



Portable analyser using two-dimensional ion chromatography with ultra-violet light-emitting diode-based absorbance detection for nitrate monitoring within both saline and freshwaters

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ARTICLE INFO

Article history:

Received 2 March 2021

Revised 28 May 2021

Accepted 21 June 2021

Available online 29 June 2021

Keywords:

Deep UV light-emitting diode

Nutrients

Water analysis

Portable

Two-dimensional IC

Matrix elimination

ABSTRACT

A portable and automated IC system with a dual-capability for the analysis of both fresh and saline environmental waters has been developed. Detection of nitrate in complex matrices such as seawater was achieved by the employment of an automated two-dimensional (heart-cut) IC method utilised in tandem with on-column matrix elimination, using a sodium chloride eluent. The system also demonstrated the capability to switch to a second mode of analysis, whereby direct one-dimensional IC analysis was employed to rapidly detect nitrite and nitrate in freshwater, with direct UV LED based absorption detection in under 3 minutes. Calibration curves using a 195 μL sample loop were generated for both freshwater and artificial seawater samples. For marine analysis, an analytical range of 0.1 mg L^{-1} – $40 \text{ mg L}^{-1} \text{ NO}_3^-$ was possible, while an analytical range (0.1 mg L^{-1} – $15 \text{ mg L}^{-1} \text{ NO}_2^-$, 0.2 – $30 \text{ mg L}^{-1} \text{ NO}_3^-$) appropriate for freshwater analysis was also achieved. Chromatographic repeatability for both marine and freshwater analysis was verified over 40 sequential runs with RSD values of $< 1\%$ demonstrated for both peak area and retention times for each mode of analysis. The selectivity of both methods was demonstrated with interference tests with common anions present in environmental waters. Recovery analysis was carried out on marine samples from Tramore Bay, Co. Waterford, Ireland, and the systems analytical performance was compared with that of an accredited IC following environmental sample analysis.

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1. Introduction

Nitrate is an oxidised form of inorganic nitrogen which naturally occurs in soils and environmental waters. The presence of nitrate within the seawater and freshwater ecosystem arises naturally through nitrogen fixation by cyanobacteria, atmospheric nitrogen, and vegetable and animal decomposition [1]. Yet despite this intrinsic nature, nitrate pollution of surface and coastal waters has become widespread over the past decades as a result of anthropogenic impacts such as sewage disposal, agriculture and industrial effluent. Elevated levels of nitrate contribute significantly to eutrophication within fresh and marine waters. This often results in algal blooms, destruction of water ecosystems and the loss of beneficial uses associated with the water [2]. Traditionally, 'grab

and lab' samples have been the standard approach for marine and freshwater monitoring, where grab samples are taken from water systems and sent to laboratories for analysis. However, clear limitations are associated with this approach in the form of sample transport, cost of labour and time [3,4]. Real-time or near real-time, *in-situ* nutrient analysers are paving the way with regard to future monitoring and understanding of environmental waters. Systems capable of generating accurate, continuous, and repeatable quantification of nutrients such as nitrate are of particular appeal, with portability and robustness being paramount for *in-situ* water analysis [5].

Various methods and strategies based upon differing analytical techniques have been explored for on-site or *in-situ* determination of nitrate within fresh and marine environmental waters [6–9]. To date, colorimetric based analysers and direct UV absorption systems have proven to be the leading strategies towards achieving *in-situ* nitrate analysers for monitoring natural waters. Lab-on-a-chip

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(LOC) based systems employing microfluidics and colorimetry with LED-based detection have shown considerable promise and have successfully been deployed *in-situ* for nutrient monitoring in a range of natural waters and waters of varying salinity [10–12]. These LOC systems offer considerable advantages over typical flow injection analysis (FIA) or segmented flow analysis (SFA) systems such as reduced reagent consumption and energy requirements. However, limitations still exist, not only as colorimetric reagents are themselves hazardous, but also in the form of challenges associated with mass manufacture of microfluidic components and assembly of LOC systems [13]. When considering direct UV optical detection systems, although numerous commercial *in-situ* analysers are available [14–17], these analysers remain at significant price points and have high power consumption requirements due to the use of UV lamps. In addition, UV nitrate probes can be impacted by matrix effects and interferences present within natural waters as a range of dissolved constituents absorb light in the UV wavelength. These include inorganic constituents, such as bromide, nitrite and hydrogen sulphide, as well as dissolved organic matter [18].

Recently, Murray *et al.* [19] reported a cost-effective portable nitrate and nitrite analyser based on rapid ion chromatography (IC) and direct UV detection using a 235 nm LED and photodiode. By coupling the UV LED based detection with rapid ion separation, selective detection of both nitrite and nitrate was achieved. The analyser was successfully deployed in a range of environmental and industrial waters and demonstrated accuracy and precision comparable to laboratory-based instrumentation. However, this IC-based nitrate analyser was not applicable to marine analysis. The sample complexity associated with saline samples, such as brackish waters typical of estuaries or coastal waters, represents a major challenge for IC analysis. The determination of nitrate in water samples with high salt content is demanding for IC due to the deleterious effects which the high levels of chloride and other anions have on the anion exchange separation. On-column matrix elimination for IC, first highlighted by Ito and Sunahara in 1988, represents a method of mitigating the matrix effects of challenging samples such as seawater by using the major matrix ion as the eluent [20]. Haddad *et al.* employed on-column matrix elimination using NaCl eluent in which the chloride matrix ion in the eluent overcame the matrix effect of saline samples and allowed for the detection of various anions, including nitrate, using IC with direct UV detection [21]. Ito *et al.*, used matrix elimination in a similar manner using dilauryldimethylammonium-coated monolithic ODS columns and direct UV detection [22]. Wang *et al.* described an alternative approach to overcome the matrix effects of seawater using a cycling-column-switching approach [23]. Within this system, low concentration anions were concentrated before final analysis, removing the effect of the matrix ion. Two-dimensional (2D) ion chromatography (both comprehensive and ‘heart-cut’ approaches) has emerged as a promising technique for the analysis of trace ions, particularly in challenging matrices. Multi-dimensional chromatography has proven to be an effective technique in maximising chromatographic separation and has shown the potential to enable superior selectivity and sensitivity [24,25].

In this research, we report a portable and environmentally conscious analyser for the detection of nitrate in marine and natural waters. The method utilises an automated 2D IC method, in combination with on-column matrix elimination using sodium chloride eluent, for the detection of nitrate in seawater matrix, with the ability to switch to one-dimensional (1D) IC analysis for direct nitrite and nitrate determination in freshwater samples. The system incorporates rapid ion chromatography with direct UV LED based optical detection for nitrate determination in under 3 minutes. Analytical performance and chromatographic repeatability were demonstrated and dynamic linear ranges were obtained

for both freshwater and seawater matrices. Environmental freshwater and seawater samples were analysed as well as blind artificial seawater samples, and the analytical performance of the developed analyser was compared to accredited laboratory instrumentation.

2. Experimental

2.1. Chemicals and reagents

All chemicals used within this study were of analytical grade. All solutions were prepared using high purity deionised water (Milli-Q). The eluent used within the analyser was 200 mM NaCl and was prepared by dilution of 5 M NaCl stock solution (Sigma Aldrich). Nitrate and nitrite stock solutions were prepared using NaNO₃ (Sigma Aldrich) and NaNO₂ (Sigma Aldrich) respectively. Artificial seawater was prepared according to the procedure set out by Metrohm in IC Application Note U-62 [26]. The following quantities of salts were added to 1 L of deionised water: 28 g NaCl, 7 g MgSO₄·7H₂O, 5 g MgCl₂·6H₂O, 1.61 g CaCl₂·2H₂O and 0.4 g NaHCO₃. For the interference studies nitrate, nitrite, carbonate, chloride, iodate, sulphate, bromide and fluoride stock solutions were prepared using NaNO₃ (Sigma Aldrich), NaNO₂ (Sigma Aldrich), Na₂CO₃ (Sigma Aldrich), NaCl (Fisher Chemicals), KIO₃ (PanReac AppliChem), Na₂SO₄ (Sigma Aldrich), KBr (Merck) and NaF (Sigma Aldrich), respectively. Working standards were prepared by diluting these stock solutions.

2.2. Portable analyser

The analyser incorporated two separation stages that operated in a manner which enabled either direct freshwater analysis or rapid matrix elimination for marine analysis in a single portable package. Anion exchange separation was achieved through the use of two 4 × 50 mm Dionex AG15 guard columns (particle diameter of 9 µm) from Thermo Fisher Scientific (Sunnyvale, CA). The twin eluent syringe pump configuration was comprised of two 2.5 mL individual glass syringes (SG Syringes, Trajan) housed within 3D printed pump assemblies. All 3D printing was performed using Onyx filament sourced from Markforged, Inc. (Massachusetts, USA) and all 3D printing of components was carried out using a Markforged Mark Two printer. The eluent syringe pumps were each coupled to one of two automated 6 port 2-position injection valves provided by VICI AG (Schenkon, Switzerland). LED-based UV absorbance detection was achieved using two low-cost detection cells, previously reported by Murray *et al.* [27], employing two 235 nm deep UV-LEDs provided by Crystal IS (Green Island, NY, USA) and two UVC photodiodes (TOCON_C1) with integrated amplifiers purchased from Sglux GmbH (Berlin, Germany). The embedded system consisted of an ARM based microcontroller (Teensy 3.6) which controlled all the timing and actuation of the syringe pumps and 6-way valves as well as the sample intake pump and sample intake syringe pump. Dedicated motor controllers (TB6612FNG) ensured the syringe pumps ran smoothly while simple on-off signals enabled the sample intake pump and 6-way valve operation. The deep UV LED intensity for each detection cell 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 easy retrieval. Electronic components were sourced from Mouser Electronics (Texas, USA). Power to the system was supplied from a Lithium-Polymer battery pack (Voltaic V88) purchased from Voltaic Systems (New York, USA). The assembled system is shown in Fig. 1. The system was housed within a 1510M Peli Case (Peli Products, Clare, Ireland). The weight of the system, including battery and full eluent, was ca.

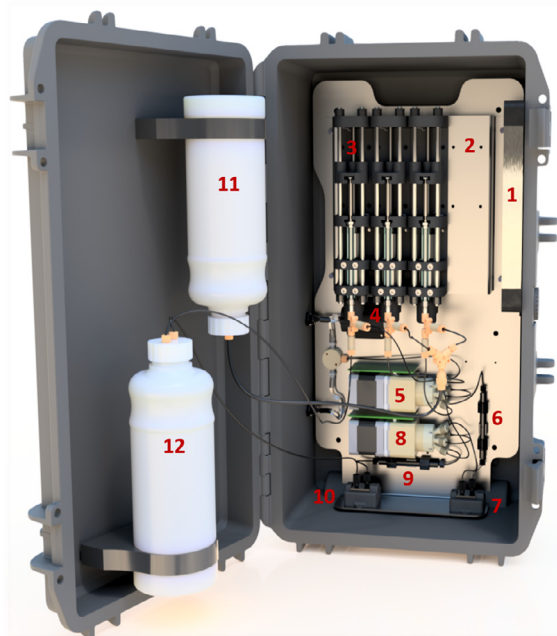


Fig. 1. Render of portable 2D IC system for freshwater and marine water analysis with components labelled. Exterior dimensions of $60 \times 37 \times 27$ cm. Legend: (1) battery; (2) electronics housing; (3) 3D printed syringe pumps; (4) 12 V sample intake pump; (5) first six-way injection valve; (6) first AG15 column; (7) first UV LED based detection cell; (8) second six-way injection valve; (9) second AG15 column; (10) second detection cell; (11) eluent storage; (12) waste storage.

13 kg. The total component cost of the fully assembled analyser was < \$3500.

2.3. Analyser operation

The fluidic schematic of the analyser is shown in Fig. 2, representing the systems operational flow. Three 3D printed syringe pumps, comparable to those described within the portable IC analyser developed by Murray *et al.* (2020), were utilised within the system [19]. The design and configuration of these syringe pumps is illustrated in Fig. A1 of the electronic supplementary information (ESI). Two 2.5 mL syringe pumps were responsible for eluent delivery and one 1 mL syringe pump was used for drawing sample from the sample reservoir through the sample loop (195 μ L), and hence filling the loop. During stage 1 of the analyser operation for marine analysis, the sample syringe and the eluent syringes operated in unison, the sample syringe drawing in sample filling the sample loop, and the eluent syringes each drawing in 2.5 mL of eluent from the eluent storage. Once these syringes were full, parallel flushing of the sample syringe and eluent syringe 1 began. The sample syringe flushed to waste and eluent syringe 1 directed flow of eluent through the first six-way valve to column 1 and detector 1, at a flowrate of 0.7 mL min⁻¹.

As eluent syringe 1 began flushing (time = 0 s), the first six-way valve remained in the load position until 24 s had passed, after which the valve automatically switched to the inject position, injecting the sample. Eluent syringe 1 continued to empty until it reached its home position defined by the activation of limit switches.

During stage 2 of analyser operation for marine analysis, the flow from detector 1 was directed to waste through the second six-way valve until 118 s had passed since the beginning of eluent syringe 1 flushing. After this time, the second six-way valve automatically switched to the load position, loading the second sample loop (800 μ L). This timing corresponded to the start of the elution

of the nitrate peak from column 1. Eluent syringe 2 began flushing after 177 s had passed, directing flow through the second six-way valve to column 2 and detector 2. The second six-way valve automatically switched to inject after 207 s had passed, corresponding to the end of the elution of the nitrate peak. The valve remained in the inject position for 17 s before automatically switching back to load position. This 17 s injection time corresponded to a sample injection volume of 198 μ L. The flow continued from the valve to column 2 and detector 2 and finally to a waste container, until eluent syringe 2 reached its home position.

When the analyser was in freshwater operational mode, the second stage of operation was by-passed and stage one directly analysed the sample using eluent syringe 1 while data acquisition was obtained from column 1 and detector 1 only.

2.4. Sample analysis and performance assessment

A combination of blind standard solutions and environmental water samples were analysed. For freshwater analysis, two Environmental Protection Agency (EPA) intercalibration standards and one river water sample were provided by the Environmental Department within TelLab (Carlow, Ireland). Nitrate concentrations determined within the freshwater samples using the portable IC analyser, employing 1D analysis, were compared to those generated by an accredited lab-based ion chromatograph, accredited according to ISO 17025 by the Irish National Accreditation Board (INAB). For marine analysis, blind artificial seawater standards were analysed using the portable IC analyser, employing 2D analysis.

Using seawater sample taken from Tramore Bay, Co. Waterford, Ireland, recovery analysis was carried out according to the spiking and recovery procedure previously reported [28,29]. This seawater sample was spiked with 5 mg L⁻¹ NO₃⁻ (Seawater A) and 7 mg L⁻¹ NO₃⁻ (Seawater B). The calculation used to determine recovery, for the spike concentration of 5 mg L⁻¹ NO₃⁻, is highlighted below.

Recovery = spiked sample conc.

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

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

The nitrate concentration present in the neat seawater sample was first determined using the portable IC through 2D analysis. This concentration was divided by 100 mL and then multiplied by 99.5 mL to account for the dilution caused by adding 0.5 mL of 1000 mg L⁻¹ NO₃⁻ standard to make up 100 mL total volume in the seawater matrix. This final value was then subtracted from the spiked sample concentration to determine the recovery as a percentage.

3. Results

3.1. Chromatographic repeatability

The repeatability of the marine analysis system employing the 2D IC configuration was assessed by analysing 40 sequential runs ($n=40$) of a 5 mg L⁻¹ NO₃⁻ artificial seawater standard. The RSD values for both peak area and retention times were below 1 % and the repeatability which was achieved is shown in Fig. 3. The peak width which was observed for nitrate during this analysis was 0.51 mins and the associated asymmetry factor (*As*) was 1.4. The repeatability demonstrated when analysing a fresh water 5 mg L⁻¹ NO₃⁻ standard using the direct 1D IC configuration is graphically presented in Fig. B1 of the ESI. The RSD values for both peak area and retention times, when performing freshwater analysis ($n=40$), were 0.71 % and 0.50 %, respectively.

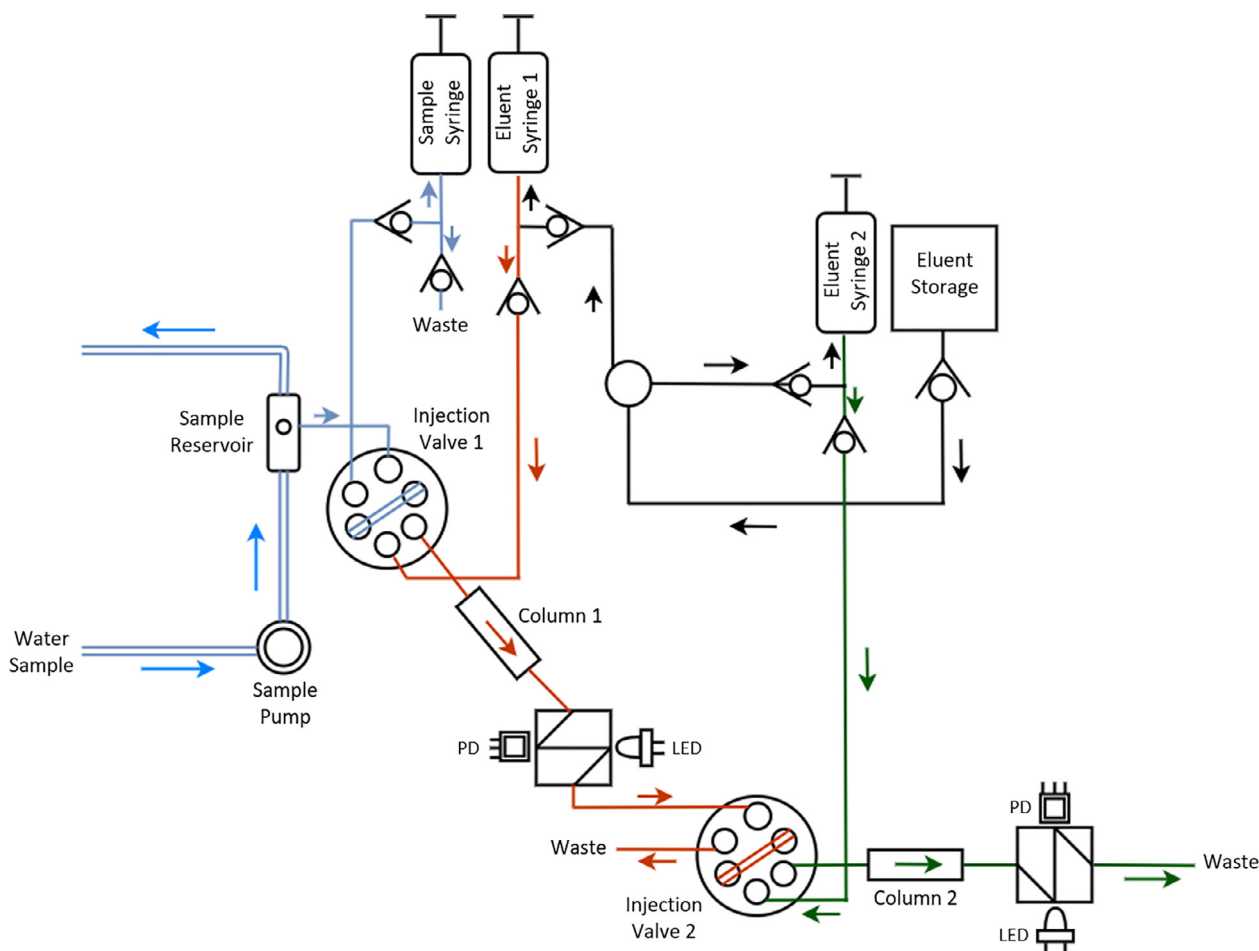


Fig. 2. Schematic representation of analyser. The flow path of NaCl eluent is shown in black. The flow path of sample through the sample reservoir and into the sample intake syringe is shown in blue. The flow path of stage 1 analysis through column one is shown in red and stage 2 analysis flow path through column 2 is shown in green.

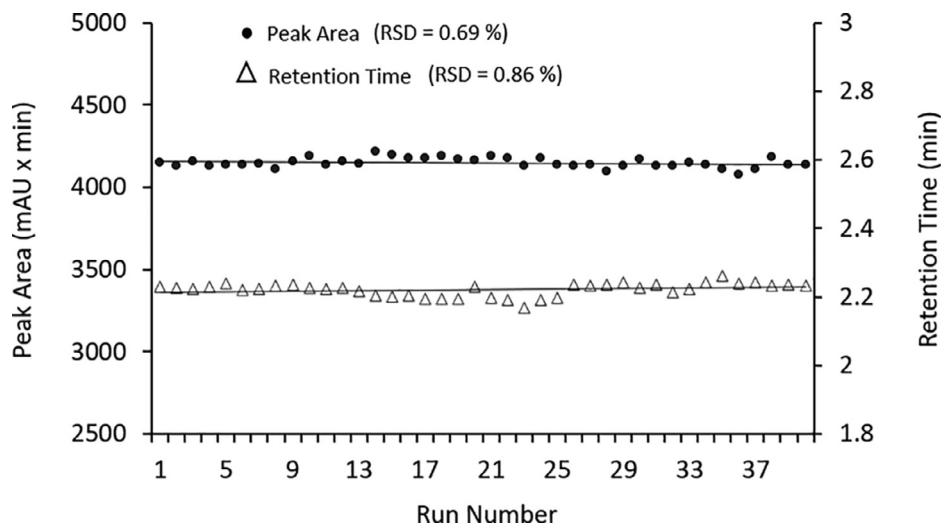


Fig. 3. Repeatability of peak area and retention time values determined using the 2D IC configuration analysing 5 mg L⁻¹ NO₃⁻ artificial seawater standard over 40 sequential runs and associated RSD values.

3.2. Assessment of interfering anions

Anions commonly found in both fresh water and seawater were investigated to ensure no co-elution was occurring when detecting nitrate. Firstly, an anion mixture containing 20 mg L⁻¹ nitrate and 10 mg L⁻¹ nitrite, fluoride, bromide, chloride, iodide, sulphate

and carbonate was analysed directly by the analyser through 1D IC. The chromatogram which was generated is depicted in Fig. 4 (a), highlighting selective detection of both nitrite and nitrate when analysing a freshwater matrix. Secondly, a 40 mg L⁻¹ nitrate artificial seawater (15210 mg L⁻¹ chloride, 2728 mg L⁻¹ sulphate, 145 mg L⁻¹ bicarbonate) standard with 10 mg L⁻¹ nitrite and iodate

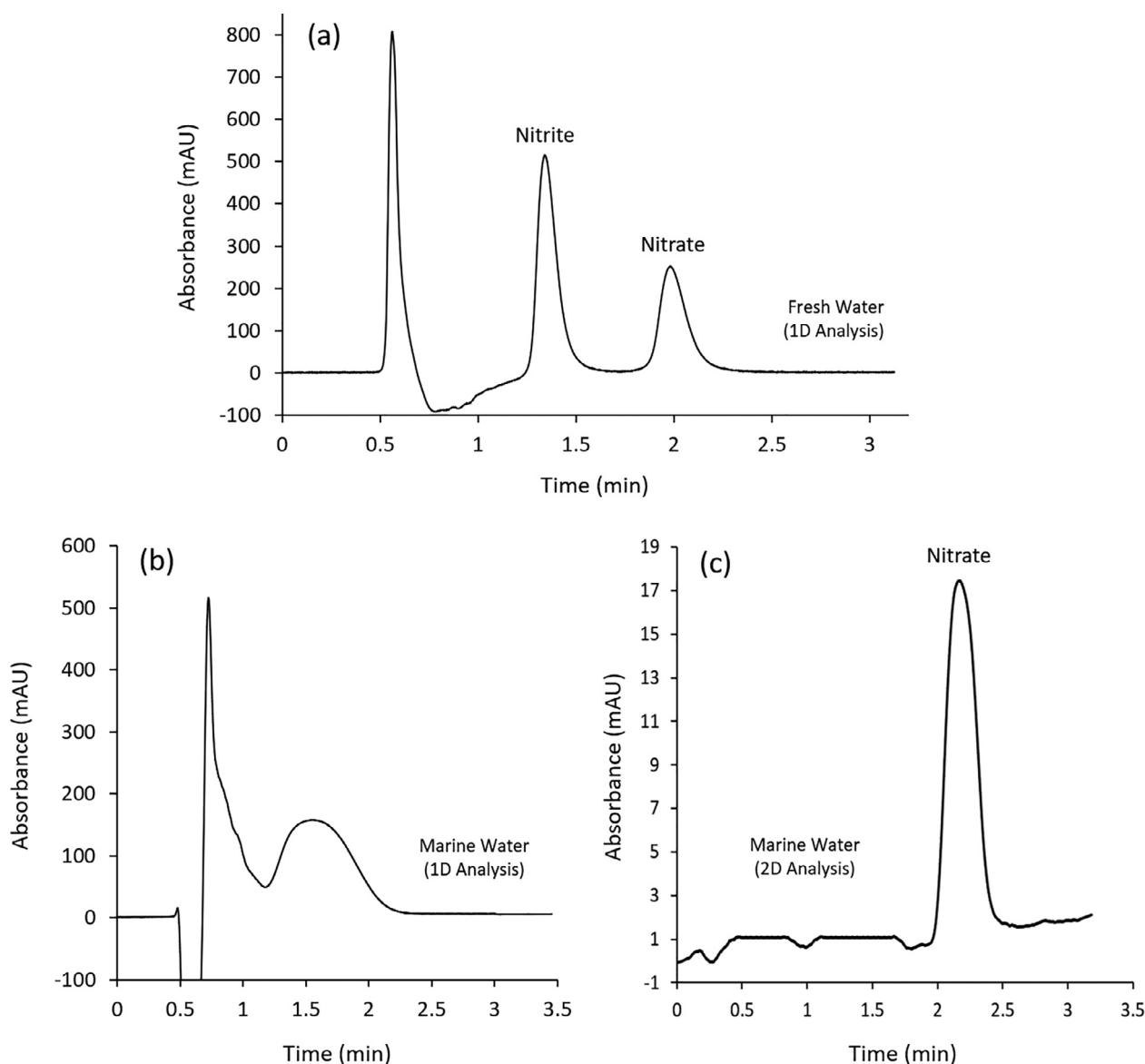


Fig. 4. (a) Chromatogram of a 10 mg L⁻¹ nitrite and 20 mg L⁻¹ nitrate freshwater standard with a 10 mg L⁻¹ mix of chloride, bromide, fluoride, sulphate and carbonate generated using 1D analysis. Eluent: 200 mM NaCl, flowrate: 0.7 mL min⁻¹, 195 μ L sample loop. (b) Chromatogram of a 40 mg L⁻¹ nitrate artificial seawater standard with 10 mg L⁻¹ nitrite and iodate and 50 mg L⁻¹ bromide using 1D analysis, highlighting co-elution and ineffective detection of nitrate (c) Chromatogram of a 5 mg L⁻¹ nitrate artificial seawater standard with 10 mg L⁻¹ nitrite and iodate and 50 mg L⁻¹ bromide using 2D analysis, highlighting selective and sensitive detection of nitrate.

Table 1

Performance of portable analyser, analysing marine samples through 2D IC analysis and freshwater samples through direct 1D IC analysis.

Analysis	Analyte	Linear Range	R ²	LOD
Marine Freshwater	Nitrate	0.1 – 40 mg L ⁻¹ NO ₃ ⁻	0.999	10 μ g L ⁻¹ NO ₃ ⁻
	Nitrite	0.1 – 15 mg L ⁻¹ NO ₂ ⁻	0.993	5 μ g L ⁻¹ NO ₂ ⁻
	Nitrate	0.2 – 30 mg L ⁻¹ NO ₃ ⁻	0.997	20 μ g L ⁻¹ NO ₃ ⁻

Table 2

Nitrate concentrations determined within environmental freshwater samples and blind artificial seawater samples using multi-dimensional IC analyser (n=3).

Sample	Analyte	Portable IC 1D (mg L ⁻¹)	Accredited IC (mg L ⁻¹)	Relative Error (%)
Freshwater A	NO ₃ ⁻	9.9 \pm 0.08	9.5 \pm 0.07	4.21 %
Freshwater B	NO ₃ ⁻	< 0.1	< 0.25	-
Freshwater C	NO ₃ ⁻	11.4 \pm 0.05	11.6 \pm 0.09	-1.72 %
Sample	Analyte	Portable IC 2D (mg L ⁻¹)	Standard Conc. (mg L ⁻¹)	Relative Error (%)
Artificial Seawater A	NO ₃ ⁻	6.92 \pm 0.08	7	-1.14 %
Artificial Seawater B	NO ₃ ⁻	2.51 \pm 0.03	2.5	0.4 %

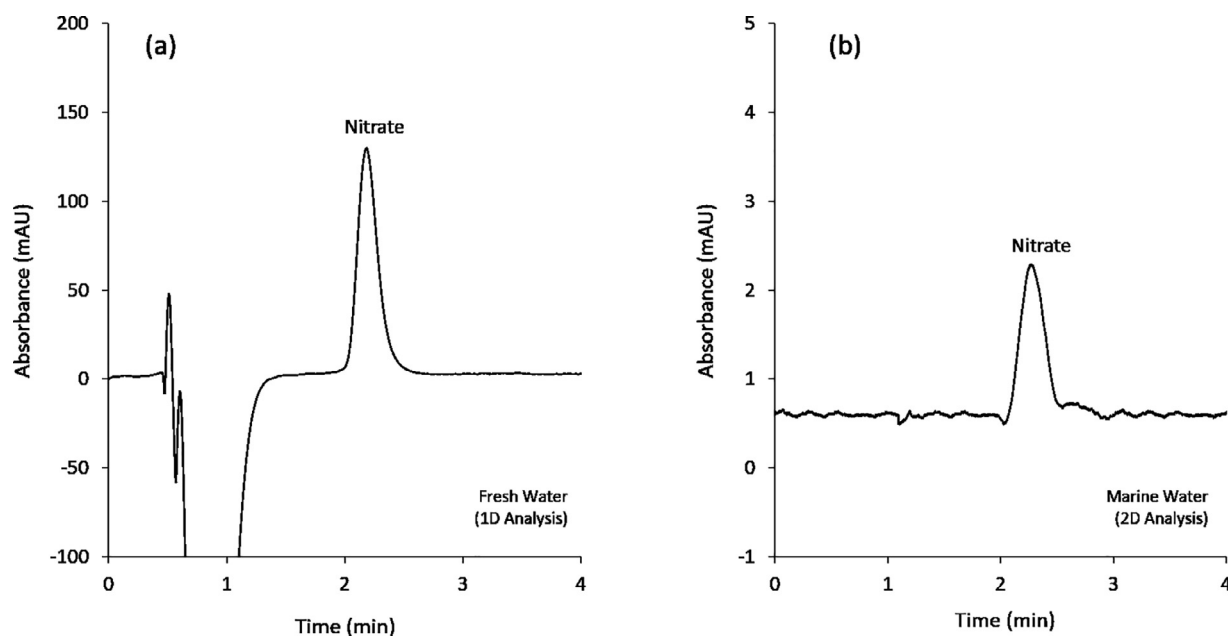


Fig. 5. (a) Chromatogram of sample Freshwater A generated using 1D IC. Eluent: 200 mM NaCl, flowrate: 0.7 mL min⁻¹, 195 μ L sample loop with AG15 guard column for separation and 235 nm LED optical detection (b) Chromatogram of environmental seawater sample generated through 2D IC.

Table 3

Concentrations determined within artificial seawater blind standards and spiked environmental seawater samples using multi-dimensional IC analyser (n=3).

Sample	Analyte	Portable IC 2D (mg L ⁻¹)	Spike Conc. (mg L ⁻¹)	Average Recovery (%)
Seawater A	NO ₃ ⁻	5.59 \pm 0.08	5	104.4 %
Seawater B	NO ₃ ⁻	7.79 \pm 0.04	7	106.1 %

and 50 mg L⁻¹ bromide was analysed using direct 1D analysis, the corresponding chromatogram is shown in Fig. 4 (b). As can be seen, severe coelution was observed and selective nitrate detection was not achieved. Following this, a 5 mg L⁻¹ nitrate artificial seawater standard with 10 mg L⁻¹ nitrite and iodate and 50 mg L⁻¹ bromide was analysed using the 2D IC analysis configuration. The generated chromatogram is shown in Fig. 4 (c). Through the application of the 2D IC, interferences and coelution associated with the high anion concentrations present within the seawater matrix are eliminated and selective detection of nitrate was demonstrated. A chromatogram for the artificial seawater matrix, without nitrite or nitrate present, following 2D IC is shown in Fig. C1 of the ESI.

3.3. Analytical performance

The detection of nitrate within marine water matrices was achieved in under 3 minutes using 2D IC employing isocratic elution using 200 mM NaCl eluent at a flowrate of 0.7 mL min⁻¹ through two AG15 columns. A sample injection of 195 μ L was utilised in combination with two 235 nm LED based optical UV detectors. The calibration ranges, using eight calibration points, and associated R² values for nitrite and nitrate are presented in Table 1. Corresponding limit of detection (LOD) values, estimated using a signal-noise-ratio (S/N) = 3, are also shown within the table [30,31]. To estimate the LOD levels, 1D analysis of an anion standard containing 1 mg L⁻¹ NO₂⁻ and 2 mg L⁻¹ NO₃⁻ (n=3), and 2D analysis of an artificial seawater standard containing 2 mg L⁻¹ NO₃⁻ (n=3) was carried out. The average background noise levels associated with each measurement and chromatogram were determined. Using this information, the estimated LOD levels were then taken as the analyte concentrations which correspond to three times the background noise level. The nitrate calibration curve for

marine analysis is illustrated in Fig. D1 of the ESI. The nitrite and nitrate calibration curves for freshwater analysis are illustrated in Fig. E1 and E2 of the ESI. Analytical ranges for freshwater analysis were achieved using calibration curves based on peak area values and a polynomial fit. Detection of nitrite and nitrate in freshwater was achieved directly using 1D IC. A single 2.5 mL eluent syringe pump using 200 mM NaCl eluent, an AG15 column, sample injection of 195 μ L with a 235 nm LED detector successfully separated the two anions in under 2.5 min.

3.4. Sample analysis

Nitrate concentrations determined within the freshwater samples using the portable IC analyser, employing 1D analysis, compared to the nitrate concentrations generated using accredited IC are shown in Table 2. The chromatogram generated for the analysis of sample 'Freshwater A' is depicted in Fig. 5 (a). For marine analysis, blind artificial seawater standards were analysed using the portable IC analyser, employing 2D analysis. The determined nitrate concentrations with associated relative errors are also reported in Table 2. Using seawater sample taken from Tramore Bay, Co. Waterford, Ireland, recovery analysis was carried out according to the spiking and recovery procedure previously reported [28,29]. The nitrate concentration present in the neat seawater sample was first determined using the portable IC through 2D analysis, chromatogram shown in Fig. 5 (b). The nitrate concentration was determined to be 0.37 mg L⁻¹ NO₃⁻. The nitrate concentrations which were determined for the spiked seawater samples and corresponding recovery values are shown in Table 3. According to standard methods for the examination of water and wastewater, a recovery value observed within the range 85–115% is seen as an acceptable recovery in terms of analytical validation. The average recovery obtained for both the spiked seawater

samples were within this acceptable range and thus demonstrated suitable analytical accuracy [28].

4. Conclusion

A portable and fully automated IC system was developed for the detection of nitrate in marine and natural waters. The system allowed for 1D or 2D IC analysis depending on the sample matrix to be analysed. For marine analysis, the developed method incorporated a 2D IC approach in combination with on-column matrix elimination techniques using two AG15 guard columns, a 200 mM NaCl eluent and detection with a low-cost 235 nm LED based absorbance detector. Direct 1D analysis was implemented for monitoring of nitrite and nitrate in freshwater samples. The use of NaCl eluent was successful, highlighting an environmentally friendly eluent and analyser.

Chromatographic repeatability was demonstrated and assessment of the effect of interfering ions was investigated. High levels of sensitivity and selectivity were shown for both the marine and freshwater analysis. Dynamic linear ranges applicable to environmental water monitoring were obtained for nitrate in marine water and for both nitrite and nitrate in freshwater. Recovery analysis was successfully carried out on seawater samples from Tramore, Co. Waterford, Ireland. The system proved successful in returning accurate and repeatable results for both marine and freshwater samples, showing its diverse application in the monitoring of a wide range of environmental waters.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Cian Fitzhenry: Investigation, Methodology, Validation, Data curation, Writing – original draft, Visualization. **Liam Jowett:** Investigation, Validation, Data curation. **Patrick Roche:** Software, Methodology. **Kevin Harrington:** Visualization. **Breda Moore:** Resources. **Brett Paull:** Conceptualization, Writing – review & editing. **Eoin Murray:** Conceptualization, Funding acquisition, Supervision, Methodology, Visualization, Writing – review & editing.

Acknowledgements

The authors would like to acknowledge financial support through the H2OMon project from the European Union Horizon 2020 Research and Innovation programme under grant agreement number 880886.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.chroma.2021.462368](https://doi.org/10.1016/j.chroma.2021.462368).

References

- [1] R. Duce, J. LaRoche, K. Altieri, K. Arrigo, A. Baker, D. Capone, et al., Impacts of atmospheric anthropogenic nitrogen on the open ocean, *Science* 320 (2008) 893–897.
- [2] N. Rabalais, R. Turner, R. Díaz, D. Justić, Global change and eutrophication of coastal waters, *ICES J. Mar. Sci.* 66 (2009) 1528–1537.
- [3] E. Murray, Y. Li, S.A. Currihan, B. Moore, A. Morrin, D. Diamond, M. Macka, B. Paull, Miniaturized capillary ion chromatograph with UV light-emitting diode based indirect absorbance detection for anion analysis in potable and environmental waters, *J. Sep. Sci.* 16 (2018) 3224–3231.
- [4] N. Aryal, M. Reba, Continuous instream monitoring of nutrients and sediment in agricultural watersheds, *J. Vis. Exp.* 127 (2017) 56036.
- [5] T.M. Schierenbeck, M.C. Smith, Path to impact for autonomous field deployable chemical sensors: a case study of in situ nitrite sensors, *Environ. Sci. Technol.* 51 (2017) 4755–4771.
- [6] L.R. Adornato, E.A. Kaltenbacher, T.A. Villareal, R.H. Byrne, Continuous in situ determinations of nitrite at nanomolar concentrations, *Deep-Sea Res. I* 52 (2005) 543–551.
- [7] D. Thouron, R. Vuillemin, X. Philippon, A. Lourenco, C. Provost, A. Cruzado, V. Garçon, An Autonomous nutrient analyzer for oceanic long-term in situ biogeochemical monitoring, *Anal. Chem.* 75 (2003) 2601–2609.
- [8] G. Duffy, F. Regan, Recent developments in sensing methods for eutrophying nutrients with a focus on automation for environmental applications, *Analyst* 142 (2017) 4355.
- [9] F. Wang, J. Zhu, L. Chen, Y. Zuo, X. Hu, Y. Yang, Autonomous and in situ ocean environmental monitoring on optofluidic platform, *Micromachines (Basel)* 11 (2020) 69.
- [10] A. Beaton, C. Cardwell, R. Thomas, V. Sieben, F. Legiret, E. Waugh, et al., Lab-on-chip measurement of nitrate and nitrite for, *Situ Anal. Natl. Waters, Environ. Sci. Technol.* 46 (2012) 9548–9556.
- [11] A.M. Nightingale, S. Hassan, B.M. Warren, K. Makris, G.W.H. Evans, E. Papadopolou, S. Coleman, X. Niu, A droplet microfluidic-based sensor for simultaneous in situ monitoring of nitrate and nitrite in natural waters, *Environ. Sci. Technol.* 53 (2019) 9677–9685.
- [12] A.D. Beaton, J.L. Wadham, J. Hawkings, E.A. Bagshaw, G. Lamarche-Gagnon, M.C. Mowlem, M. Tranter, High-resolution in situ measurement of nitrate in runoff from the Greenland ice sheet, *Environ. Sci. Technol.* 51 (2017) 12518–12527.
- [13] A. Rios, M. Zougagh, M. Avila, Miniaturization through lab-on-a-chip: Utopia or reality for routine laboratories? A review, *Anal. Chim. Acta* 740 (2012) 1–11.
- [14] TriOS, OPUS UV spectral sensor <https://www.trios.de/en/opus.html> (accessed 14 May 2019).
- [15] YSI incorporated, IQ SensorNet NitraVis® Sensors <https://www.ysi.com/nitravis>, (accessed 14 May 2019).
- [16] Sea Bird Scientific, SUNA V2 Nitrate Sensor <https://www.seabird.com/nutrient-sensors/suna-v2-nitrate-sensor/family?productCategoryId=54627869922>, (accessed 16 May 2019).
- [17] s:can Messtechnik GmbH, spectro:lyser spectrometer probe <https://www.s-can.at/products/spectrometer-probes>, (accessed 13 May 2019).
- [18] B.A. Pellerin, B.A. Bergamaschi, B.D. Downing, J.F. Saraceno, J.A. Garrett, L.D. Olsen, Optical Techniques for the Determination of Nitrate in Environmental Waters: Guidelines for Instrument Selection, Operation, Deployment, Maintenance, Quality Assurance, and Data Reporting, US Geological Survey, Virginia, 2013.
- [19] E. Murray, P. Roche, M. Briet, B. Moore, A. Morrin, D. Diamond, B. Paull, Fully automated, low-cost ion chromatography system for in-situ analysis of nitrite and nitrate in natural waters, *Talanta* 216 (2020) 12095.
- [20] K. Ito, H. Sunahara, Ion chromatography of iodide ion in seawater using concentrated sodium chloride solution as eluent, *Bunseki Kagaku* 37 (1988) 292.
- [21] Marheni, P.R. Haddad, A. McTaggart, On-column matrix elimination of high levels of chloride and sulfate in non-suppressed ion chromatography, *J. Chromatogr. A* 546 (1991) 221–228.
- [22] K. Ito, R. Nomura, T. Fujii, M. Tanaka, T. Tsumura, H. Shibata, Determination of nitrite, nitrate, bromide, and iodide in seawater by ion chromatography with UV detection using dilauryldimethylammonium-coated monolithic ODS columns and sodium chloride as an eluent, *Anal. Bioanal. Chem.* 404 (2012) 2513–2517.
- [23] R. Wang, N. Wang, M. Ye, Y. Zhu, Determination of low-level anions in seawater by ion chromatography with cycling-column-switching, *J. Chromatogr. A* 1265 (2012) 186–190.
- [24] R. Shellie, P. Haddad, Comprehensive two-dimensional liquid chromatography, *Anal. Bioanal. Chem.* 386 (2006) 405–415.
- [25] H. Wagner, B. Pepich, C. Pohl, D. Later, K. Srinivasan, R. Lin, et al., Selective method for the analysis of perchlorate in drinking waters at nanogram per liter levels, using two-dimensional ion chromatography with suppressed conductivity detection, *J. Chromatogr. A* 1155 (2007) 15–21.
- [26] Metrohm AG, IC Application Note U-62, Ammonium, nitrite, and nitrate in artificial seawater applying UV/VIS detection, Metrohm, Herisau, 2013.
- [27] E. Murray, P. Roche, K. Harrington, M. McCaul, B. Moore, A. Morrin, D. Diamond, B. Paull, 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* 1603 (2019) 8–14.
- [28] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, Standard Methods For The Examination Of Water And Wastewater, Port City Press, Baltimore, 2005.
- [29] E. Murray, E.P. Nesterenko, M. McCaul, A. Morrin, D. Diamond, B. Moore, A colorimetric method for use within portable test kits for nitrate determination in various water matrices, *Anal. Methods* 9 (2017) 680–687.
- [30] E. Desimoni, B. Brunetti, About estimating the limit of detection by the signal to noise approach, *Pharm. Anal. Acta* 6 (2015) 1–4.
- [31] K.R. Elkin, Portable, fully autonomous, ion chromatography system for on-site analyses, *J. Chromatogr. A* 1352 (2014) 38–45.