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Spectrophotometric flow system using vanadomolybdophosphate detection chemistry and a liquid waveguide capillary cell for the determination of phosphate with improved sensitivity in surface and ground water samples

M. Sofia A.C. Neves[a], M. Renata S. Souto[b], Ildikó V. Tóth[a], Sérgio M.A. Victal[a], M. Cláudia Drumond[a], António O.S.S. Rangel[a,*]

[a] Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal
[b] Universidade Fernando Pessoa, Faculdade de Ciências da Saúde, Rua Carlos da Maia 296, 4200-150 Porto, Portugal

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ABSTRACT

A flow injection procedure based on the vanadomolybdate method for the determination of dissolved reactive phosphorus in water samples is described. The system includes a liquid waveguide long pathlength cell connected to a charge coupled device (CCD) spectrophotometer. Calibration was linear up to 500 μg P L^{-1}, with a detection limit of 17 μg P L^{-1} and a quantification limit of 56 μg P L^{-1}. An injection throughput of 60 determinations h^{-1} and repeatability (R.S.D.) of 2.2% were achieved. Potential interference from silicate was effectively masked by addition of a tartaric acid stream. The accuracy of the proposed methodology was assessed through analysis of a certified reference material and recovery tests on water samples. The developed procedure allows the determination of phosphorus in water samples at trace levels with high sensitivity, reduced reagent consumption and low waste production.

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1. Introduction

Phosphorus is an essential element for the growth of plants and animals. It is the limiting nutrient in fresh water ecosystems, and an increase in its concentration usually leads to an increase in the aquatic vegetation. This process may result in eutrophic conditions and depletion of oxygen in water, due to the heavy oxygen demand of microorganisms as they decompose organic material. The disturbance of the normal functioning of the ecosystem will eventually cause degradation in water quality. European Union directive sets the limit of 100 μg L^{-1} P-PO_4^{3-} as an indicator level for probable problematic algae growth [1].

In water samples, phosphorus can be found in the form of different inorganic and organic species and can be present in either the dissolved, colloidal or particulate form. The dominant and most stable inorganic species is dissolved in reactive phosphorus [2–4]. Reference procedures are usually based on phosphorus determination in this form, on aliquots of previously filtered samples. Most of them are based on the colorimetric assay of phosphomolybdate or vanadophosphomolybdate heteropoly acids. Orthophosphate reacts with molybdate in acidic medium to yield 12-molybdophosphoric heteropolyacid; subsequently, detection is undertaken either on the molybdophosphate reduction product (molybdenum blue method) or on the yellow vanadomolybdate complex [2,5,6]. The molybdenum blue method became broadly used due to its higher sensitivity and lower susceptibility to interferences [4,7,8], than the vanadophosphomolybdate method. Nevertheless, the low concentration levels imposed by legislation are difficult to achieve. Therefore, the development of new methodologies capable of monitoring trace phosphate levels in environmental samples with adequate precision, has gained importance [9].

Flow injection analysis (FIA) is a widespread and well established approach to determine phosphorus. In fact, the first publication on FIA is dedicated to phosphate determination [10] and discusses both the yellow vanadomolybdate and the molybdenum blue method. Compared to the blue molybdenum method, the yellow vanadomolybdate analytical procedure can present some advantages that make it more suitable for flow systems: (i) the use of a single reagent mixture with extended stability makes the method suitable for field portable applications and for unattended operation in water monitoring [11,12] and (ii) the formation of a fine precipitate, accompanying the development of the blue colour, does not occur. However, maybe because of its limited sensitiv-

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* Corresponding author. Tel.: +351 225580064; fax: +351 225090351.
E-mail address: aorangel@esb.ucp.pt (A.O.S.S. Rangel).

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ity, the yellow vanadomolybdate method has been rarely used in flow systems. This limitation might be overcome by resorting to instrumental advances in spectrophotometry. Recently, with the development of the liquid waveguide capillary cell (LWCC), the increase of the flow cell pathlength can be easily achieved without deteriorating other analytical characteristics of the method. The long pathlength spectrophotometric measurements can increase the method sensitivity by up to two orders of magnitude [4,13,14].

The objective of this work was to develop a flow system based on the vanadomolybdate method, capable of quantifying phosphate at trace concentrations in waters, using a LWCC coupled to a charge coupled device (CCD-array) detector. Different flow strategies were employed and the effect of silicate (the most commonly referred interfering compound) on the analytical measurements was assessed.

2. Experimental

2.1. Reagents and solutions

All chemicals presented an analytical reagent grade. Solutions and reagents were prepared with deionised water (with specific conductance lower than 0.1 μS cm^{-1}) and subsequent dissolution was done in appropriate solvents. Due to the low phosphorus level analysed in the LWCC flow system, all solutions were prepared with ultra-pure water (Barnstead-Easypure-LF) in volumetric material that was previously rinsed with this type of water.

Phosphorus stock solution (100 mg L^{-1}) was prepared dissolving potassium dihydrogen phosphate (KH_2PO_4) previously dried overnight at 105 °C. Silicate stock solution (100 mg L^{-1}) was prepared by dissolving sodium metasilicate pentahydrate ($Na_2SiO_3{\cdot}5H_2O$). Working phosphorus and silicate standard solutions were prepared daily by suitable dilution of the stock solutions.

A 10 mM tartaric acid solution was prepared dissolving 0.37 g of L(+) tartaric acid ($C_4H_6O_6$) in 0.25 L of water.

The vanadomolybdate reagent was a solution of 25 g L^{-1} ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] and 1.9 g L^{-1} ammonium monovanadate (NH_4VO_3), in either 2 M or 3.25 M HCl.

All groundwater samples were filtered through a 0.45 μm Whatman cellulose acetate membrane. Mineral water samples had no previous treatment. Two surface waters certified reference materials were used: SPS-SW2 (Spectrapure, Oslo, Norway) and QC RW1 (VKI, Denmark).

2.2. Flow manifolds and instrumentation

The preliminary flow injection system used in this work is shown in Fig. 1(a). The initial conditions were based on the American Public Health Association (APHA) recommended batch procedure [5].

A peristaltic pump (Gilson, Minipuls 3) and Tygon PVC tubes were used to propel water (carrier, C), and reagent (R) solution into the system at flow rates of 3.2 and 0.8 mL min^{-1}, respectively.

The tubing (0.8 mm i.d.) connecting the different parts of the flow systems was made of poly(tetrafluoroethylene) with Gilson end fitting and connectors.

Sample and standard injections in the flow injection set-up were made using a Rheodyne type 5020 six-port rotary injection valve. Carrier and reagent streams then merged in a laboratory made acrylic Y-shaped connector used as confluence point and the resulting solution further mixed while passing a reaction coil (170 cm).

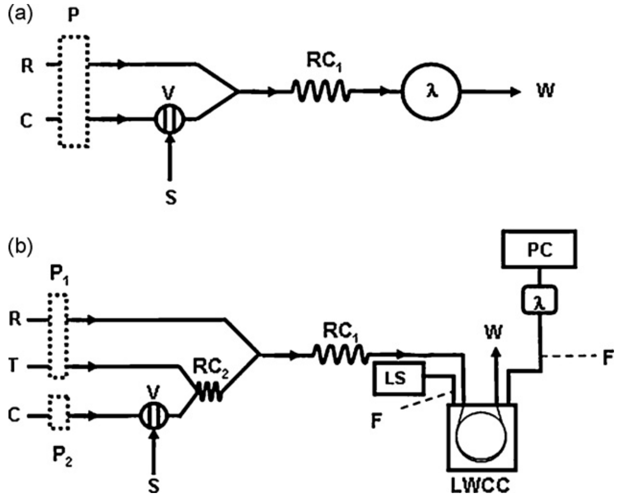

Fig. 1. Flow injection manifolds: (a) set-up used in preliminary studies and (b) manifold used for the determination of phosphorus in waters with long pathlength liquid core waveguide technology. R, vanadomolybdate reagent; C, carrier (deionised water); T, tartaric acid solution; P_i, peristaltic pump; S, sample or standard solution; V, injection valve; RC_1, reaction coil (170 cm); RC_2, reaction coil (50 cm); λ, detector (conventional or CCD array spectrometer); PC, computer; F, optical fibre; LS, light source; LWCC, liquid waveguide capillary cell; W, waste.

Another flow configuration (Fig. 1(b)) was used to reduce the effect of the silicate interference, with a stream of tartaric acid merging the carrier stream after the injection port. A reactor coil of 50 cm was used to enhance mixture between these solutions. Carrier (ultra-pure water), tartaric acid and reagent flow rates were reset to 2.7, 0.7 and 0.8 mL min^{-1}, respectively with the aid of a second peristaltic pump.

Different detection systems were used. For the manifold presented in Fig. 1(a), a Thermo Spectronic Helios Gamma UV–vis Spectrophotometer equipped with a Hellma model 178.712-QS flow cell (10 mm light path, inner optical volume 30 μL), connected to a Kipp & Zonen BD112 recorder was used. Subsequently this detector was replaced by an OceanOptics (Dunedin, FL, USA) USB2000-FLG Spectrometer (slit: 200 μm, grating: 600 lines blazed at 500 nm; bandwidth 380–1020 nm) connected via a 400 μm fibre optical cable (model P400-2-UV–vis) to the flow cell, placed in an Ocean Optics CUV cell support (Fig. 1(a)). A Mikropack (Ostfildern, Deutschland) Deuterium–halogen light source, model DH-2000-BAL was used with a 400 μm illumination optical fibre (model P400-2-UV–vis). Registration of the analytical signal was made using the OOIBase32 Spectrometer Operating Software. Dual-wavelength spectrophotometry was used to reduce the refractive index effect and the blank absorbance of the vanadomolybdate reagent. The analytical wavelength was 380 nm and the reference wavelength 600 nm; the absorbance signal at 600 nm was subtracted from the one at 380 nm for schlieren effect [15] correction. The collected absorbance data was treated and analysed in a lab-developed Microsoft Excel based software.

Afterwards, the conventional flow cell was replaced by a World Precision Instruments (Sarasota, FL, USA) liquid waveguide capillary cell, with a pathlength of 100 cm, model 2100. The absorbance change was monitored at 446 nm. During the optimisation process, it was observed that the LWCC gave the best day-to-day performance when sequentially flushed with 1 M NaOH, 1 M HCl and ultra-pure water (in counter current) at the end of each day.

2.3. Reference procedure

To assess the quality of the results obtained with the different analytical systems, results were compared with those given by the American Public Health Association recommended reference

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