
Ion chromatograph with 3D printed absorbance detector for indirect UV absorbance detection of phosphate in effluent and natural waters

Lace Annija ¹, Byrne Aideen ¹, Bluett Simon ⁴, Malaquin Laurent ², Raimbault Vincent ², Courson Remi ³, Hayat Zain ², Moore Breda ¹, Murray Eoin ^{1,4,*}

¹ Research & Development T.E. Laboratories Ltd. (TelLab) Tullow Carlow, Ireland

² LAAS-CNRS Université de Toulouse CNRS Toulouse F-31400 ,France

³ IFREMER, Laboratoire Détection Capteurs et Mesures (REM-RDT-LDCM) F,rance

⁴ Research & Development Aquamonitrix Ltd. Carlow ,Ireland

* Corresponding author : Eoin Murray, email address : emurray@aquamonitrix.ie

Abstract :

An ion chromatography system employing a low-cost 3D printed absorbance detector for indirect UV detection towards portable phosphate analysis of environmental and industrial waters has been developed. The optical detection cell was fabricated using stereolithography 3D printing of nanocomposite material. Chromatographic analysis and detection of phosphate was carried out using a CS5A 4×250 mm analytical column with indirect UV detection using a 255 nm light emitting diode. Isocratic elution using a 0.6 mM potassium phthalate eluent combined with 1.44 mM sodium bicarbonate was employed at a flow rate of 0.75 ml min⁻¹. A linear calibration range of 0.5 to 30 mg L⁻¹ PO₄³⁻ applicable to environmental and wastewater analysis was achieved. For retention time and peak area repeatability, RSD values were 0.68 % and 4.09 %, respectively. Environmental and wastewater samples were analysed with the optimised ion chromatography platform and the results were compared to values obtained by an accredited ion chromatographer. For the analysis of environmental samples, relative errors of < 14 % were achieved. Recovery analysis was also carried out on both freshwater and wastewater samples and recovery results were within the acceptable range for water analysis using standard ion chromatography methods.

Keywords : Indirect ultra violet detection, Ion chromatography, Phosphate, SLA detection cell, Water analysis

1. Introduction

Phosphorous is an essential nutrient for plant and animal species in aquatic ecosystems. It is mostly found in the form of phosphate [1]. Increased levels of phosphate in water systems can lead to eutrophication which is one of the most common water quality issues worldwide [2]. Eutrophication results in the increased growth of harmful algae, which during decomposition releases toxins and reduces the available amount of dissolved oxygen in waters. This deteriorates water quality and leads to loss of biodiversity [3]. The main sources of phosphate in freshwater include wastewater effluents, farm run-off, fertilisers and industrial waste [4].

To date, the majority of water monitoring has been based on manual sampling followed by laboratory analysis using a range of different methods. However, the high cost of sample analysis makes it unsuitable for high frequency monitoring [5]. In addition, most manual sampling methods are carried out on weekly or monthly samples, which cannot determine seasonal or daily variations in water quality [6]. Consequently, environmental monitoring using on-site or *in-situ* methods is needed for data collection at high temporal and spatial frequency [7]. Ideally, the analytical analyser for on-site or *in-situ* monitoring should be compact, robust, cost effective and environmentally compatible with the ability to deliver reliable measurements over prolonged periods of time [8]. A wide range of different analytical methods have been applied for *in-situ* sensor development for water monitoring, including chemiluminescence [9], electrochemistry [10, 11] and colorimetry [12, 13]. Several electrochemical sensor prototypes of promise have been developed for phosphate detection in water [14, 15]. Despite the fast analysis times and the high sensitivity demonstrated in laboratory-based tests, these electrochemical sensors require further development and extensive field assessment.

Since Manz introduced the concept of miniaturised total analysis systems (μ TAS) there has been a growing interest in the application of microfluidic systems for environmental monitoring [16, 17]. Microfluidic or lab-on-a-chip (LOC) detection systems have many advantages over large scale chemical sensors, including reduced reagent consumption, low power requirement and increased sample turnover time [18]. Over the past decade, colorimetric assays have been extensively utilised within LOC systems for *in-situ* and portable phosphate determination in various waters, and a number of *in-situ* and online phosphate analysers employing colorimetry are commercially available [19-25]. The LOC *in-situ* phosphate analyser developed by the National Oceanography Centre, Southampton can be seen as a leading phosphate analyser. This portable analyser has successfully been deployed within a broad range of environmental waters over long deployment periods delivering high levels of accuracy and precision [26-28]. Despite these high levels of analytical performance in the field, challenges arise in terms of mass manufacture of microfluidic components and assembly of LOC systems which has hampered these *in-situ* systems and other LOC colorimetric based systems from routine use and adoption on a mass scale [29, 30].

When considering the determination of inorganic anions such as phosphate in complex water matrices such as wastewater, ion chromatography (IC) with suppressed conductivity detection is a widely-used technique within a laboratory setting [31]. Ion chromatography methods have numerous advantages over colorimetric methods, including no requirement for multiple reagents, simple sample pre-treatment and high selectivity in complex samples [31]. When considering portable IC, Hauser *et al.* (2001) reported a portable battery powered ion chromatography system suitable for in-field analysis. Determination of a wide range of species, including inorganic ions and organic acids was demonstrated employing three electrochemical detection methods [32]. In recent years, developments in automation techniques and advancements in photovoltaic and battery technologies have enabled the development and deployment of portable chromatographic analysers [33-36]. Elkin (2014) reported a portable conductivity-based IC system for anion determination in river water and the system employed an eluent reflux device to minimise eluent consumption [35]. However, when considering long term deployment in the field, IC with conductivity detection can be heavily impacted by ambient temperature fluctuations [37].

Murray *et al.* (2020) described a portable and deployable IC-based analyser for nitrite and nitrate determination in both freshwater and wastewater [36]. Selective detection of these anions was achieved using a 235 nm LED coupled with a photodiode for direct UV detection. During field deployments the analyser demonstrated high precision and accuracy comparable to accredited laboratory-based methods. When considering phosphate determination in water, direct UV detection is not feasible due to the non-UV absorbing nature of this anion. As a means of overcoming this, indirect UV detection can be employed as a strategy for phosphate detection [38-40].

In this work, we describe the development of a phosphate determination method employing IC with indirect UV LED detection towards the generation of a simple, portable analyser for phosphate monitoring in both freshwater and wastewater matrices. The analyser was based on IC employing isocratic elution using potassium phthalate-based eluent with an IonPac CS5A analytical column for anion separation and indirect UV LED based optical detection. The detection system utilised a 3D printed detection cell, fabricated through stereolithography, with a 255 nm LED and UV photodiode. The IC system was integrated with a cation trap cartridge to eliminate transition metal interference for accurate phosphate determination in wastewaters. Freshwater and wastewater samples, along with blind freshwater samples, were analysed and the analytical performance of the developed method and configuration was compared to an accredited lab-based IC system.

2. Materials and methods

2.1 Reagents and materials

All chemicals used within this study were of analytical grade. All solutions were prepared using high purity deionised water (Milli-Q). Sodium tetraborate and potassium phthalate eluent was prepared using $\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$ (Sigma Aldrich) and $\text{C}_8\text{H}_5\text{KO}_4$ (labkem), respectively. Sodium bicarbonate buffer was prepared using sodium bicarbonate and sodium hydroxide (Sigma Aldrich). Tris buffer was prepared with Tris(hydroxymethyl)aminomethane (Panreac), whereas Bis-tris buffer was prepared from Bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane (Sigma Aldrich). Phosphate stock was prepared using KH_2PO_4 (PanReac AppliChem). For the interference study nitrate, nitrite, carbonate, chloride, iodate, sulphate, bromide and fluoride stock solutions were prepared

using NaNO_3 (Sigma Aldrich), NaNO_2 (Sigma Aldrich), Na_2CO_3 (Sigma Aldrich), NaCl (Fisher Chemicals), KIO_3 (PanReac AppliChem), Na_2SO_4 (Sigma Aldrich), KBr (Merck) and NaF (Sigma Aldrich), respectively. Working standards were prepared by diluting the stock solutions.

2.2 Ultra Violet Optical Detector

The absorbance detector was based on a z-shape format and was fabricated using SLA printing. The detector is shown in Fig. 1, further design renders and photos of the 3D printed optical detection cell are shown in figure A1 of the electronic supplementary information (ESI). The fluidic design of the detector was based upon the design previously reported by Murray *et al.* [41]. The cell was 56 x 32 x 15 mm in size, the z-shaped channel had a diameter of 1 mm and the optical path of the cell was 2.5 cm. Cells were fabricated using a DWS 29J+ 3D stereolithographic system in DL260 resin from DWS Systems (Italy). DL260 resin was selected as it is a nano-filled ceramic material which ensures the printed detector cell resists bending after fabrication allowing for constant optical alignment between the LED and the photodetector. DL260 resin also has a broad chemical resistance. The system used a 405 nm laser source, providing a 30 μm writing resolution [42]. DL260 is a nanoceramic composite material with a density of 1.3 g mL^{-1} , a flexural modulus of 1.8 GPa and a static water contact angle of $77^\circ \pm 3^\circ$. The parts were printed with a constant slice thickness of 30 μm and a laser hatching value of 30 μm . The detector cell was printed with a laser speed set to 2800 mm s^{-1} for the first 62 layers composing the basal part of the design and increased to 5800 mm s^{-1} for the remaining layers. All parts were developed in ethanol in an ultrasonic bath for 1 min. Microfluidic channels were further developed by manually injecting 5 mL of ethanol using a plastic syringe connected to the device inlet. The total fabrication time, comprising 3D printing and device development, was 150 minutes. Fused silica glass windows were assembled to the 3D printed detector using TESA 61210 double sided-tape, which was cut by xurography using a Graphtec FC8600-60 cutting plotter. This adhesive displays good chemical resistance and is resistant to UV light, ensuring good sealing of the assembly over time.

2.3 Ion Chromatography Configuration

The fluidic configuration of the phosphate analyser is shown in Fig. 2, and incorporates design aspects of the portable IC system previously reported by Murray *et al.* [36]. Eluent delivery was provided using a compact dual piston pump (Knauer, Berlin, Germany). An automated 1 mL syringe pump was used for introducing sample into the system for analysis. The syringe pump was designed and fabricated as previously reported [36], and the gas-tight syringe was purchased from Trajan Scientific (Melbourne, Australia). An automated 6 port 2-position injection valve was provided by VICI AG (Schenkon, Switzerland). Separation was achieved using a 4 × 50 mm IonPac CG5A guard column with a 4 × 250 mm IonPac CS5A analytical column (Thermo Fisher, Sunnyvale, California). The particles used within these columns had a diameter of 9 µm, capable of both anion and cation separation through the presence of both sulfonic acid and alkanol quaternary ammonium functional groups. Samples were automatically drawn through a Dionex InGuard Na trap cartridge (Thermo Fisher, Sunnyvale, California) to remove transition metals prior to separation and analysis. LED-based indirect UV detection was achieved using the 3D printed detection cell with a 255 nm UV-LED (Digi-Key, Minnesota, USA) and a UVC photodiode (TOCON_C1) with integrated amplifier purchased from Sglux GmbH (Berlin, Germany). The embedded system consisted of an ARM based microcontroller (Teensy 3.6) which controlled the timing and actuation of the sample intake pump, the sample syringe pump and the 6-way valve. The 255 nm UV LED intensity was controlled through a constant current driver (AL8805) for stable operation. UVC photodiode signals were sampled using a 16-bit analog to digital converter (ADS1115). Separation data processed by the microcontroller was stored on an SD card for retrieval. Electronic components were sourced from Mouser Electronics (Texas, USA). Inline check valves and tubing connectors were purchased from Kinesis (Altrincham, UK) and Sigma Aldrich (St. Louis, MO). The analytical system was housed within a 1510 M Peli Case (Peli Products, Ireland).

2.4 Eluent optimisation

In ion exchange chromatography, pH is an important parameter for separation and is readily adjusted and controlled by means of buffer substances. To achieve optimum elution and repeatable detection of phosphate within water matrices, a mobile phase with a constant

pH is required. In Methods for the Examination of Waters and Associated Materials analysis, published in 1990 [43], an anion exchange chromatography method with indirect UV detection of inorganic anions using potassium phthalate combined with sodium tetraborate was described for potential phosphate determination. However, following initial assessments using sodium tetraborate in combination with potassium phthalate as the eluent, an unstable eluent pH was observed overtime resulting in poor and inconsistent chromatography. To stabilise eluent pH and to optimise phosphate detection, a range of different buffers were assessed, including, Tris, Bis Tris, sodium hydroxide and sodium bicarbonate.

2.5 Sample analysis and performance assessment

A range of water samples were obtained for testing using the portable IC system, including a public amenity visitor centre effluent sample (Co. Offaly, Ireland), effluent from a residential care facility and an industrial food processing effluent. In addition, blind water samples were prepared and analysed. To further assess the accuracy of the IC configuration, a range of various environmental samples were spiked and recovery analysis was carried out following the procedure described by Eaton [44, 45]. A river water sample (Wexford, Ireland), an effluent from a waste water treatment plant (Wicklow, Ireland), the residential care facility and industrial food processing effluent samples were spiked with $5 \text{ mg L}^{-1} \text{ PO}_4^{3-}$ and recovery was obtained using the following calculations:

$$\text{Recovery} = \text{spiked sample conc.} - ((\text{unspiked sample conc.} / 100 \text{ mL}) \times 99.5 \text{ mL})$$

$$\text{Recovery \%} = \text{recovery} / \text{spike concentration} \times 100$$

Concentrations of phosphate in the environmental samples were firstly determined using the portable phosphate analyser. The obtained concentrations were divided by 100 and then multiplied by 99.5 to take into consideration the dilution caused by adding 0.5 mL of $1000 \text{ mg L}^{-1} \text{ PO}_4^{3-}$ standard to make up 100 mL total volume in the real water sample matrix. The obtained value was then subtracted from the spiked sample concentration to calculate recovery.

3. Results and discussion

3.1 Eluent assessment

When using sodium tetraborate in combination with potassium phthalate as the eluent, an unstable eluent pH was observed overtime as the RSD for daily pH measurements exceeded 30 % after 2 days. Poor eluent pH stability was observed for all buffers assessed, with the exception of sodium bicarbonate. For this reason, sodium bicarbonate was selected as it enabled eluent stability at pH 8.8. The pH stability of the eluent, consisting of 0.6 mM potassium phthalate and 1.44 mM sodium bicarbonate was assessed by analysing and monitoring the retention time of a 10 mg L⁻¹ PO₄³⁻ standard over twelve days. Three measurements were obtained on a daily basis using the same eluent. The results, including the % RSD values for each day, are outlined in figure B1 of the ESI. Satisfactory precision was achieved over the twelve-day analysis with an overall retention time RSD of 3.74 % obtained. The eluent demonstrated sufficient stability for use within the portable phosphate analyser and demonstrates potential when considering future deployment of the analyser in remote environmental locations for extended periods of time.

3.2 Analytical performance

The optimised IC method enabled phosphate determination under 10 minutes which is comparable to commercial phosphate analysers [46, 47]. Satisfactory resolution was achieved and a wide linear calibration plot was obtained ranging from 0.5 to 30 mg L⁻¹ PO₄³⁻ (R² = 0.999). The phosphate linear curve generated by the analyser is shown within figure C1 of the ESI. The limit of detection (LOD) was calculated using a signal-to-noise ratio (S/N) = 3 as previously reported [48, 35]. Following assessment, it was estimated to be 0.4 mg L⁻¹ PO₄³⁻. The signal response and detection of 0.5 mg/L PO₄³⁻ is highlighted in the chromatogram shown in figure D1 of the ESI. To estimate the LOD, analysis of a 0.7 mg L⁻¹ PO₄³⁻ standard was carried out. The average background noise level associated with the measurement and chromatogram was determined. Using this information, the estimated LOD level was then taken as the phosphate concentration which corresponded to three times the background noise level [46]. The interference of common anions was investigated to ensure that coelution of phosphate with other anions would not be present during environmental sample analysis. In the study, chloride, iodate, fluoride, carbonate,

Accepted Article

sulphate, bromide, nitrate and nitrite were selected as these anions are commonly found in environmental waters. An anion mixture containing 10 mg L⁻¹ of these nine commonly found anions along with phosphate was analysed using the portable IC set up. As can be seen in Fig. 3, selective detection of phosphate was achieved and the determination of phosphate was not affected by the presence of other anions.

3.3 Chromatographic repeatability

To assess the repeatability of the portable IC platform for phosphate analysis, 52 sequential chromatograms were produced for the nine-anion standard solution with 10 mg L⁻¹ phosphate present within the standard. Prior to the first injection, the system was equilibrated with the eluent for approximately 15 min and automatic injection was configured. The 10 mg L⁻¹ phosphate anion mix standard solution was injected every 10 min. The repeatability of the retention times and peak areas are presented in Fig. 4. The relative standard deviation (RSD) of peak area and retention time for the 52 successive runs was 4.07 % and 0.68 % respectively. These repeatability results highlight the potential of the method and the portable platform when considering phosphate quantification in environmental water samples.

3.4 Water sample analysis

All samples were analysed in triplicate. The performance of the portable IC analyser was assessed by comparing the obtained phosphate results to an accredited lab-based ion chromatograph, accredited according to ISO 17025 by the Irish National Accreditation Board (INAB). Accuracy of the portable IC configuration was obtained by calculating the relative % error for phosphate between the portable and accredited IC system. Table 1 shows the phosphate concentrations determined within each sample using the portable IC configuration versus the accredited lab-based IC system. Examples of chromatograms generated by the portable IC system are shown in Fig. 5.

The phosphate concentrations which were determined for the spiked environmental water samples and corresponding recovery values are shown in Table 2. Average recovery for environmental samples spiked with phosphate ranged between 95.5 – 115.7 % which lies within the recommended recovery range for IC methods set by Environmental Protection Agency's (EPA) methods [49]. In addition, according to standard methods for the

examination of water and wastewater, a recovery value observed within the range 85–115% is an acceptable recovery in terms of analytical validation [44].

5. Concluding Remarks

A portable IC configuration and method for the determination of phosphate in water has been developed and demonstrated in a laboratory setting. The method employed isocratic elution using buffered potassium phthalate eluent at pH 8.8 with a CS5A 4×250 mm analytical column in series with a CG5A 4×50 mm guard column. Indirect UV detection of phosphate was achieved using a 3D printed detection cell with a 255 nm LED and photodiode. The SLA 3D printing of the detection cell enabled the generation of a low-cost, mechanically robust monolithic detector, with fabrication time compatible with medium scale production. The IC set up demonstrated good performance in terms of repeatability and precision. In addition, a LOD of 0.4 mg L⁻¹ PO₄³⁻ and a linear detection range between 0.5–30 mg L⁻¹ PO₄³⁻ applicable to a wide range of environmental and industrial wastewaters was achieved. Environmental samples were analysed using the portable IC system and the results were compared to an accredited IC system with relative errors < 14 % obtained. Average recovery ranged between 95.48 – 115.7 % following a recovery assessment carried out for both fresh water and wastewater samples. Overall, the developed phosphate detection method shows a great potential for phosphate monitoring in both freshwater and wastewater matrices and has the potential for use within deployable monitoring applications in the field. Further work will be focused on development of an embedded system and communications to enable complete automation of the analyser for remote *in situ* phosphate monitoring in the field.

Acknowledgements

The authors would like to acknowledge financial support through the H2Omon project from the EU Horizon 2020 Research and Innovation programme under grant agreement number 880886. The authors would also like to acknowledge financial support from the Holifab project, EU Horizon 2020 Pilots Programme under grant agreement number 760927. This work was partly supported by LAAS-CNRS micro and nanotechnologies platform (member of the Renatech French national network) and by the MultiFAB project funded by

FEDER European Regional Funds and French Région Occitanie under grant agreement number 16007407/MP0011594.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

6. References

- [1] Robards K., McKelvie I. D., Benson R. L., Worsfold P. J., Blundell N. J., Casey H., Determination of carbon, phosphorus, nitrogen and silicon species in waters. *Anal. Chimica Act.* 1994, 287, 147–190.
- [2] Anderson D. M., Glibert P. M., Burkholder J. M., Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. *Est.* 2002, 25, 704-726.
- [3] Carpenter S. R., Caraco N. F., Correll D. L., Howarth R. W., Sharpley A. N., Smith V. H., Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. App.* 1998, 8, 559-568.
- [4] Mainstone C. P., Parr W., Phosphorus in rivers—ecology and management. *Sci. Total Environ.* 2002, 282, 25-47.
- [5] Cleary J., Maher D., Diamond D., in: Mukhopadhyay S., Mason A. (Eds.), Smart Sensors for Real-Time Water Quality Monitoring. Springer, Berlin 2013, pp. 125-148.
- [6] Johnson K.S., Needoba J.A., Riser S. C., Showers W. J., Chemical sensor networks for the aquatic environment. *Chem. Rev.* 2007, 107, 623-640.
- [7] Worsfold P. J., Challenges in the Determination of Nutrient Species in Natural Waters. *Microchim. Acta* 2006, 154, 45–48.
- [8] Bowden M., Sequiera M., Krog J.P., Gravesen P., Diamond D., Analysis of river water samples utilising a prototype industrial sensing system for phosphorus based on micro-system technology. *J. Environ. Monit.* 2002, 4, 767-771.
- [9] Gross E.M., Durant H.E., Hipp K.N., Lai R.Y., Electrochemiluminescence detection in paper-based and other inexpensive microfluidic devices. *ChemElectroCh.*, 2017, 4, 1594-1603.

- [10] Contreira-Pereira L., Yucel M., Omanovic D., Brulport J. P., Le Bris N., N., Compact autonomous 12oltametric sensor for sulfide monitoring in deep sea vent habitats. *D. Sea Res. Part I: Ocean. Res. Pap.* 2013, *80*, 47-57.
- [11] Pankratova N., Cuartero M., Cherubini T., Crespo G.A. and Bakker E., In-line acidification for potentiometric sensing of nitrite in natural waters. *Anal. Chem.* 2017, *89*, 571-575.
- [12] Racicot J.M., Mako T.L., Olivelli A., Levine M., A Paper-Based Device for Ultrasensitive, Colorimetric Phosphate Detection in Seawater. *Sen.* 2020, *20*, 2766.
- [13] Khongpet W., Yanu, P., Pancharee S., Puangpila C., Hartwell S.K., Lapanantnoppakhun, S., Yodthongdee Y., Paukpol A., Jakmunee J., A compact multi-parameter detection system based on hydrodynamic sequential injection for sensitive determination of phosphate, nitrite, and nitrate in water samples. *Anal. Met.* 2020, *12*, 855-864.
- [14] Barus C., Romanytsia I., Striebig N., Garcon V., Toward an in-situ phosphate sensor in seawater using Square Wave Voltammetry. *Tal.* 2016, *160*, 417–424.
- [15] Jonca J., Giraud W., Barus C., Comtat M., Striebig N., Thouron D., Garcon V., Reagentless and silicate interference free electrochemical phosphate determination in seawater. *Elect. A.* 2013, *88*, 165-169.
- [16] Manz A., Graber N., Widmer H. A., Miniaturized total chemical analysis systems: a novel concept for chemical sensing. *Sens. Actuators, B* 1990, *1*, 244-248.
- [17] Nightingale A.M., Beaton A.D., Mowlem M.C., Trends in microfluidic systems for in situ chemical analysis of natural waters. *Sens. Actuators, B* 2015, *221*, 1398-1405.
- [18] Whitesides G. M., The origins and the future of microfluidics, *Nature*, 2006, *442*, 368–373.
- [19] Slater C., Cleary J., Lau K.T., Snakenborg D., Corcoran B., Kutter J. P., Diamond D., Validation of a fully autonomous phosphate analyser based on a microfluidic lab-on-a-chip, *Water Sci Technol.* 2010, *61*, 1811–1818.
- [20] Donohoe A., Lacour G., McCluskey P., Diamond D., McCaul M., Development of a cost-effective sensing platform for monitoring phosphate in natural waters. *Chemosen.* 2018, *6*, 57.
- [21] Legiret F.E., Sieben V.J., Woodward E.M.S., Abi Kaed Bey S.K., Mowlem M.C., Connelly D.P., Achterberg E.P., A high performance microfluidic analyser for phosphate

- measurements in marine waters using the vanadomolybdate method, *Talanta*, 2013, 116, 382-387.
- [22] http://www.systea.it/index.php?option=com_k2&view=item&id=223:systea-spa-wiz-probe&Itemid=175&lang=en (accessed Aug 2, 2021)
- [23] <https://www.seabird.com/hydrocycle-po/product?id=54721314201> (accessed Sept 9, 2021).
- [24] <https://www.partech.co.uk/measurements/phosphate/> (accessed Sept 8, 2021).
- [25] <https://www.xylemanalytics.com/en/iq-analyzer-for-orthophosphate--wtw> (accessed Sept 8, 2021).
- [26] Birchill A.J., Beaton A.D., Hull T., Kaiser J., Mowlem M., Pascal R., Schaap A., Voynova Y.G., Williams C., Palmer M., Exploring Ocean Biogeochemistry Using a Lab-on-Chip Phosphate Analyser on an Underwater Glider, *Front. Mar. Sci.*, 2021.
- [27] Clinton-Bailey G.S., Grand M.M., Beaton A.D., Nightingale A.M., Owsianka D.R., Slavik G.J., Connelly D.P., Cardwell C.L., Mowlem M.C., A Lab-on-Chip Analyzer for in Situ Measurement of Soluble Reactive Phosphate: Improved Phosphate Blue Assay and Application to Fluvial Monitoring, *Environ. Sci. Technol.* 2017, 51, 9989–9995.
- [28] Grand M.M., Clinton-Bailey G.S., Beaton A.D., Schaap A.M., Johengen T.H., Tamburri M.N., Connelly D.P., Mowlem M.C., Achterberg E.P., A Lab-On-Chip Phosphate Analyzer for Long-term In Situ Monitoring at Fixed Observatories: Optimization and Performance Evaluation in Estuarine and Oligotrophic Coastal Waters, *Front. Mar. Sci.*, 2017.
- [29] Ríos A., Zougagh M., Avila M., Miniaturization through lab-on-a-chip: Utopia or reality for routine laboratories? A review, *Anal. Chim. Acta*, 2012, 740, 1–11.
- [30] Schierenbeck T.M., Smith M.C., Path to impact for autonomous field deployable chemical sensors: a case study of in situ nitrite sensors, *Environ. Sci. Technol.* 2017, 51, 4755–4771.
- [31] Michalski R., Ion chromatography applications in wastewater analysis. *Sep.* 2017, 5, 16.
- [32] Kappes, T., Galliker, B., Schwarz, M. A., & Hauser, P. C., Portable capillary electrophoresis instrument with amperometric, potentiometric and conductometric detection, *Trends Anal. Chem* 2001, 20, 133-139.

- [33] Boring, C. B., Dasgupta, P. K., & Sjögren, A., Compact, field-portable capillary ion chromatograph, *J. Chromatogr. A* 1998, 804, 45-54.
- [34] Kiplagat I.K., Kubáň P., Pelcová P., Kubáň V., Portable, lightweight, low power, ion chromatographic system with open tubular capillary columns, *J. Chromatogr. A* 2010, 1217, 5116-5123.
- [35] Elkin K.R. Portable, fully autonomous, ion chromatography system for on-site analyses, *J. Chromatogr. A*, 2014, 1352, 38-45.
- [36] Murray E., Roche P., Briet M., Moore B., Morrin A., Diamond D., Paull B., Fully automated, low-cost ion chromatography system for *in-situ* analysis of nitrite and nitrate in natural waters, *Talanta* 2020, 216, 12095.
- [37] Madden J.E., Lopez L., Yang H., Moore D.G., Technical Note 179: Effect of Temperature on IC Signal Noise, Thermo Fisher Scientific, California 2016.
- [38] Naish P.J., Indirect Ultraviolet Detection for Ion Chromatography-Its Optimisation and Application, *Analyst*, 1984, 109.
- [39] Connolly D., Paull B., Fast ion chromatography of common inorganic anions on a short ODS column permanently coated with didodecyldimethylammonium bromide, *J. Chromatogr. A*. 2002, 953, 299-303.
- [40] Breadmore M.C., Haddad P.R., Fritz J.S., Optimisation of the separation of anions by ion chromatography–capillary electrophoresis using indirect UV detection, *J. Chromatogr. A* 2001, 920, 31-40.
- [41] Murray E., Roche P., Harrington K., McCaul M., Moore B., Morrin A., Diamond D., Paull B., Low cost 235 nm ultra-violet light-emitting diode-based absorbance detector for application in a portable ion chromatography system for nitrite and nitrate monitoring, *J. Chromatogr. A* 2019, 1603,8-14.
- [42] Juskova P., Ollitrault A., Serra M., Viovy J.L., Malaquin L., Resolution improvement of 3D stereo-lithography through the direct laser trajectory programming: Application to microfluidic deterministic lateral displacement device, *Anal. Chim. Acta*, 2018, 1000, 239-247.
- [43] HMSO, The Determination of Anions and Cations, Transition Metals, Other Complex Ions and Organic Acids and Bases in Water by Chromatography, London 1990.
- [44] Eaton A.D., Clesceri L.S., Rice E.W., Greenberg A.E., Standard methods for the examination of water and wastewater. Port City Press, Baltimore 2005.

- [45] Fitzhenry C., Jowett L., Roche P., Harrington, K., Moore B., Paull B., Murray E., Portable analyser using two-dimensional ion chromatography with ultra-violet light-emitting diode-based absorbance detection for nitrate monitoring within both saline and freshwaters, *J. Chromatogr. A* 2021, 1652, 462368.
- [46] https://www.yokogawa.com/eu/solutions/products-platforms/process-analyzers/liquid-analyzers/wet-chemistry-analyzers/we440-phosphate-analyzer/#Details__Features (accessed April 14, 2021).
- [47] <https://www.3s-analyzers.eu/wp/wp-content/uploads/2020/07/Phosphate-Blue-Colorimeter-Datasheet.pdf> (accessed April 15, 2021).
- [48] Murray E., Li Y., Currivan S.A., Moore B., Morrin A., Diamond D., Macka M., Paull B., Miniaturized capillary ion chromatograph with UV light-emitting diode based indirect absorbance detection for anion analysis in potable and environmental waters, *J. Sep. Sci.* 2018, 16, 3224-3231.
- [49] <https://www.epa.gov/sites/default/files/2015-06/documents/epa-300.1.pdf> (accessed August 12, 2021).

Fig. 1: Design of UV LED absorbance detector fabricated using SLA. Legend: (1) UV photodiode and electronic board; (2) printed photodiode holder; (3) fused silica glass UV-transparent windows (12.5 × 2 mm); (4) chemical resistant double-sided tape; (5) Detector cell; (6) UV LED holder; (7) surface mount UV LED and electronic board; (8) cell holder.

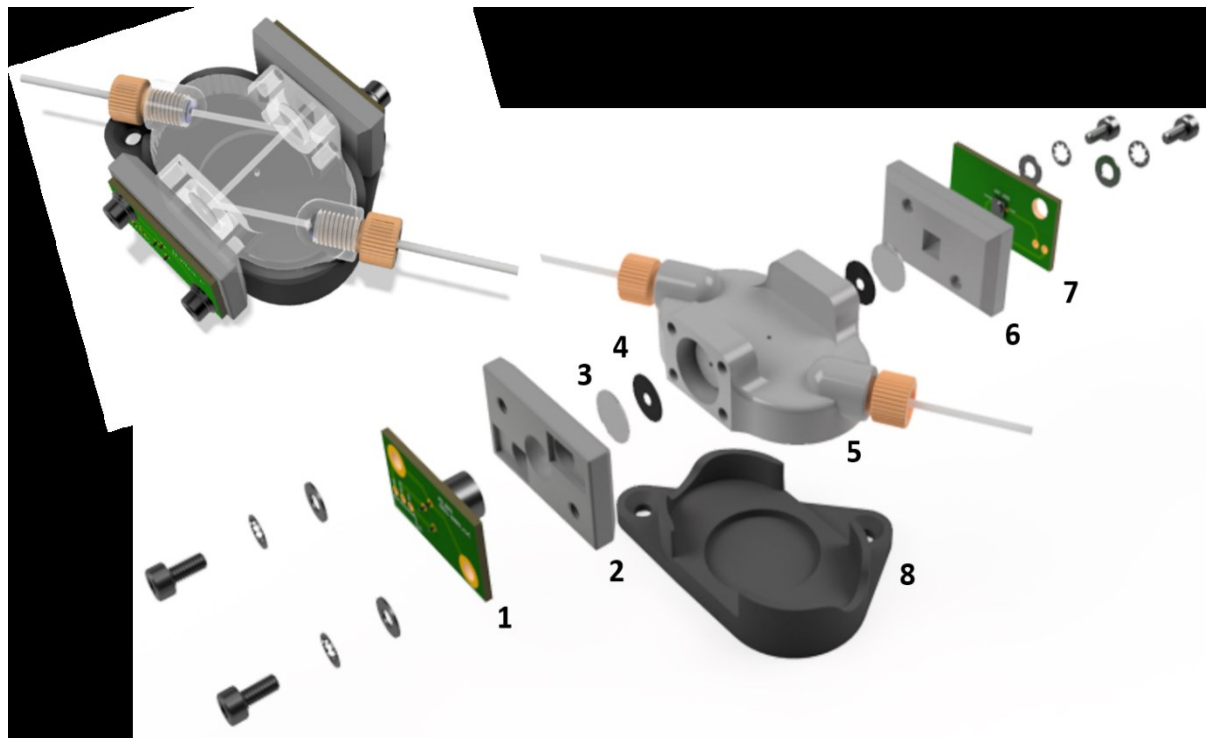


Fig. 2: (Top) Schematic representation of portable chromatographic set up for phosphate analysis. The flow path of water sample through the sample reservoir is shown in blue. An aliquot of sample taken from the reservoir is drawn through the cation trap cartridge and is introduced into the system via the sample loop of the six-way valve, this flow path is shown in green. The flow path of the buffered potassium phthalate eluent is shown in black. (Bottom) Render of portable phosphate analyser with components labelled. Exterior dimensions of 23 cm x 36 cm x 57 cm. System weight 13 kg. Legend: (1) eluent container; (2) waste container; (3) piston pump; (4) injection valve; (5) battery; (6) control board and electronics; (7) 3D printed UV LED detection cell; (8) analytical column.

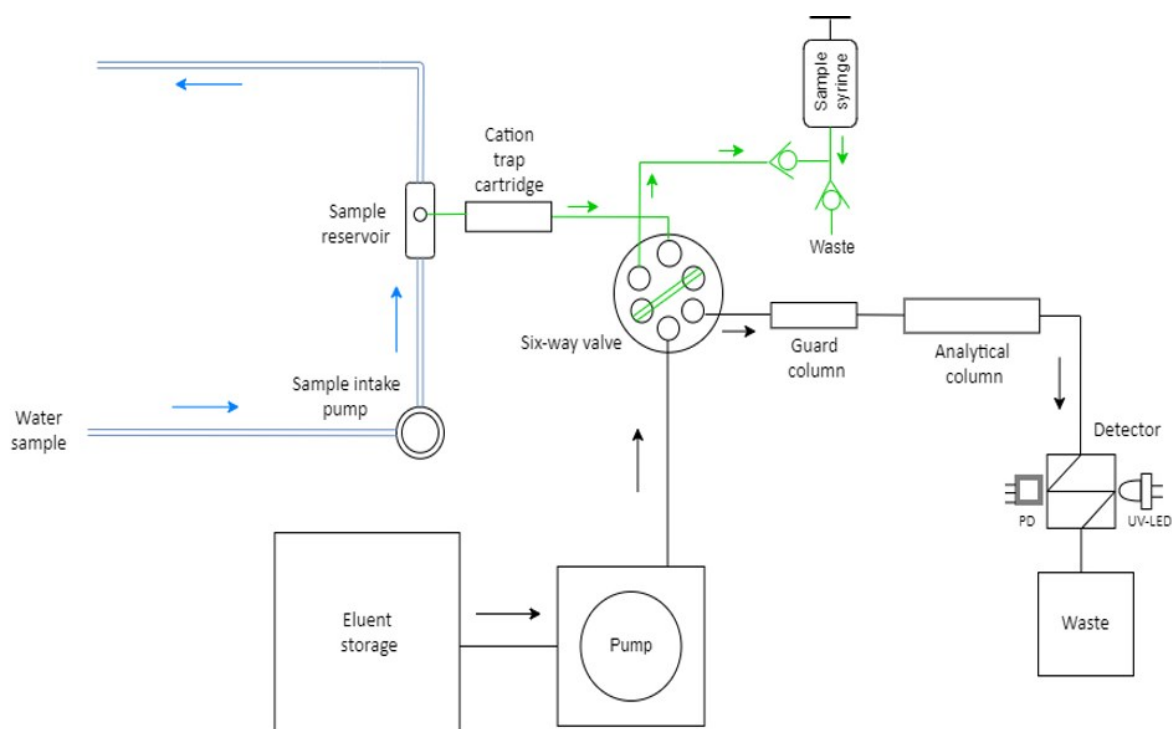


Fig. 3: Chromatogram of nine-anion standard containing $10 \text{ mg L}^{-1} \text{ PO}_4^{3-}$, SO_4^{2-} , CO_3^{2-} , IO_3^- , Br^- , F^- , Cl^- , NO_2^- and NO_3^- . The standard was analysed using a $75 \text{ }\mu\text{L}$ sample loop and 0.6 mM potassium phthalate eluent at a flow rate of 0.75 mL min^{-1} with a Dionex CG5A $4 \times 50 \text{ mm}$ guard column and Dionex CS5A $4 \times 250 \text{ mm}$ analytical column employing the 3D printed detector with 255 nm LED and photodiode for detection.

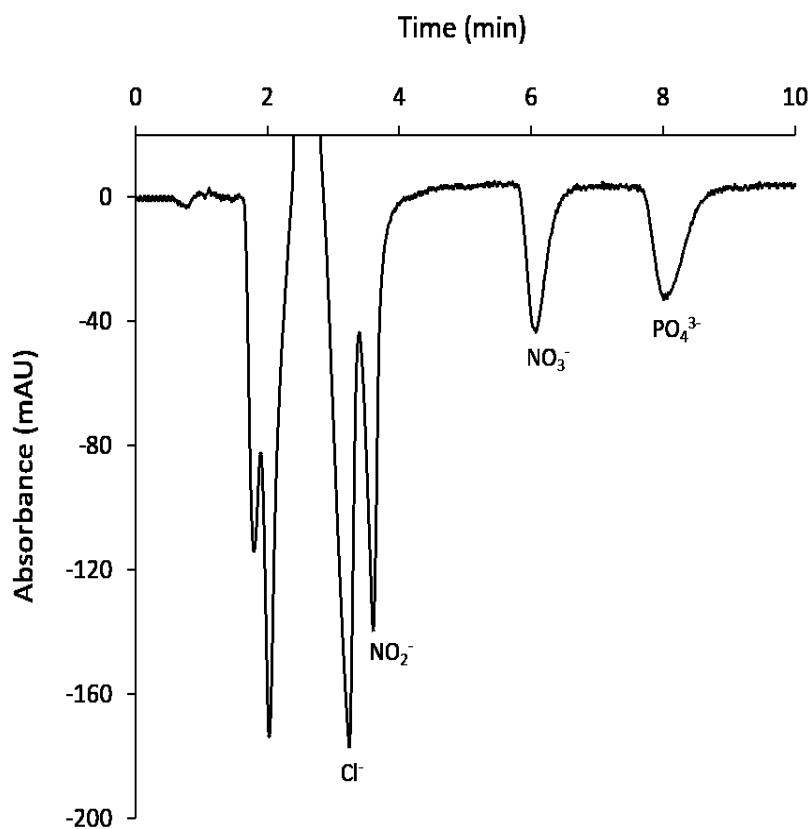


Fig. 4: Repeatability of peak area and retention time values determined using the portable analyser, analysing $10 \text{ mg L}^{-1} \text{ PO}_4^{3-}$ standard over 50 sequential runs and associated RSD values.

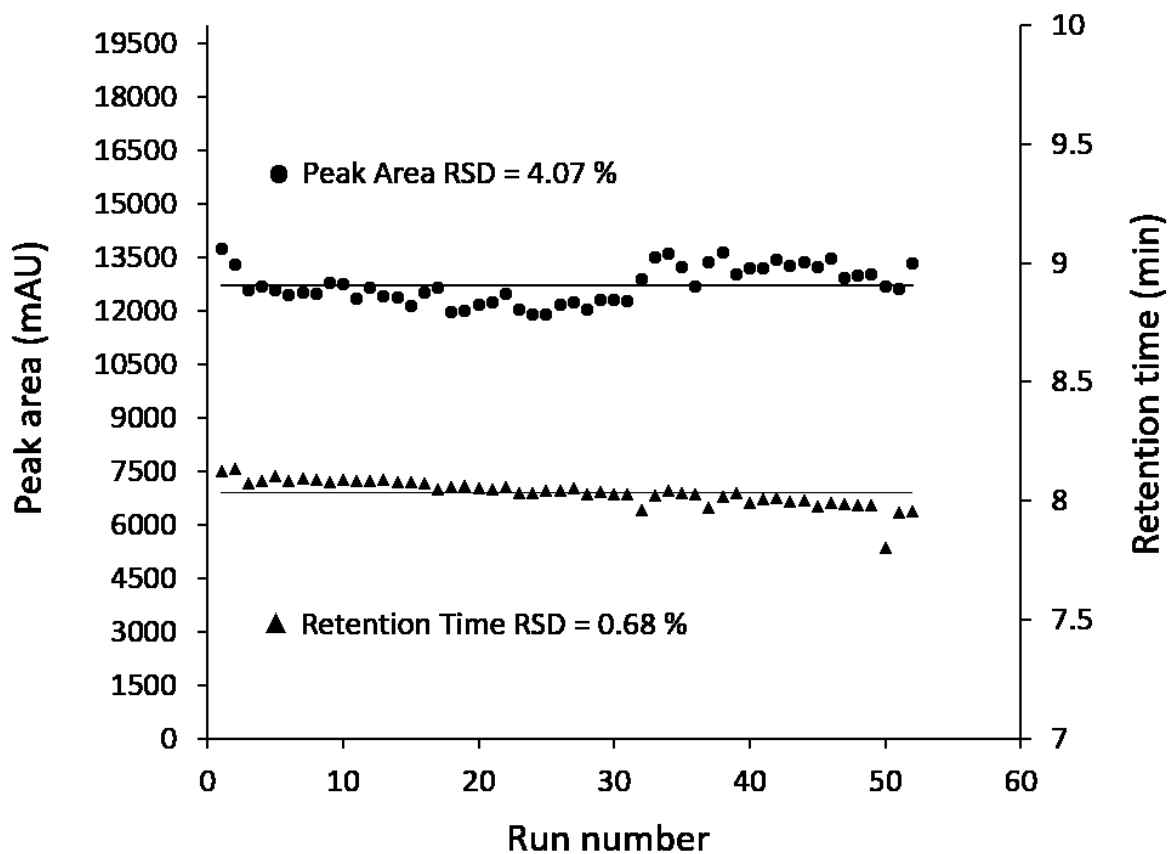


Fig. 5: (Left) Chromatogram of industrial process effluent sample; (Right) chromatogram of spiked river water sample. Samples were analysed using a 75 μL sample loop and 0.6 mM potassium phthalate eluent at a flow rate of 0.75 mL min^{-1} with a CG5A 4 \times 50 mm guard column and CS5A 4 \times 250 mm analytical column employing the 3D printed detector with 255 nm LED and photodiode.

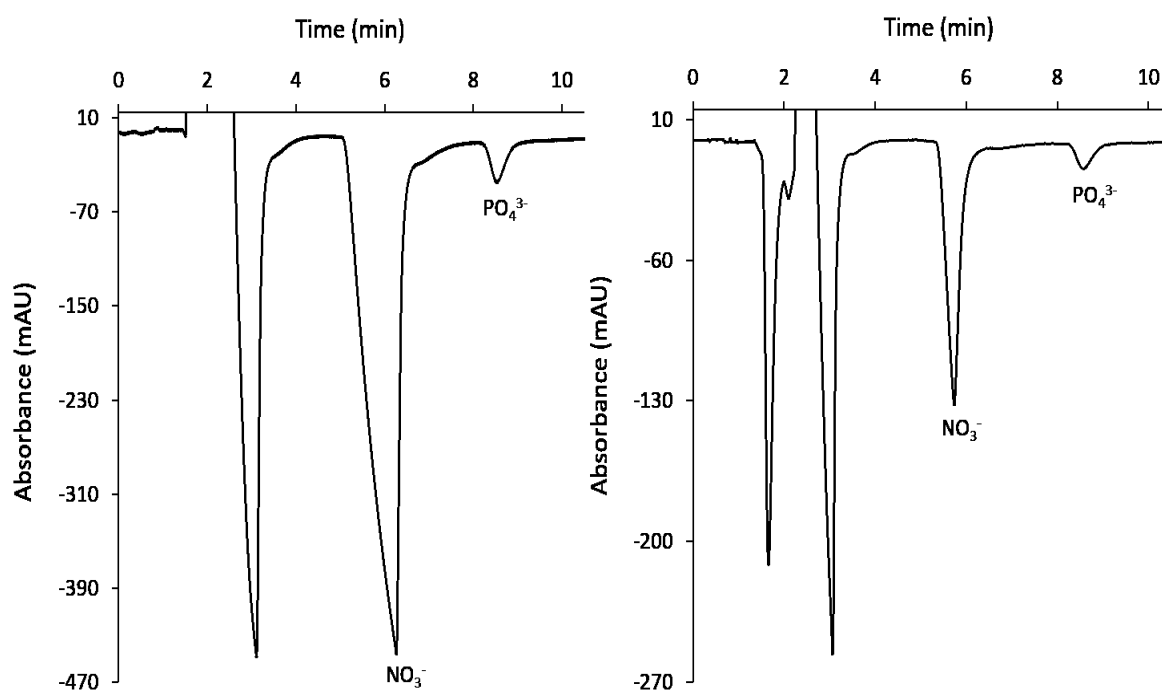


Table 1: Phosphate concentrations obtained using portable IC configuration versus phosphate concentrations generated using accredited IC (n=3).

Sample	Portable IC (mg L ⁻¹ PO ₄ ³⁻)	Accredited IC (mg L ⁻¹ PO ₄ ³⁻)	Relative error (%)
Residential care facility effluent	1.3 ± 0.64	1.5 ± 0.11	- 13.3
Industrial food processing effluent	24.1 ± 0.62	27.0 ± 0.26	- 10.7
Public amenity visitor centre effluent	7.3 ± 0.25	7.8 ± 0.13	- 6.4
Freshwater A	6.8 ± 0.34	6.6 ± 0.08	1.9
Freshwater B	3.5 ± 0.16	3.8 ± 0.06	- 7.8

Table 2: Concentrations determined within fresh and spiked environmental water samples determined with portable phosphate analyser (n=3).

Sample	Portable IC (mg L ⁻¹ PO ₄ ³⁻)	Spike (mg L ⁻¹ PO ₄ ³⁻)	Average recovery (%)
Residential care facility effluent	1.28 ± 0.61	5	98.5
Waste water treatment plant effluent	0.99 ± 0.80	5	108.8
Industrial food processing effluent	9.98 ± 0.60	5	115.7
River water sample	< 0.5	5	95.5