

Trace metal analysis of oilfield-produced water from Clair ridge offshore platform using microwave plasma atomic emission spectrometry

Hauwa Abubakar Rasheed ^{1, 2,*} and Chizoma Nwakego Adewumi ^{2, 3}

¹ Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, Bayero University, Kano, Nigeria.

² Department of Chemistry, Faculty of Natural and Applied Sciences, Veritas University, Abuja, Nigeria.

³ Waste to Wealth Research Team, Nile University of Nigeria, Plot 681, Cadastral Zone C, Airport Road, Jabi, Abuja Federal Capital Territory, Nigeria.

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Abstract

Oilfield Produced water, a by-product of oil and gas production, often contains a range of dissolved and suspended constituents that may pose environmental concerns if discharged untreated. In this study, Microwave-Induced Plasma Atomic Emission Spectroscopy (MIP-AES) was employed for the quantitative determination of trace metals in produced water samples. Calibration curves for all analyzed elements exhibited excellent linearity ($R^2 \geq 0.999$), confirming the method's accuracy and suitability for multi-element analysis. The concentration of sodium was found to be 2596.03 ± 43.20 ppm, indicating high salinity, consistent with the known saline characteristics of the North Sea water often injected into reservoirs. Significant levels of copper, iron, and potassium were also detected, suggesting possible contributions from natural formation water chemistry, mineral dissolution, and corrosion of production infrastructure. The lack of phosphorus detection was probably caused by either chemical transformation into undetectable forms or concentrations below detection limits. The findings demonstrate that MIP-AES is a sensitive, economical, and reliable method for routinely monitoring the quality of produced water, with consequences for environmental management and discharge regulation compliance.

Keywords: Limit of quantification; Oilfield Produced water; Trace metals; Calibration; Limit of Detection

1. Introduction

Oilfield Produced water (OPW) is the largest volume waste stream generated during oil and gas exploration and production [1]. Beyond dissolved salts, hydrocarbons, and treatment chemicals, it frequently contains trace metals, including mercury (Hg), lead (Pb), copper (Cu), chromium (Cr), arsenic (As), phosphorus (P), and nickel (Ni), originating from geological formations, drilling fluids, and equipment corrosion. From an environmental perspective, trace metals are non-biodegradable and exhibit toxicological effects on aquatic biota, even at parts per billion levels. They can bioaccumulate in fish and shellfish, persist in sediments for decades, and ultimately enter the food chain, posing chronic ecological and health hazards [2].

The determination of trace metals in OPW is essential for evaluating environmental risks, regulatory compliance, and operational integrity in oil and gas activities [3]. Strict discharge restrictions for trace metals in produced water are enforced by both national and international regulatory bodies, including the Nigerian Department of Petroleum Resources (DPR), the OSPAR Commission, and the United States Environmental Protection Agency (USEPA). Exceeding these limits can lead to legal penalties, reputational damage, and operational shutdowns. Continuous monitoring ensures compliance with environmental legislation and supports environmental impact assessment (EIA) processes

* Corresponding author: Hauwa Abubakar Rasheed

[4]. From an operational standpoint, trace metal concentrations provide insight into corrosion rates, scaling tendencies, and the efficiency of OPW treatment systems. Tracking variations in metal levels can also aid in source identification, distinguishing between formation-derived metals and those introduced through drilling or production processes [5]. Ultimately, regular trace metal analysis in produced water supports sustainable oil and gas production, safeguards environmental and public health, and reinforces corporate social responsibility commitments in line with global sustainability targets, such as the United Nations Sustainable Development Goals (SDGs) [6].

Microwave-Induced Plasma Atomic Emission Spectroscopy (MIP-AES) is a powerful tool that uses a microwave magnetic field and nitrogen gas to sustain the plasma that is used as an excitation source [7]. With a traditional torch, a strong plasma is produced when nitrogen, a diatomic gas, is used as the plasma gas. Either bottled gas or a nitrogen generator, which offers a reliable, high-temperature source in standard torches (around 5000 K), can be used to supply nitrogen. A central channel that is colder and appropriate for atomizing samples produces emission lines from atomization with great intensity. [8], [9]. MIP-AES is increasingly preferred for trace metal analysis because it offers a balance between analytical performance, operational simplicity, and cost-effectiveness. Unlike conventional techniques such as colorimetry or flame photometry, which are often limited by lower sensitivity, single-element capability, and lengthy procedures, MIP-AES provides rapid, simultaneous multi-element detection with excellent sensitivity, enabling accurate quantification of metals at trace and ultra-trace levels [10]. Compared to more sophisticated methods such as inductively coupled plasma mass spectrometry (ICP-MS) or high-performance liquid chromatography (HPLC) coupled with elemental detection, MIP-AES is more affordable to acquire and operate, particularly as it utilizes nitrogen from ambient air rather than expensive argon, and it requires less stringent laboratory conditions and maintenance [11]. Furthermore, it maintains strong performance and less susceptibility to matrix interferences while accommodating a broad variety of sample matrices with little preparation. This investigation was prompted by these characteristics, which make MIP-AES a desirable option for routine trace metal analysis. This study's aim was to utilize MIP-AES in determining the concentrations of sodium (Na), potassium (K), iron (Fe), P, and Cu in OPW samples. A calibration curve and standard solutions were used to indirectly quantify the amounts of each element in the samples.

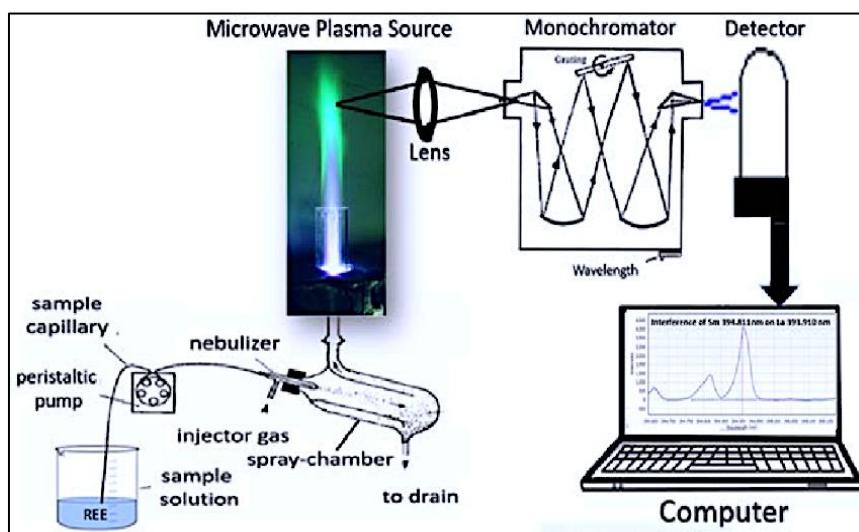


Figure 1 MIP-AES setup [11]

2. Materials and methods

2.1. Preparation of stock solutions and standards

HNO_3 (65%) and HCl (37%) were purchased from Merck, Darmstadt, Germany. The following salts [NaCO_3 , $\text{Fe}(\text{NO}_3)_2$, K_2CO_3 , $\text{Cu}(\text{NO}_3)_2$, and NaPe_4] were also procured from Karmel, Tianjin, China. For all dilutions, 1% of HNO_3 and HCl in 3:1 was used for metal digestion [12]. Stock solutions for each salt were prepared by dissolving the salts in distilled water first and then the acid solution to attain 1000 ppm of K, Na, Fe, P, and Cu. Six different concentrations of standard solutions (0.01, 0.1, 0.5, 1, 5, and 10 ppm) were prepared as well.

2.2. Sample collection and preparation

Three samples of OPW from the Clair Ridge offshore platform within the North Sea, Aberdeen, Scotland, were carefully collected, sealed in an airtight container, and labeled meticulously for later use.

2.3. Instrumentation

Trace metal analysis was conducted using the Agilent 4100 Microwave Induced Plasma Atomic Emission Spectroscopy operated in time-resolved mode and a custom-written Excel spreadsheet, including a Dean Dixon outlier test for all sample triplicates. Nitrogen used in this instrument was generated from the air using a generator. The OPW sample was very clear; therefore, no further filtration was required. The sample was then taken and placed in three tubes. The six standard solutions, along with the blank sample (1% HNO_3) and OPW samples, were analyzed in three replications. Each element was set at a specific wavelength as shown in Table 1. The elemental analysis for the standard solutions was then run, and calibration curves were observed from the software and found acceptable except for phosphorus, which gave a very low R^2 value indicating poor calibration. For potassium and sodium, the OPW had to be diluted 100 times and 1000 times, respectively, using 1% HNO_3 and analyzed again to obtain the intensities within the acceptable range. The 1000-times-diluted sample gave Na intensities within range. A calibration curve using the intensities of the standard solutions, and the concentrations was performed for each metal to determine the line equation, which was then used to calculate the actual concentration of the metals in the OPW.

Table 1 Instrument operating conditions

Parameters	Fe	Cu	K	Na
Wavelength (nm)	371.993	327.395	769.897	589.592
Viewing position	110	-30	0	-10
Nebulizer pressure (kPa)	180	180	180	180
Read time (s)	3	3	3	3
Number of replicates	3	3	3	3
Sample uptake time (s)	15	15	15	15
Stabilization time (s)	15	15	15	15
Pump rate (rpm)	15	15	15	15
Gas flow	Nitrogen gas 20 L^{-1} min, Air 25 L^{-1} min			
Power of Magnetron output	6480 KJh^{-1}			
Detector	CCD detector (back-thinned solid state)			

3. Results and discussion

In standard solutions made from 1000 ppm stock solutions, Table 2 displays the individual concentrations and intensities of each element. The varying intensities are ascribed to the varying concentrations of each metal in the samples. It displays the differences in the elements' intensities. Compared to the transition metals (Fe and Cu), the alkali metals (K and Na) had greater intensities. This is due to the alkali metals' ease of ionization. Phosphorus, on the other hand, couldn't be detected by the instrument as evidenced by the negative intensity due to low ionization potential or absence of the metal in question. Sodium was found in the highest concentration among the detected metals, consistent with the saline nature of formation water. This is expected, as Na is a dominant cation in deep formation brines, derived mainly from the dissolution of halite (NaCl) and other sodium-bearing minerals over geological timescales. Iron levels are attributable to both the dissolution of iron-bearing minerals such as siderite ($\text{Fe}_{\text{2}}\text{CO}_3$) within the reservoir rock and corrosion of steel tubing, casings, and pipelines. Cu likely originates from corrosion of brass or bronze components in pumps, valves, and fittings, as well as potential residual contamination from drilling or completion fluids. The detection of cadmium even at low concentrations is notable due to its toxicity and may be linked to trace occurrences in formation minerals or as an impurity in other production chemicals. Overall, the detection of Fe, Cu, Cd, and Na underscores the need for continuous monitoring of trace metals in produced water, as even low-level discharges can accumulate in aquatic environments and pose long-term ecological risks.

The absence of phosphorus, despite its potential use in scale inhibitors, highlights the importance of understanding geochemical interactions and chemical fate within the production system. These results not only provide baseline data for environmental risk assessment but also offer valuable insights for corrosion control, treatment system optimization, and compliance with regulatory discharge limits. Although phosphate species are sometimes present in produced water due to the use of phosphate-based scale inhibitors, these compounds may not have been employed in the wells under investigation. Furthermore, phosphates and phosphonates readily precipitate with calcium and other divalent cations to form insoluble salts or adsorb onto mineral surfaces, thereby reducing their aqueous concentrations before sampling [8]. Phosphonate inhibitors, if injected, may also undergo thermal degradation under reservoir conditions, producing breakdown products that are not detected as elemental phosphorus by MIP-AES. In cases where phosphorus is present, its concentration might still fall below the detection limit of the instrument, particularly in high-salinity matrices where spectral interferences can reduce sensitivity [11].

Table 2 Concentrations and intensities of Na, K, Cu, Fe and P

	Sodium (Na)		Potassium K)		Copper (Cu)	Iron (Fe)	Phosphorus (P)
	Concentration (ppm)	Intensity					
Blank	0	0	0	0	0	0	-6954.4
SD 1	0.01	44960.9	4840.16	776.5	356	-6988.48	
SD 2	0.1	54800.01	6948.86	12789.82	516.58	-6996.5	
SD 3	0.5	98085.44	12702.89	27218.35	1130.84	-6975.43	
SD 4	1	211732.48	24821.04	54997.86	2477.54	-6966.15	
SD 5	5	978120.13	121028.47	277,874.53	11174.72	-6880.6	
SD 6	10	1890984.51	227985.95	539540.5	24625	-6695.1	

The calibration curve for iron is shown in Figure 1, and the actual concentration of iron in OPW as determined by the calibration curve is shown in Table 3. It was discovered that the concentration of iron was 0.0424 ± 0.005 . This result agrees with previous findings; especially for reservoirs that do not have integrity problems like corrosion and scaling, such a low concentration of iron is predicted.

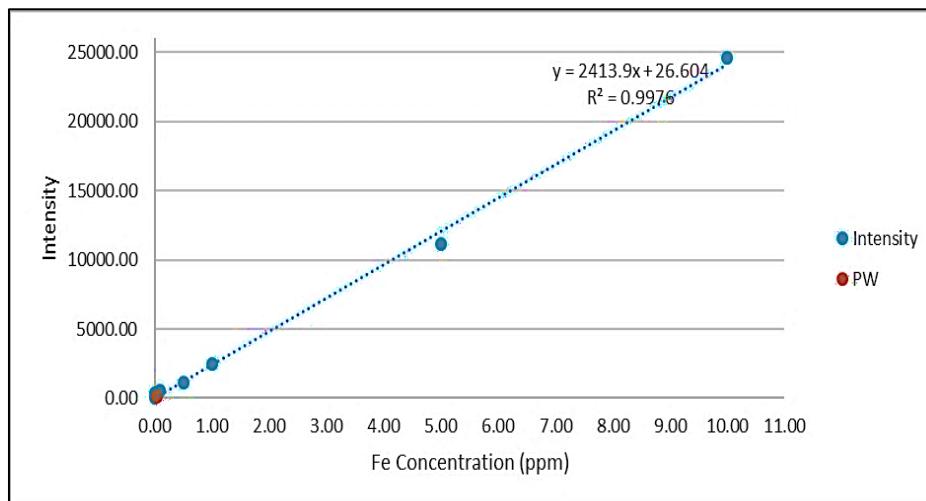
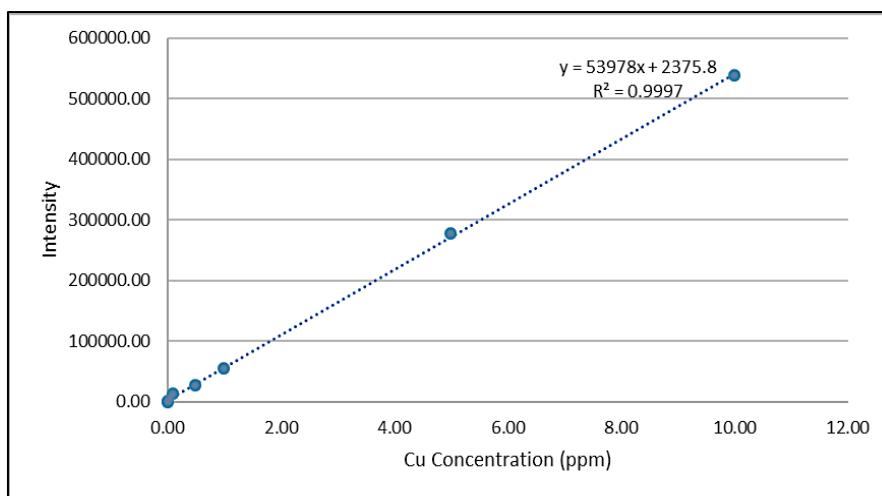


Figure 2 Calibration curve of Fe

Table 3 Concentration of Fe in OPW sample (without dilution)

Sample	Fe Concentration (ppm)	Intensity
PW sample 1	0.0419	127.65
PW sample 2	0.0419	127.74
PW sample 3	0.0428	129.80
Mean \pm SD	0.0422 ± 0.0005	

Figure 2 shows the calibration curve of Cu presented in standards. The calibration curve is acceptable as well. Table 4, on the other hand, shows the intensities of Cu in the unknown sample. Like Fe, the process water was used without dilution because the intensities were very low, and so the chances of detecting Cu in the diluted sample will be less. The negative values of concentration shown indicated that the amount of Cu is lower than the instrument detection limit (Table 5).

**Figure 3** Calibration curve for Cu**Table 4** Concentration of Cu in OPW (without dilution)

Sample	Cu Concentration (ppm)	Intensity
OPW sample 1	0.0230	1132.14
OPW sample 2	0.0271	915.30
OPW sample 3	0.0259	975.25
Mean \pm SD	0.0253 ± 0.0021	

Table 5 Calculation of LOD and LOQ of the measured elements

Element	Slope	Blank SD	LOD (ppm)	LOQ (ppm)
Cu	53978.0	89	0.005	0.016
Fe	2413.9	8	0.011	0.033
Na	187540.0	8622.68	0.152	0.460
K	22704.0	54.87	0.008	0.024

Figure 3 shows the calibration curve of K presented in a series of standards. The calibration curve has a regression factor R^2 of 0.9991 as observed, which indicates excellent linearity. The OPW was diluted 10 times because the intensities were found to be higher than the range in the standard solutions as depicted in Table 6. This is because K is easily ionized and is also found in quantifiable amounts (2.793 ± 0.0295) in sea water also contributing to salinity.

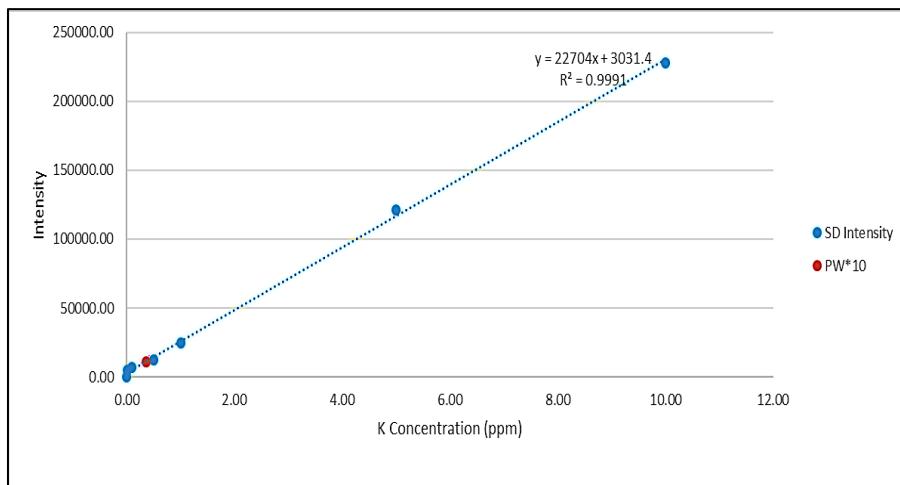


Figure 4 Calibration curve for K

Table 6 Concentration of K in OPW

Sample	Measured concentration (ppm)	Dilution Factor	Actual concentration (ppm)	Intensity
OPW sample 1	0.2816	10	2.816	9425.68
OPW sample 2	0.3760	10	2.760	11568.71
OPW sample 3	0.4304	10	2.804	12803.16
Mean + SD	2.793 ± 0.0295			

Figure 4 shows the calibration curve of Na. The intensity values for the standard solutions are observed to be high, which is due to high Na ionization potential. When the undiluted sample was analyzed in the instrument, the color of the plasma was observed to change from blue to orange due to very high concentrations; therefore, the OPW was diluted further 1000 times. Na is usually present in high concentrations in the OPW, but the range varies from field to field. The actual concentration of Na was found to be

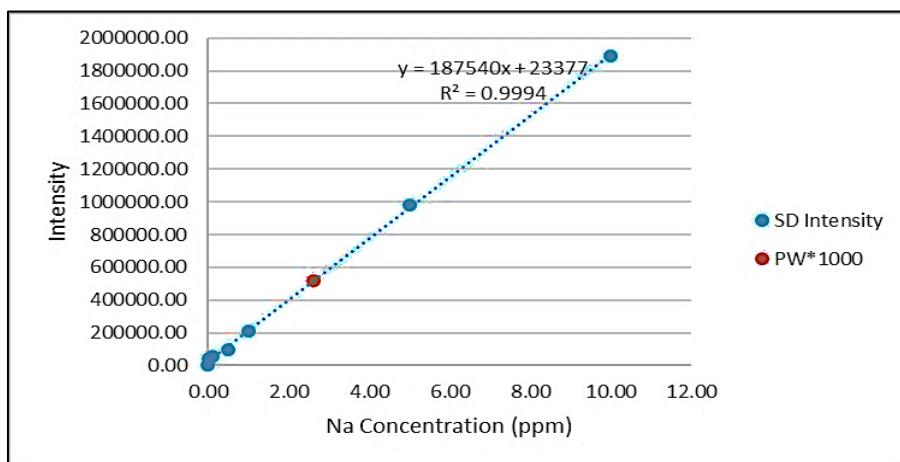


Figure 5 Calibration curve for Na

Table 7 Na concentration in OPW

Sample	Measured Concentration (ppm)	Dilution Factor	Actual concentration (ppm)	Intensity
PW sample 1	2.5480	1000	2548.0	501231.13
PW sample 2	2.6084		2608.4	512563.21
PW sample 3	2.6317		2631.7	525687.05
Mean	2596.03±43.20			

Table 8 shows the Limit of Detection (LOD) and Limit of Quantitation (LOQ) for the measured elements. These are used to describe the smallest concentration of a measurand that can be reliably measured by an analytical procedure. The LODs and LOQs were calculated from the filtration blanks instead of analysis blanks for all metals. This is a rather conservative approach, leading to higher LODs and LOQs. The LODs and LOQs for the trace element analysis are given in Table 2. For trace metals, all measured concentrations were above the LOQ, while phosphorus showed concentrations below the LOD and LOQ. LOD and LOQ were calculated from the blank standard deviation and slope of each element calibration curve as per equations (1) and (2):

$$\text{LOD} = 3.3 \frac{SD}{slope} \quad \dots \quad (1)$$

$$\text{LOQ} = 10 \frac{SD}{slope} \quad \dots \quad (2)$$

4. Conclusion

The analysis of OPW using MIP-AES demonstrated the technique's reliability and sensitivity for detecting trace metals, even at low concentrations. Significant levels of Na, K, Cu, and Fe, reflecting possible contributions from formation water chemistry, corrosion of production infrastructure, and mineral dissolution. The nature of the OPW was saline with a Na concentration of 2596.03±43.20 ppm, indicating high sodium chloride content, which is typical for North Sea offshore platforms. Phosphorus was not detected due to very low LOD or total absence in the OPW. However, the phosphorous could be present in the process water from chemical residuals that are produced with oil and gas, such as scale inhibitors. Phosphate scale inhibitors are very commonly used in the oil and gas industry due to their stability at higher temperatures and their effect on both carbonate and sulphate scale. Overall, MIP-AES proved advantageous over conventional methods due to its cost-effectiveness, multi-element capability, and minimal sample preparation, making it a suitable approach for routine monitoring of produced water quality and assessing its environmental implications.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no competing interests. The authors declare they have no financial interests.

Authors contribution

Hauwa A. Rasheed: Conceptualization, Investigation, writing original draft. Chizoma N Adewumi: resources, revising and editing the manuscript.

Consent for publication

All authors give the consent to the publication of their data.

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