



**HAL**  
open science

## Ion chromatograph with three-dimensional printed absorbance detector for indirect ultraviolet absorbance detection of phosphate in effluent and natural waters

Annija Lace, Aideen Byrne, Simon Bluett, Laurent Malaquin, Vincent Raimbault, Rémi Courson, Zain Hayat, Breda Moore, Eoin Murray

### ► To cite this version:

Annija Lace, Aideen Byrne, Simon Bluett, Laurent Malaquin, Vincent Raimbault, et al.. Ion chromatograph with three-dimensional printed absorbance detector for indirect ultraviolet absorbance detection of phosphate in effluent and natural waters. *Journal of Separation Science*, 2022, 45 (5), pp.1042-1050. 10.1002/jssc.202100897 . hal-03796005

**HAL Id: hal-03796005**

**<https://laas.hal.science/hal-03796005v1>**

Submitted on 9 Jan 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Ion chromatograph with three-dimensional printed absorbance detector for indirect ultraviolet absorbance detection of phosphate in effluent and natural waters

Annija Lace <sup>1</sup>, Aideen Byrne <sup>1</sup>, Simon Bluett <sup>1</sup>, Laurent Malaquin <sup>2</sup>, Vincent Raimbault <sup>2</sup>, Remi Courson <sup>4</sup>, Zain Hayat <sup>2</sup>, Breda Moore <sup>1</sup>, Eoin Murray <sup>1,3</sup>

1. Research & Development, T.E. Laboratories Ltd. (TelLab), Tullow, Carlow, Ireland
2. LAAS-CNRS, Université de Toulouse, CNRS, F-31400, Toulouse, France
3. Research & Development, Aquamonitrix Ltd., Carlow, Ireland
4. Current affiliation : IFREMER - Laboratoire Détection, Capteurs et Mesures (REM-RDT-LDCM), France

**Correspondence:** Corresponding Author: Dr Eoin Murray, Research & Development, T.E. Laboratories Ltd. (TelLab), Carlow, Ireland. Phone: +353 868412294. Fax: +353 599152886. Email: EMurray@aquamonitrix.ie

**Abbreviations:** IC, ion chromatography; LED, light emitting diode; SLA, Stereolithography

**Keywords:** Indirect UV detection / Anion detection / Phosphate / SLA detection cell / Water analysis

## **Abstract**

An ion chromatography (IC) method employing a low cost, 3D printed UV absorbance detector incorporating a 255 nm light emitting diode (LED) for portable phosphate analysis in environmental and industrial waters has been developed. The optical detection cell was fabricated using stereolithography (SLA) 3D printing of nanocomposite material. Chromatographic analysis of phosphate was carried out using a CS5A 4×250 mm analytical column in series with CG5A 4×50 mm guard column at a flow rate of 0.75 ml min<sup>-1</sup> based on indirect UV detection using a 255 nm LED. Isocratic elution using a 0.6 mM potassium phthalate eluent combined with 1.44 mM sodium bicarbonate was employed. A Linear calibration range from 0.3 to 30 mg L<sup>-1</sup> applicable to environmental water analysis was achieved. For retention time and peak area repeatability, RSD value was 0.68 % and 4.09 %, respectively. Environmental water samples were analysed with the optimised IC system and the results were compared to values obtained by an accredited IC system. For environmental samples treated with Dionex Inlet Guard sample preparation cartridge 9×24 mm the relative errors were < 14 %. Recovery analysis was carried out on both freshwater and waste water samples.

## 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 phosphate presence in water systems can lead to eutrophication which is one of the most common water quality issues worldwide [2]. Eutrophication results in increased growth of harmful algae, which during decomposition release toxins and reduces the available amount of dissolved oxygen. This, in turn, deteriorates the 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 fresh water monitoring is 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 should be compact, robust, cost effective and environmentally compatible with 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, including chemiluminescence [9], electrochemistry [10,11] and colorimetry [12,13]. Electrochemical sensor prototypes have been developed for phosphate detection in water [14,15]. Despite the fast reaction times and the high sensitivity demonstrated in laboratory-based tests, these methods require further development and extensive field assessment.

Since Manz introduced the idea of miniaturised total analysis systems ( $\mu$ TAS) there has been a growing interest in microfluidic system application to environmental monitoring [16]. Microfluidic or lab on chip detection systems have many advantages over large scale chemical sensors, including reduced reagent consumption, low power requirement and increased sample turnover time [17]. To date, the majority of lab on chip methods have been based on

colorimetry due to their simplicity and applicability to microfluidic detection systems [18]. However, development of colorimetric reagent-based sensing devices is challenging as they require effective operating fluidic components, electronics, power board and communications. To date, production of detectors is costly, time consuming and requires inter disciplinary expertise. Therefore, there is a need for improved incorporation of fluidic and electronic components at a reduced overall cost [19].

In recent years, numerous researchers have developed autonomous lab on chip phosphate analysers based on colorimetric detection which have been deployed in range of environmental waters with complex matrices. Grand et al. [20] developed a lab on a chip sensor based on molybdenum blue method. The measurements were not affected by high salinity or presence of coloured dissolved organic matter. The phosphate analyser was deployed in estuarine water for 56 days period demonstrating good infield accuracy for the first month of deployment. Similarly, Clinton-Bailey et al. [21] generated a lab on a chip analyser for phosphate detection in environmental water using phosphate blue method. The solar powered sensor operated on a stop-flow regime. The analyser demonstrated high accuracy during nine-week infield deployment.

Duffy *et al.* [22] developed a fully integrated lab on a disc analyser for phosphate detection in water using molybdenum blue method. The device used centrifugal force by rotation of the disc to mix reagents and samples. The detection system included an LED-photodiode detector which measured absorbance of light at 880 nm. The device was applied for river water and waste water treatment plant effluent analysis, showing a good agreement with spectrophotometric method. However, further work on detector's hardware is needed; while portable, this lab on a disc approach also cannot be applied to in-situ continuous measurement due to necessity of manual sampling and filtering before loading in the analyser. Despite the encouraging results obtained with portable colorimetric sensors, the manufacture of reagent-based detection systems is very challenging and expensive [23]. In addition, the life time of portable colorimetry-based methods is significantly limited due to reagent stability [24].

In this paper we propose a novel phosphate detection system-based ion chromatography with indirect UV detection. Several indirect UV detection methods have been reported for

phosphate determination in water [25-27], however, up to date there are no reports on portable indirect UV detection systems. The work described in this paper is aimed towards the development of a portable *in-situ* analyser for phosphate in both freshwater and wastewater matrices. The analyser is based on ion chromatography using 0.6 mM potassium phthalate eluent. The detection system incorporates indirect UV LED based optical detection for phosphate determination. 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 ion chromatograph.

## **2. Materials and methods**

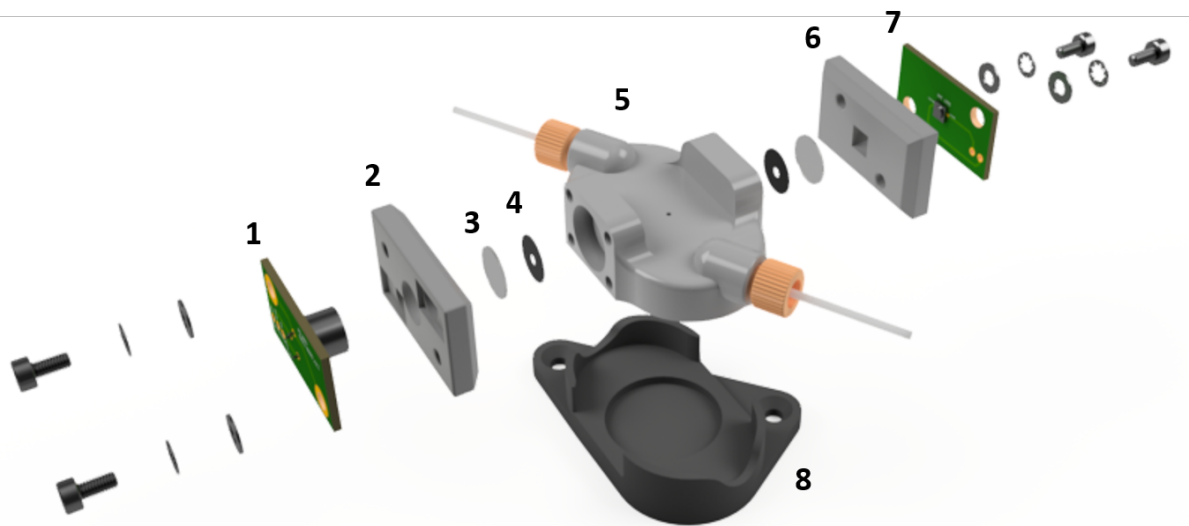
### **2.1 Reagents and materials**

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). Phosphate stock was prepared using  $\text{KH}_2\text{PO}_4$  (PanReac AppliChem). For the interference study nitrate, nitrite, carbonate, chloride, iodate, sulphate, bromide and fluoride stock solutions were prepared using  $\text{NaNO}_3$  (Sigma Aldrich),  $\text{NaNO}_2$  (Sigma Aldrich),  $\text{Na}_2\text{CO}_3$  (Sigma Aldrich),  $\text{NaCl}$  (Fisher Chemicals),  $\text{KIO}_3$  (PanReac AppliChem),  $\text{Na}_2\text{SO}_4$  (Sigma Aldrich),  $\text{KBr}$  (Merck) and  $\text{NaF}$  (Sigma Aldrich), respectively. Working standards were prepared by diluting the stock solutions.

### **2.2 UV Optical Detector**

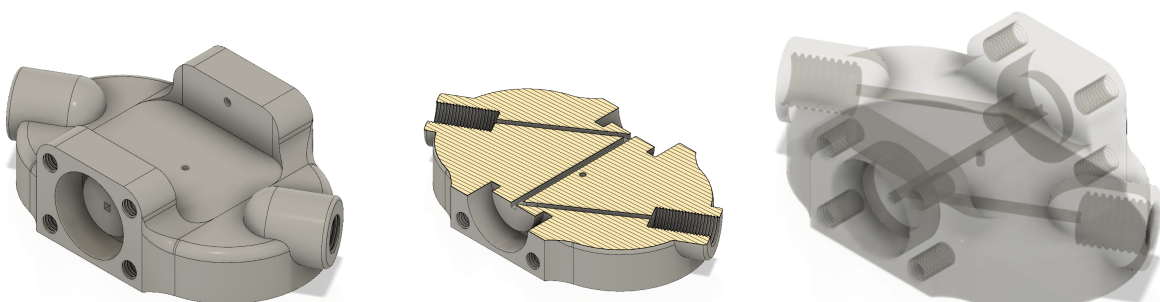
The optical detector was based on a z-shape format and was fabricated using SLA printing. The detector is shown in figure 1. The fluidic design of the detector was based upon the design previously reported by Murray *et al.* [28]. The cell was 56.2 x 32.4 x 15.6 mm in size and 11,38mL in volume. Cells were fabricated with a 3D stereolithographic system DWS 29J+ in DL260 from DWS Systems (Italy). The system uses a 405 nm laser source and provides a 30 $\mu\text{m}$  writing resolution (Ref : 10.1016/j.aca.2017.11.062). DL260 is a nanoceramic composite material with a density of 1.3g/mL, a flexural modulus of 1,8GPa and a static water contact angle of 77 $^\circ$ +/-3 $^\circ$ . The parts were printed with a constant slice thickness of 30 $\mu\text{m}$  and a laser hatching value of 30 $\mu\text{m}$ . The detector cell was printed with a laser speed set to

2800 mm/s for the first 62 layers composing the basal part of the design and increased to 5800 mm/s for the remaining layers. All other printed parts were obtained with a 5800mm/S laser speed. All parts were developed in ethanol in an ultrasonic bath for 1 min. Microfluidic channels were further developed by manually injecting 5mL of ethanol using a plastic syringe connected to the device inlet. The total fabrication time, comprising 3D printing and device development, was 2h30 min per chip. ~~a microfluidic z-shaped channel with a diameter of 500  $\mu$ m and optical path of 2.15 cm was micro-milled.~~ The internal volume of the z-cell channel was 11  $\mu$ L, the square-shaped microchannels being 500 $\mu$ m wide. Fused silica glass windows are assembled to the 3D printed detector using TESA 61210 double sided-tape, which is cut by xurography using a Graphtec FC8600-60 cutting plotter. This adhesive features good chemical resistance to polar and non-polar chemicals, and is resistant toward UV light, ensuring good sealing of the assembly over time.

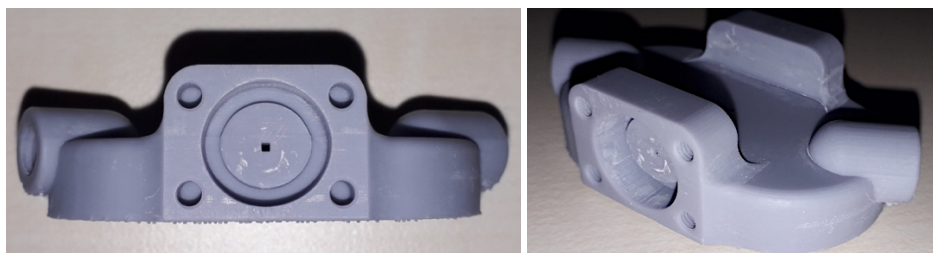


**Figure 1:** Design of 3D printed UV LED absorbance detector fabricated using SLA. Legend: (1) UV photodiode and electronic board; (2) 3D printed photodiode holder; (3) fused silica glass UV-transparent windows (12.5 × 2 mm); (4) chemical resistant double-sided tape ; (5) 3D printed detector cell; (6)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

Question : Shall we provide the design, at least, the internal architecture of the chip (part n°5) as well as the fluidic connectors ? and eventually parts N °2 and 6 ? Shall we also give information about the connectors ?



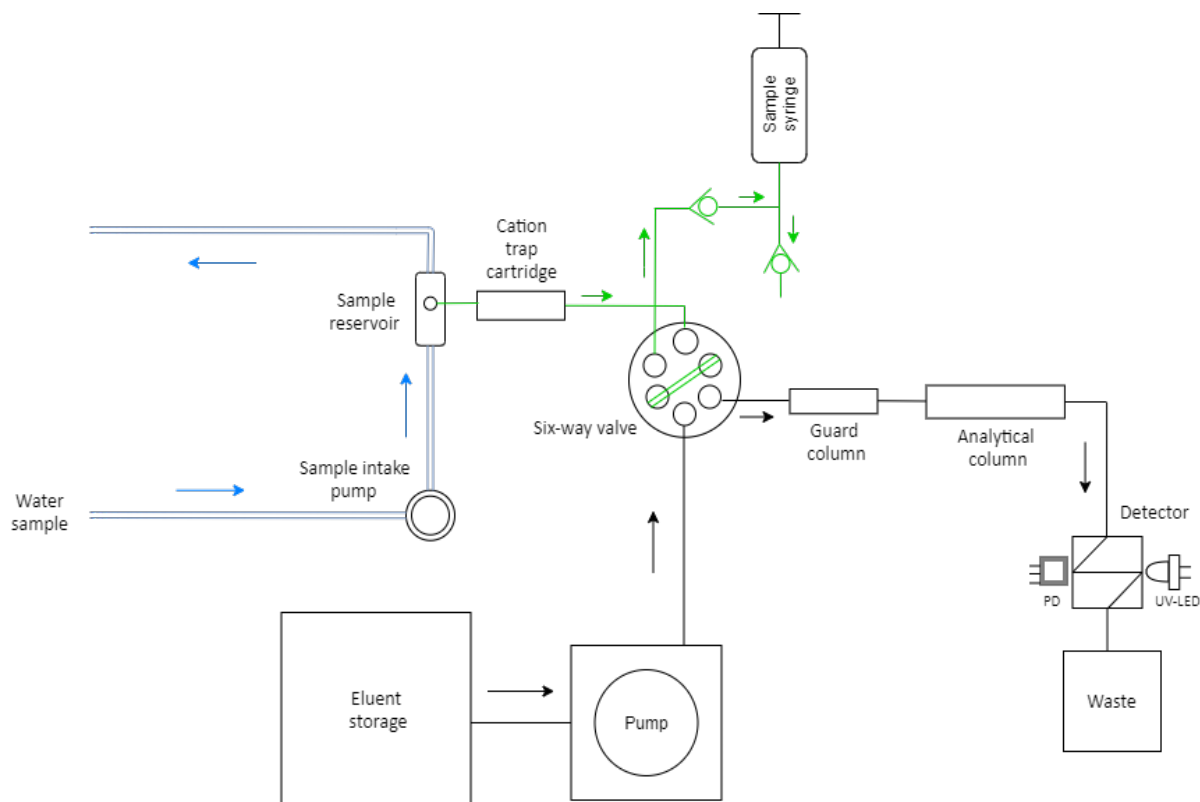
We could also show the final 3D printed device (some. examples below, we can show better images if needed)



### 2.3 IC Configuration

The automated portable phosphate analyser described in this paper was based on the IC system reported by Murray et al. [29]. The phosphate analyser fluidic configuration is shown in figure 2. The syringe pumps were manufactured from low-cost components coupled with a 3D printed base and a pusher block. Sample and eluent were pumped using 1 ml gas tight luer lock glass syringes (Sigma Aldrich, Wicklow, Ireland). A 6 port 2-position injection valve (VICI AG, Schenkon, Switzerland) with automated hybrid stepper motor (Radionics, Dublin, Ireland) was used. Syringes were flushed and filled using 12 V brushed geared DC motors (Pololi, Las Vegas, USA). Efficient and fast separation was achieved using a 4×250 mm in series with 4×50 mm IonPac CS5A guard column. Indirect UV detection was carried out using 255 nm UV-LED (Crustal IS, Green Island, NY, USA) and UVC photodiode. For eluent storage. 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, Clare, Ireland). Cost?





**Figure 2:** 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 a 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.

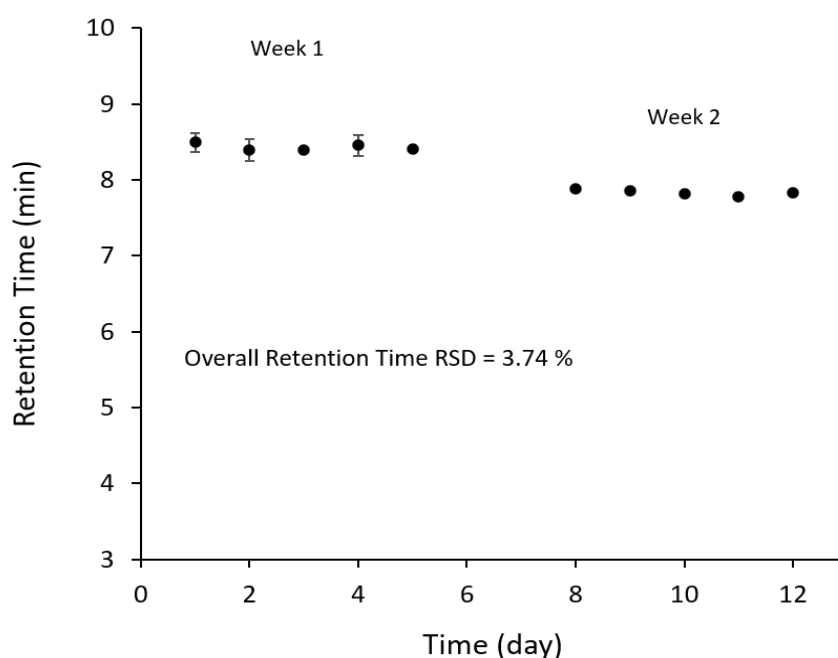
## 2.4 Eluent optimisation

Buffered eluents with controlled pH are required for optimum elution of ions from ion exchange systems. In *Methods for the Examination of Waters and Associated Materials analysis*, published in 1990 [30], an anion exchange chromatography method with indirect UV detection of inorganic anions using potassium phthalate combined with sodium tetraborate was described for phosphate determination. However, when using sodium tetraborate in combination with potassium phthalate as the eluent, a constant eluent pH overtime could not be achieved resulting in poor and unstable chromatography overtime. In order to achieve robust and stable eluent pH a range of different buffers were assessed, including, Tris, Bis Tris, sodium hydroxide and sodium bicarbonate. From these various buffers, sodium bicarbonate was selected due to its non-toxic nature and it enabled stable eluent pH. The stability and performance of potassium phthalate and sodium bicarbonate eluent was assessed by continuous analysis of  $10 \text{ mg L}^{-1}$  phosphate sample.

### 3. Results and discussion

#### 3.1 Eluent assessment

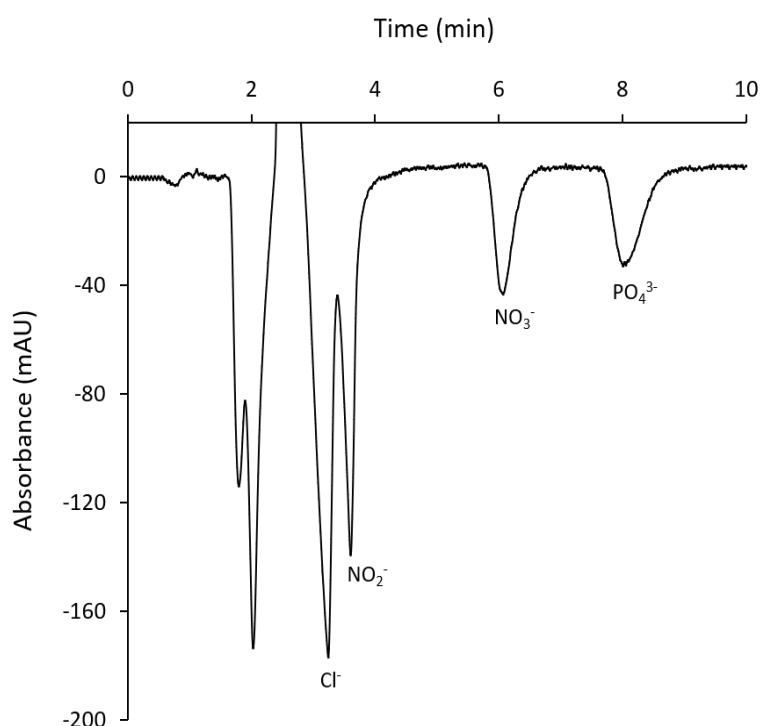
The pH stability of the eluent, consisting of 0.6 mM potassium phthalate and 1.44 mM sodium bicarbonate was assessed by analysing and monitoring the retention time of a  $10 \text{ mg L}^{-1} \text{ PO}_4^{3-}$  standard over twelve days. Three measurements were obtained on a daily basis using the same eluent. The results, including the % RSD values for each day, are outlined in figure 4. Satisfactory precision was achieved over the twelve-day analysis with RSD of 3.74 %. 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.



**Figure 4:** Within-day ( $n=3$ ) and between-day ( $n=10$ ) precision data for  $10 \text{ mg L}^{-1} \text{ PO}_4^{3-}$  retention time using 0.6 mM potassium phthalate combined with 1.44 mM sodium bicarbonate buffer. Overall average retention time was 8.12 min and the between day % RSD was 3.74.

### 3.2 Analytical performance

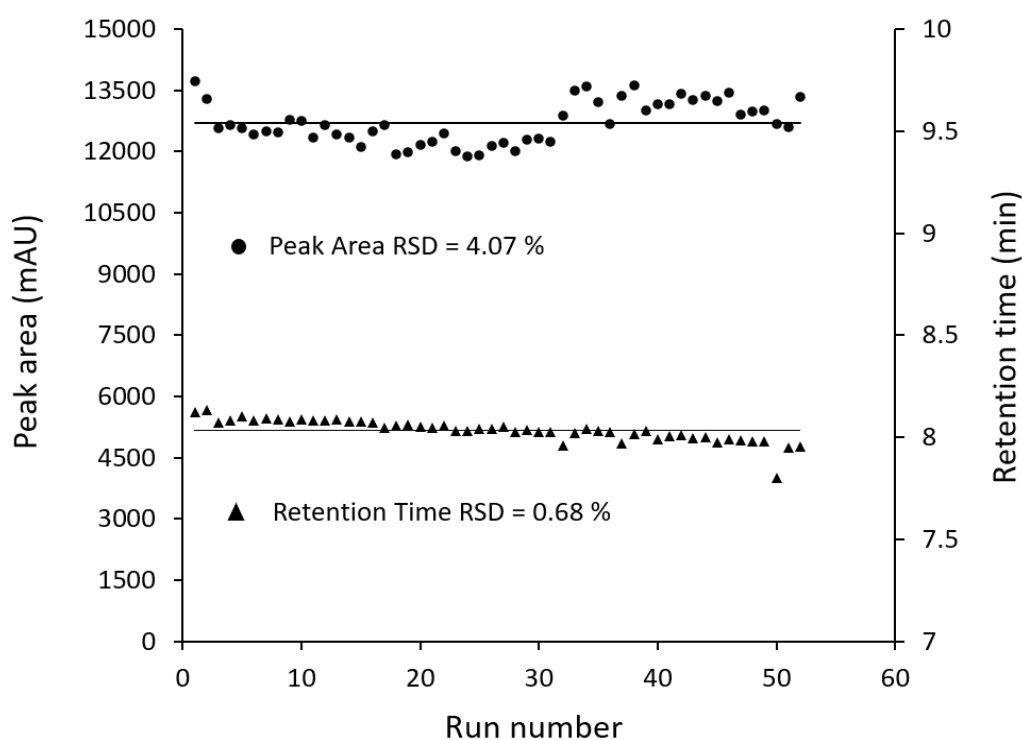
The optimised IC method enabled phosphate determination under 10 min run time which is comparable to commercial phosphate analysers [31, 32]. Satisfactory resolution was achieved and a sufficiently wide linear calibration plot was obtained ranging from 0.3 to 30 mg L<sup>-1</sup> ( $R^2 = 0.999$ ). The phosphate linear curve generated by the analyser is shown within Figure A1 of the ESI. The limit of detection was calculated using a signal-to-noise ratio (S/N) = 3 which corresponded to 0.322 mg L<sup>-1</sup>. The limit of quantification (LOQ) was 1.07 mg L<sup>-1</sup> which was obtained by using S/N = 10 [Add Ref EM]. 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, sulphate, bromide, nitrate and nitrite were selected as these anions are commonly found in environmental waters. An anion mixture containing 10 mg L<sup>-1</sup> of these nine commonly found anions along with phosphate was analysed using the portable IC set up. As can be seen in figure 3, selective detection of phosphate was achieved and the determination of phosphate was not affected by the presence of other anions.



**Figure 3:** Chromatogram of nine-anion standard containing 10 mg L<sup>-1</sup> PO<sub>4</sub><sup>-3</sup>, SO<sub>4</sub><sup>-2</sup>, CO<sub>3</sub><sup>-2</sup>, IO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>. The standard was analysed using a 75 µL sample loop and 0.6 mM potassium phthalate eluent at a flow rate of 0.75 mL min<sup>-1</sup> with a Dionex CG5A 4×50 mm guard column and Dionex CS5A 4×250 mm analytical column employing the 3D printed detector with 255 nm LED and photodiode for detection.

### 3.3 Chromatographic repeatability

To assess the repeatability of the portable IC platform, 52 sequential chromatograms were produced for a nine-anion standard solution. Prior to the first injection, the system was equilibrated with the eluent for approximately 20 min and automatic injection was configured. The 10 mg L<sup>-1</sup> phosphate standard solution was injected every 10 min. The repeatability of the retention times and peak areas are presented in figure 5. 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 a suitable robustness associated with the method and the portable platform when considering phosphate quantification in environmental water samples.



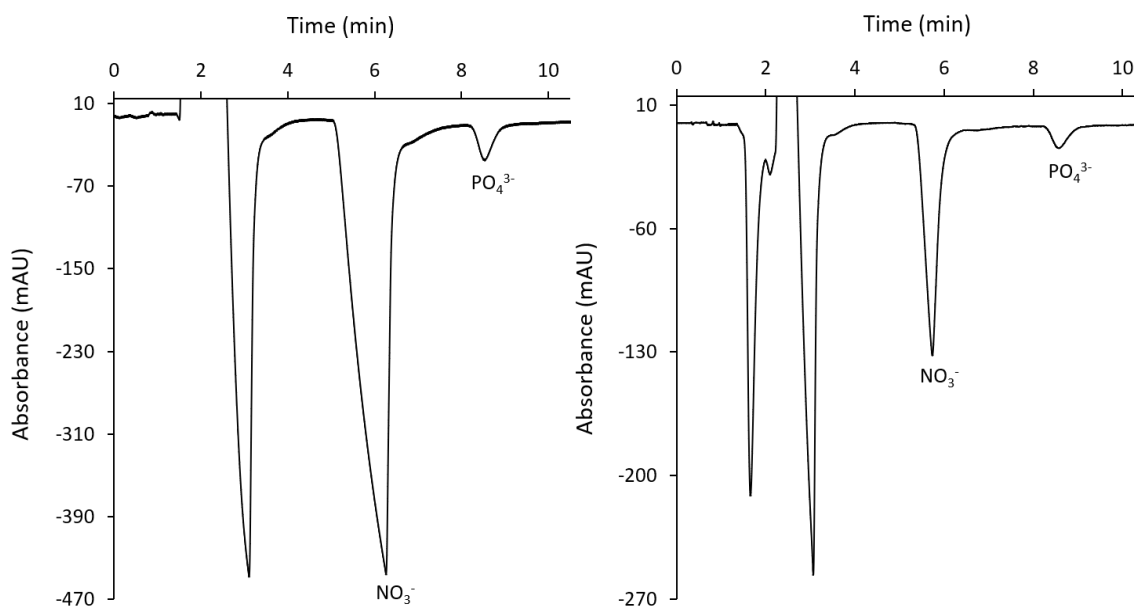
**Figure 5:** Repeatability of peak area and retention time values determined using the portable analyser, analysing 10 mg L<sup>-1</sup> PO<sub>4</sub> standard over 50 sequential runs and associated RSD values.

### 3.4 Water sample analysis

Water samples obtained from various locations, including a visitor center, effluent from residential care facility and industrial food processing effluent were analysed by the portable IC system. In addition, blind artificial fresh water samples were prepared and analysed. Prior to analysis, all samples were filtered using 0.2  $\mu\text{m}$  nylon filters and Whatman Grade 1 filter paper to remove suspended particles. All samples were analysed in triplicate. The performance of the portable IC detection system was assessed by comparing the obtained results to an accredited IC system. Accuracy of the portable IC configuration was obtained by calculating the relative % error between the portable and accredited IC system. Samples were treated with Dionex InGuard Na sample preparation cartridge 9 $\times$ 24 mm which was installed within the analyser to remove interfering transition metals from the water sample. Table 2 shows the phosphate concentrations determined within each sample using the portable IC system versus the accredited lab-based IC system. Examples of chromatograms generated by the portable IC system are shown in figure 6.

**Table 2:** Phosphate concentrations obtained using portable IC configuration versus phosphate concentrations generated using accredited IC ( $n=3$ ).

Sample	Portable IC ( $\text{mg L}^{-1} \text{PO}_4^{3-}$ )	Accredited IC ( $\text{mg L}^{-1} \text{PO}_4^{3-}$ )	Relative error (%)
Residential care facility effluent	1.3	1.5	13.3
Visitor center water sample	24	28	14.3
Industrial food processing effluent	7.2	7.8	7.7
Freshwater A	6.8	6.6	1.9
Freshwater B	3.5	3.8	7.8



**Figure 6:** (Left) Chromatogram of industrial process effluent sample; (Right) chromatogram of spiked river water sample. Samples were analysed using a 75  $\mu\text{L}$  sample loop and 0.6 mM potassium phthalate eluent at a flow rate of 0.75  $\text{mL min}^{-1}$  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.

In order 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 [33] [Add Ref EM]. Environmental samples from Teagasc catchment, waste water treatment plant, residential care facility and industrial food processing effluent 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 with 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. The phosphate concentrations which were determined for the spiked environmental water samples and corresponding recovery values are shown in Table 3.

Average recovery for environmental samples spiked with phosphate ranged between 98.4-115.69 % which lies within the recommended recovery range for ion chromatography methods set by EPA method [34].

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

<i>Sample</i>	<i>Portable IC (mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>)</i>	<i>Spike (mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>)</i>	<i>Average recovery (%)</i>
Residential care sample	1.28	5	98.48
Waste water treatment plant (Baltinglass)	0.99	5	108.80
Industrial food processing effluent	9.98	5	115.69
River water sample	< 0.5	5	95.48

#### 4. Concluding Remarks

A portable IC configuration and method for the determination of phosphate in water has been developed and demonstrated in a laboratory. The method employed isocratic elution using buffered potassium phthalate eluent 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. *Question: We could mention the advantages of 3D printing : mechanically robust monolithic device, direct integration of connectors, low cost and 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 0.3 mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup> and a linear detection range between 0.3-30 mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup> applicable to a wide range of environmental waters was achieved. Environmental samples were analysed using the portable IC system and the results were compared to an accredited IC system with relative errors < 15 % obtained. Recovery assessment was successfully carried out for both fresh water and waste water samples. Overall, the developed phosphate detection method shows a great potential for phosphate monitoring in both freshwater and waste water. 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 (grant agreement number 16007407/MP0011594)



## 5. 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. *Sc. of the Tot. Env.* 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. *Microch. Ac.* 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. of Env. 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 voltammetric 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., Pencharee 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. *Sen. and act. B: Chem.* 1990, 1, 244-248.
- [17] Whitesides G. M., The origins and the future of microfluidics. *Nat.*, 2006, 442, 368–373.
- [18] Nightingale A.M., Beaton A.D. , Mowlem M.C., Trends in microfluidic systems for in situ chemical analysis of natural waters. *Sen. and Act.s B: Chem.* 2015, 221, 1398-1405.
- [19] 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.
- [20] 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. in Mar. Sc.* 2017, 4, 255.
- [21] Clinton-Bailey G.S., Grand M. M., Beaton A. D., Nightingale A. M., Owsianka D. R., Slavik G. J., Connelly D.P., Cardwell C. I., 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. *Env. Sc. & tech.* 2017,51, 9989-9995.
- [22] Duffy G., Maguire I., Heery B., Nwankire C., Ducree J., Regan F., PhosphaSense: A fully integrated, portable lab-on-a-disc device for phosphate determination in water. *Sens. and Act. B: Chem.* 2017, 246, 1085–1091.
- [23] Donohoe A., Lacour G., McCluskey P., Diamond D., McCaul M., Development of a Cost-Effective Sensing Platform for Monitoring Phosphate in Natural Waters. *Chemosen.* DOI: 10.3390/chemosensors6040057
- [24] Pol R., Cespedes F., Gabrie D., Baeza M., Microfluidic lab-on-a-chip platforms for environmental monitoring. *TrAC T. in Anal. Chem.* 2017, 95, 62-68.

- [25] Connolly D., Paull B., Fast ion chromatography of common inorganic anions on a short ODS column permanently coated with didodecyldimethylammonium bromide. *J Chromatogr. A*. DOI: 10.1016/s0021-9673(02)00108-5
- [26] Ohta K., Simultaneous separation of common mono-and divalent cations by ion chromatography with indirect photometric detection using an unmodified silica gel column and tyramine–oxalic acid–15-crown-5 as eluent. *Anal.* 2000, *125*, 269-272.
- [27] Small H., Miller T.E., Indirect photometric chromatography. *Anal.Chem.* 1982, *54*, 462-469.
- [28] HMSO, The Determination of Anions and Cations, Transition Metals, Other Complex Ions and Organic Acids and Bases in Water by Chromatography, London 1990.
- [29] 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.
- [30] 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. *Tal.* 2020, *216*, 12095.
- [31] <https://www.3s-analyzers.eu/wp/wp-content/uploads/2020/07/Phosphate-Blue-Colorimeter-Datasheet.pdf> (last time accessed April 15, 2021).
- [32] <https://www.yokogawa.com/solutions/products-platforms/process-analyzers/liquid-analyzers/wet-chemistry-analyzers/we440-phosphate-analyzer/> (last time accessed April 14, 2021).
- [33] 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.
- [34] <https://www.epa.gov/sites/default/files/2015-06/documents/epa-300.1.pdf> (last time accessed August 12, 2021).