Development of a sequential injection system for the determination of nitrite and nitrate in estuarine waters

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Framework

◆ The growth of global awareness about the importance of monitoring water bodies in order to protect water quality has led to search for fast, automatic and reliable methods of parameters determination.

Sequential Injection Analysis (SIA)

✓ Robustness and versatility - potential for multi determinations

✓ Low consumption of reagents and sample along with low production of effluents

✓ High degree of automation

◆ Monitoring nitrate and nitrite level in estuarine waters aims to control the possible contamination by the excess of fertilizers which can result in the eutrophication of the water body – application to three estuaries in northern Portugal.

Manifold and operation conditions
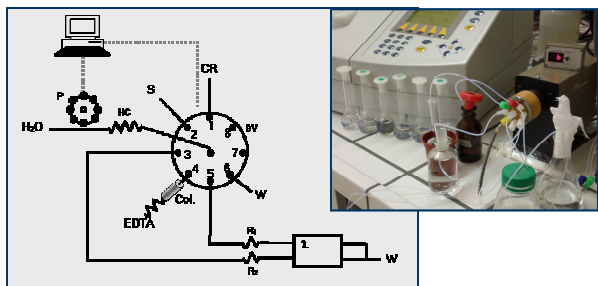
P – peristaltic pump; SV – selection valve; λ – spectrophotometer at 543 nm; HC – holding coil (30 cm); Col. - cadmium column; R_1 - reactors; CR – colour reagent (sulphanilamide 20 g/L, N1NED 2 g/L in H_3PO_4 1.5 M); S – sample or standard; EDTA – conditioner (EDTA 0.55 g/L with NH_4Cl 21 g/L); W – waste.

Protocol sequence

Step	SV position	Time (s)	Pump speed	Pump direction	Volume (µL)	Description
A	4	4.5	30	a	214	Aspiration of conditioner (EDTA)
B	2	2.5	30	a	119	Aspiration of sample/standard
C	4	10	10	b	148	Propelling to column for reduction
D	8	4	40	b	243	Propelling to waste to wash holding coil
E	1	9	40	a	548	Aspiration of colour reagent
F	2	9.2	40	a	560	Aspiration of sample/standard
G	3	55	40	b	2800	Propelling to detector, mixture of reagent and sample and measurement (nitrite determination)
H	4	3	10	a	44	Aspiration for preparation of the port
I	8	2	40	b	122	Propelling to waste to wash holding coil
J	1	5	40	a	304	Aspiration of colour reagent
L	4	3.4	20	a	102	Aspiration of reduced sample/standard
M	5	45	40	b	2738	Propelling to detector, mixture of reagent and sample and measurement (nitrate+nitrite determination)
N	4	5	30	a	238	Aspiration of conditioner (EDTA) to wash the column
O	8	5	40	b	304	Propelling to waste to wash holding coil

◆ Griess reaction for determination of nitrite and reduction of nitrate to nitrite with cadmium column.

◆ Flow cell of 2 cm optical path for nitrite determination and of 1 cm optical path for nitrate+nitrite determination.

Features of the SIA methodology

✓ **Typical calibration curves (7 curves):**

✓ nitrite: Abs = 0.0471 ± 0.0026 $[NO_2^-]$ + 6E-04 ± 8.8E-03

✓ nitrate: Abs = 0.00332 ± 0.00032 $[NO_3^-]$ + 7.81E-02 ± 1.96E-02

✓ **Limit of detection (LOD) and quantification (LOQ)**

✓ nitrite: LOD = 0.12 µM; LOQ = 0.39 µM

✓ nitrate: LOD = 4.3 µM; LOQ = 14.2 µM

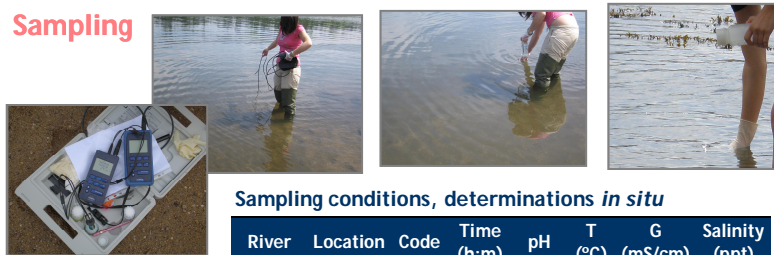## Estuaries water from 3 Portuguese rivers

Cávado River

Location 3

Ave River

Location 3

Douro River

Location 2
Location 1
Location 3

Sampling

Sampling conditions, determinations *in situ*

River	Location	Code	Time (h:m)	pH	T (ºC)	G (mS/cm)	Salinity (ppt)
Ave	3	RA3	-	8.60	-	0.47	< 2
Cávado	1	RC1	12:15	7.67	18.5	15.2	10.0
	2	RC2	11:15	6.87	20.4	2.0	< 2
	3	RC3	13:15	7.19	21.5	0.72	< 2
Douro	1	RD1	12:15	8.16	21.1	29.2	18.4
	2	RD2	11:15	8.30	21.6	29.2	18.0
	3	RD3	10:15	7.90	22.6	22.7	6.8

Results

Comparison between the results obtained with the developed SIA methodology and with the reference procedure (a colorimetric determination).

SIA = $9.71 \times 10^{-1} \pm 0.0504$ Ref. Met. + $6.14 \times 10^{-2} \pm 0.0900$
$R^2 = 9.95 \times 10^{-1}$
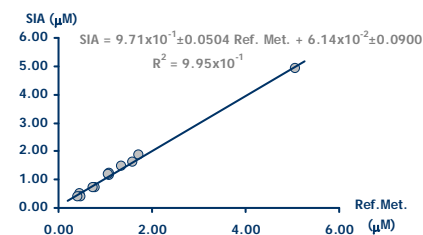
Application to the monitorisation of nitrites and nitrates level in the mentioned estuaries water, with direct introduction of the sample.

Sampling date	River /location	Sample ID	Nitrite (µM ± SD)	Nitrate + nitrite (µM ± SD)	Nitrate (µM ± SD)
11-07-2008	Ave 3	RA3	4.91 ±0.16	241 ±7	236 ±7
06-05-2008	Cávado 1	RC1	0.66 ±0.02	55.0 ±0.5	54.4 ±0.5
	Cávado 2	RC2	1.47 ±0.01	76.5 ±4.1	75.1 ±4.1
	Cávado 3	RC3	1.60 ±0.19	106 ±2.4	105 ±2
10-07-2008	Douro 1	RD1	<LOQ -	122 ±9	122 ±9
	Douro 2	RD2	0.70 ±0.04	122 ±5	121 ±5
	Douro 3	RD3	0.88 ±0.05	308 ±5	307 ±5
24-07-2008	Douro 1	RD1'	0.68 ±0.08	48.0 ±7.6	47.3 ±7.5
	Douro 2	RD2'	1.28 ±0.00	62.2 ±0.5	60.9 ±0.5
	Douro 3	RD3'	2.57 ±0.02	71.1 ±1.5	68.5 ±1.5

❖ Both the values of nitrite and nitrate increase by moving up river.

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