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A high performance microfluidic analyser for phosphate measurements in marine waters using the vanadomolybdate method



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ABSTRACT

We report a high performance autonomous analytical system based on the vanadomolybdate method for the determination of soluble reactive phosphorus in seawater. The system combines a microfluidic chip manufactured from tinted poly (methyl methacrylate) (PMMA), a custom made syringe pump, embedded control electronics and on-board calibration standards. This “lab-on-a-chip” analytical system was successfully deployed and cross-compared with reference analytical methods in coastal (south west England) and open ocean waters (tropical North Atlantic). The results of the miniaturized system compared well with a reference bench-operated phosphate auto-analyser and showed no significant differences in the analytical results (student’s *t*-test at 95% confidence level). The optical technology used, comprising of tinted PMMA and polished fluidic channels, has allowed an improvement of two orders of magnitude of the limit of detection (52 nM) compared to currently available portable systems based on this method. The system has a wide linear dynamic range 0.1–60 μM, and a good precision (13.6% at 0.4 μM, *n*=4). The analytical results were corrected for silicate interferences at 0.7 μM, and the measurement frequency was configurable with a sampling throughput of up to 20 samples per hour. This portable micro-analytical system has a low reagent requirement (340 μL per sample) and power consumption (756 J per sample), and has allowed accurate high resolution measurements of soluble reactive phosphorus in seawater.

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1. Introduction

Phosphorus is a key nutrient in the marine environment and is involved in a range of biochemical processes [1,2]. Phosphate is the primary source of phosphorus for marine phytoplankton uptake and is essential for their growth and reproduction [3]. Although depleted levels of phosphate can limit primary production in marine ecosystems [4], an increase in phosphate concentrations due to anthropogenic inputs [5] can lead to excessive phytoplankton growth, with potentially adverse effect on water quality including nuisance blooms. Perturbations of phytoplankton communities have been directly linked to enhanced phosphate loadings [6]. Consequently, limits for phosphate concentrations in natural waters are being reduced by regulatory organisations [7]. This evolution of international water quality policy is increasing the need for the accurate determination of phosphate with sensitive automated analytical systems.

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Various analytical techniques have been applied to measure soluble reactive phosphorus (SRP) in seawater, including ion chromatography [8,9] and electrochemistry [10]. However, flow analysis techniques [11] remain the first choice for seawater analysis [12] because of their selectivity, sensitivity and accuracy. The molybdenum blue method is the most commonly used analytical approach, involving a reaction between orthophosphate and a molybdate donor reagent, with subsequent reduction of the product to a blue coloured complex using ascorbic acid [13]. Alternative colorimetric techniques which are also based on the formation of heteropoly acids with molybdenum, can be used for SRP determination, including the vanadomolybdophosphoric method [14], as described here.

In situ analysis of phosphate is required to address the need for data at high spatial and temporal resolution [15–17]. This approach removes potential alterations of water samples during the sampling, sample handling and storage; these steps all constitute the main sources of contamination in standard analytical methodologies [18]. In the past, a range of autonomous analytical systems based on wet-chemistry have been developed for the determination of phosphate in natural waters [19–24]. One of the main challenges for the development of *in situ* chemical systems involves the reduction of their physical size. Large instruments are

difficult to deploy, often expensive, and cannot be used on smaller marine platforms (e.g. buoys, remotely operated vehicles, CTD rosette frames). In addition, there are restrictions on the length of time that instruments can be deployed autonomously due to limitations on reagent and power availability, and often limited reagent stability.

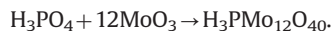
To address these limitations we have applied “lab-on-a-chip” technology [25–27] to miniaturise already sensitive and accurate chemical methods. This approach addresses many of the technical constraints of *in situ* deployments and preserves the high performance of chemical analysis in natural waters. This study describes an automated low power and low reagent consuming microfluidic analyser to monitor SRP in marine waters. The microfluidic analyser uses the stable vanadomolybdate reagent and was field-tested and compared with bench-top analytical systems in coastal and open ocean waters. The combination of a stable reagent, low reagent use and low power consumption makes the micro-analyser a viable and economical option for implementation on various deployment platforms for monitoring phosphate in marine and freshwater systems.

2. Material and methods

2.1. Chemical method

The determination of SRP reported here is based on the rapid direct reaction of orthophosphate with an acidified vanadomolybdate reagent which produces a yellow coloured complex [28–31]. This “yellow” method was chosen for the stability of the reagent mixture over time, reported to be over one year, compared with four to six weeks for the classical “blue” method [32]. The inorganic phosphorus species in seawater include orthophosphoric acid, dihydrogen phosphate, and hydrogen phosphate, and

their abundance at equilibrium depends on the pH. Under acidic conditions, orthophosphoric acid is dominant and reacts with molybdate ions to form molybdophosphoric acid:



In the presence of vanadate ions, this complex will form vanadomolybdophosphoric acid, $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, with a molar absorptivity of $3.6 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 385 nm [14].

The vanadomolybdate stock solution used in this study was prepared with 7.2 g ammonium molybdate (A-7302, Sigma, Dorset, England) and 0.36 g ammonium metavanadate (20555-9, Aldrich, Dorset, England) dissolved in 95 mL concentrated hydrochloric acid (Sigma-Aldrich, ACS reagent 37%) and made up to 1 L with high purity water (MilliQ, Millipore, $> 18.2 \Omega \text{ cm}^{-1}$). Phosphate working standards were prepared from a stock solution of 3 mM phosphate (0.40827 g L^{-1} of potassium dihydrogen phosphate, Sigma-Aldrich), and prepared using low nutrient sea-water (LNSW), collected from North Atlantic surface waters and aged in the laboratory for at least one year. A silicate stock standard of 1 mM (0.188 g L^{-1} of sodium hexafluorosilicate, Sigma-Aldrich) was used to spike solutions for studies into silicate interference on the phosphate measurements. The error generated by the silicate interference was investigated by preparing a 50 nM phosphate standard in LNSW with additions of silicate that ranged from 1 μM to 100 μM , corresponding to levels found in natural waters (World Ocean Atlas 2009, NOAA).

2.2. Microfluidic analyser description

The optical absorption measurement of the yellow complex provides a simple measurement of SRP. High power UV-LEDs (XRL-375-5E, 375 nm, 19–26 mW, Roithner) were used as a light source, and photodiodes (TSL257-LF, Texas Advanced Optoelectronic Solutions Inc.) for the absorbance detection [33]. Both LEDs and

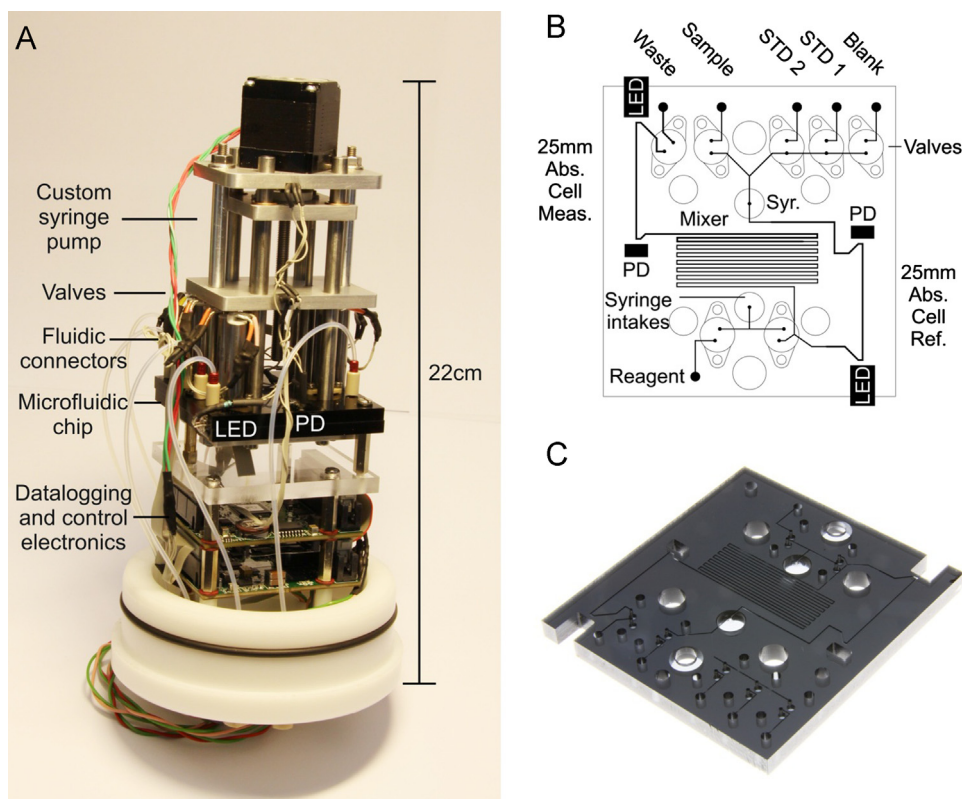


Fig. 1. (a) Photograph of the micro-analyser, including a custom syringe pump, valves, microfluidic chip and electronics. The system measures 22 cm high and 10 cm in diameter. (b) Microfluidic chip schematic. (c) Photograph of the chip prior to bonding (micro-milled in tinted-PMMA).

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