Spectrophotometric Determination of Phenol in Natural Waters by Trichloromethane Extraction Method after Steam Distillation

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Authors' contributions

This work was carried out in collaboration among all authors. Author WOM designed the study, performed the statistical analysis; wrote the protocol and the first draft of the manuscript. Authors SG and CAW managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The concentrations of phenol in natural waters were determined so as to ascertain water quality as water intended for human consumption. Total phenols were determined by molecular spectrophotometry, after steam distillation, complexation with 4-aminoantipyrene and extraction into trichloromethane. The dynamic range was 0 - 300 mg/L. Experiments were carried out in the Central Science Laboratory Complex, Taraba State University-Jalingo Nigeria. The research work was completed in 4 months. The experimental method was applied in the analysis of environmental samples (river water and groundwater) collected within Jalingo metropolis of Taraba State, North Eastern Nigeria. Significant amount of phenols were found in the in the natural water samples with a range of 0.2891 - 0.3952 mg/L. The results indicated high pollution of phenol as the values exceeded the tolerance level of 0.0005 mg/L and maximum contaminant level of 0.005 mg/L for

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phenol allowed by European Communities and Japan's Ministry of Health, Labour and Welfare respectively for water intended for human consumption. The qualities of natural waters were impaired in terms of phenol and therefore the need for post treatment to make them safe for water intended for human consumption. The water bodies should also be monitored from time to time to ascertain the level of phenol.

1. INTRODUCTION

Phenol is an aromatic organic compound with the molecular formula C_6H_5OH. It is a white crystalline solid that is volatile. It is a component of industrial paints strippers used in the aviation industry and other chemically resistant coatings. Phenol derivatives are also used in the preparation of cosmetics [1].

It has also wide spread application in the pharmaceutical, dyes, paper, pesticides and petrochemical industries etc. The industrial effluents from the aforementioned industries are often discharged in natural water bodies. Due to its toxicity, its presence could have significant detrimental effects on water quality or animals as well as some plants even at very low concentration. For these reasons eleven common phenols: pentachlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-nitrophenol, 2,4-dimethylphenol, 2-nitrophenol, 2-chlorophenol and phenol have been included in the lists of priority pollutants [2]. Excessive presence of phenol and its derivatives in natural water sources is considered a serious threat to human health and overall water quality [3].

Quality assessment of natural waters in Jalingo metropolis, Taraba State, North Eastern Nigeria has faced serious neglect over the years with no or scanty work cited in literatures. This work is poised to investigate the concentrations of total phenol in natural waters intended for human consumption.

2. MATERIALS AND METHODS

2.1 Materials

All reagents were analytical grade. All plastic and glassware utilized were pre-washed with detergent water solution and rinsed with tap water.

2.2 Sampling Methods

Natural water samples were collected from river Magwoi, river Nukkai, and groundwater. The sample point was in Jalingo metropolis of Taraba State, North-Eastern Nigeria, located between latitude 8º47' to 9º01' N and longitude 11º09' to 11º30' E. The samples were obtained by grab sampling technique following procedures described by [4]. The map of Taraba showing, Jalingo the location of the sampling area is displayed in Fig. 1.

2.3 Preparation of Analytical Reagents

All analytical reagents were prepared with boiled distilled water following standard procedures. Working standards were prepared from sock standard.

2.4 Standardization of Phenol

Phenol was standardized by bromination of phenol following standard procedure adopted by [4]. 1.000 g of phenol was accurately weighed and dissolved in one litre volumetric flask using distilled water and made up to the mark and labeled as stock standard. 20 mL of phenol from the stock standard solution was taken in an iodine flask, 40 mL of distilled water, 20 mL of Winkler's solution $[KBr + KBrO_3]$ were added and the flask was shaken. Then 5 mL of concentrated hydrochloric acid was added and allowed to stand for 10 minutes after which 10 mL of $K_3[Fe(CN)_6]$ solution was added. The mixture was titrated against sodium thiosulphate (that was initially standardised by potassium dichromate) until the colour changed to pale-yellow, then 2 drops of starch indicator was added and the titration continued until the first colour disappeared. The burette reading was recorded. The titration was repeated with fresh samples until three concordance readings were obtained. Phenol concentration was calculated using the formula:

Phenol (mg/L) = 7.842[(AB- C)].

Where

C = Volume of sodium thiosulphate used for the sample

A= Volume of sodium thiosulphate used for the blank

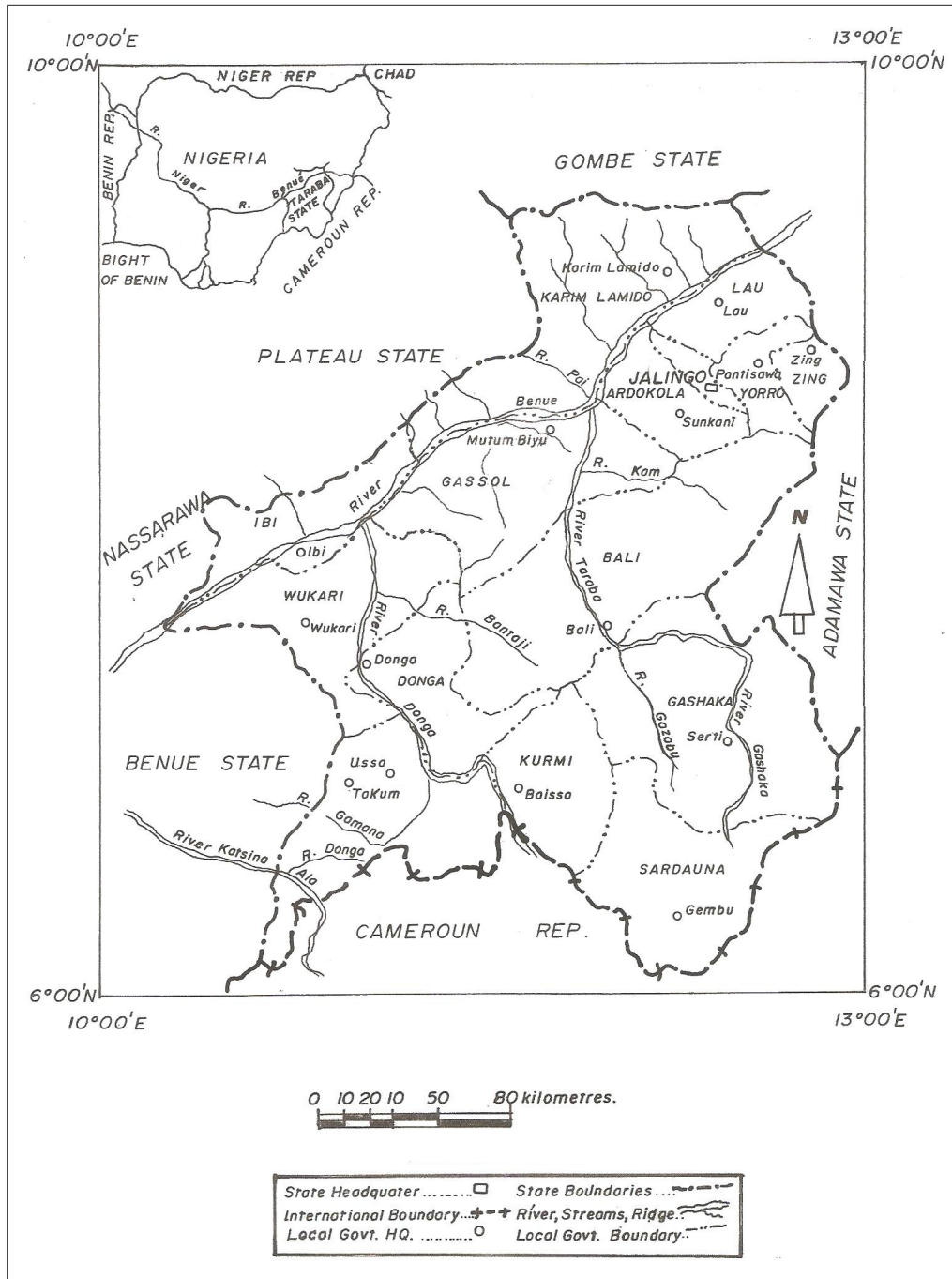B = Volume of Winkler's reagent used for the sample divided by 10

Fig. 1. A map of Taraba showing Jalingo, location of the sampling area

2.5 Construction of Calibration Curve

Calibration linearity for phenol determination was investigated by making replicates of five different concentrations. Calibration curve was constructed using working standards of phenol and a blank following standard method adopted by [4]. 300 mL distilled water blank and a series of 300 mL phenol standards containing 100 mg, 150 mg, 200 mg, 250 mg and 300 mg phenol. To the blank and standards, 10 mL of the buffer solution was added to each and the pH adjusted to about pH 10. The solution was transferred into 500 mL separating funnel, followed by the addition of 3 mL of 4-aminoantipyrene and 3 mL of potassium ferric cyanide solution thoroughly mixed and allowed to stand for 10 minutes to develop colour. The colour was extracted with 20 mL trichloromethane added to the separating funnel and shaken 20 times twice. Each extract was filtered with Whatman No. 42 filter paper containing 5 g layer of anhydrous sodium sulphate and the dry extracts were collected into clean conical flasks. The dry extracts were analysed at a wavelength of 510 nm on T-60 UV-Visible spectrophotometer (Model 2007, made in United Kingdom). Phenol concentration was calculated by the formula:

Phenol (mg/L) =

$$\frac{\text{Instrument reading (mg/L)} \times \text{dilution factor}}{\text{mL of sample used for colorimetric analysis}}$$

2.6 Recovery Study

Recovery tests were tried on two replicate samples of distilled water which were spiked with phenol at final concentration of 40 mg/L. The phenol in each case was extracted using trichloromethane, dried with sodium sulphate. The dry extracts were analysed at a wavelength of 510 nm on UV-Visible spectrophotometer.

2.7 Determination of Phenol in Natural Waters by Steam Distillation

The analytical procedure adopted was similar to that recommended by [5,6] with modification. An aliquot of 300 mL of the sample was transferred in a round bottom flask and a side condenser was fitted to the flask. The solution was heated by a mantle until 275 mL of distillate were collected. Addition of some 50 mL of distilled water in the flask was followed, to finish the steam-distillation until 300 mL of total distillate

volume was collected. 300 mL of the sample was taken in triplicates to which 10 mL of buffer solution was added to each sample and pH adjusted to 10. The solution was transferred into 500 mL separating funnel, followed by the addition of 3 mL of 4-aminoantipyrene and 3 mL of potassium ferric cyanide solution thoroughly mixed and allowed to stand for 10 minutes to develop colour. The colour was extracted with 20 mL trichloromethane added to the separating funnel and shaken 20 times twice. Each extract was filtered with Whatman No. 42 filter paper containing 5 g layer of anhydrous sodium sulphate and the dry extracts were collected into clean conical flasks. The dry extracts were analysed at a wavelength of 510 nm on UV-Visible T-60 spectrophotometer (2007 model, made in United Kingdom).

Calculation, mg/L Phenol =

$$\frac{\text{Instrument reading (mg/L)} \times \text{dilution factor}}{\text{mL of sample used for colorimetric analysis}}$$

3. RESULTS AND DISCUSSION

3.1 Standardisation of Phenol via Titrimetric Method

The result obtained from the standardisation of phenol by titrimetric titration was 817.69 mg/L served as the concentration of the stock standard and indicated that the phenol used in the work was of high quality (81.77%). This determination was crucial to obtaining working standards which were used to construct calibration curve for the determination of the concentration phenol in water on UV-Visible spectrophotometer.

3.2 Calibration Curve

The calibration curve obtained by a series of aqueous standards of phenols was linear. The results are shown in Table 1 and curve displayed in Fig. 2.

Table 1. Calibration curve

Concentration (mg/L)	Absorbance
50	0.096
100	0.1965
200	0.4020
250	0.5140
300	0.6120

The regression equation was C=0.0021A- 0.0092 and the correlation coefficient was r =0.9998 which was very close to unity. The slope of the calibration curve (change in the response signal per unit analyte concentration) is the calibration sensitivity [7]. The calibration curve was linear and therefore sensitivity was constant and independent of concentration. The calibration sensitivity was found to be 0.0021 and a linear dynamic range of 0–300 mg/L.

3.3 Recovery Study

The result of the recovery study is shown in Table 2.

The mean recovery was found to be 97.65% as in Table 2. The repeatability, as expressed by the coefficient of variation of these analyses was CV=11.6%. This fairly good precision was achieved by keeping identical time intervals for mixing of reagents, colour development and solvent extraction. The analytical method required close control of pH since colour intensity was affected. The most intense colouration resulted at pH 9 -10. Therefore the solution being buffered at pH 10 enhanced maximum sensitivity and good reproducibility of analytical results. The high mean recovery percent of phenol and low coefficient of variations (Table 2) practically corroborated the sensitivity of the method and thus its suitability for the analysis of environmental samples.

3.4 Determination of Phenol in Natural Waters

The results obtained for the determination of phenol in natural waters is displayed on Table 3.

The 1st replicate values for river Nukkai, groundwater and the 3rd replicate value for river Magwoi were considered as outliers and therefore were not included in the statistical computation. The results were of high precision as indicated by low coefficient variation (CV) being less than 5% (Table 3). It has been reported in literature that coefficient of variation of 5% or less connotes good method performance [8]. Earlier investigators have reported values of phenol concentration in the range of 0.004 – 0.012 mg/L for rivers, lakes and stream waters located in Northern Greece [9]. The values of phenol concentration in natural waters obtained in this work were considerably higher compared with those reported by [9]. Although another researcher [10] reported a higher value of 1 mg/L for phenol in tap water. The high load of phenol in all the water samples used in the work was due to degradation of lignin of plants particularly for rivers Nukkai and Magwoi. The groundwater had lower concentration of phenol compared to those of the river water (Table 3). The plausible explanation could be that it was protected against human activities (such as washing of motorcycles, automobiles, bicycles, clothing,

Table 2. Mean percent recovery of phenol

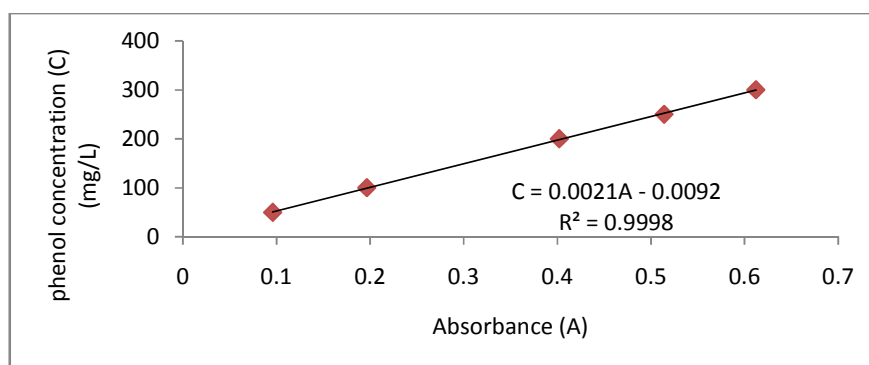| Concentration of phenol (mg/L)	Replicate 1 (mg/L)	Replicate 2 (mg/L)	Mean ± standard deviation	Relative standard deviation (RSD)	Coefficient of variation (CV)	% Recovery
40	42.64	36.19	39.415±4.560839	0.1157	11.57	97.65

Fig. 2. Calibration curve for the determination of phenol in water

Table 3. The concentrations of total phenol in natural waters

Sample source	Replicate 1 phenol (mg/L)	Replicate 2 phenol (mg/L)	Replicate 3 phenol (mg/L)	Mean± standard deviation	Relative standard deviation (RSD)	Coefficient variation (CV) %
River Magwoi	0.3825	0.4079	0.3099	0.3952±0.01796	0.004545	4.50
River Nukkai	0.3067	0.3301	0.3378	0.3340±0.00550	0.016471	1.65
Groundwater	0.3065	0.2940	0.2841	0.2891±0.00700	0.024217	2.42

bathing etc.), municipal and industrial discharges being not easily accessible compared to river waters. It is of interest to note that the rivers are surrounded by vast farm lands that were used to engage in agricultural activities from time to time. The high concentration of phenol in these water bodies gave an indication of its presence from industrial sources such as petroleum products from washing of automobiles and insecticide, herbicide, fungicide and pesticide remains from agricultural activities.

The presence of phenol even in low concentration of 1 ppb, some phenols in drinking water supplies have been reported to lead to objectionably tasting and odoriferous chlorophenols on chlorination [10]. The detrimental health implications of the toxicity of phenol cannot be compromised. Phenol and its vapour have been reported to be corrosive to the eyes, skin, the respiratory tract; inhalation of phenol vapour may cause lung excessive accumulation of serum in tissues [11]. It also has harmful effects on the central nervous system and the heart resulting in seizures and coma [12]. Long-term or repeated exposure may have harmful effects on liver and kidneys and there is no evidence that phenol causes cancer in humans [11].

4. CONCLUSION

In conclusion, the quality of natural water bodies should be monitored from time to time to ensure safe level for phenol. The European Community (EC) Directive specifies a legal tolerance level of 0.0005 mg/L for each phenol in water intended for human consumption [14] and the Japan's Ministry of Health, Labour and Welfare specified a maximum contaminant level (MCL) of 0.005 mg/L for phenols in drinking water [15]. Water treatment agencies must take into cognizance the need of post treatment of water bearing phenol to make it free of odour and bitter taste on chlorination thereby making the water safe for municipal water supplies intended for human consumption. The water bodies should also be

monitored from time to time to ascertain the level of phenol.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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