ELSEVIER

Determination of nanomolar concentrations of phosphate in natural waters using flow injection with a long path length liquid waveguide capillary cell and solid-state spectrophotometric detection

Laura J. Gimbert [a,b,*], Philip M. Haygarth [b], Paul J. Worsfold [a]

[a] School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK
[b] Cross Institute Programme for Sustainable Soil Function (SoilCIP), Institute of Grassland and Environmental Research (IGER), North Wyke Research Station, Okehampton, Devon EX20 2SB, UK

Abstract

A flow injection manifold incorporating a 1 m liquid waveguide capillary cell and a miniature fibre-optic spectrometer for the determination of low phosphorus concentrations in natural waters is reported. The limit of detection (blank + 3 S.D.) was 10 nM using the molybdenum blue chemistry with tin(II) chloride reduction. The sensitivity of the flow injection manifold was improved by 100-fold compared with a conventional 1 cm flow cell. The response was measured at 710 nm and background corrected by subtracting the absorbance at 447 nm. Interference from silicate was effectively masked by the addition of 0.1% (m/v) tartaric acid and results were in good agreement ($P = 0.05$) with a segmented flow analyser reference method for freshwater samples containing 1 μM phosphate.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Flow injection; Phosphate; Liquid waveguide capillary cell; Solid-state spectrophotometry; Natural waters

1. Introduction

Phosphorus (P) is an essential element for all life including plant growth and photosynthesis in algae [1–3], and excessive phosphorus concentrations can result in eutrophication of natural waters. Phosphorus exists in different forms in natural waters, soil leachates, and agricultural runoff with the most commonly measured fractions being dissolved reactive phosphorus, total dissolved phosphorus and total particulate phosphorus [4–7]. The dissolved fraction, operationally defined as the fraction that passes through a conventional 0.2 or 0.45 μm membrane, contains inorganic and organic compounds such as orthophosphate, inositol phosphates, nucleic acids, phospholipids, phosphoamides, phosphoproteins, sugar phosphates and condensed phosphates [4,5,8,9]. The particulate fraction, operationally defined as the material retained by the membrane, comprises material of biological origin (animal, plant, bacterial), weathering products (primary and secondary minerals), and authigenic minerals formed by direct precipitation of inorganic phosphorus or sorption to other precipitates [8,10–12]. Both the dissolved and particulate fractions will also have phosphorus associated with colloidal material, defined as the 0.001–1 μm fraction [13–15].

There are a number of different methods for the determination of P species [11], with spectrophotometric methods the most widely used for phosphate, often in conjunction with flow injection analysis (FIA). Motomizu and Li recently reviewed trace and ultra trace methods for P determination with FIA [16] and concluded that detection based on chemiluminescence was the most sensitive with a limit of detection of 1 nM [17]. Spectrophotometric methods for the determination of phosphate are usually based on the Murphy and Riley molybdenum blue reaction [11,18–20], but sensitivity is limited by the use of conventional 1 cm path length cells:

$$PO_4{}^{3-} + 12MoO_4{}^{2-} + 27H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12H_2O \quad (1)$$
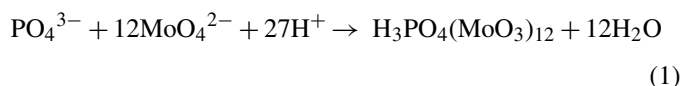
* Corresponding author at: School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK. Tel.: +44 1752 232402; fax: +44 1752 233009.
E-mail address: lgimbert@plymouth.ac.uk (L.J. Gimbert).

$$H_3PO_4(MoO_3)_{12} \xrightarrow{\text{reduction}} \text{phosphomolybdenum blue} \qquad (2)$$

An additional challenge with the molybdenum blue chemistry is the interference from related species, particularly silicate (Si). The silicomolybdenum blue complex has a broad absorbance band ($\lambda_{\max}$ 790 nm) that overlaps the 710 nm typically used for phosphomolybdenum blue detection [21]. Silicate interference can be reduced or eliminated using lower temperatures (silico-molybdenum blue complex formation is favoured at higher temperatures, i.e. 40–65 °C) or by reducing the pH [19,22]. Masking agents such as tartaric acid can also be effective provided that they are added before the molybdophosphate or molybdosilicate species have formed [17,23].

Zhang and Chi [24] obtained a limit of detection of 0.5 nM phosphate using a gas-segmented continuous flow analyser and a 2 m liquid waveguide capillary cell (LWCC) with the molybdenum blue method using ascorbic acid as the reductant. This system was applied to seawater [24] and river water samples [25]. The Beer–Lambert law states that absorbance is proportional to the path length of the cell (flow or static) but long path length cells normally suffer from serious attenuation of the light source. However, with a LWCC attenuation is minimised by the light being totally internally reflected [24] using a Teflon AF fluoropolymer which has a refractive index lower than that of water (~1.33). A capillary of fused silica coated with Teflon AF enables light travelling through the capillary to be totally internally reflected at the AF–silica interface provided that the incident angle, on going from the optically more dense medium (water) to the less dense medium (AF–clad silica tubing) exceeds the critical angle [26]. The refractive index (schlieren) interference using segmented flow analysis with a LWCC has been quantified using samples of different salinities and measuring the absorbance. When the refractive index at the sample/carrier interface does not match, the absorbance measurements require a correction for the refractive index interference [24]. The effect of potential matrix interferences such as silicate in natural waters has not been reported with LWCCs.

There are generic attractions in combining FIA with a LWCC flow cell, including enhanced sensitivity compared with conventional flow cells and a more rapid response and portability compared with segmented flow analysers. However, combining the two has significant challenges including refractive index effects and long-term stability.

The aim of this work was therefore to optimise a flow injection manifold incorporating a 1 m LWCC for the sensitive detection of phosphate in natural waters using the molybdenum blue chemistry. Tin(II) chloride was used as the reductant rather than ascorbic acid due to the faster kinetics [4,18,27]. The effect of silicate interference on the FIA-LWCC manifold was significantly reduced by the addition of tartaric acid and the accuracy determined by comparative analysis of freshwater samples using an air-segmented analyser.

2. Experimental

2.1. Reagents and solutions

All glassware and bottles were cleaned overnight in nutrient free detergent (Neutracon®, Decon Laboratories, UK), rinsed three times with ultra-pure water (Elga Maxima®, 18.2 MΩ), soaked in 10% (v/v) HCl for 24 h, again rinsed three times with ultra-pure water and dried at room temperature.

All solutions and reagents were prepared with ultra-pure water and all reagents were of AnalaR grade (VWR International, Dorset, UK) or equivalent, unless otherwise stated. A 3 mM PO$_4$-P stock solution was prepared by dissolving 0.4393 g of potassium dihydrogen orthophosphate (oven dried for 1 h at 105 °C) in 1 L of ultra-pure water. Working standards in the range 0.01–1 μM were prepared by dilution of the stock solution.

Two reagents were prepared, ammonium molybdate (10 g ammonium molybdate and 35 mL sulphuric acid in 1 L ultra-pure water), and tin(II) chloride (0.2 g tin(II) chloride, 2 g hydrazinium sulphate and 28 mL sulphuric acid in 1 L ultra-pure water). Tartaric acid solution (1%, w/v) was prepared by dissolving 1 g in 100 mL ultra-pure water and diluting to the appropriate concentration as required. The silicate standards were prepared by dilution of a silicate SpectrosoL® solution (1000 mg L^{-1}) to give working standards in the range 0.5–2.0 mg Si L^{-1}.

2.2. Instrumentation and procedures

The flow injection manifold used in this work is shown in Fig. 1. The starting conditions were based on the method used by Hanrahan et al. [28] and are summarised in Table 1. The manifold was re-optimised after incorporation of a long path length 1 m LWCC. A peristaltic pump (MiniPuls 2, Gilson, Villiers-le-Bel, France) was used to propel the ammonium molybdate and tin(II) chloride reagent streams at flow rates of 0.30 mL min^{-1}. A second peristaltic pump (Mini S840, Ismatec, Surrey, UK)
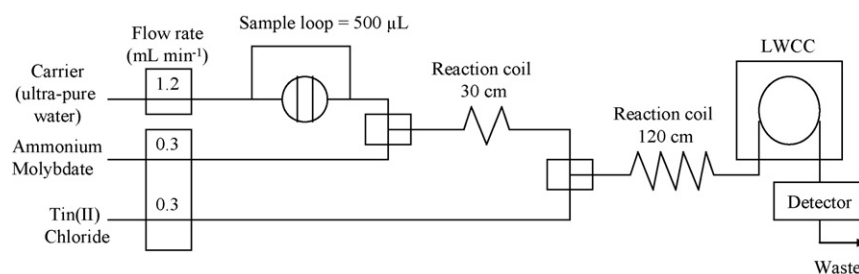

Fig. 1. FIA-LWCC manifold for the determination of PO$_4$-P with optimised flow rates and reaction coil lengths. One peristaltic pump was used for the carrier and one for the reagents. A third peristaltic pump was used to fill the sample loop.