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QUANTITATIVE ANALYSIS OF HEAVY METALS IN PRODUCED WATER FROM NDX 011 IN NIGER-DELTA OIL FIELD

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ABSTRACT: *Oil and gas production is usually accompanied by water (brine), which is referred to as produced water. As oil and gas production declines, the quantity of water production from same reservoir increases. These produced waters have many components, which mostly have adverse environmental impacts. One of such components are the heavy metals which are numerous. Produced water sample from Niger Delta crude oil was investigated for five (5) heavy metals. The analysis was carried out using an Ultraviolet Visible Spectrophotometer. The analysis was carried out (in line with industry standard) on the produced water sample in order to determine the concentrations of the heavy metals present. The results obtained from this analysis showed that the concentrations of one out of the five heavy metals investigated (Arsenic (As)) was more than the allowable limits set by regulatory bodies. Arsenic (As), Boron (B), Manganese (Mn), Tin (Sn), and Barium (Ba) have concentrations of 0.9599mg/L, 0.0955mg/L, 0.000433mg/L, 0.31730mg/L, and 0.0019mg/L respectively compared with maximum limits set by the regulatory bodies as 0.3mg/L Arsenic, 5mg/L Boron, 0.004mg/L Manganese, 10mg/L Tin and 1.3mg/L Barium. This showed that the produced water from oil and gas activities in Niger Delta region of Nigeria should be tested and treated for Arsenic and other present heavy metals that may have concentrations higher than standard limits set by regulatory bodies before disposal and/or re-use.*

KEY WORDS: Produced water, Heavy metals, Crude Oil, Niger-Delta.

INTRODUCTION

Production of hydrocarbon oil from subsurface reservoirs is often accompanied by water (brine). The extracted water is referred to as ‘produced water’. As oil and gas depletion increases, the volume of produced water rises and is compelled to exceeds the volume of the hydrocarbon produced before the reservoir is depleted beyond economic profit. Produced waters often have a defining down turn on the economic development of an oilfield and the oil and gas reservoir, due to the cost of producing the oilfield waters over the feasible period of production. These produced waters have many components, which mostly impact negatively on the environment. One of such components are the heavy metals, Obodo, et al (2004).

Produced water can be defined as the water brought from the hydrocarbon bearing reservoir during the extraction of oil and gas. Oil and gas are usually discovered along side water in the subsurface reservoir, where the water having a higher density than the oil and gas lays underneath the hydrocarbons in the reservoir. This water which occurs naturally in the reservoir is called formation water, interstitial water or sometimes, connate water. Oil and gas wells can initiate water production after production has occurred for a long time, depending on the reservoir energy drive mechanism.

Origin of Produced Water

In an oil and gas reservoir, the pore spaces in the rock matrix contain the natural fluids at chemical equilibrium. Because reservoir rocks are mostly of sedimentary origin, water which is present at the time of rock genesis is therefore trapped in the pores of the rock. Water may also move or migrate according to the hydraulic pressures, which might be induced by geological processes that also form the reservoirs. In oil and gas reservoirs, some of the water may be displaced during hydrocarbon extraction, but some water will always remain in the rock pores. If the reservoir rock was originated in a sea or ocean, then it will be saline, Utvik, et al (1999).

Reservoir rocks deposited in lakes, rivers or estuaries have fresher or less saline water. Originally, the water is in chemical equilibrium with the original inorganic (mineral) salt of the rock, but upon invasion of the hydrocarbon (oil and gas), a new equilibrium with those new phases will be attained. Therefore, both equilibria and chemical reaction dynamics are associated with the inorganic (mineral) phases and the oil and gas phases.

Composition of Produced Water

Produced water are chemically complex fluids. They usually contain high levels of dissolved solids, with salinity ranging from 12 to 160 ppt (parts per thousand); metals concentrations which is higher than those of receiving waters (in discharge); and up to 25 ppm (parts per million) oil and grease, Ayad, et al (2010). Radioactive isotopes are also prevalent in produced oilfield waters Concentrations of radium 226 in brines often exceed regulatory criteria established for other industries. Monocylic aromatic hydrocarbons (benzene, toluene, ethyl benzene, xylenes), polycyclic aromatic hydrocarbons, and related hetrocyclic aromatic compounds are also constituents of produced oilfield waters and are considered major toxicants in produced oilfield waters Heavy metals in produced waters include cadmium, copper, chromium, lead, mercury, nickel, zinc etc.

These composition and behavior of produced waters often change with addition of treating agents, along with the presence of compressed gas, oil, and present solids. The composition of produced waters is an exclusive source of information about a particular reservoir. This is because of the high variability in the composition of produced waters in different fields.

Effects of Produced Water

One of the greatest implications of produced water in the last two decades has been the environmental impact and regulatory practices. In many cases, government regulations limit the available options, and this may define the degree of characterization from sampling to analysis imposed on the operator. Because of the environmental impacts these produced waters may have, there are different regulations guiding the disposal of the produced water. Oil and grease, temperature, pH, and heavy metal concentrations are some of the main quality parameters used in the regulation of the discharge of produced water to the environment. The main effects of produced waters encountered in the oil and gas industry are deposition of insoluble scale and corrosion of meta, Utvik, et al (1999).

The untreated produced waters that are re-injected into the reservoir have some environmental effects that include:

- excess solids which cause clay deflection.
- excess soluble salts which can cause plants to dehydrate and die.
- reduced oxygen level enough to damage aquatic species.
- injection formation plugging due to suspended solids, which results in injection pressure increase and decrease in the produced water injection flow rate.
- scale problem which causes well bore clogging and fluid flow prevention.
- environmental impact due to chemical additive like corrosion inhibitor and H_2S scavenger

Heavy Metals

Heavy metals are metals, metalloids or any metallic element with relatively high density, toxic even at low concentrations, Aka and Akuma, (20120. They have harmful effects. Examples of the commonly encountered ones in produced water are lead, cadmium, mercury, copper, zinc, chromium, cobalt, etc. Naturally, heavy metals are elements of the earth's crust which can neither be degraded nor destroyed. They are mainly formed in underground and surface water by their deposition through rainwater. They have varying effects on the environment when they find their ways into the environment through different human activities. Heavy metals are also classified based on density, atomic weight, chemical toxicity in relation to living organisms. An alternative term to heavy metals is 'toxic metals' of which no consensus of exact definition exists. These metals include cobalt, chromium, copper, manganese, molybdenum, tin, silver, arsenic and boron, e.t.c. Heavy metals may be classified as "trace elements" because they occur in concentrations of less than 1% (frequently below 0.01% or 100 mg/L) in rocks of the earth's crust. These trace elements or heavy metals are often called micronutrients such as zinc; copper and manganese are useful to crops, while cobalt, manganese, copper and zinc are useful to live stock. The metals that cannot be bio-degraded chemically in nature include cobalt, zinc, manganese, magnesium, copper, lead, nickel, cadmium and mercury. They get incorporated into the plant enduring the growth of the parent plant and remain undamaged. Some heavy metals, when present at high concentrations, lead to poisoning and these include lead, zinc, cadmium, mercury, nickel, copper, etc.

The requirement, doses and tolerance levels of essential or trace elements are decided on the basis of effects on growth, health, fertility and other relevant criteria.

In Medicine and Chemistry, heavy metals are defined and include all toxic metals, irrespective of their atomic weights, members of the group VI, VII, VIII, IX and X elements of the transition series of the periodic group inclusive.

Environmental Effects of Heavy Metals in Produced Waters

The environmental implications of these toxic wastes, especially heavy metals, when discharged directly (untreated) into water bodies and estuaries cannot be overemphasized, Eboatu and Okonwo.(1999). Although 75 percent of the earth is covered by water, only a very small portion of it can be consumed directly by man. Ground water is an important source of drinking water for humans. It contains over 90% of the fresh water and it is an important reserve of good quality and consumable water. These are the waters being contaminated by industrial activities. Example is the effect of effluent discharge from oil production platforms into the rivers and estuaries of the Niger-Delta region in Nigeria, which have affected the agricultural activities, particularly fishing, and have contaminated the drinking water of the host communities in this region. International Occupational Safety and Health Information Centre in their journal of 1999, stated that heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs.

The water pollution by heavy metals has become a question of considerable public and scientific concern in the light of the evidence of their toxicity to human health and biological systems. Heavy metals receive particular concern considering their strong toxicity They exist in water in colloidal, particulate and dissolved phases with their occurrence in water bodies being either of natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents). Some of the metals are essential to sustain life. Calcium, magnesium, potassium and sodium must be present in human body for normal functions. Also, cobalt, copper, iron, manganese, molybdenum and zinc are needed at low levels as catalyst for enzyme activities.

MATERIALS AND METHOD.

Apparatus:

Ultraviolent – Visible Spectrophotometer was the main equipment used in this work. It is based on absorption of light in visible or ultraviolet region. Absorption of ultraviolet or visible light occurs simultaneously with an electron jumping into an excited state from ground state and this explains why transition metal ions and conjugated organic compounds can be analyzed by this method

Experimental Procedure:

Collection and Preparation of Produced water sample:

Produced water sample was collected from OML 00A1 in the Niger-Delter region of Nigeria, owned by a Multinational Oil Company. The sample was transferred to an airtight container which was appropriately labeled and taken to the laboratory for analysis.

Determination of Arsenic (As) Concentration:

Arsenic (III) stock solution (1000 μgmL^{-1}) was prepared by dissolving 0.17g of $NaAsO_2$ in 100 mL of water. Working standard was prepared by appropriate dilution of stock. Toluidine blue (0.01 %), hydrochloric acid (1 M), potassium iodate (2 %) and sodium acetate (1 M) were used.

Procedure

i. 0.17g of Sodium Arsenate ($NaAsO_2$ –the stock) was dissolved in 100mL of distilled water.
ii. 0.05g of Toluidine blue was dissolved in 100mL of distilled water.
iii. 86ml of concentrated HCl was diluted to 1litre with distilled water.
iv. 2g of Potassium Iodate (KI) was dissolved in 100mL of distilled water.
v. 13.61g of Sodium Acetate was dissolved in 100mL of distilled water.

Standard Working Solution:

(i) Aliquots of sample solution containing 1mL; 5m, 10mL; and 15mL of Sodium Arsenate were transferred into a series of volumetric flasks. Iml of potassium iodate, 1ml of HCL, 0.5ml of toludine blue and 2ml of sodium acetate (which causes change in colour of the solution as a result of iodine liberation) were added to each of the flash, and each was made up to 20ml using distilled water.

(ii) 20mL of the produced water sample was measured and transferred into a flask. 1mL of Potassium Iodate (2 %, 1ml to convert arsenic (v) to arsenic (III)), 1ml of dilute hydrochloric acid (1M), 0.5ml of toludine blue, 2ml of sodium acetate were added to the produced water sample in the flask and left for 2 minutes.

(iii) After 2 minutes the absorbance of each of the flash was measured using the UV-Vis spectrophotometer at a wavelength of 628nm. Calibration of the spectrometer before use was done with distilled water.

(iv) The results were used to plot a calibration graph which was used to determine the concentration of Arsenic in produced water.

Determination of Boron (B) Concentration:

Procedure

(i) A stock solution containing 100ppm of Boron was prepared by dissolving 5.71g of boric acid in 1000 ml of distilled water (stock solution)

(ii) 2.0g of ascorbic acid were dissolved in 100ml of distilled water, with 5ml of azomethine reagent (conditioning reagent) added to it.

(iii) 40g of ammonium acetate were dissolved in 100ml of water, 125ml of glacial acetic acid alongside 6.7g of EDTA (disodium salt) and 60mL of thioglycolic acid were all added and properly mixed to form a buffer solution.

Standard Working Solution:

(i) 1mL, 2mL; 3mL,4mL of the stock were taken and transferred to four different conical flask, 4mL of the buffer solution as well as 2mL of ascorbic acid solution were added to each of the flask. Each of the flasks was made up to 20mL using distilled water.

(ii) 5mL of the produced water sample was taken and put in a conical flask, 4mL of the buffer solution and 2mL of the ascorbic acid were also added to the flask and make up to 20mL with distilled water.

(iii) The blank solution consists of 5mL distilled water; 4mL buffer solution and also make up to 20mL with distilled water which was used to calibrate the spectrometer before use.

(iv) The solutions were left to stand for 30 minutes and then analyzed using the UV-Vis spectrometer at a wavelength of 410nm and the absorbance taken.

(v) The results were used to plot a calibration curve, which was used to determine the concentration of Boron in the produced water sample.

In the same manner, the concentrations of other metals (manganese, Tin and Barium) in the produced water sample were determined from the calibration curve of each of the metal.

RESULTS AND DISCUSSION

The results obtained from the analysis are shown on Tables 1, 2, 3, 4 and 5, and these were used to plot the various calibration graphs (figures 1, 2, 3, 4, 5) for each heavy metals. The calculations made from these results showed the concentrations for each five heavy metals in the produced water in (mg/L), shown in table 6. The analysis of these results and calculations showed that for every liter of the produced water gotten from the OML 00A1 well, there are: 0.9595mg/L of Arsenic; 0.0955 mg/L of Boron; 0.000433 mg/L of Manganese; 0.31739 mg/L of Tin; and 0.0019mg/L of Barium respectively. These were the concentrations of the five heavy metals analyzed.

The regulatory standard of these heavy metals in produced waters are shown in Table 7 below.

Comparing the values from the analysis with the regulatory standard values of these heavy metals, it is obvious that the concentrations of one of these heavy metals analyzed exceeds the regulatory standard limit. The heavy metal with concentration that exceeds regulatory standard limit is arsenic (As), while Manganese (Mn), Boron (B), Tin (Sn) and Barium (Ba) have concentrations within the regulatory limits. Heavy metals are unfriendly metals that have adverse effect on man, plants, animals and the environment at large especially when their concentrations get beyond the allowable limits. Therefore, their concentrations in produced water and other waste water should surely be taken care of before discharge or re-use as the case may be. From the result obtained in Arsenic, it implies that if the produced water is not properly treated for arsenic before disposal, it will have harmful effects on marine life (offshore) and can cause environmental problems. The produced water, if not properly treated before re-use or discharge can also have adverse effect on the oilfield materials and equipment.

Calculation.

From the calibration graphs plotted

Y= mx + c

$$Concentration\ of\ heavy\ metal\ in\ produed\ water \left(\frac{mg}{L}\right) = \frac{X \times 1000}{volume\ of\ produced\ water\ sample}$$

Where:

Y= Absorbance of the produced water sample

m= slope of the graph

x = concentration of heavy metal (mg/L)

c = interception of the graph on the y-axes

Table 1: UV-Vis Spectrophotometer Absorbance Readings for Arsenic

Sample	**Volume Concentration (mL)**	**Absorbance**
Blank	0	.0.00
A	1	0.84
B	5	0.61
C	10	0.49
D	15	0.39

Table 2: UV-Vis Spectrophotometer Absorbance Reading for Boron.

Sample	**Concentration (Mg/l)**	**Absorbance**
Blank	0.000	0.000
A	0.005	0.023
B	0.010	0.041
C	0.015	0.068
D	0.020	0.082

Table 3: UV-Vis Spectrophotometer Absorbance Reading for Manganese (Mn)

Sample	**Concentration (mg/L)**	**Arbsobance**
Blank	0	0
A	0.00080	0.40
B	0.00040	0.19
C	0.00016	0.06
D	0.00008	0.03

Table 4: UV-Vis Spectrophotometer Absorbance Reading for Tin (Sn)

Sample	**Concentration (mg/L)**	**Arbsobance**
Blank	0	0
A	0.00008	0.001
B	0.00016	0.002
C	0.0004	0.007
D	0.0008	0.020

Sample	Concentration (mg/L)	Absorbance
Blank	0	0
A	0.0001	0.08
B	0.0002	0.14
C	0.0005	0.19
D	0.0010	0.24

Table 5: UV-Vis Spectrophotometer Absorbance Reading for Barium (Ba)

Heavy metal	**Arsenic (Ar)**	**Boron (B)**	**Manganese (mn)**	**Tin (Sn)**	**Barium (Ba)**
Conc. in produced water (mg/l)	0.9595	0.0955	0.000433	0.31739	0.0019

Table 6: Concentration of heavy metals in produced water

Table 7: Standard values as set by regulatory bodies (Fakhru'l-Razi A., *et al*)

Heavy Metals	**Maximum value(mg/L)**
Arsenic	0.3
Chromium	0.02
Boron	5
Manganese	< 0.004
Tin	10
Barium	1.3

CONCLUSIONS

The analysis of the five (5) selected heavy metals (Arsenic (As), Boron (B), Manganese (Mn), Tin (Sn), and Barium (Ba)) in the produced water sample showed that the concentration of arsenic (As) exceeded regulatory standard limit.

This heavy metal (Arsenic (As)) with such high concentration in a produced water can be harmful to our environment if the produced water is not well treated before discharge or re-use. Therefore, there is need to adequately treat produced water for Arsenic and other heavy metals that may exceed the regulatory standard limits. Treatment can be done through adsorption or any other chemical method or metal removal from solution, according to regulatory standard procedures, considering efficiency and economical evaluation of the treatment method.

It is recommended that more attention should be paid to these non-prevalent and dangerous heavy metals in the oil industry before discharge or re-use as the case may be. Oil industry should be mandated to obey discharge and re-use regulations set by the regulatory bodies.

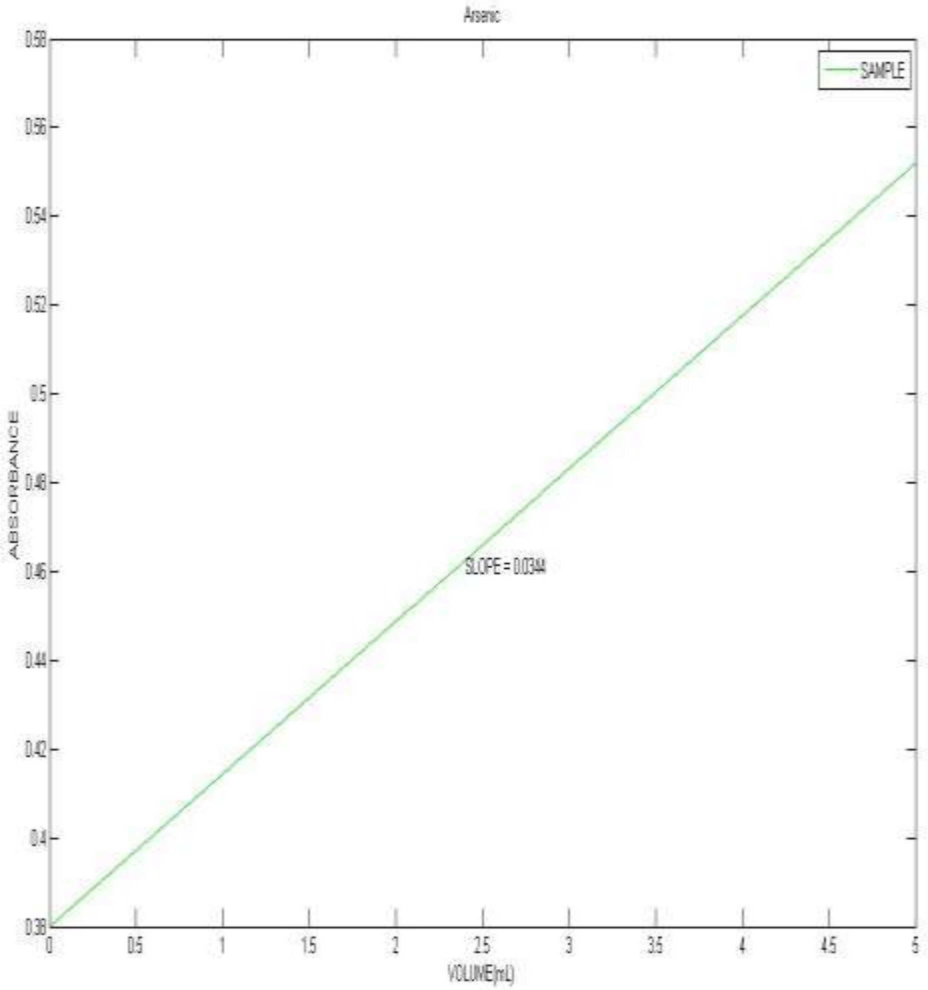

Figure 1. Calibration graph of Absorbance against Arsenic concentration

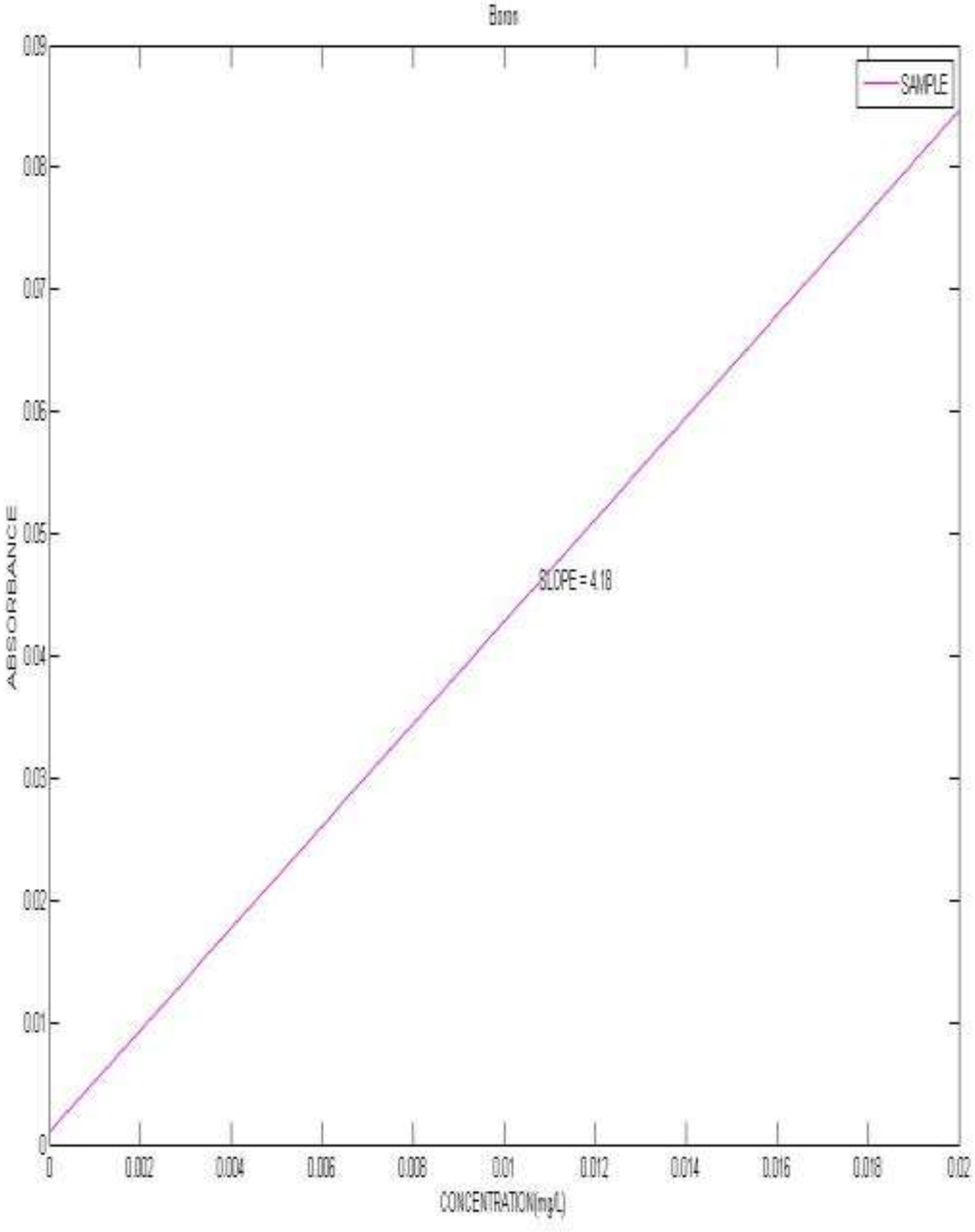

Figure 2 Calibration graph of Absorbance against Boron concentration.

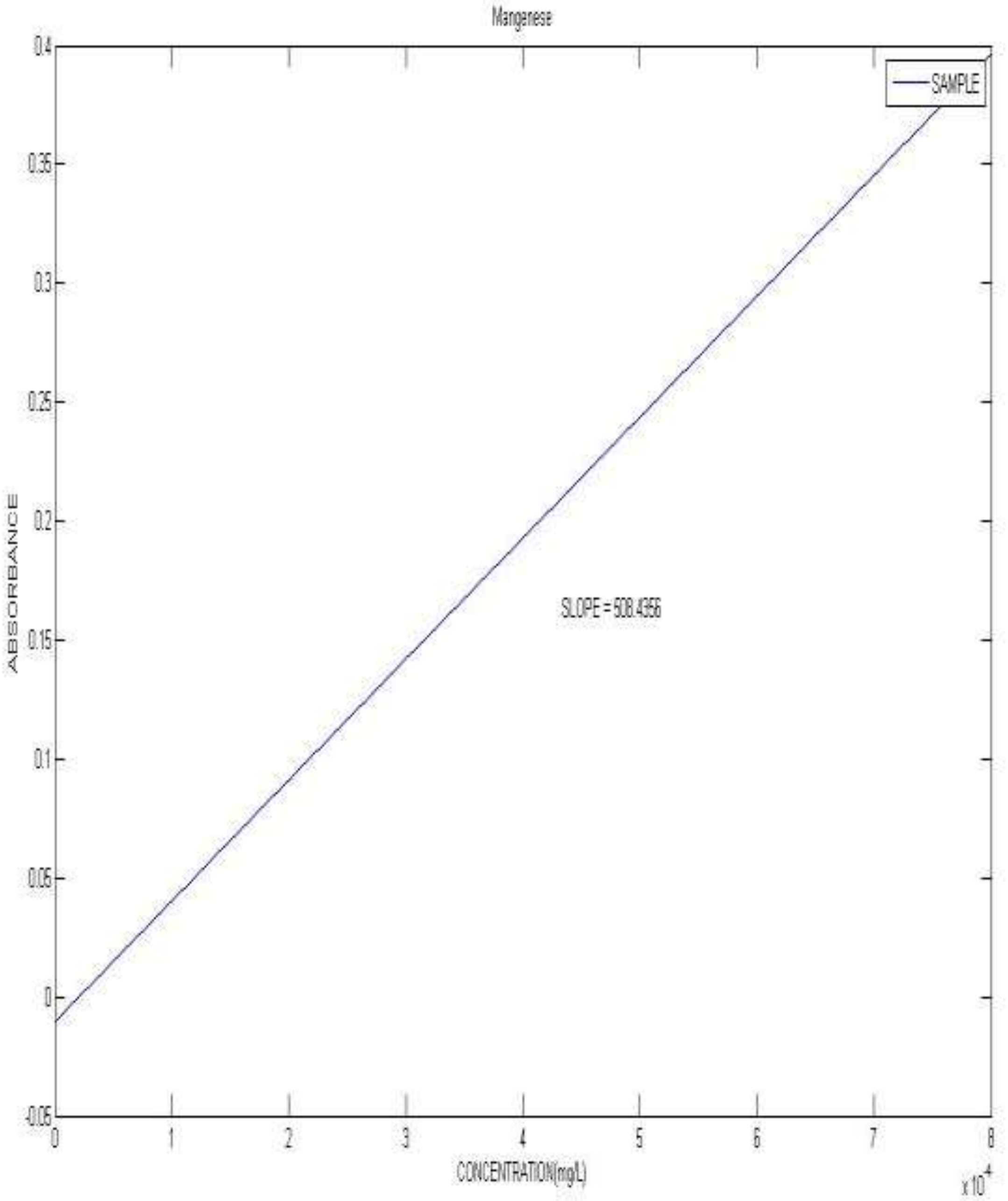

Figure 3: Calibration graph of Absorbance against Manganese concentration

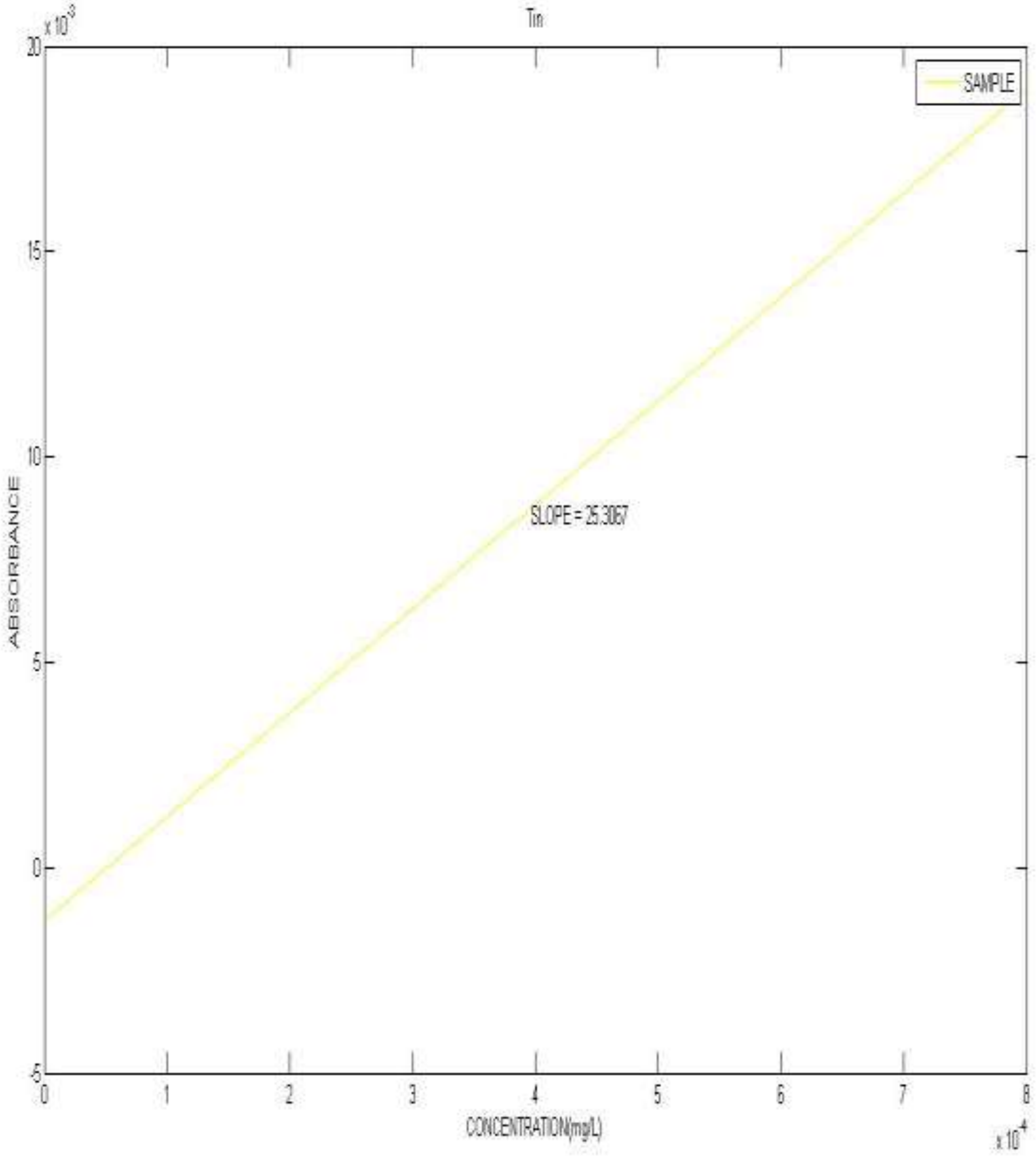

Figure 4: Calibration graph of Absorbance against Tin concentration

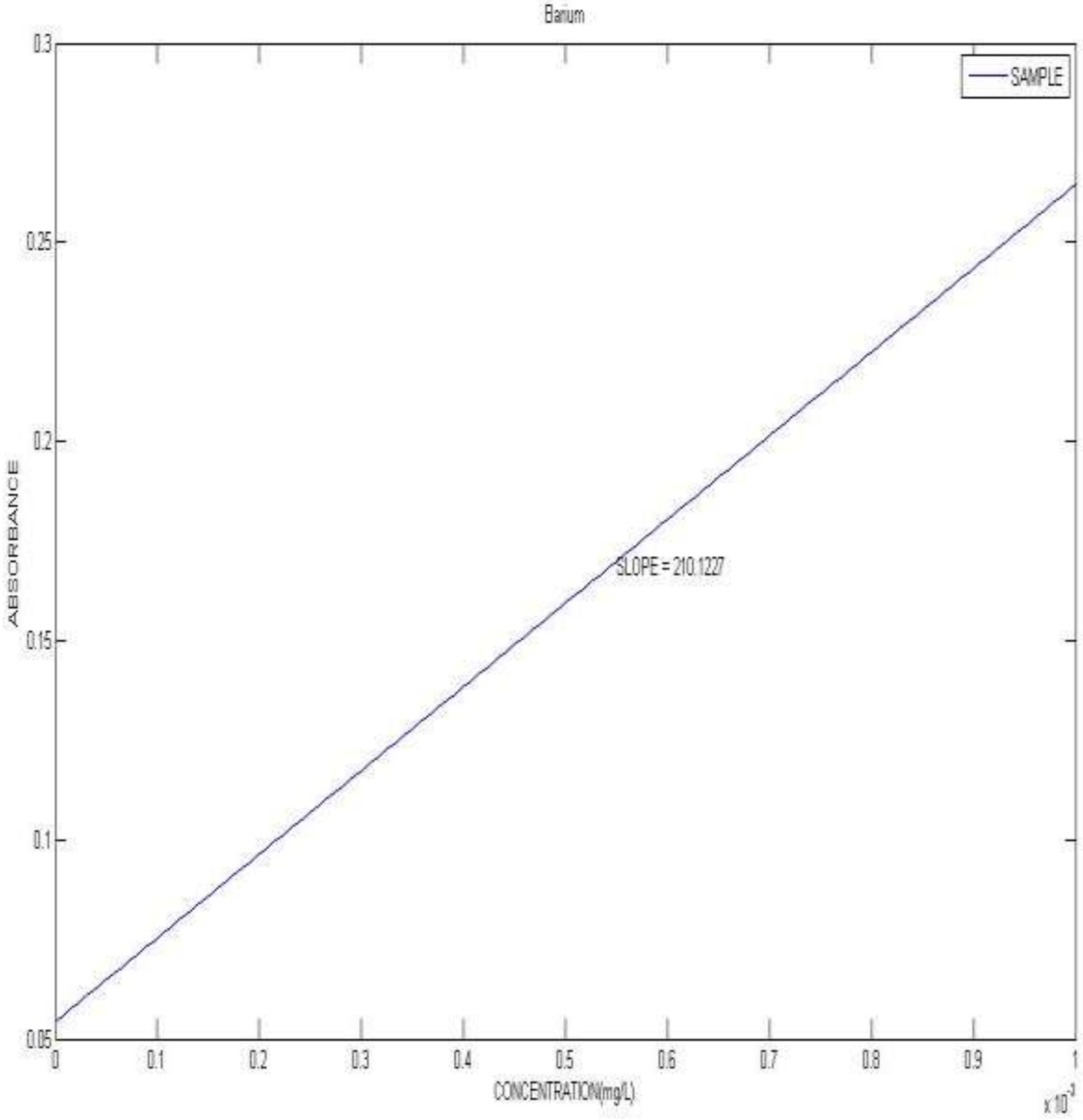

Figure 5: Calibration graph of Absorbance against Barium concentration

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