



Sequential injection system for the spectrophotometric determination of ammonium in Portuguese estuarine waters

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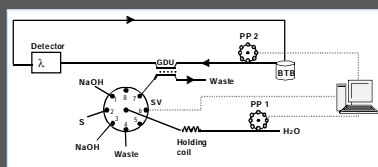
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Objectives

- Development of a sequential injection system for ammonium determination in a wide dynamic range, using a green chemistry approach (no consumption of reagent)
- Application to water samples with high salinity gradient: estuarine waters, interstitial waters, marine waters and well waters

Sequential injection method



Manifold for the determination of ammonium: SV, selection valve; GDU, gas diffusion unit; PP, peristaltic pumps; BTB, bromothymol blue indicator; S, sample/standard.



Step	SV position	Time (s)	Pump 1 speed	Pump 1 direction	Volume (μL)	Pump 2	Description
A	1	3.3	40	a	200	off	Aspiration of NaOH
B	2	14.8/13.2*	40	a	900/800*	off	Aspiration of sample/standard
C	3	3.3	40	a	200	off	Aspiration of NaOH
D**	2	13.2	40	a	800	off	Aspiration of sample/standard
E**	3	3.3	40	a	800	off	Aspiration of NaOH
F	7	50	30	b	3000	off	Propelling the mixture of hydroxide and sample to the donor channel of the GDU
G	4	45	20	b	1350	on	Propelling the BTB in the acceptor channel to detector

* time for step B for the dynamic range 0.1 - 1 ppm.
** steps included only for the dynamic range 0.1 - 1 ppm.



Features of the developed system

Dynamic range	Calibration curve	LOD	LOQ	RSD, % (mg/L)	Determination rate (h ⁻¹)	NaOH consumption/determination
1.0 - 5.0 mg/L (55-222 μM)	A = 0.0863±0.0098 mg NH ₄ ⁺ /L + 0.078±0.019	-	138 μg/L (7.7 μM)	2.1% (2.46±0.05)	28	0.40 mg

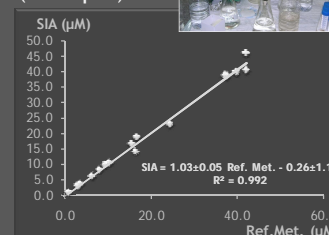
⚡ No BTB consumption (per determination) due to recirculation

Conclusions

- Wide quantification range
- Determination of ammonium in estuarine waters and also in marine and well waters
- Effective determination within a wide salinity gradient, ranging from < 2 to 35

Application to estuarine samples

Some samples were filtered (0.45 μm)



Sample source	Sample ID	Salinity	Ref. Met. conc.±SD (μM)	SIA, conc.±SD (μM)	%RD
Ave estuary	F1	7.16	15.5±0.2	16.4±1.8	5.8
	F2	0.80	16.7±0.4	18.7±0.7	12.2
	F3	0.11	24.3±2.5	22.9±0.3	-5.6
Well waters	PW1	27.3	0.89±0.04	0.82±0.42	-7.6
	A1	6.1	37.4±2.4	38.5±0.7	2.9
	A2	1.4	39.6±0.5	39.7±0.3	0.2
Lima estuary	A3	0.2	41.9±0.5	40.3±0.7	-3.8
	PF5a	< 2	3.59±0.05	3.54±0.68	-1.4
	PF10a	< 2	3.09±0.15	2.90±0.47	-6.1
Cávado estuary	PF10b	< 2	3.09±0.15	3.08±0.16	-0.3
	L2	3.8	6.38±0.07	6.11±0.81	-4.2
	C1	15.6	16.4±0.2	14.0±1.3	-14.6
Marine waters	C2	2.0	37.0±0.3	38.6±0.5	4.4
	C3	0.4	41.9±0.4	45.8±0.6	9.4
Well waters	P1	33.1	8.05±0.06	8.10±0.61	0.6
	P6	33.2	10.3±0.1	10.4±0.3	1.0
	P9	35.0	9.38±0.20	9.7±0.2	3.2



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