Spectrophotometric determination of ammonium in coastal waters using a multicommuted flow injection system

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Objectives

- Development of a multicommuted flow system for the determination of ammonium in saline waters
  - Recirculation of the solutions ⇒ reduction of reagents consumption and waste generation
  - In-line elimination of interfering species
    - Introduction of a gas diffusion unit
    - Addition of a complexing agent to the carrier solution

Manifold and protocol sequence

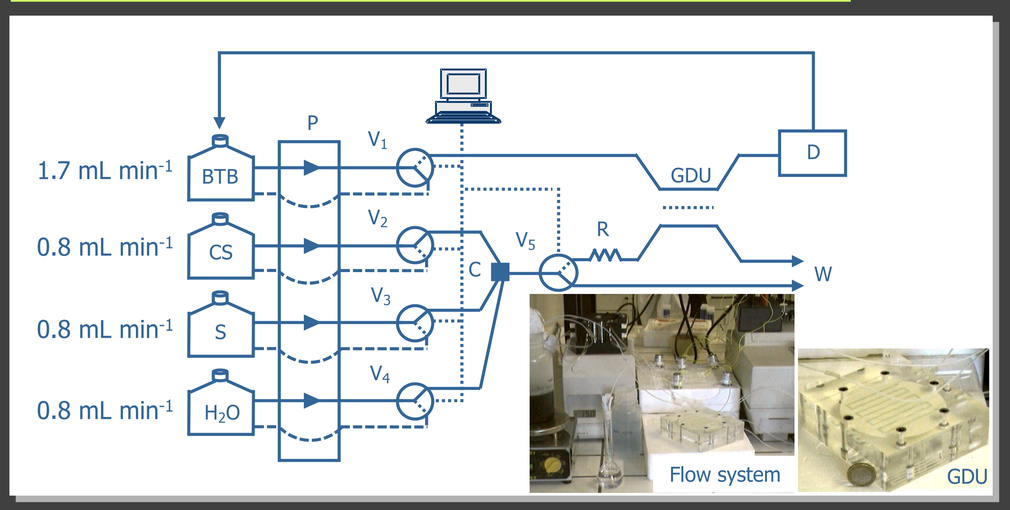


Figure 1. Multicommuted flow system for the spectrophotometric determination of ammonium in coastal waters. BTB: bromothymol blue 0.06 mmol L^{-1}; CS: NaHO 0.5 mol L^{-1} + potassium sodium tartrate 70 g L^{-1}; S: sample or standard; P: peristaltic pump, V_i: solenoid valves in position "on" (continuous line) or "off" (dotted line); C: confluence; R: reaction coil (100 cm); GDU: gas diffusion unit; W: waste; D: detector (620 nm)

Step	Description	Position of the commutation valves					Time / s
		V_1	V_2	V_3	V_4	V_5	
1	Wash connection between V_3 and V_5	N	F	N	F	N	15
2	Wash connection between C e V_5	F	F	F	N	N	15
3	Wash acceptor and donor channels	F	N	F	F	F	20
4	Sample introduction	F	N	N	F	F	18
5	Sample introduction and stop BTB flow	N	N	N	F	F	12
6	Stop BTB flow	N	N	F	F	F	48
7	Propel acceptor stream towards the detector; signal registration	F	N	F	F	F	90

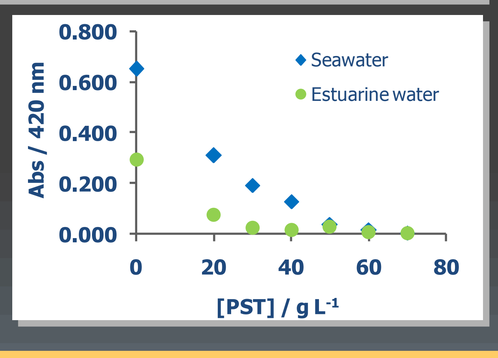
The letters N e F correspond to positions "on" and "off" of the commutation valves, respectively

Evaluation of complexing agents

- After mixing the sample with the alkaline solution, the formation of a precipitate was observed ⇒ evaluation of the efficiency of different complexing agents: read absorbance (turbidity) of a solution containing sample + NaHO + complexing agent

Complexing agent	Maximum Concentration tested / g L^{-1}	Abs / 420 nm
Sodium citrate	180	0.367
EDTA	70	0.017
Potassium sodium tartrate (PST)	70	0.005

Potassium sodium tartrate was selected as the complexing agent ⇒



Interference study

Added species	Concentration found in saline waters	Tested concentration#	Relative deviation / %
Methylamine / nM	600	800	3.4
Dimethylamine / nM	400	2000	2.7
Trimethylamine / nM	500	1000	2.4
Ethylamine / nM	1400	1500	3.0
Diethylamine / nM	100	3000	2.1
Triethylamine / nM	N/A*	3000	4.3
Triethanolamine / nM	N/A*	8000	-3.1
Urea / μM	3	10	-0.5
HCO_3^- / mg L^{-1}	140	200	4.1
CO_3^{2-} / mg L^{-1}	80	100	4.4
Hg^{2+} / mg L^{-1}	0.0002	1	2.2
S^{2-} / mg L^{-1}	0.1	10	1.6
Ca^{2+} / mg L^{-1}	400	500	0.6
Mg^{2+} / mg L^{-1}	1300	1500	1.9
K^+ / mg L^{-1}	400	500	4.0
Sr^{2+} / mg L^{-1}	8	20	3.7
SO_4^{2-} / mg L^{-1}	2700	3000	4.5
Br^- / mg L^{-1}	70	100	0.5
H_3BO_3 / mg L^{-1}	30	50	2.0
F^- / mg L^{-1}	1	10	-0.5

*N/A – not available; #using a standard solution of 100 μg L^{-1} NH_4^+; interferents were tested separately

Application to real saline samples

Recovery assays

$[NH_4^+]$ added / μg L^{-1}	Recovery / %				
	A1	A2	A3	A4	A5
50.0	102 ± 2	101 ± 5	99.2 ± 2.8	96.5 ± 5.8	99.0 ± 2.2
200	99.8 ± 3.8	102 ± 2	94.9 ± 1.8	98.8 ± 4.4	95.7 ± 1.1
500	96.7 ± 1.6	103 ± 2	96.4 ± 0.5	102 ± 1	98.9 ± 0.6
800	99.9 ± 1.4	102 ± 1	98.9 ± 0.6	100 ± 1	99.5 ± 0.6

Samples: A1, A2, A3 - seawaters; A4, A5 - estuarine waters

Certified Reference Material VKI QC RW1

- Acceptance limits: 100.2 – 101.5 μg N L^{-1}
- Preparation of the reference material in the sample to be analysed

Sample	A2	A3	A4	A5
[N] / μg L^{-1}	101.1	100.5	100.7	101.2
Standard deviation (n = 10)	1.6	1.6	1.3	2.0

Figures of merit

Working range / μg L^{-1} NH_4^+	50.0 - 1000
Sensitivity (n = 12) / AU mg^{-1} L	0.524 ± 0.016
Intercept (n = 12) / AU	0.176 ± 0.034
Detection limit / μg L^{-1} NH_4^+	18
Quantification limit / μg L^{-1} NH_4^+	35
Relative standard deviation (n = 10) / %	1.6
Determination rate/ h^{-1}	20

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