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Study of Analytical Method for Measure Phosphorus in Groundwater by UV Spectroscopy Visible

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Abstract:- In the present work, a spectrophotometric method was used for the determination of phosphorus in water samples from artesian wells of cities in the southwest of Bahia-Brazil. The method was based on the reaction of ammonium molybdate in acid medium with orthophosphate ions to form a complex, after reduction with ascorbic acid and quantification by spectrophotometry. The maximum wavelength of the complex formed was at 880 nm. The calibration curve showed a linear relationship between phosphorus concentrations and absorbance in the concentration range of 0.04 to 1.0 mg L^{-1} with a linear correlation coefficient equal to 0.993. The method quantification limit was evaluated at 0.04 mg L^{-1}. The addition and phosphorus recovery tests showed that there was no matrix interference in the procedure. The RSD value was less than 0.07% and recovery was within the range of 97.2 to 98.8%, indicating good precision and accuracy of the method. The phosphorus concentration in the samples analyzed was between 0.134 ± 0.002 to 1.106 ± 0.053 mg L^{-1}, exceeding the maximum limit established by CONAMA for freshwater, belonging to Class I.

Keywords:- *Spectrophotometry; Water; Quality.*

I. INTRODUCTION

Groundwater is of fundamental importance in public and private water supply worldwide. Around 1.5 billion people living in urban centers and a large portion of the rural population have their needs supplied by groundwater [1].

The main advantages of using underground water are related to (i) the low cost of well construction in contrast to the cost of surface water abstraction works, (ii) the supply alternative for small and medium urban populations or rural communities and (iii) the fact that it generally presents good quality for human consumption [2].

In Brazil, the distribution of underground water, like rainfall, is not uniform throughout the country. Some regions have an abundance of this resource and others have extreme scarcity. The amount of water available in the country is sufficient to meet the demand for water needed for the use of the Brazilian population, however, a large part of the people do not have access to this benefit [3].

Currently, the monitoring of phosphorus in water has been considered extremely relevant in public policies that deal with water quality as a life-sustainer and for public supply purposes [4]. This nutrient may be present naturally in water by dissolution of rocks, decomposition of organic matter, by the soil, among others, and may be caused by human action, through the discharge of untreated effluents and the use of chemical fertilizers in agriculture [5]. Although phosphorus is very important for all forms of life, the excess in water is responsible for the process of eutrophication, which causes the accumulated growth of algae and heterotrophic bacteria, modifying the physical-chemical character of water, reducing the amount of dissolved oxygen and precipitating heavy metals such as iron [6].

UV-VIS spectrophotometry has been widely employed for the determination of chemical species in various samples and evaluation of their possible toxic effects. The technique has as its principle the quantitative measurement and analysis of specific light spectrum used in biological and physicochemical investigations. The concentrations in the analyzed solutions are defined from the amount of light absorbed during the process.

In view of the above, the present work aimed to study a method for determining the concentration of soluble phosphorus in water samples from artesian wells in the southwestern region of Bahia using UV-VIS spectrophotometry as an analytical technique.

II. EXPERIMENTAL METHODOLOGY

The samples were collected in glass vials previously washed with diluted hydrochloric acid and rinsed several times with ultrapure water. In order to preserve them until the moment of the analysis, the samples were filtered and stored under refrigeration at 4°C. The analyses were performed in the Analytical Chemistry Laboratory of the University Southwest Bahia, Campus de Vitória da Conquista, where 5 samples of artesian well water from the following municipalities were analyzed: José Gonçalves, Veredinha, Barra do Choça, Itarantim and Cândido Sales.

Each sample was analyzed in triplicate, with the objective of evaluating the precision of the method applied. In the samples identified by the letters A, B, C, D, and E, the phosphorus concentrations were determined.

The experimental procedure consisted in the preparation of a calibration curve using standard phosphorus solutions with concentrations between 0.0 and 1.0 mg L^{-1}. Subsequently, 8.00 mL of a reagent mixture consisting of 60.00 mL of H_2SO_4 2.5 mol L^{-1}, 20.00 mL of $C_8H_4K_2O_{12}Sb_2$, 20.00 mL of $(NH_4)_6Mo_7O_{24}$ and 0.7000 g

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of $C_6H_8O_6$ was added to these solutions. The blank solution was made following the previous procedure, i.e., using all reagents except the phosphorus stock solution. After preparing the solutions, the absorbance was determined for each known concentration and the graph of the calibration curve was drawn to obtain the straight line equation and the respective correlation coefficient.

To prepare the samples, each was filtered using a system composed of a Buchner funnel, a kitassat, and a vacuum pump. After filtration, 50.00 mL of the sample was pipetted and transferred to a 125 mL erlenmeyer flask. Using a pasteur pipette, two drops of the 0.1% (w/v) phenolphthalein indicator were added to the samples. Each sample was then titrated using 3 mol L^{-1} NaOH solution until the titrate changed color. After titration the samples were neutralized with H_2SO_4 solution. Subsequently, 8.00 mL of the reagent mixture was added to each sample. After that, a 10 minute interval was allowed for the reaction to take place.

The absorbance measurements for phosphorus determination were performed in a UV-VIS spectrophotometer (Celm, E 225D visible) using 1 cm silicate glass cuvettes with a wavelength equal to 880 nm. Finally, the samples had the phosphorus concentrations determined by interpolation to the previously prepared calibration curve.

III. RESULTS AND DISCUSSION

The method used for phosphorus determination was based on a specific reaction for ortho-phosphate ions, using previously filtered water samples. All forms of phosphorus present in natural waters, whether in ionic or complexed form, are found in the form of phosphate [7].

Ammonium molybdate was reacted in an acid medium with the orthophosphate ions so that formation of ammonium phosphomolybdate occurred. Ascorbic acid was employed to reduce the product formed to a complex of intense blue coloration. As the reduction reaction with ascorbic acid is relatively slow, the reaction speed was increased by employing potassium antimony double tartrate to act as a catalyst. The color of the complex formed was shown to be proportional to the phosphorus concentration.

The graphical representation of the wavelength values (X) versus absorbance allowed the determination of the maximum absorbance value of the complex formed at 880 nm, as shown in Figure 1.

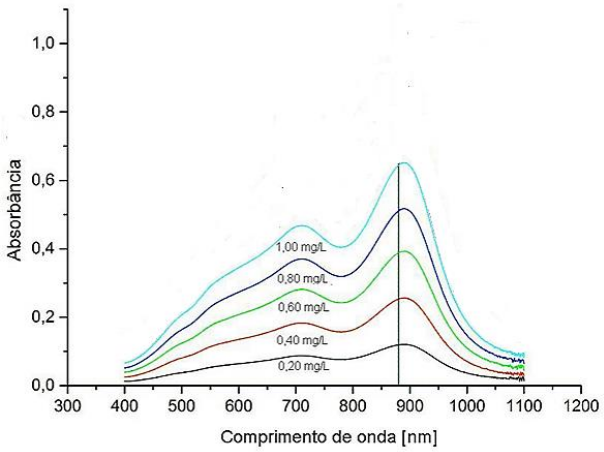

Fig. 1: Absorption spectrum of the blue phosphorus complex formed

The linearity of the method was evaluated to characterize the ability to obtain results directly proportional to the concentration of phosphorus in the sample, within a specific range [8]. For this purpose, different solutions with exact and known concentrations of PO_4^{3-} were introduced into the spectrophotometer, and the instrumental response was recorded. This response was corrected for the value obtained with the blank, which measured the response of the analytical method for impurities or interfering species in the reagents. This parameter was measured by statistical analysis of variance, obtaining significant results for the linear regression and non-significant results for the linearity deviation ($p < 0.05$).

Thus, the calibration curve was constructed with the purpose of obtaining a mathematical relationship between absorbance and concentration. This relationship was found by means of the straight line equation shown in Table 1. The correlation coefficient found for the mean curve was 0.993, demonstrating a linear response of the equipment for the concentration range used in obedience to Beer's law.

Parameter	Results
Linearity range (mg L^{-1})	0.040 a 1.0 mg L^{-1}
Equation of the straight line	$Y = 0.721 [PO_4^{3-}] – 0.021$
Slope (b) ± standard deviation	0.021 ± 0.124
Slope (a) ± standard deviation	0.721 ± 0.82
Correlation Coefficient (R)	0.993

Table 1: Data referring to the linearity of the method studied

The sensitivity of the method was analyzed by determining the limits of detection (LD) and quantification (LQ). For these parameters the calculated values were 0.015 and 0.040 mg L^{-1}, LD and LQ, respectively. Analyzing the LQ value lower than the minimum concentration established in the quantification interval, it can be seen that the applied method presents excellent sensitivity.

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The precision, expressed as relative standard deviation of ten determinations, was equal to 0.07%. This parameter was evaluated in a water sample with a PO_4^{3-} concentration of approximately 0.50 mg L^{-1}.

The accuracy was evaluated by addition and recovery tests of PO_4^{3-} in water samples. The samples showed recovery of PO_4^{3-} ranging from 97.2% to 98.8%. The results obtained indicate that the method has a good accuracy and did not suffer any influence of the matrix on the analytical procedure applied.

Table 2 shows the mean concentrations of phosphorus determined in water samples A, B, C, D, and E from artesian wells. Along with the concentration values, the respective standard deviations are presented, considering that all samples were analyzed in triplicate to evaluate the precision of the measurements.

It can be observed that the phosphorus concentration determined in the samples ranged between 0.134 ± 0.002 and 1.106 ± 0.053 mg L^{-1} as shown in Table 2. There is no Brazilian legislation related to the maximum amount of phosphorus allowed in waters from artesian wells intended for human consumption. However, the Dutch legislation determines that the level of phosphorus in underground waters does not generate problems when its concentration is equal or lower than 0.05 mg L^{-1} [9].

Sample	Concentration (mg L^{-1})
A	1.106 ± 0.053
B	0.143 ± 0.001
C	0.157 ± 0.001
D	0.135 ± 0.001
E	0.134 ± 0.002

Table 2: Mean values of phosphorus concentrations (mg L^{-1}) with their respective standard deviations in the analyzed artesian well samples

The results obtained in this study showed that all samples have phosphorus concentrations above 0.05 mg L^{-1}. These concentration values, suggest that the analyzed water samples are not indicated for human consumption. The concentration values found in this study were similar to those reported by [9], in which 25% of the samples from artesian wells analyzed had phosphorus concentration values higher than those recommended by Dutch legislation.

Artesian wells located in agricultural areas have higher phosphorus values when compared to wells located in urban areas [10]. This fact highlights that the water from artesian wells can be altered depending on where it is drilled. In this context, the use of fertilizers in rural areas favors the contamination of water tables, consequently increasing the concentration of phosphorus in the water. Among the samples analyzed, sample A presented the highest concentration of phosphorus. This fact can be justified due to the location of the artesian well, which has crops in its surroundings and, consequently, the contamination by phosphorus may have been caused by widely used fertilizers.

According to Resolution No. 357/2005 of the National Council of Environment (CONAMA), freshwater, belonging to class I, intended for domestic supply (after simplified treatment), irrigation of vegetables and fruits that are consumed raw, among other requirements, must have a total phosphorus content of up to 0.025 mg L^{-1}.

Thus, given this data, it is possible to observe that the analyzed waters present a phosphorus concentration above the maximum limit allowed. Although the studies of water quality for irrigation depend on a set of physical, chemical and biological characteristics, it is possible to affirm that the water samples analyzed are not appropriate for irrigation as far as the concentration of phosphorus is concerned.

IV. CONCLUSION

The values of phosphorus determined in the samples of artesian well water exceeded the levels considered appropriate for human consumption, which can lead to a series of diseases. The values of phosphorus concentration determined in the samples also indicated that they are not appropriate for the practice of irrigation in crops.

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