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Study of Digestion Efficiency on Spectrophotometric Determination of Phosphate In Water Sample by Flow Injection Analysis

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Abstract. A method suitable for the determination of phosphate in water samples is presented. The flow injection (FI) manifold contain a PTFE reaction coil wrapped around a low power UV lamp and is based on the spectrophotometric determination of Orthophosphate and mineralized organic phosphate at 690 nm after reduction of phosphomolybdate to molybdenum blue with tin(II) chloride. The linear range was 0-1.5 mg L^{-1} P, with a detection limit (3 s) of 7 µg L^{-1} and a sample throughput of 40 h^{-1}. The tolerance of interference from Fe(II), Al(III), and Fe(III) was achieved using on-line sample pre-treatment by a strong acid ion exchange column.
Keywords: Digestion, Spectrophotometric, Phosphate, Flow injection, water sample.

Introduction

The measurement of phosphorus species in natural water may be determined as a part of water quality monitoring. But, the importance of environmental interest in phosphorus relates to role in the determination of the amount of bioavailability phosphorus as a limiting nutrient for growth of algae and the process of eutrophication (Benson *et al*., 1996; Meaney *et al*., 2002). In aquatic system, phosphate occurs in wide variety of inorganic an organic form. While the may exist in either, colloidal particulate and dissolved forms, and the dissolved fraction can consist of compounds such as orthophosphates, inositol phosphates, nucleic acids, sugar phosphates and condensed phosphates (Filella *et al*., 2006).

The majority of manual and automated methods of phosphate determination are based on the spectrophotometric determination of phosphorus as phosphomolybdenum blue (McKelvie *et al*., 1995; Peat *et al*., 1997). The determination of phosphate is most commonly based on the formation of the heteropoly acid, 12-molybdophosphoric acid (12-MPA) under acidic condition (Neves *et al*, 2008). The absorbance of the 12-MPA then be measured, or it may be reduced to form the highly colored phosphomolybdenum blue (PMB), using a variety of reductant. Better sensitivity can be achieved if 12-MPA is reduced to form PMB. A wide variety of reductant has been employed for this purpose i.e. tin (II) chloride (Motomizu *et al*., 2005).

Flow injection analysis (FIA) is a widespread and well established approach to determine phosphorus (Mesquita *et al*., 2011; Estella *et al*., 2005; Fernandes *et al*., 2002). Orawan *et al*. (2005) have also described the flow injection manifold for rapid sequential determination of Dissolved Organic Phosphate in natural water. Determination of phosphate necessitates pre digestion of water sample prior to detection as orthophosphate species. Orthophosphate can react readily with acidic molybdate to form 12-phosphomolybdic acid, which on reduction with tin (II) chloride yields the strongly colored phosphomolybdenum blue species. Complete conversion of particulate and filterable component requires conditions that are conducive to the dissolution of phosphate mineral phases, hydrolysis of phosphate esters, and oxidation of organic phosphate.

Numerous methods have been proposed which the digestion efficiency should be assessed by using a range of appropriate phosphorus model compound and standard reference material. A range of suitable model compounds for this compound has been suggested by Kerouel and Aminot (1996). In this study, we investigate the digestion

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efficiency of model phosphate by alkaline peroxodisulphate and combined with photo oxidation in PTFE reactor wrapped around a low power UV using flow injection analysis system.

Materials and Methods

Apparatus

The Flow Injection designed was used throughout and mixing coil with length of 30 and 60 cm. Ismatec pump were used for carrier and reagent delivery.

Sample (600 µL) was injected using a motor rheodyne injection valve. The UV source was a germicidal U tube that had a major emission line at 254 nm an d a power consumption of 40 W. Oxygen and ozone bubbles formed during photooxidation were removed using two 10 cm length of knotted tubing.

The absorbance was measured with a spectrophotometer fitted with a 10-mm path length glass flow-through cuvette and output recorded on an analogue chart recorder

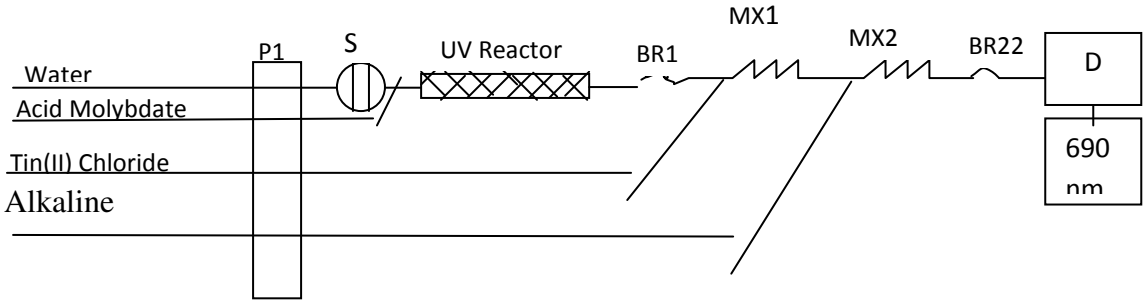

Fig. 1. Flow injection manifold for spectrophotometric determination of phosphate: carrier (Milli-Q water, flow rate 1.38 ml min^{-1}); acid molybdate (R2, flow rate 0.94 ml min^{-1}); tin(II) chloride(R3, flow rate 0.55 ml min^{-1}); P1,peristaltic pump 1; P2, peristaltic pump 2 (flow rate 0.64 ml min^{-1}), alkaline peroxodisulfate (R1); I, rotary injection valve; SN, solenoid valve; BR, bubble-removal tubing (10 cm long), MX1, mixing coil 1 (90 cm x 0.5 mm i.d.); MX2, mixing coil 2 (60 cm x 0.5 mm, i.d.); D, detector (690 nm)

Reagents

The Alkaline peroxodisulfate solution (R1) was prepared by dissolving potassium peroxodusulphate, 4.0% (Merck) in di-sodium tetraborate, 34% (Merck).

The Acid molybdate solution (R2) was prepared by dissolving, 8.1 x 10^{-3} mol L^{-1} ammonium heptamolybdate tetrahydrate (Merck)) in sulfuric acid, 0.63 mol L^{-1} (BDH, AnalaR).

Tin(II) chloride solution (R3) was prepared by dissolving tin(II) chloride, 8.9 x 10^{-4} mol L-1 (Fisons, Australia) and hydrazinium sulfate, 0.015 mol L-1 (Fisons, Australia) in sulfuric acid , 0.50 mol l-1 (BDH, AnalaR)

A stock standard solution of phosphate was prepared by dissolving potassium dihydroden orthophosphate 100 mg P l-1 (impurity 99.5%, BDH, AnalaR). Working solution was freshly prepared by dilution of stock with water.

Recoveries of model phosphorous compounds

Model phosphate compounds used in the recovery experiments were chosen to represent a good efficiency of digestion, viz., potassium dihydrogen orthophosphate (BDH, 99.5%); sodium tripolyphosphate (Ajax); phytic acid (Sigma); adenosin-5`-monophosphate (Boehringer Mannheim); 2-aminoethyl phosphoric acid (Aldrich, 97%); bis-2-nitrophenyl phosphate (Sigma, 99%); D-glucose-6-phosphate (Sigma, 98%), phenyl phosphate (Sigma).

Interferences

Separate solutions of interfering ions (Mg(II), Al(II), La(III), Fe(II)), Fe(III), Cu(II) and (La(III) were prepared by dissolving of magnesium chloride hexahydrate (Sigma),

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aluminum sulfate (M&B Laboratory Chemicals), Copper sulphate (Ajax), lanthanum chloride (Ajax),and ferric sulfate hydrate (Ajax).

Ion exchange column for sample pre-treatment

The columns were packed with Dowex W50 X8 (BDH) cation exchange resin (5.0 cm x 1.0 cm i.d.). The resin was initially cleaned in 10 % (v/v) concentrated H_2SO_4 and tehn flused with Milli-Q grade water. The columns was regenerated by flushing on-line with 10 % (v/v) concentrated sulphuric acid followed by Milli-Q water after each use.

Results and Discussion

Optimization of FI manifold

Initially the flow rates reported by McKelvie et al. (1996) were used (1.3 ml min-1) for the water carrier and peroxydisulphate streams. Samples were injected not the carrier stream and subsequently merged with the peroxydisulphate stream. To minimize sample dilution however the peroxydisulphate concentration was increased to 50 g L^{-1} rom 40 g L^{-1}. to avoid problem with back pressure, the i.d. of the PTFE reactor coil was increased from 0.3 to 0.5 mm with minimal effect on dispersion.

Analytical performance

The linear range and detection limit of the system were determined using orthophosphate standards in the range 0 – 1.5 mg/L phosphate. In the concentration range of 0.05 – 0.50 mg P l-1, calibration graph for orthophosphate and phytic acid standard solution were similar (for orthophosphate: y = 0.1438x + 0.5973; r2 = 0.9984: for phytic acid: y = 0.1065x + 0.4889; r2 = 0.9982. The relative standard deviations (n=5) for standards above 0.5 mg/L were generally <1 %.). The sensitivity of the system was 0.2699 AU per mgL-1 phosphate and the detection limit was 7 µg/L, calculated using 3 s (n = 5) of the blank signal.

Efficiency of digestion method

Six Model phosphate compounds used in the recovery experiments were chosen to represent a good efficiency of digestion. Recoveries of model phosphorous compounds were used to form representative of phosphate compound in water sample. It was found that the recoveries for 0.3 mg l^{-1} P in organic phosphorus were good as shown in Table 2.

Table 2. Recoveries of model Phosphorus compound

Phosphorus compound	Recoveries (%)
Phytic acid	97 ±0.1
Phenyl phosphate	105 ±0.1
D-glucose-6-phosphate	90 ±0.1
2-aminoethyl phosphonic acid	98 ±0.1
p-nitrophenyl phosphate	99 ±0.1
Adenosin monophosphate	93±0.1
Sodium tripolyphosphate	6.0 ±0.1
Orthophosphate	100±0.1

Interferences study

The principal problem when using alkaline peroxydisulphate and photooxidation process in photoreactor is susceptible to interference from metal ions, e.g., Fe(III) and Al(III) which form complexes and precipitates with orthophosphate at high pH. These can be classified into three types, those that also form molybdate complexes resulting in enhanced absorbance, those that form compound with orthosposphate and inhibit the formation of phosphomolydenum blue. A strong cation exchange column in the H^+ form was introduced as a sample pretreatment line with the aim of eliminating interference form metal ions. The recoveries of the result obtained applying a strong cation exchange column were shown in Table 3.

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Table 3. Recoveries of standard solution containing interferences before and after sample pretreatment using cation exchange column

Interferences	Before	After
Fe(II)	42 ±0.1	97 ±1.6
Al(III)	180 ±0.1	99±0.1
Fe(III)	135 ±0.3	98±0.6
Mg(II)	54±0.2	60±0.5
La(III)	62±0.1	86±0.2
Cu(III)	2 ±0.1	30 ±0.1

Conclusions

The flow injection manifold describe is suitable for the determination of phosphate in water sample. A combination of photooxidation and peroxodisulphate digestion gave a good recoveries on model phosphorus compound.

Acknowledgments

The author would like to thanks to Technical Program Skill Development Project (TPSDP) for financial support. Special thanks to Assoc. Prof Ian McKelvie and Mrs. Barlah Rumhayati, the staff and Ph.D student of Water Studies Centre, Monash University for their assistance on this work.

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