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FLOATATION — SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS AS BRILLIANT GREEN-MOLYBDOPHOSPHATE ION-PAIR

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Abstract: Orthophosphate in natural waters is determined spectrophotometrically as Brilliant Green-Molybdophosphate ion-pair. The ion-pair is floated as a membrane-like substance at the interface between the aqueous and diethyl ether phases. After discarding the aqueous phase, the excess of Brilliant Green extracted into the diethyl ether alongwith the ion-pair is removed by shaking with 25 ml of 1.0 M hydrochloric acid. The floated ion-pair is dissolved in methanol and absorbance is measured at 625 nm against methanol. The calibration graph is linear upto 1 μg with a relative standard deviation of 3.2% at 0.3 μg phosphate phosphorus. The detection limit is 2.5 μg l^{-1} which is twice of the standard deviation of the reagent blank. The apparent molar absorptivity for orthophosphate phosphorus is $1.25 \times 10^4 l\ mol^{-1}cm^{-1}$. Arsenic (V), citrate, tartrate and sulphate interfere.

Keywords: Phosphorus determination; molybdophosphate; brilliant green; floatation spectrophotometry; natural waters.

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INTRODUCTION

A variety of sensitive spectrophotometric and spectrofluorometric methods are available for the determination of phosphorus as orthophosphate in environmental, clinical and agricultural samples. Mostly they are based on various modifications and improvements in yellow molybdophosphate and molybdenum blue methods. A variety of cationic dyes such as malachite green[1-6], rhodamine B[7-10], ethyl violet[11], methylene blue[12], Ravanol[13], bis[2-(5-chloro-2-pyridylazo)-5-diethyl(amino) phenolate] cobalt (III) chloride[14], phenosafranine[15] and crystal violet[16,17] are used for ion-association of molybdophosphate anion.

The resultant ion-pairs are either extracted into organic solvent or floated on the surface of interface of aqueous and organic phases and then dissolved or extracted with the help of another organic solvent or a mixed solvent system, or pre-concentrated by membrane filtration, flow injection or stopped flow time difference analysis. The absorbance of resultant coloured phase is measured at a wavelength of maximum absorbance. Some of these methods[4,9] are claimed to be suitable down to ppb phosphorus level.

In the present communication, a floatation-spectrophotometric method for the determination of orthophosphate phosphorus has been described. Brilliant green, a cationic dye, has been used as ion-pairing reagent for molybdophosphate anion. This dye has been reported for the determination of perchlorate[18] and iodide[19].

The molybdophosphate (P) anion, formed as a result of reaction between orthophosphate and molybdate anions in acidic media, is floated in the form of ion-pair with brilliant green (BG) at the interface of aqueous-diethyl ether phase. After washing with hydrochloric acid to remove excess of BG, floated brilliant green-molybdophosphate (BG-P) ion-pair in diethyl ether is dissolved in methanol and absorbance is measured at 625 nm. The method is successfully applied for the determination of phosphorus at ppb level in natural water samples. This method has the advantage over some reported ones[7,8] in removal of excess of ion-pairing reagent from diethyl ether phase with chloroform and equally compatible[9] in using a less toxic hydrochloric acid (over chloroform) for this purpose. Various experimental parameters are studied to evaluate the usefulness of the method.

EXPERIMENTAL

Equipment

Perkin Elmer Lambda 3B UV-VIS Spectrophotometer with matched 10 mm glass cells was used for all absorbance measurements. A Corning pH meter with a combined glass electrode was used for pH measurements.

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Reagents

All chemicals were analytical-grade reagents from Merck and used without further purification. Distilled water was used throughout.

1000 µg/ml standard stock solution of phosphorus was prepared by dissolving 4.394 g of KH_2PO_4 in water and making up the volume to one litre. To make 0.2 M ammonium molybdate solution, 3.531g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (MW 1235.9) was dissolved in 100 ml water. 1.255 g of BG($C_{27}H_{34}N_2O_4S$, MW 482.64, 96%) was dissolved in 250 ml water to make 0.01M solution and stored in amber bottle. It was prepared freshly every week and diluted as required. H_2SO_4 (95-98%) and HCl (37%) were appropriately diluted with water to make 3.0 M and 1.0 M solutions respectively and stored in polyethylene bottles.

Recommended Procedure

Take sample solution containing upto 1µg of phosphorus in a 50 ml beaker and add 5 ml of 3.0 M sulphuric acid, 7 ml of 0.2 M ammonium molybdate and 5 ml of 1.2×10^{-4} M BG solution. Dilute the mixture upto 20 ml with water, mix well and let stand for 20 minutes at 30-35°C to ensure the reaction to occur. Transfer the solution into a 100 ml separating funnel, add 10ml of diethyl ether, shake thoroughly for 2 minutes to float the BG-P ion-pair and discard the aqueous phase. Remove the excess of BG extracted into diethyl ether by shaking the funnel for 1 minute with 25 ml of 1.0 M hydrochloric acid. Again discard the aqueous phase and add 15 ml of methanol to the organic phase and mix well for 30 seconds to dissolve the floated ion-pair. Transfer the solution into a 25 ml measuring flask, make up the volume with diethyl ether and measure the absorbance at 625 nm against methanol. Follow the same procedure for standards and reagent blank containing no phosphorus.

RESULTS AND DISCUSSION

Selection of Solvent and λ_{max}

A number of organic solvents such as benzene, cyclohexane, amyl alcohol, chloroform and diethyl ether were studied for the extraction/floatation of BG-P ion-pair. Diethyl ether gave satisfactory results for floated ion-pair because excess of BG extracted into diethyl ether was easily removable by shaking with 1.0 M hydrochloric acid.

Dissolution of floated ion-pair was examined in acetone, methanol, butanol, benzyl alcohol and carbon tetrachloride. Methanol gave better results and was chosen for its easy handling and comparatively less toxic nature. Maximum and minimum absorbance for the ion-pair and reagent blank respectively was observed at 625 nm. It was found to be independent of various reagents employed in aqueous system.

Selection of Acid and Effect of its Concentraton

To adjust the acid concentration in aqueous media for BG-P ion-pair formation, commonly used acids (HNO_3, HCl, $HClO_4$ and H_2SO_4) were examined. Maximum absorbance was found with sulphuric acid.

Effect of concentration of sulphuric acid was studied by the sequence described in the procedure and varying the concentration of the acid (5 ml, 1.5 - 4.0 M). Maximum difference in absorbance intensity of the ion-pair and reagent blank was observed when acid concentration of aqueous phase was adjusted to 0.75 M.

Molybdate Concentration

The effect of the concentration of molybdate on the ion-pair formation is shown in Fig.1. A constant and maximum absorbance is observed at molybdate concentration above 5×10^{-2}M in aqueous phase. An optimum concentration, 7×10^{-2}M, was maintained by 7 ml of 0.2 M molybdate solution.

Brilliant Green Concentration

Effect of the concentration of BG on the absorption intensity of BG-P ion-pair is given in Fig.2. The absorption intensity becomes constant and maximum above 2.4×10^{-5}M BG concentration in aqueous media.

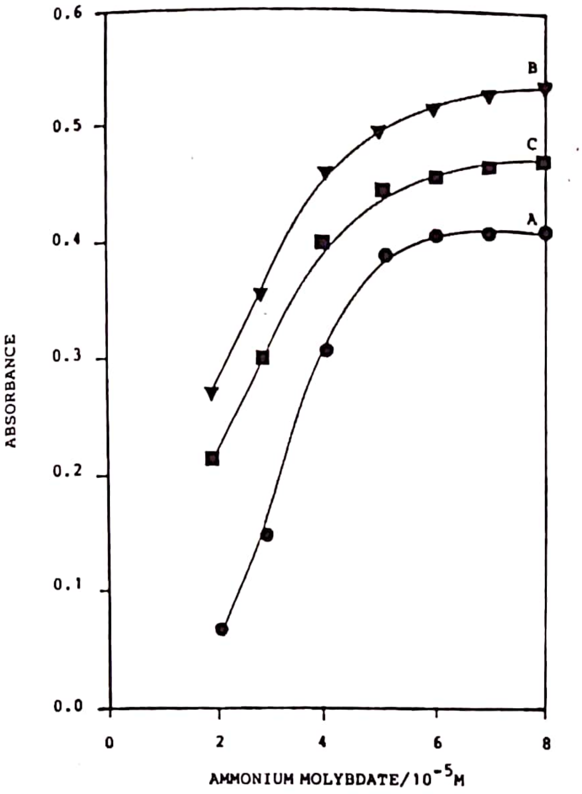

Fig.1 Effect of the concentration of molybdate on the ion-pair formation.

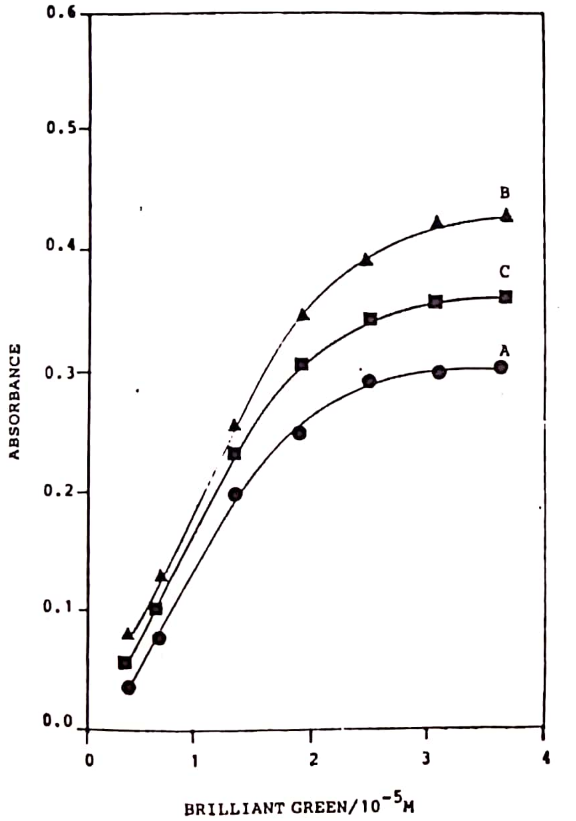

Fig.2 Effect of the concentration of BG on the absorption intensity of BG-P ion-pair.

Therefore, concentration of BG in aqueous phase was adjusted to 3.0 x 10^{-5}M.

Removal of Excess of BG

In order to remove excess of BG extracted into diethyl ether phase, water and various concentrations of hydrochloric acid (0.5 - 3.5 M) were examined. 1.0 M hydrochloric acid (20 ml) gave better absorption intensity for the ion-pair and lower absorption for reagent blank. To study the effect of volume of 1.0 M hydrochloric acid on the removal of excess of BG prior to the dissolution of BG-P ion-pair, various volumes of 1.0 M acid (10 - 50 ml) were employed. The results in Fig.3 show that better removal is obtained with 20-30 ml aliquots of the acid. Therefore, 25 ml portion of 1.0 M hydrochloric acid was used to remove the excess of BG.

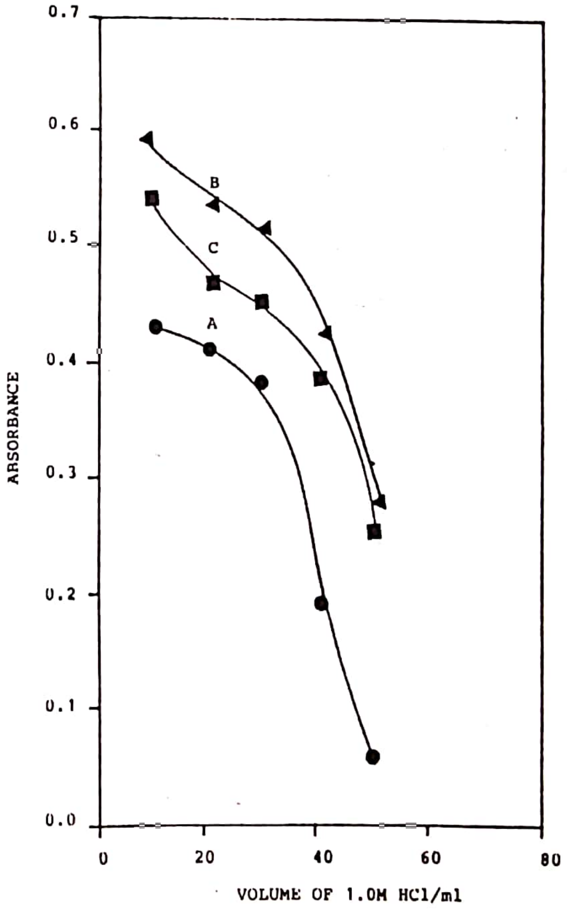

Fig.3 Effect of the volume of 1.0 M hydrochloric acid on the removal of excess of BG prior to the dissolution of BG-P ion-pair.

Spectroscopic Characteristics

Absorption intensity of a series of standard solutions of orthophosphate-phosphorus (0.05 - 3µg) was measured as described in procedure. The calibration graph was linear upto 1 µg with a relative standard deviation of 3.2% at 0.3 µg of phosphorus for 7 determinations. The highest apparent molar absorptivity as calculated from the slope was 1.25 x 10^4 l mol^{-1} cm^{-1} at 625 nm. The calculated detection limit was twice of the standard deviation of reagent blank, i.e. 2.5 µg l^{-1}.

Effect of Foreign Ions

The effect of foreign ions on the determination of 0.3 µg phosphate-phosphorus by the proposed method is summarized in Table 1. From the data, it appears that a large number of anions and cations do not show significant interference. Many of them can be tolerated upto equivalent amount of phosphorus taken. Tartrate by suppressing and arsenic (V), citrate and sulphate by enhancing the absorption of system interfere severely, while Cr(III), Fe(III), fluoride, iodide and perchlorate interfere slightly by suppressing the absorption intensity.

Table 1

Effect of foreign ions on the determination of 0.3 µg phosphorus

Ion	Added As	Amount Taken/µg	Phophorus Found/µg
None		-	0.30
K^+	KCl	0.3	0.32
Na^+	NaCl	0.3	0.29
Mg^{2+}	$MgCl_2.6H_2O$	0.3	0.28
Co^{2+}	$CoCl_2.6H_2O$	0.3	0.32
Al^{3+}	$KAl(SO_4)_2.12H_2O$	0.3	0.29
As^{5+}	$Na_2HAsO_4.7H_2O$	0.3	0.50
Fe^{3+}	$Fe_2(SO_4)_3.xH_2O$	0.3	0.26
Cr^{3+}	$CrCl_3.6H_2O$	0.3	0.27
Cr^{6+}	$K_2Cr_2O_7$	0.3	0.30
Tartrate	$Na_2C_4H_4O_6.2H_2O$	0.3	0.24
Citrate	Tri-Sodium Citrate	0.3	0.42
HCO_3^-	$NaHCO_3$	0.3	0.32
NO_3^-	$NaNO_3$	0.3	0.28
SO_4^{2-}	Na_2SO_4	0.3	0.40
SiO_4^{4-}	Na_4SiO_4	0.3	0.28
F^-	NaF	0.3	0.27
I^-	KI	0.3	0.26
ClO_4^-	$KClO_4$	0.3	0.26

Determination and Recovery of Phosphate-Phosphorus in Natural Waters

Orthophosphate phosphorus contents in some natural water samples collected from Northern areas of Pakistan were determined by the proposed method using a 2 ml aliquot. Standard addition technique was used for accurate measurements. The results are given in Table 2. The range of recoveries of phosphorus in natural water samples is 85 - 112% which is satisfactory.

Table 2

Recovery of phosphate-phosphorus in some natural water samples

Sample	P/µg Added	P/µg Found	Recovery %	Ethyl violet method[11] (P/µg)
1. Gomal Water	-	0.60	-	0.61
	0.2	0.80	100	-
	0.5	1.35	110	-
2. Nilter River	-	0.80	-	0.82
	0.2	0.98	90	-
	0.5	1.32	104	-
3. Hunza River	-	2.60	-	2.50
	0.2	2.78	98	-
	0.5	3.11	102	-
4. Glacier Water (Hunza Valley)	-	0.96	-	1.00
	0.2	1.20	112	-
	0.5	1.48	104	-
5. Kaghan Water	-	2.60	-	2.70
	0.2	2.79	95	-
	0.5	3.10	100	-
6. Spring Water	-	1.00	-	0.97
	0.2	1.17	85	-
	0.5	1.48	96	-

Water samples were also analysed with ethyl violet method[11]. The results (Table 2) were in good agreement to that of the proposed method.

CONCLUSION

The proposed method is sensitive down to ppb levels of orthophosphate-phosphorus. Excess of ion-pairing reagent is easily removable with 25 ml portion of 1.0 M hydrochloric acid. The method compares well with Rhodamine B-Phosphate ion-pair method[9] in these aspects. It has the advantage over others[7,8] which employ a comparatively toxic solvent, chloroform, for the extraction of excess of ion-pairing reagent. The proposed method may be applied to natural water samples.

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