Spectrophotometric analysis of phosphate concentration in agricultural soil samples and water samples using molybdenum blue method

Funmilayo Enitan Adelowo and Solomon Oluwole Oladeji

Department of Pure and Applied Chemistry. Ladoke Akintola University of Technology. P. M. B. 4000. Ogbomoso. Nigeria. Email: oladeji_oluwole@yahoo.com, feadelowo@lautech.edu.ng.

Abstract. Phosphorus has a strong affinity for soil thereby increasing the rate of dissolved phosphorus that will be transported in runoff. The most important contributing factor for increasing in phosphates levels are natural and human factors such as dumping of refuse from nearby areas, use of fertilizers and human excretes. The phosphate levels in the soil and water samples (expressed in part per million) was analyzed by molybdenum blue phosphorus method using a simple analytical and UV-visible spectrophotometric method and the phosphates level was measured at 740 nm. The calibration curve was formed using concentrations of 0.5-3.0 mg/L. The samples analyzed showed high levels of phosphates which could be due to domestic, natural and agricultural factors.

Keywords: Phosphates levels; Molybdenum blue phosphorus method; Calibration curve; Pollutants; UV-visible spectrophotometer.

Received June 30, 2016

Accepted December 22, 2016

Released December 31, 2016



Open Acess Full Text Article



ORCID © 0000-0001-7748-6131 Funmilayo Enitan Adelowo © 0000-0002-8534-7331 Solomon Oluwole Oladeji

Introduction

The chemistry of soil indicates that it contains several chemical components ranging from organic to inorganic compounds. Scientifically, it is defined as the outermost or weathered superficial layer of the earth's crust. They are consists mainly of decomposed parent rock material (organic matter), mineral (inorganic) matter, water, air and organisms (Weier, 1973). Soil is a complex system which includes Soil and water is one of the major constituents of the earth. Geographically, the earth crust contains 70% of water (hydrosphere) (Oladeji et al., 2016). From recent researches, scientists discovered that soil and water contains many metals, chemical constituents or compounds. Some of these include phosphates, nitrates and sulphates amongst others. From soil the plant absorbs water and solutes necessary for its continued well-being.

Phosphorus is an important nutrient that occurs widely in the environment. It is the key elements necessary for the growth of plants and animals and also, assists in metabolism. In the earth crust, it is the eleventh most abundant element on the surface of the earth and is most commonly found as phosphate (Chaube and Gupta, 1983). Eutrophication of surface water is caused by increase level of phosphate in water and this increases the growth of algae thereby reduce the light intensity and level of dissolved oxygen in the water. Researches and recent report indicates the high utilization of phosphates in detergents, fertilizers, sugar industries amongst others, thus the determination of phosphorus is important to water analyst and limnologist (Kharat and Pagar, 2009). Due to these reports, various phosphate determination procedures titrimetry, complexogravimetry, absorption colorimetry, atomic spectroscopy, flow injection analysis, and spectrophotometry methods (Verma, 1988; Bøtker et al., 1994). In the attempt to quantitate the phosphate level, spectrophotometric methods have been preferred because it involves no extraction, sosphicated instruments and easily accessible. The commonest spectrophotometric includes molybdovanadate ammonium and molybdate methods (Vogel, 1999). In ammonium molybdate spectrophotometric method, reducing agents such as tin(II) chloride, ascorbic acid and 1-amino-2naphthol-4-sulfonic acid are often preferred. It also involves the formation of molybdophosphoric acid from ortho phosphate and an excess of molybdate in acidic solution followed by reduction to give molybdenum blue. The concentrations or phosphate levels in the sample is proportional to the intensity of colour produced and the absorbance is measured spectrophotometrically at а certain wavelength. In the attempt to reduce the health and environmental hazards by phosphate contamination,

spectrophotometrically analysis of phosphate in soil and water sample is inevitable.

Materials and methods

Chemicals and reagents

All the chemicals and reagents used were analytical reagent grade unless otherwise stated and the solutions were prepared in double distilled water.

Instruments

The absorbance were determined using ultraviolet visible spectrophotometer, model WPAS 104 UK with 1 cm matched quartz cells.

Preparation of standard solutions (stock solution)

potassium About 0.717 g of dihydrogenphosphate (KH_2PO_4) was accurately weighed and dissolved in double distilled water and the volume was made 500 mL in a volumetric flask. The working phosphate solutions different of concentrations were prepared by serial dilution of the stock solution (Oladeji et al., 2016).

Preparation of working solution of ammonium molybdate

About 1.7081 g of ammonium molybdate was accurately weighed and dissolved in 100 mL of warm water; a milky colouration was observed, cooled and transferred into 250 mL volumetric flask.

Preparation of dilute hydrochloric acid

A measured amount of concentrated hydrochloric acid solution was diluted and made up to mark in a 100 mL of volumetric flask.

Preparation of dilute trioxonitrate (V) acid

A measured amount of 50 mL of concentrated trioxonitrate (V) acid solution was diluted and made up to mark in a 100 mL of volumetric flask.

Preparation of hydrazine hydrate

About 0.125 g of hydrazine sulphate was accurately weighed and dissolved with double distilled water in a clean beaker in a 100 mL standard flask and made up to calibrated mark.

Soil sample collection and preparation.

Soil sample was taken from Goddex and Linkway Farms in Ogbomoso. The sample was dried for 10 days, sieved and stored for further analysis.

Water sample collection and preparation

About 50 mL of water samples were collected in March, 2016 from three major rivers (Arowomole, Odoje and Alapata Rivers) located in the Southern part of Ogbomoso, Nigeria. The water samples were filtered using filter paper No. 42. The filtered samples was then stored in clean sample bottle.

Soil sample analysis for phosphates

About 2 g of the soil sample was accurately weighed and placed in a 250 mL conical flask, 60 mL of HCl and HNO3 (ratio of 3 to 1) was added and shaken in a mechanical shaker for 30 min. The digestion was done for 6 h:30 min. This was then filtered using filter paper Whatmann No. 41. About 15 mL of the filtered digested sample was taken, 3 mL of ammonium molybdate, 2 mL of hydrazine sulphate was added and kept in a water bath for 30 min. The blue colour observed was spectrophotometrically measured (Amponsah et al., 2014).

Water sample analysis for phosphates

About 15 mL of the filtered water sample was accurately measured, 3 mL of ammonium molybdate, 2 mL of hydrazine sulphate was added and kept in a water bath for 30 min. The blue colour observed was measured spectrophotometrically (Amponsah et al., 2014).

Results and discussion

Determination of maximum absorbance

The absorption spectral data of the potassium dihydrogenphosphate used as standard against the reagent blank (water) exhibit the wave length of maximum absorbance around 740 nm.

Calibration curve for the standard (KH₂PO₄)

The molybdenum blue method is based on the formation of phosphomolybdate. At effective analytical conditions, the amount of phosphates is proportional to the intensity of colour (blue) in the stock solution (KH_2PO_4) . The calibration curve of the absorbance from UV-visible spectrophotometer the of concentrations 0.5-3.0 mg/L, respectively, is given below in Figure 1 from Table 1.

Phosphate analysis in soil and water samples

The analytical results of phosphate analysis in soil and water samples are shown in Table 2. The phosphates concentration in soil and water was obtained by interpolating the calibration curve in Fig 1. The highest concentration of phosphate was obtained from Goddex Farms (S_{F1}) with a concentration of 2.80 mg/L, the lowest being Odoje River with concentration (W_2) of 1.480 mg/L. The uses of fertilizers, detergents, fungicides and even paints have been discovered to be the major pollutants in Ogbomoso, Nigeria. There is no healthbased guideline proposed for phosphate consumption, thou, medically high intake of phosphate can cause health problems like cancer, ulcers, kidney problems, brain damage and gastrointestinal effects. The use of fertilizers, herbicides, fungicides in farm help improve the quality of farm produce. The environmental protection agency has a recommended limit for phosphates levels in soil and water bodies. For streams and rivers the Environmental Protection Agency recommended limit is 0.1 mg/L. The following recommendations are also given for phosphate consumptions: total phosphorus; no more than 0.1 mg/L for streams which do not empty into reservoir, 0.05 mg/L for streams discharging into reservoirs and 0.025 mg/L for reservoirs (Oladeji et al., 2016). It is recommended that health authorities be notified of sources of drinking. Man made sources of phosphate include human sewage, agricultural run-off from crops, sewage from animal feedlots, pulp and paper industry, vegetable and fruit processing, chemical and fertilizer manufacturing, and detergents (McCoy, 2011).

Table 1. The absorbance, A_T obtained from different concentration (mg/L) of potassium dihydrogenphosphate.

	Ст	$\mathbf{A}_{\mathbf{T}}$
1.	0.00	0.000
2.	0.50	0.230
3.	1.00	0.386
4.	1.50	0.580
5.	2.00	0.759
6.	2.50	0.831
7.	3.00	1.172

Where CT = concentration (mg/L); $A_T = absorbance$.



Figure 1. The calibration curve for the standard solution (KH₂PO₄)

The highest concentration of phosphates at Goddex Farms (S_{F1}) could be attributed to the mixed farming activities in the farm. There was an indication that the use of manure (cow dung) and inorganic fertilizers (phosphate fertilizers) was the usual practice in this farm. The use of fertilizers in agriculture is paramount when compare with herbicides, fungicides and nematocides uses. The high level of phosphates in soil samples taken from maize fields (SF1 and SF2) could be due to the use of phosphates fertilizers and have higher level when compared to soil samples

taken from lands sprayed with phosphates fungicides. In water samples, the high level of phosphates was recorded in Arowomole River (W_1). This could be due to the industrial, human and farming activities in the community. The dumping of refuse, sewage, human waste could also be a major factor. The laundry activities, car-washing, block industry and also farming activities are also major contributing factors (McCoy, 2011). Also, in Alapata River, W_3 , residents close to this water source uses phosphate containing detergents.

Table 2. The absorbance of the water samples and their corresponding concentrations obtained from the calibration curve.

Sampling Area	Ст
W1	1.650
W2	1.480
W3	1.510
SF1	2.800
SF2	2.650
SP1	1.970
SP2	2.050

Where C_T concentration (mg/L)

The increased eutrophication have some negative environmental and human impacts such as reduced aesthetic and recreational value of lakes, river and stream as well as the seasonal depletion of the water dissolved oxygen content, and this could leads to destruction and even death of fish as well as other ecosystem disruptions (Smith et al., 1999).

The soil and water samples showed that all the samples exceeded the recommended phosphate concentration level. The high concentration of phosphates is due to natural and human factors such as erosion, leaching and weathering and also, runoff from nearby farm and nearby residential areas.

Conclusion

The spectrophotometric analysis using ammonium molybdate as reductants proved effective analytical for the determination of phosphate. It involves the phosphomolybdate reduction of by dihydrogenphosphate. potassium The phosphate concentration in the samples was measured at 740 nm. The phosphates levels are high in all the samples when compared to the Environmental Protection Agency. This could be due to natural such as erosion and weathering, agricultural and also human activities. In the attempt to prevent the effects of high phosphates, the use of phosphate containing materials such be reduce and the people in these area should be enlighten on the health effects on these phosphate levels can cause.

Acknowledgements

The authors are grateful to the Laboratory Technologists of the Applied Department of Pure and LAUTECH. Chemistry, Ogbomoso, Nigeria, for the assistance and encouragement during the course of the research.

Conflicts of interest

Authors declare that they have no conflict of interests.

References

Amponsah, D.; Etsey, G.; Nagai, H. Determination of amount of phosphate and sulphate in soil samples from university of Cape Coast Farm. **International J. Sci. Tech. Res.**, v. 3, no. 7, 2014.

Bøtker, H. E.; Kimose, H. H.; Helligsø, P.; Nielsen, T. T. Analytical evaluation of high energy phosphate determination by high performance liquid chromatography in myocardial tissue. **Journal of Molecular and Cellular Cardiology**, v. 26, no. 1, p. 41-48, 1994. http://dx.doi.org/10.1006/jmcc.1994.1006 Chaube, M. A.; Gupta, V. K. Spectrophotometric determination of phosphate in polluted waters by solvent extraction of molybdenum blue. **Analyst**, v. 108, p. 1141-1144, 1983.

http://dx.doi.org/10.1039/AN9830801141

Kharat S. J.; Pagar, S. D. Determination of phosphate in water samples of Nashik District Rivers by UV-visible spectroscopy. **E-Journal Chem.**, v. 6, Suppl. 1, p. S515-S521, 2009. http://dx.doi.org/10.1155/2009/913609

McCoy, M. Goodbye phosphates. **Chemical** and Engineering News, v. 89, no. 4, p. 12-17, 2011. Available from: https://pubs.acs.org/cen/coverstory/89/8904cover.html. Accessed on: Jun. 23, 2016.

Oladeji, S. O.; Adelowo, F. E.; Odelade, K. A. Evaluation of phosphate level in water samples (Ogbomoso Rivers) using UV-visible spectrophotometric method. **Int. J. Sci. Res. Env. Sci.**, v. 4, no. 4, p. 102-108, 2016. http://dx.doi.org/10.12983/ijsres-2016-p0102-0108

Smith, V.; Tilman, G.; Nekola, J. Eutrophication: impacts of excess nutrient in freshwater, marine and terrestrial ecosystems. **Environ. Pol.**, v. 100, no. 1/3, p. 179-196, 1999. http://dx.doi.org/10.1016/S0269-7491(99)00091-3

Verma, N. C. System of technical control for cane sugar factories in India. The Sugar Technologists Association of India, 1988.

Vogel, A. A text book of quantitative chemical analysis. 5. ed. London: Longmans, 1991.

Weier T. E.; Stocking C. R.; Barbour, M. G. An introduction to plant Biology. 5. ed. Davis, California: University of California, 1973.

License information: This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.