Recent advances and future trends in Flow Injection and their application to Chemical Oceanography

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Raquel B. R. Mesquita¹,
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Flow analysis as an efficient monitoring tool

- Analysis automation
- Real-time determinations
- On-line monitoring
- Low consumption values
- Multi-parametric determinations
- Speciation
Natural waters

- Wide concentration ranges
- Variable salinity
- Colour and/or turbidity
- Chemical forms
- Spatial and temporal variability

Complex matrix

- Real time assessment
  - Speciation
  - Interferences

Automation: Flow analysis
Flow methods vs Classical methods

Classical methodologies

× High reagent consumption
× High sample volumes
× High reaction time
× Higher contact between the analyst and the reagents
× Sample pretreatments often required

Flow methodologies

✓ Reduced reagent and sample consumption
✓ Lack of physical-chemical equilibrium
  ✓ Reduction in the reaction time
✓ Automation – increased security of the analyst
✓ Possibility of in-line sample pretreatments
Flow Injection Analysis - FIA

Described in 1975

✓ No physical nor chemical equilibrium
✓ Controlled dispersion – same conditions for standards and samples
✗ Continuous reagent flow
✗ One manifold per determination

Sequential Injection Analysis (SIA)
Sequential Injection Analysis - SIA

Described in 1990
- Non continuous flow
- Minimization of reagent/sample consumption
- Multi-parametric determinations
- Higher degree of automation
Sequential Injection Analysis - SIA

Detection system:
- Optical
- Electrochemical
- ...

Separation units:
- Gas diffusion
- SPE
- ...

Pre-treatment units:
- Digestion
- Dilution
- ...
The configuration of the basic SI instrument can be expanded by a variety of peripherals that fall into two categories: detectors and solution handling devices.
Water monitoring

In situ measurements
- pH
- Temperature
- Salinity
- Turbidity
- Dissolved Oxygen

Routine determinations
- Nitrogen ($NO_x$, $NH_x$, $N_{total}$)
- Phosphorus (phosphate)
- Carbon (DIC, DOC, TC)
SIA for transitional waters quality assessment

North west of Portugal
- Porto (>1 million pop.)
- Viana do Castelo
- Braga

Estuary of Câvado
- 1.600 km²
- rural and disperse urban area

Estuary of Ave
- 1.400 km²
- farm and industrial area

Estuary of Douro
- 98.000 km²
- urban area (vol. Discharge > 500 m³/s)
Monitored estuaries

Douro
(41.1°N, 08.6°W)

Cávado
(41.5°N, 08.7°W)

Ave
(41.3°N, 08.7°W)
Nutrients monitorization \((\text{NO}_x)\)

Simultaneous determination of nitrite and nitrate

CR, colour reagent (sulfanilamide, 20 g/L; N1NED, 2 g/L; Phosphoric ac., 0.5 M); S, sample/standard; EDTA, 0.4 g/L and ammonium chloride 20 g/L; Col., Cd column

Nutrients monitorization (NH$_x$)

Determination of ammonium and ammonia


BTB, 180 µM; S, sample/standard; NaOH 25 mM; Ppi, peristaltics pumps; SV, selection valve; GDU, gas diffusion unit
Nutrients monitorization (NO$_x$, NH$_x$ e PO$_4^{3-}$)

**Development of a sequential injection system for the determination of nitrite and nitrate in waters with different salinity: Application to estuaries in NW Portugal**

Raquel Beatriz Ribeiro Mesquita,$^{ab}$ Maria Teresa Soares Oliveira Barbosa Ferreira,$^a$
Ricardo Luiz Alves Segundo,$^a$ Catarina Fernanda Carvalho Pinheiro Teixeira,$^b$ Adriano Agostinho Bordalo$^b$
and António Osmaro Santos Silva Rangel$^{ab}$

Elimination of salinity interference using a multireflective cell

Bi parametric determination with in-line nitrate reduction

**Development of a flow method for the determination of phosphate in estuarine and freshwaters—Comparison of flow cells in spectrophotometric sequential injection analysis**

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Adriano A. Bordalo$^b$, Ian D. McKelvie$^d$, António O.S.S. Rangel$^{ab}$

Separation of the analyte from the sample with a GDU and no reagent consumption recirculation mode
## Parameter Quantification range Calibration curves LOD (µM) LOQ (µM) Determination rate (h⁻¹)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantification range</th>
<th>Calibration curves</th>
<th>LOD (µM)</th>
<th>LOQ (µM)</th>
<th>Determination rate (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>0.033-0.332 mM</td>
<td>$A = 0.631 \pm 0.050$ $[\text{NH}_4^+] + 0.087\pm0.029$</td>
<td>4.9</td>
<td>16.3</td>
<td>31</td>
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<tr>
<td>Phosphate</td>
<td>5.54 – 49.9 µM</td>
<td>$H_0 = 0.091 \pm 0.008$ $[\text{PO}_4^{3-}] - 0.089 \pm 0.057$</td>
<td>2.3</td>
<td>2.5</td>
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<tr>
<td>Nitrite</td>
<td>0.50 – 8.00 µM</td>
<td>$A = 5.06\times10^{-2} \pm 1.02\times10^{-3}$ $[\text{NO}_2^-] - 1.24\times10^{-4}$ $\pm 4.68\times10^{-3}$</td>
<td>0.11</td>
<td>0.36</td>
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<tr>
<td>Nitrate</td>
<td>12.5 – 305 µM</td>
<td>$A = 3.17\times10^{-2} \pm 7.57\times10^{-5}$ $[\text{NO}_3^-] - 8.38\times10^{-2}$ $\pm 1.19\times10^{-2}$</td>
<td>3.7</td>
<td>12.2</td>
<td>33</td>
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</table>

### Table of Estuarine Conditions

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<tr>
<th>ID</th>
<th>pH</th>
<th>Conductance (mS/cm)</th>
<th>Salinity</th>
<th>$\text{PO}_4^{3-}$ (µM±SD)</th>
<th>$\text{NO}_2^-$ (µM±SD)</th>
<th>$\text{NO}_3^-$ (µM±SD)</th>
<th>$\text{NH}_4^+$ (µM±SD)</th>
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<tr>
<td>Estuário 1</td>
<td>7,89</td>
<td>49,9</td>
<td>36,6</td>
<td>42,9 ± 2,5</td>
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<td>Estuário 2</td>
<td>7,89</td>
<td>0,227</td>
<td>&lt; 2</td>
<td>28,2 ± 0,0</td>
<td>1,16 ± 0,19</td>
<td>343 ± 67</td>
<td>4,14 ± 0,12</td>
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<tr>
<td>Estuário 3</td>
<td>6,21</td>
<td>1,455</td>
<td>&lt; 2</td>
<td>1,22 ± 0,06</td>
<td>1,07 ± 0,14</td>
<td>182 ± 6</td>
<td>24,5 ± 4,3</td>
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<tr>
<td>Estuário 4</td>
<td>6,31</td>
<td>0,276</td>
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<td>&lt; LQ</td>
<td>1,12 ± 0,14</td>
<td>115 ± 4</td>
<td>10,3 ± 2,9</td>
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<tr>
<td>Estuário 5</td>
<td>6,27</td>
<td>11,67</td>
<td>7,4</td>
<td>&lt; LQ</td>
<td>0,959 ± 0,067</td>
<td>23,4 ± 0,8</td>
<td>44,8 ± 4,0</td>
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<td>Estuário 6</td>
<td>6,59</td>
<td>1,393</td>
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<td>1,28 ± 0,17</td>
<td>4,06 ± 0,08</td>
<td>114 ± 2</td>
<td>9,8 ± 0,8</td>
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</table>
Nutrients monitorization - carbon speciation

Determination of DIC, TC (DOC), CO₂ and alkalinity

Fig. 1. Sequential injection manifold for carbon speciation in bathing waters: SV, eight port selection valve; Pi, peristaltic pumps; HC, holding coil (400 cm); RC, reaction coil (143 cm); Iₜ, connection tubes of 4, 3.5, and 46.5 cm length respectively; λ, spectrophotometer (611 nm); MRC, multi-reflection cell coupled to light-emitting diode (660 nm); GDU, gas diffusion unit equipped with an hydrophobic membrane; c, Y-shaped confluence; UV reactor, 4 m long reaction tube around a UV lamp; BTB, bromothymol blue indicator (90 μM BTB in 0.2 mM dihydrogen phosphate); BG, bromocresol green (0.11 g L⁻¹ BG in 2 mM acetic acid); Sample/Standard, sample or standard for DIC, TC and CO₂ determination; acidified peroxodisulfate, 1.2% of peroxodisulfate in 0.5 M H₂SO₄; H₂SO₄/Sₐlk, sulphuric acid (0.01 M) for DIC and TC determination or alkalinity standard or sample; W, waste.
Micro SIA – Lab on valve (LOV)

Described in 2000

Typical sample and reagent volumes: 5 to 25 µL/assay
Consumption of carrier solution: 100 to 250 µL
Solid Phase Extraction - SPE

Objectives

- Sample clean-up
- Analyte pre-concentration

DEFINITION OF SOLID PHASE EXTRACTION

A solid phase extraction (SPE) consists of bringing a liquid or gaseous test portion/solution in contact with a solid phase, or (ad)sorbent, whereby the analyte is selectively adsorbed on the surface of the solid phase. The solid phase is then separated from the solution and other solvents (liquids or gases) are added. The first such solvent is usually a wash to remove possible adsorbed matrix components; eventually an eluting solvent is brought into contact with the sorbent to selectively desorb the analyte.

Solid Phase Extraction - SPE

Non-Automated format
- time consuming
- low reproducibility

Automation
- Solid Phase Micro-Extraction (Needle trap, in-tube…)
- Flow-based methods (FIA, SIA)

SPE FLOW-BASED FORMAT

Reusable

Renewable (bead injection)
Reusable SPE - SIA

Determination of enzymatic activity (alkaline phosphatase)

\[ p\)-Nitrophenyl phosphate + H\(_2\)O \rightarrow p\)-Nitrophenol + Pi \]
Use of solid phase extraction for the sequential injection determination of alkaline phosphatase activity in dynamic water systems

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b Laboratory of Hydrobiology, Institute of Biomedical Sciences Abel Salazar (IBAS) and Institute of Marine Research (CIIMAR), Universidade do Porto, Lg. Abel Salazar 2, 4050-003 Porto, Portugal

* Corresponding author.

Fig. 2. Sequential injection (SI) manifold for the spectrophotometric determination of alkaline phosphatase activity: P, peristaltic pump; SV, eight-port selection valve; HC, 4.25 m holding coil; S, sample or enzyme standard; CR NTA, column with NTA resin charged with Zn2+ ions; DB 50, diethanolamine buffer (0.2 M diethanolamine buffer with 0.10 mM MgCl2); S PNP, enzyme substrate pNPP 30 mM; S pNP, pNP standard; EB 50, elution buffer (8 M of urea, 100 mM of KH2PO4 and 100 mM of Tris–HCl); RC, 95 cm reaction coil; λ, spectrophotometer (405 nm); W, waste.
Bead injection 
renewable solid phase spectrometry in micro SI format
Bead injection renewable SPS
Renewable SPE using microSI-LOV

Exploiting the bead injection LOV approach to carry out spectrophotometric assays in wine: Application to the determination of iron

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Fig. 1. (a) Configuration of the Bi-LOV manifold. (b) Position of the bead column in the flow cell. SP, syringe pump; PP, peristaltic pump; HC, holding coil; FC, flow cell; SCN\textsuperscript{−}, 1.5 M; H\textsubscript{2}O\textsubscript{2}, 0.3 M; W, waste; ST, PTFE stopper; PP, PEEK plug; B, beads; FO, fibre optics.
Renewable SPE using microSI-LOV

Determination of total protein content in white wine

NTA resin

Protein

$\text{Cu}^{2+}$

Freshly prepared beads

Beads after one working day

Coloring reaction (Lowry method)
Dear Colleagues,

It is our pleasure to announce and invite you to participate in the: 18th International Conference on Flow Injection Analysis – ICFIA, September 15-20, 2013, Porto, Portugal

18th ICFIA – [www.spq.pt/eventos/ICFIA](www.spq.pt/eventos/ICFIA)

Contact e-mail: icfia18@gmail.com
GREEN CHEMISTRY APPROACH FOR IRON DETERMINATION IN BATHING WATERS

Exploiting the lab on valve concept to study the 3,4-HPO chelator as non-toxic reagent for the determination of iron in coastal and inland bathing waters
Coastal and inland balnear waters

Important to monitor some aesthetic parameters

High impact waters

More often quality assessment

Public health
# 3,4-HPO Ligands

<table>
<thead>
<tr>
<th>3,4-HPO Ligand</th>
<th>Structure</th>
<th>Chemical formula</th>
<th>Molecular weight</th>
<th>pKa $\text{Hmmp}$</th>
<th>pKa $\text{Hdmpp}$</th>
<th>pKa $\text{Hetpp}$</th>
<th>pKa $\text{Hempp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Hydroxy-2- methyl-4-pyridinone</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>$\text{C}_6\text{H}_7\text{O}_2\text{N}$</td>
<td>126.14</td>
<td>$\text{pKa}_1 = 3.62 \pm 0.05$</td>
<td>$\text{pKa}_2 = 9.48 \pm 0.05$</td>
<td>$\text{pKa}_1 = 3.69 \pm 0.01$</td>
<td>$\text{pKa}_2 = 9.61 \pm 0.03$</td>
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<tr>
<td>3-Hydroxy-1, 2- methyl-4-pyridinone</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>$\text{C}_7\text{H}_9\text{O}_2\text{N}$</td>
<td>139.15</td>
<td>$\text{pKa}_1 = 3.62 \pm 0.05$</td>
<td>$\text{pKa}_2 = 9.48 \pm 0.05$</td>
<td>$\text{pKa}_1 = 3.69 \pm 0.01$</td>
<td>$\text{pKa}_2 = 9.61 \pm 0.03$</td>
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<tr>
<td>2-Ethyl-3-hydroxy-4-pyridinone</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>$\text{C}_7\text{H}_9\text{O}_2\text{N}$</td>
<td>139.15</td>
<td>$\text{pKa}_1 = 3.63 \pm 0.04$</td>
<td>$\text{pKa}_2 = 9.62 \pm 0.05$</td>
<td>$\text{pKa}_1 = 3.62 \pm 0.05$</td>
<td>$\text{pKa}_2 = 9.61 \pm 0.03$</td>
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<tr>
<td>2-Ethyl-3-hydroxy-1-methyl-4-pyridinone</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>$\text{C}<em>8\text{H}</em>{11}\text{O}_2\text{N}$</td>
<td>153.16</td>
<td>$\text{pKa}_1 = 3.53 \pm 0.02$</td>
<td>$\text{pKa}_2 = 9.46 \pm 0.05$</td>
<td>$\text{pKa}_1 = 3.63 \pm 0.04$</td>
<td>$\text{pKa}_2 = 9.62 \pm 0.05$</td>
</tr>
</tbody>
</table>
μSI-LOV manifold for iron determination with 3,4-HPO ligand Hmpp

SP, syringe pump; HC, holding coil; OF, optical fibers
Parameters for iron quantification with 3,4-HPO ligand Hmpp

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Used value</th>
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<tbody>
<tr>
<td>Volumes</td>
<td></td>
</tr>
<tr>
<td>Ligand</td>
<td>40 µL</td>
</tr>
<tr>
<td>Buffer</td>
<td>5 µL</td>
</tr>
<tr>
<td>Sample</td>
<td>50 µL</td>
</tr>
<tr>
<td>Buffer composition</td>
<td>[HCO₃⁻] =0.25 M</td>
</tr>
<tr>
<td></td>
<td>pH=10.5</td>
</tr>
<tr>
<td>Flow rate for determination</td>
<td>20 µL/s</td>
</tr>
</tbody>
</table>

The decrease of ligand concentration results in slope decrease and intercept increase.

Concentration of ligand solution 12 mg/L
Interference assessment

Major ions possibly present in water and bivalent (and trivalent) metal ions

Table 4. Assessment of possible interfering ions in the determination of iron according to legislated values; UNFAO, United Nations Food and Agriculture Organization.

<table>
<thead>
<tr>
<th>Possible interfering ion</th>
<th>Legislation maximum values (irrigation\textsuperscript{a} or streams\textsuperscript{b} waters)</th>
<th>Tested concentration of interfering ion in a standard 0.4 mg Fe\textsuperscript{3+}/L (mg/L)</th>
<th>Interference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UNFAO (mg/L)</td>
<td>Portugal (mg/L)</td>
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</tr>
<tr>
<td>Al\textsuperscript{3+}</td>
<td>5\textsuperscript{a}</td>
<td>20\textsuperscript{a}</td>
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<tr>
<td>Ca\textsuperscript{2+}</td>
<td>15\textsuperscript{b}</td>
<td>50\textsuperscript{b}</td>
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<td>Co\textsuperscript{2+}</td>
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<td>Cu\textsuperscript{2+}</td>
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<td>Mg\textsuperscript{2+}</td>
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<td>2.8</td>
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Features of the developed µSI-LOV method

<table>
<thead>
<tr>
<th>Dynamic range (mg/L)</th>
<th>Calibration curve ( A = m.[Fe^{3+}] + b )</th>
<th>LOD (µg/L)</th>
<th>LOQ (µg/L)</th>
<th>Quantification rate (h⁻¹)</th>
<th>Reagent/sample consumption</th>
<th>Effluent production (µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 - 1.00</td>
<td>( y = 0.0488 (±0.0008) ) ([Fe^{3+}] + 0.0030 (±0.0004)) ( R^2 = 0.999 )</td>
<td>23</td>
<td>77</td>
<td>90</td>
<td>0.48 mg Hmpp [Fe^{3+}] 0.11 mg NaHCO₃ [Fe^{3+}] 0.16 mg HNO₃ [Fe^{3+}] 50 µL</td>
<td>350</td>
</tr>
</tbody>
</table>

Limitations for coastal waters application

- Lower dynamic range
- Decrease the quantification limit
- Iron preconcentration
- Use of NTA Superflow resin
- Solid phase spectrometry (SPS)
μSI-LOV for iron determination with 3,4-HPO ligand with preconcentration in NTA resin

SP, syringe pump; HC, holding coil; OF, optical fibers

NTA resin (B) for iron preconcentration: Measurement based on solid phase spectrometry

⇒ SPS
Salinity interference minimization with the SPS method

µSI-LOV
for iron determination

µSI-LOV-SPS
for iron speciation

[slope (L/mg)]

salinity added

0.000
0.050
0.100
0.150
0.200
0.250
0.300
0.350
0.400
0.450
0.000
0.010
0.020
0.030
0.040
0.050
0.060
0.000
0.10
20
30
40
0
10
20
30
40
0.00
10
20
30
40
0.00

Bathing waters
Coastal bathing waters locations

Porto urban area
Exploiting the use of 3,4-HPO ligands as non-toxic reagents for the determination of iron in natural waters with a sequential injection approach

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