CATÓLICA
UNIVERSIDADE CATÓLICA PORTUGUESA
ESCOLA SUPERIOR DE BIOTECNOLOGIA

*Flow X, 2006*

# A multicommuted flow injection system with a multi-channel propulsion unit: spectrophotometric determination of $N\text{-}NH_4^+$

Sara M. Oliveira, Teresa I. M. S. Lopes, Ildikó V. Tóth and António O. S. S. Rangel

Escola Superior de Biotecnologia, Porto, Portugal

# Introduction

**Separation processes in flow analysis**

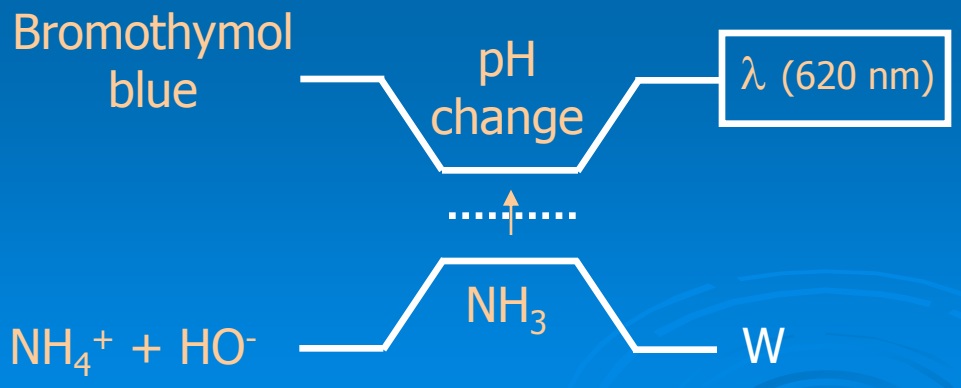
- Objectives
  - Avoid matrix problems
  - Enhance selectivity
  - Pre-concentrate/dilute
- Limitations
  - Overpressure conditioning
    - Propulsion process
    - Manifold configuration
    - Flow technique
  - Mostly used in FIA systems
    - High reagents consumption and waste generation

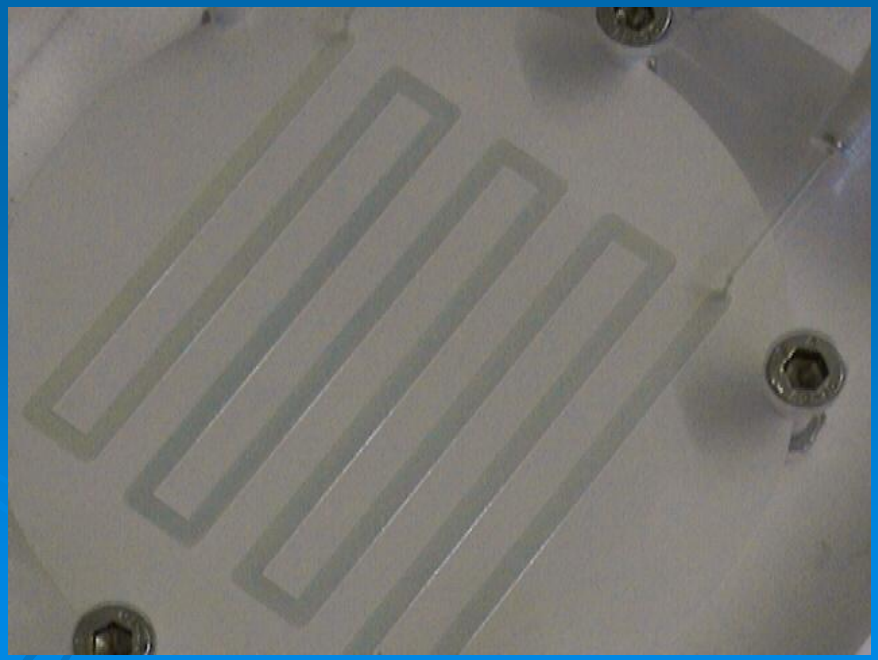
# Introduction

- Multicommutation system with the pumping device placed before the solenoid valves
  - Minimisation of the formation of unwanted air bubbles
  - Easy adaptation of a separation device to the manifold
  - Minimisation of reagent consumption and waste generation
    - Propulsion of the solutions into the flow network or re-circulation to their own vessel
    - Possibility of reagent recycling

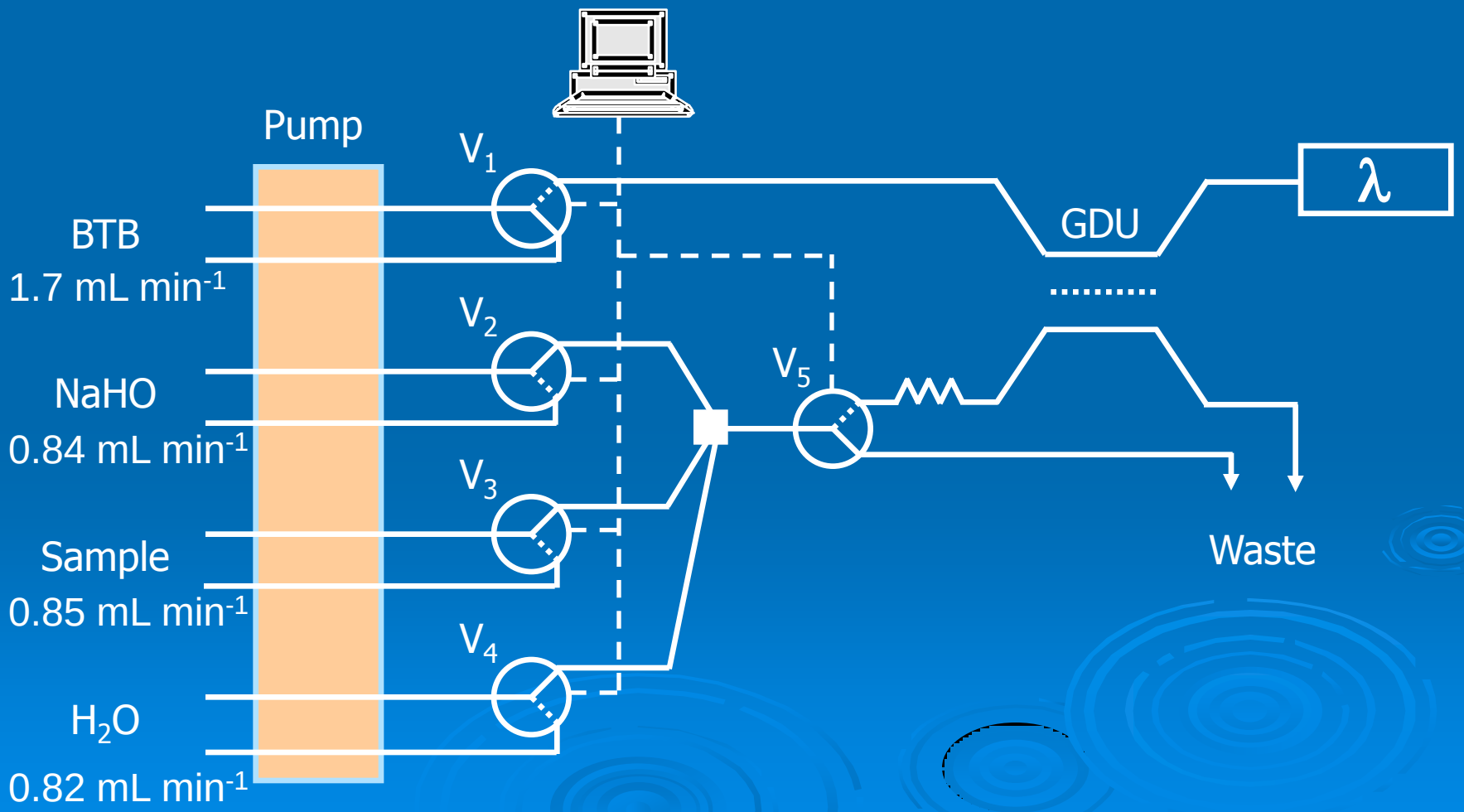
# Introduction

- Application of the system to a reaction with low selectivity
  - Spectrophotometric determination of ammonium nitrogen using an acid-base indicator
- Incorporation of a gas diffusion unit
  - Transfer the analyte from a donor stream (sample) to an acceptor solution (detector)

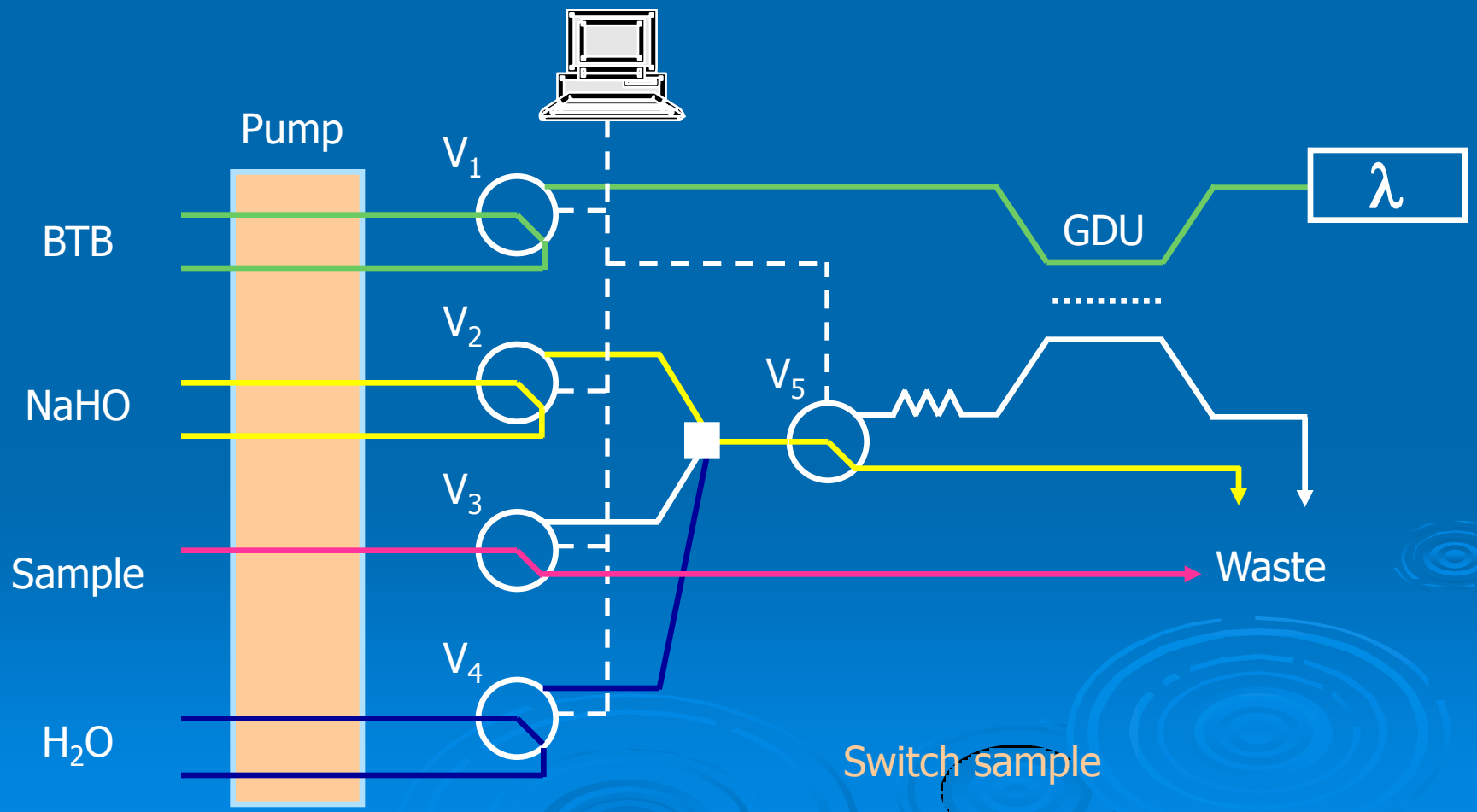


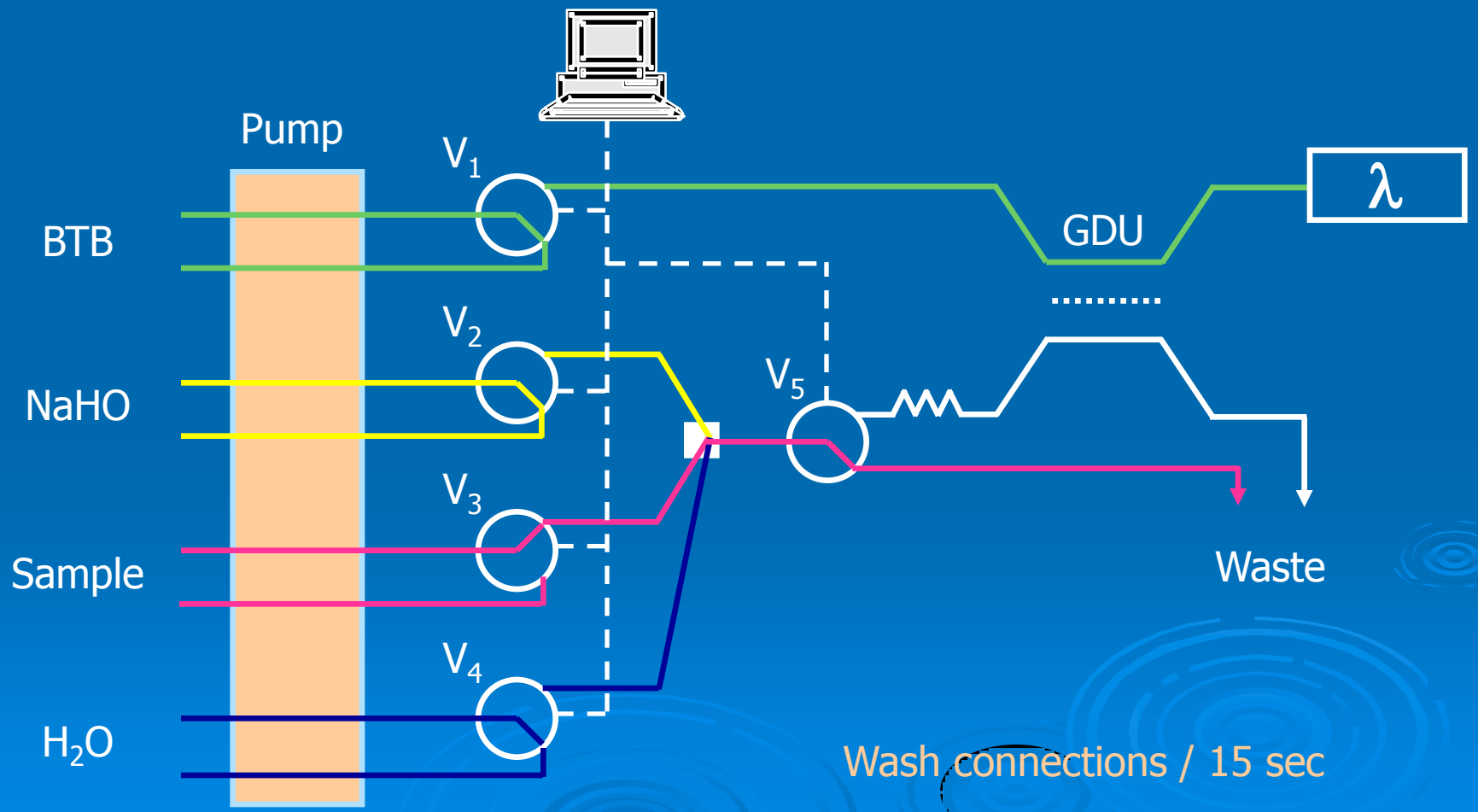
# Multicommuted manifold



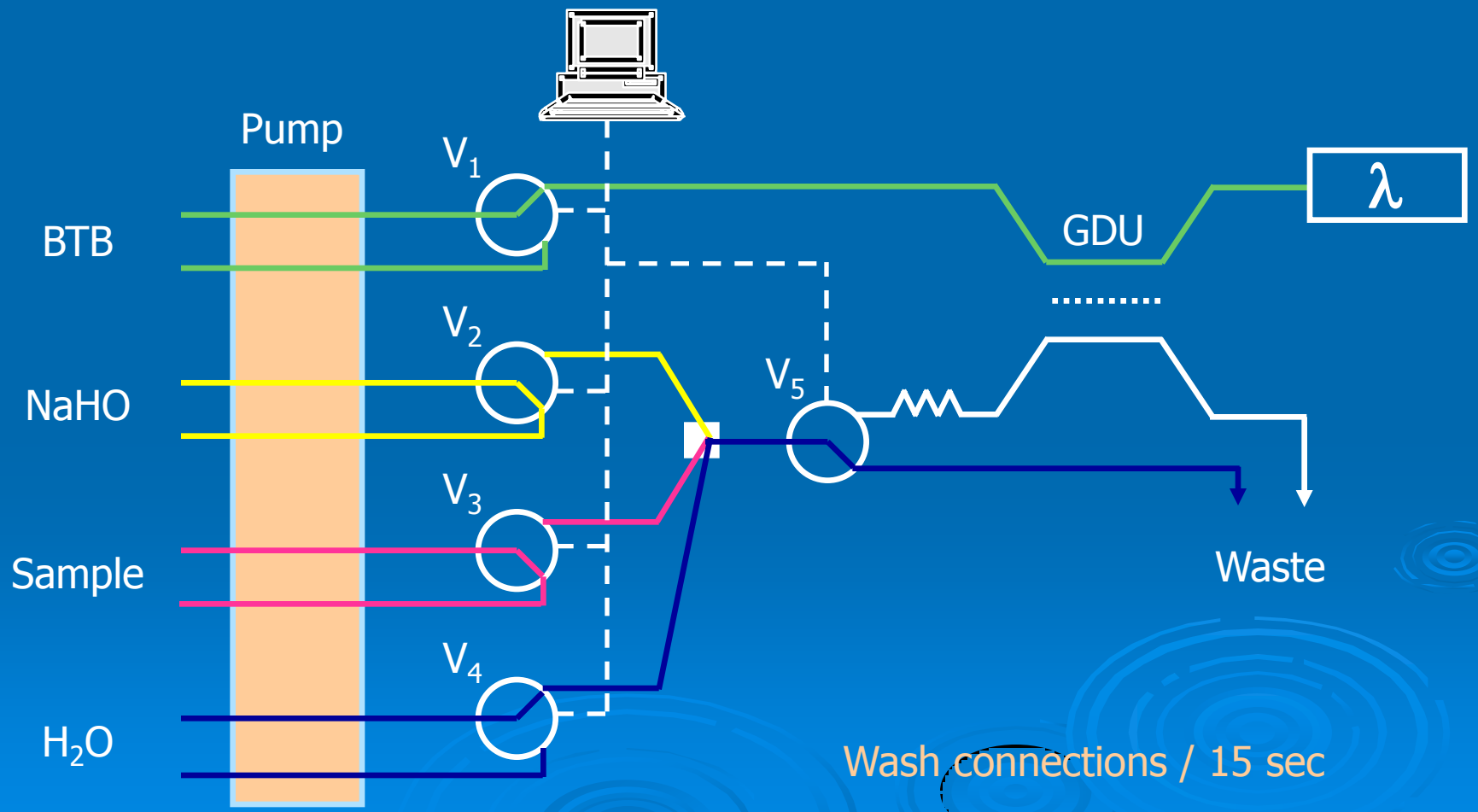
# Analytical sequence



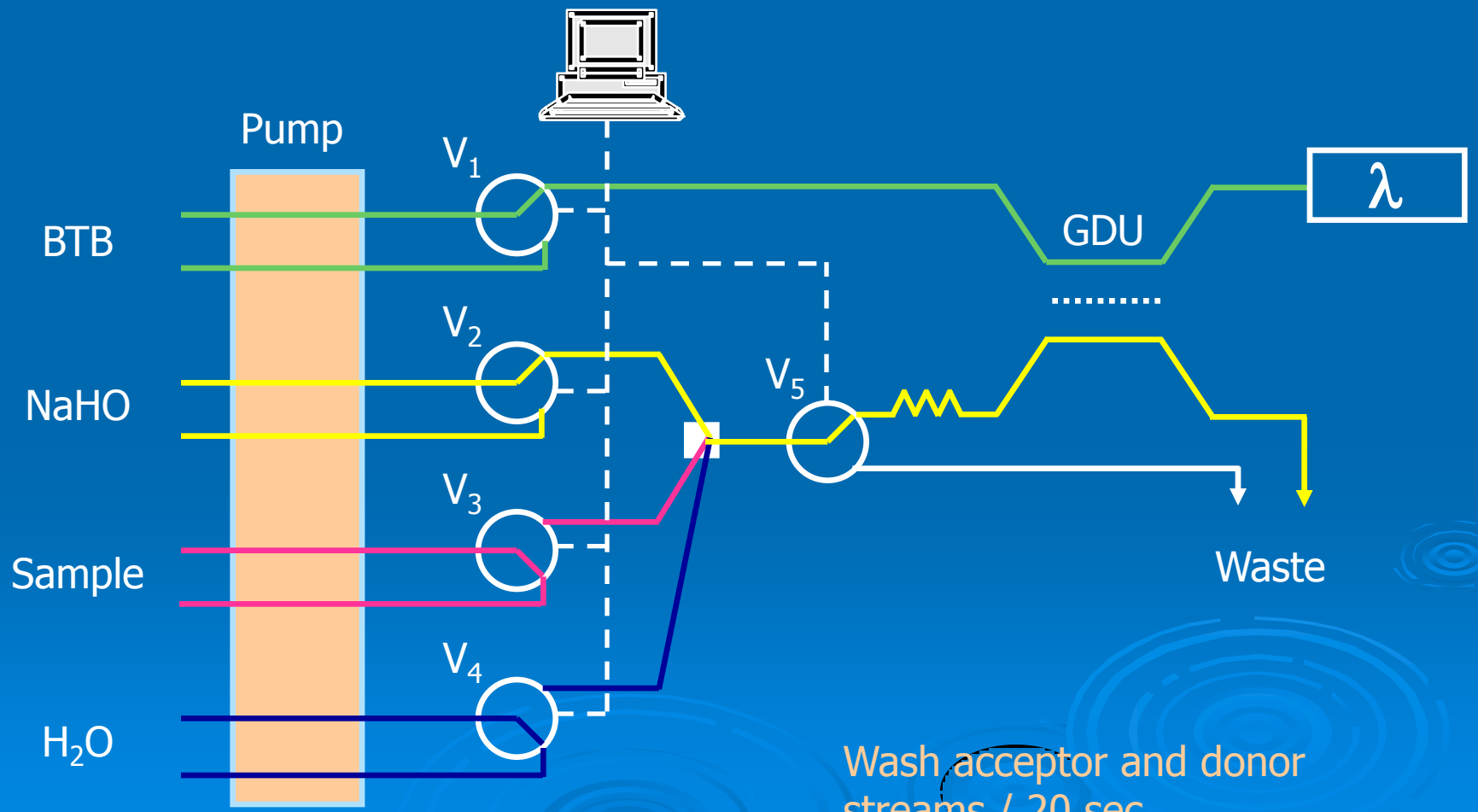
# Analytical sequence



# Analytical sequence

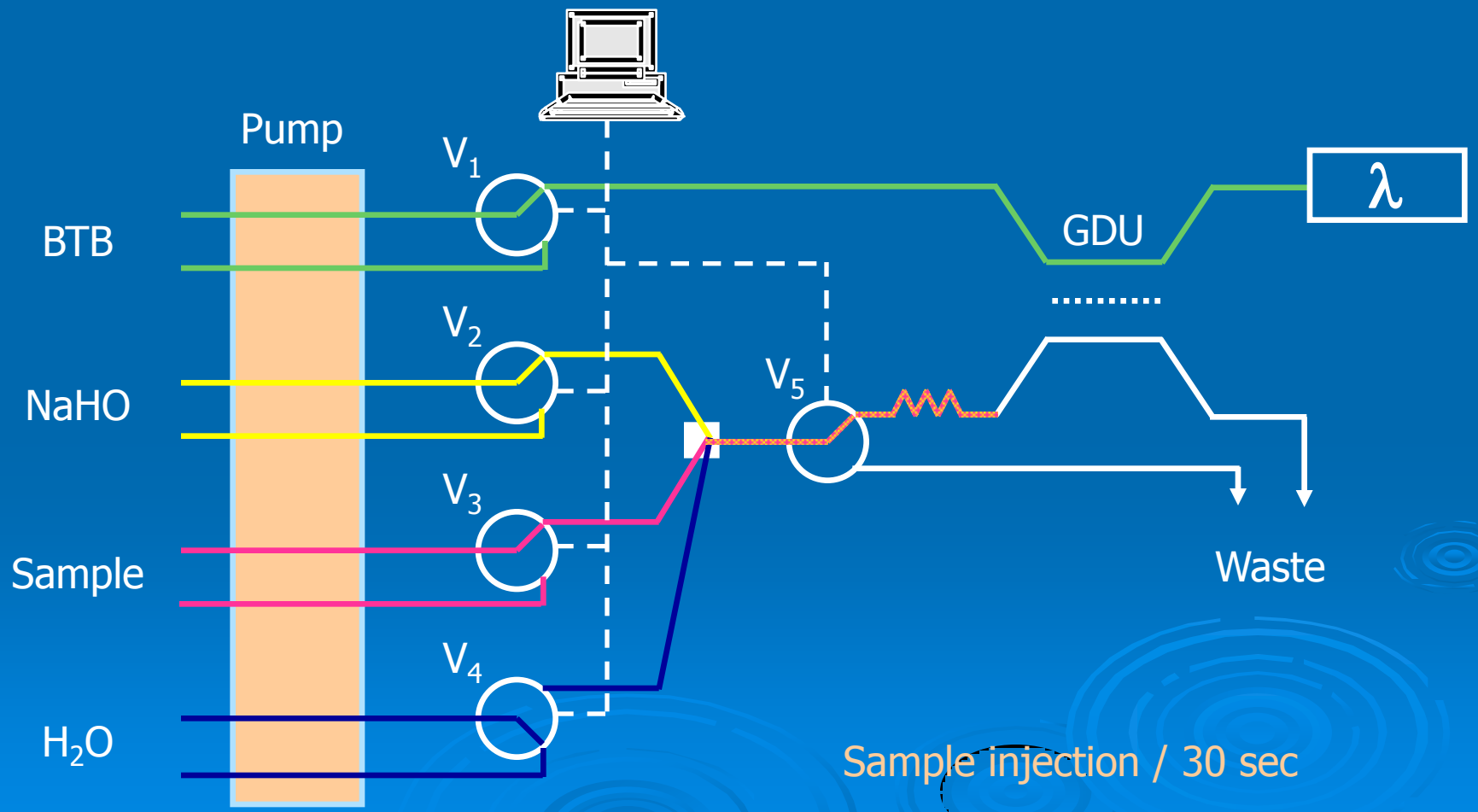


# Analytical sequence

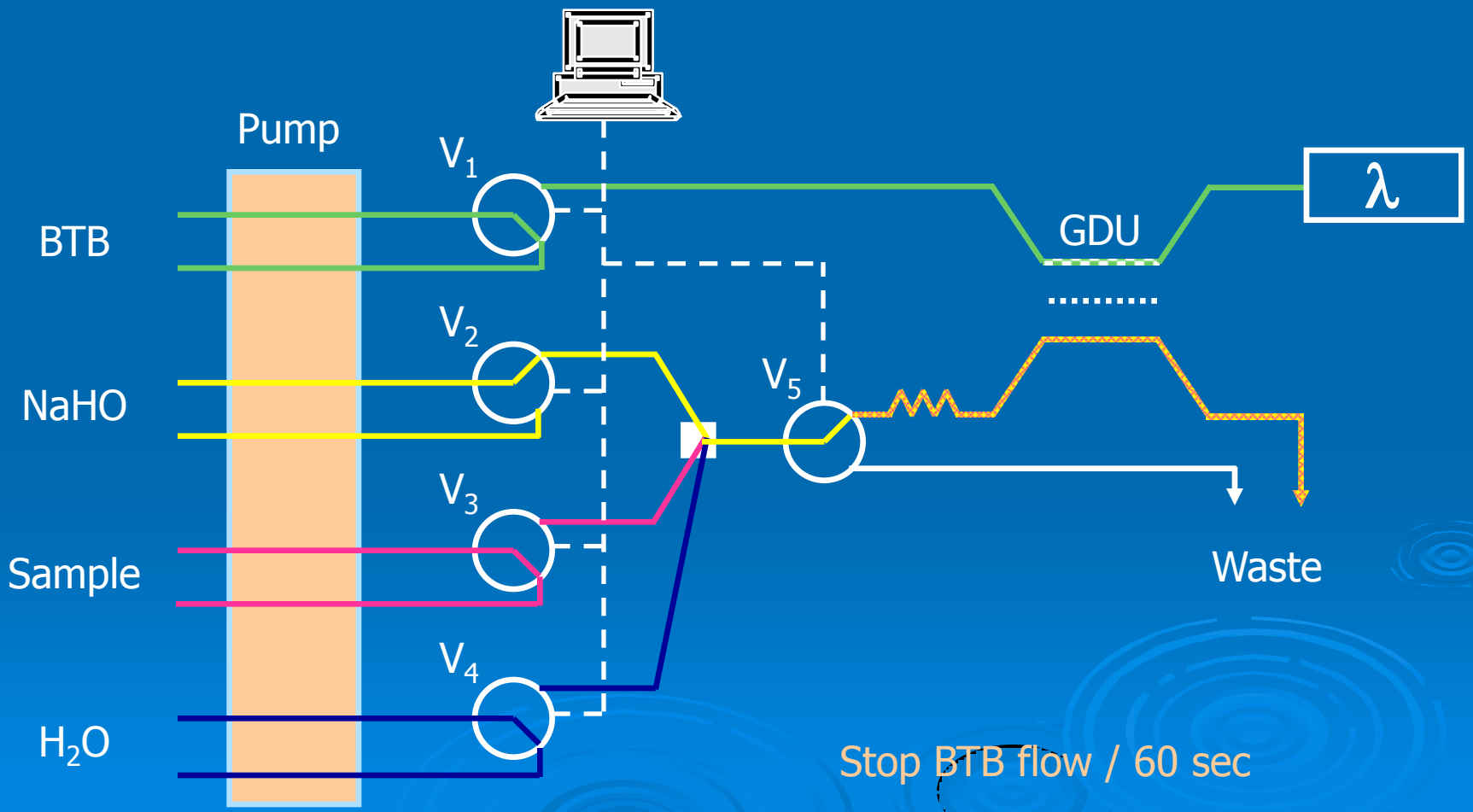



Wash acceptor and donor streams / 20 sec

# Analytical sequence

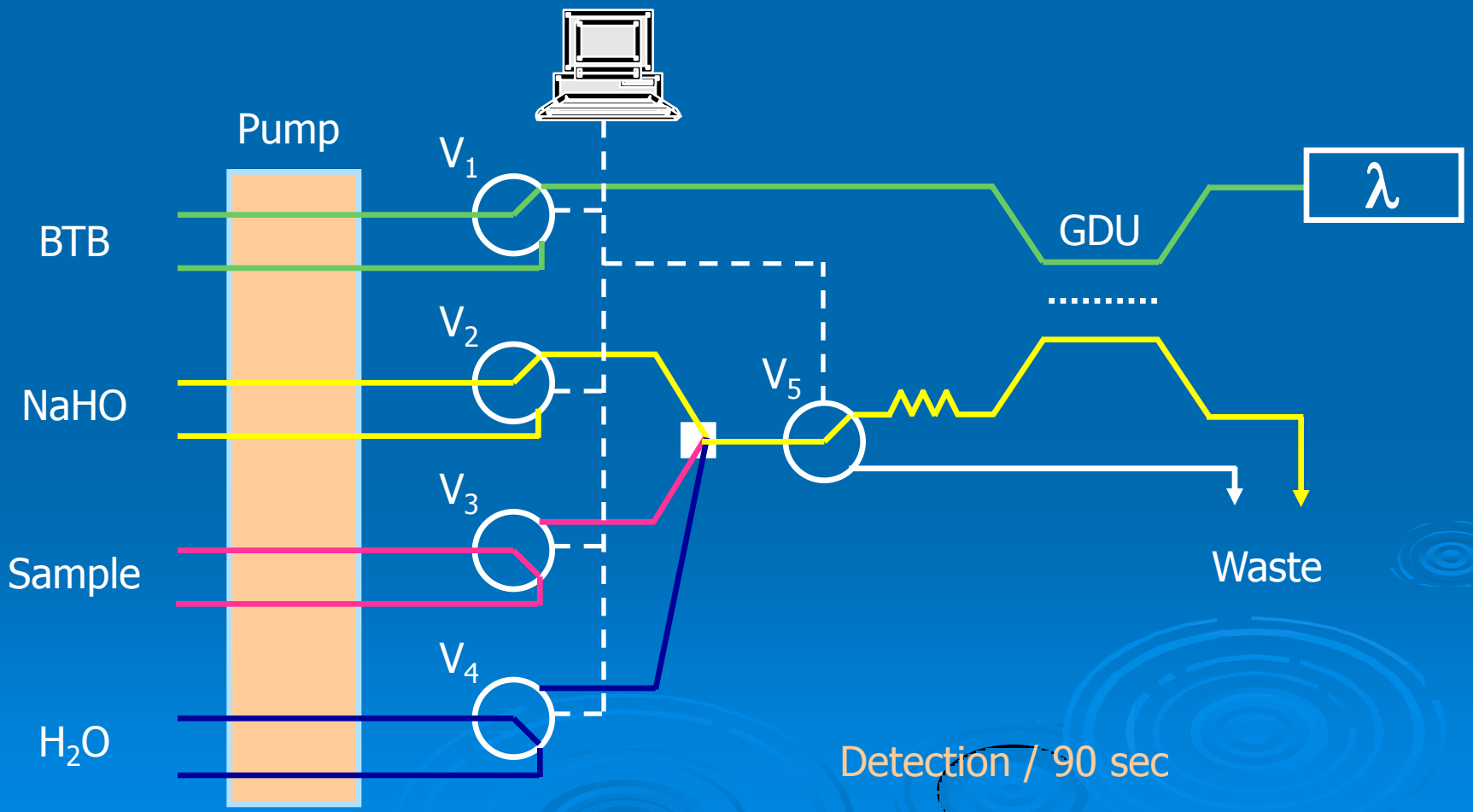


# Analytical sequence

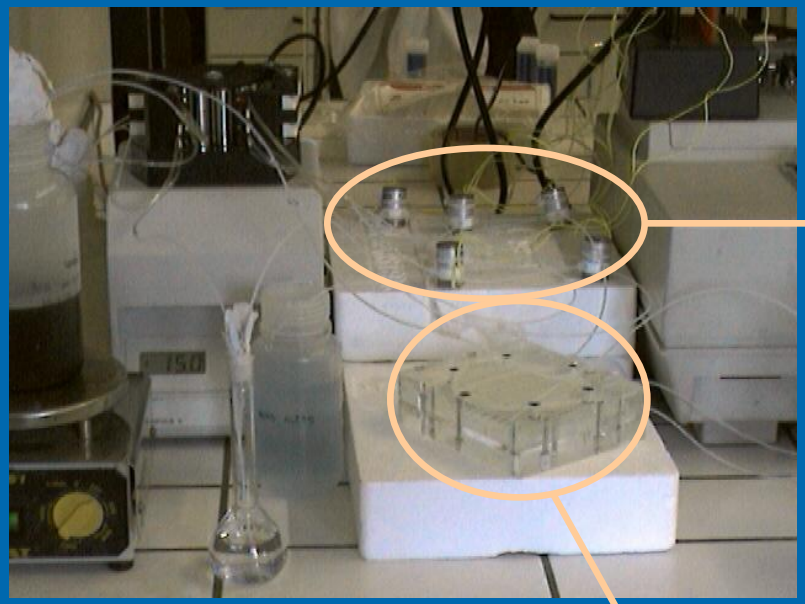



Stop BTB flow / 60 sec

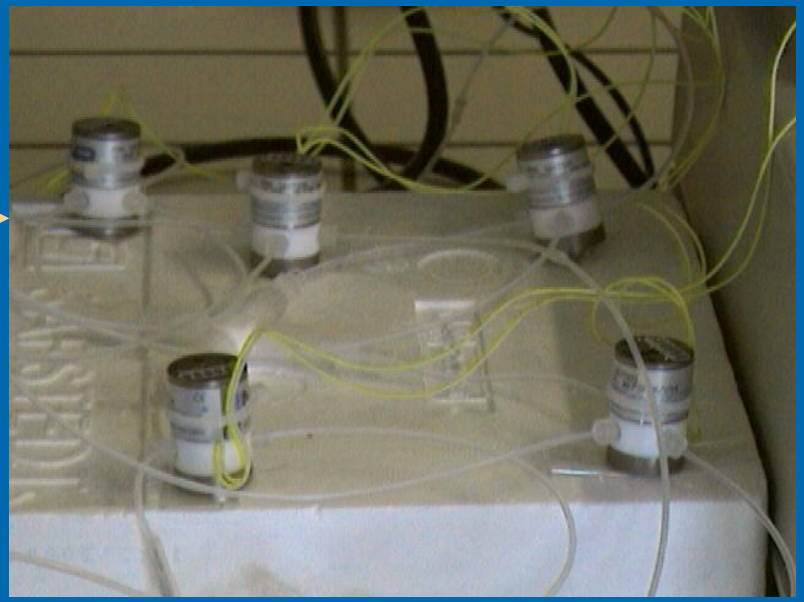
# Analytical sequence



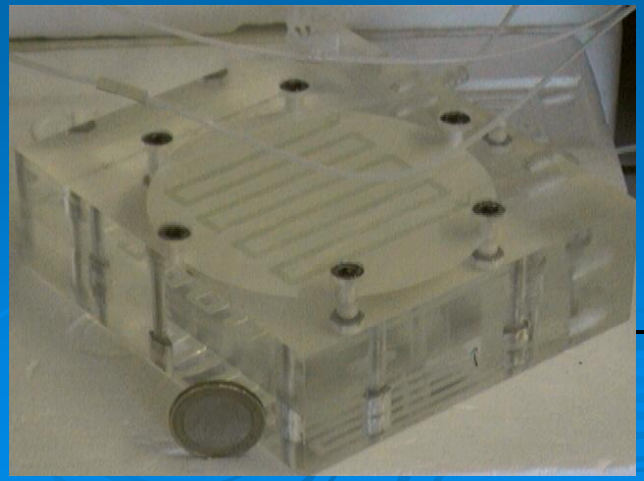
# In the laboratory



Flow manifold



Network of solenoid valves



Gas diffusion device

# Development of the flow system

| Variable studied | Range | Chosen Value |
|---|---|---|
| Temperature (donor solution) | 25 – 80ºC | 25ºC |
| Ultrasonic treatment | Yes / No | No |
| Flow cell optical path | 10 mm / 20 mm | 10 mm |
| BTB pH | 5.8 – 7.6 | 6.8 |
| Acceptor flow rate | 1.1 – 2.3 mL $min^{-1}$ | 1.7 mL $min^{-1}$ |
| Donor flow rate | 1.1 – 2.0 mL $min^{-1}$ | 1.7 mL $min^{-1}$ |
| Sample volume | 208 – 553 μL | 415 μL |
| Stop period of BTB solution | 0 – 80 s | 60 s |
| NaHO concentration | 0.01 – 0.5 mol $L^{-1}$ | 0.1 mol $L^{-1}$ |
| BTB concentration | 0.02 – 0.1 mmol $L^{-1}$ | 0.06 mmol $L^{-1}$ |

# Development of the flow system

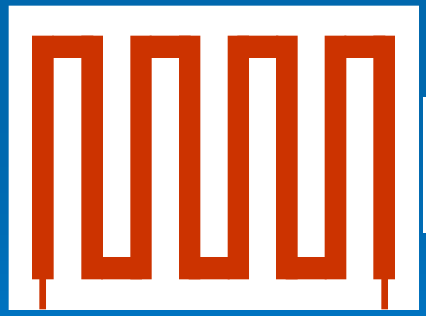
- Configuration and area of the gas diffusion device

A = 108 $mm^2$

s = 0.0165 AU $mg^{-1}$ L

A = 142 $mm^2$

s = 0.0177 AU $mg^{-1}$ L



GDU chosen

A = 1524 $mm^2$

s = 0.0804 AU $mg^{-1}$ L

A = 146 $mm^2$

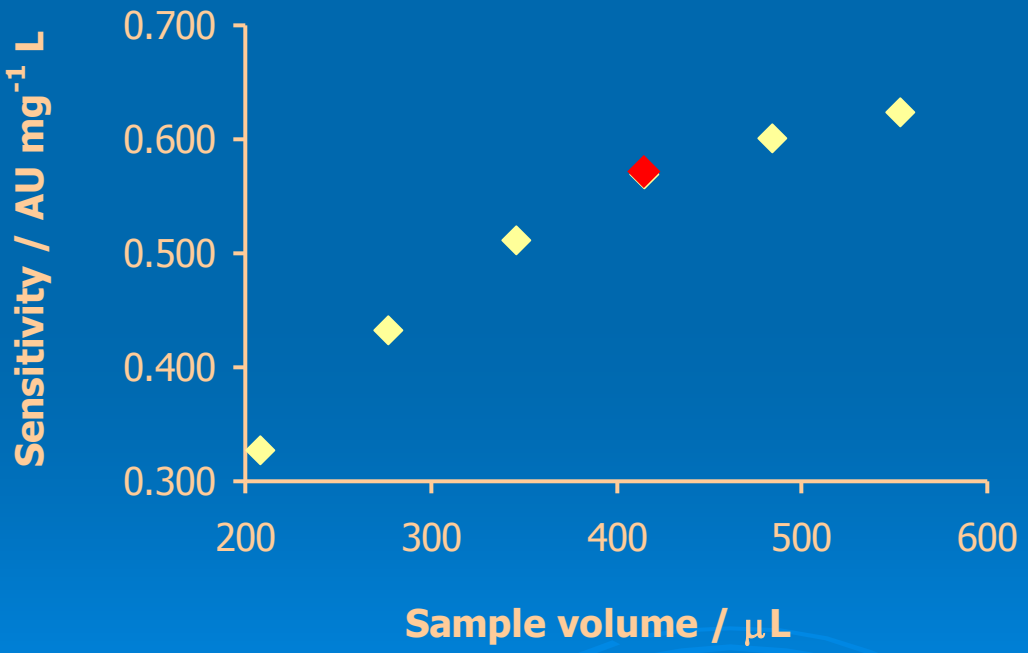
s = 0.0553 AU $mg^{-1}$ L

s = sensitivity

Experiments done with a FIA system; $NH_4^+$ concentration range = 1 – 20 mg $L^{-1}$

# Development of the flow system

- Sample volume

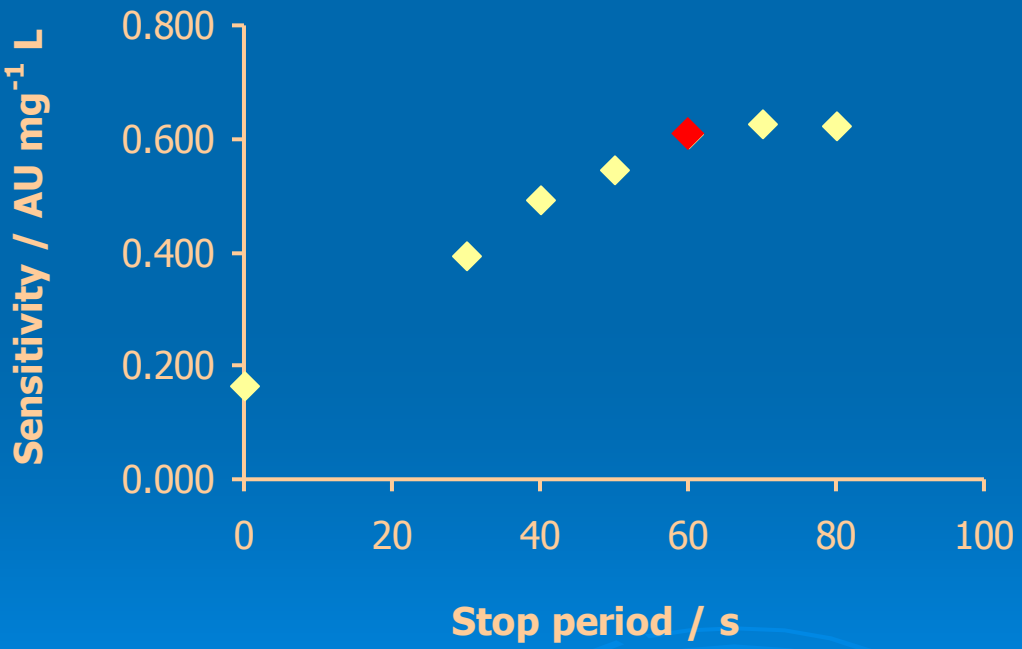



A sample volume of 415 µL corresponded to 96% of the sensitivity relative to the maximum volume tested

$NH_4^+$ concentration range = 50 – 1000 µg $L^{-1}$

# Development of the flow system

- Stop period of the BTB solution

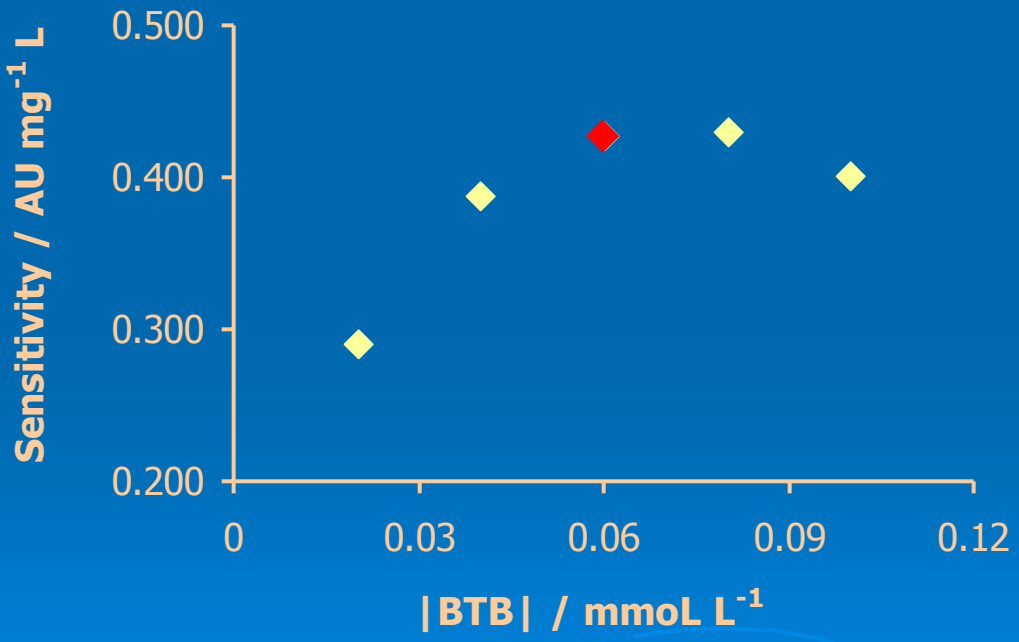



The flow of the acceptor stream was stopped for a period of 60 seconds

$NH_4^+$ concentration range = 50 – 1000 μg $L^{-1}$

# Development of the flow system

- Acceptor solution concentration




A concentration of 0.06 mmol $L^{-1}$ of BTB was selected for further work

$NH_4^+$ concentration range = 50 – 1000 μg $L^{-1}$

# Development of the flow system

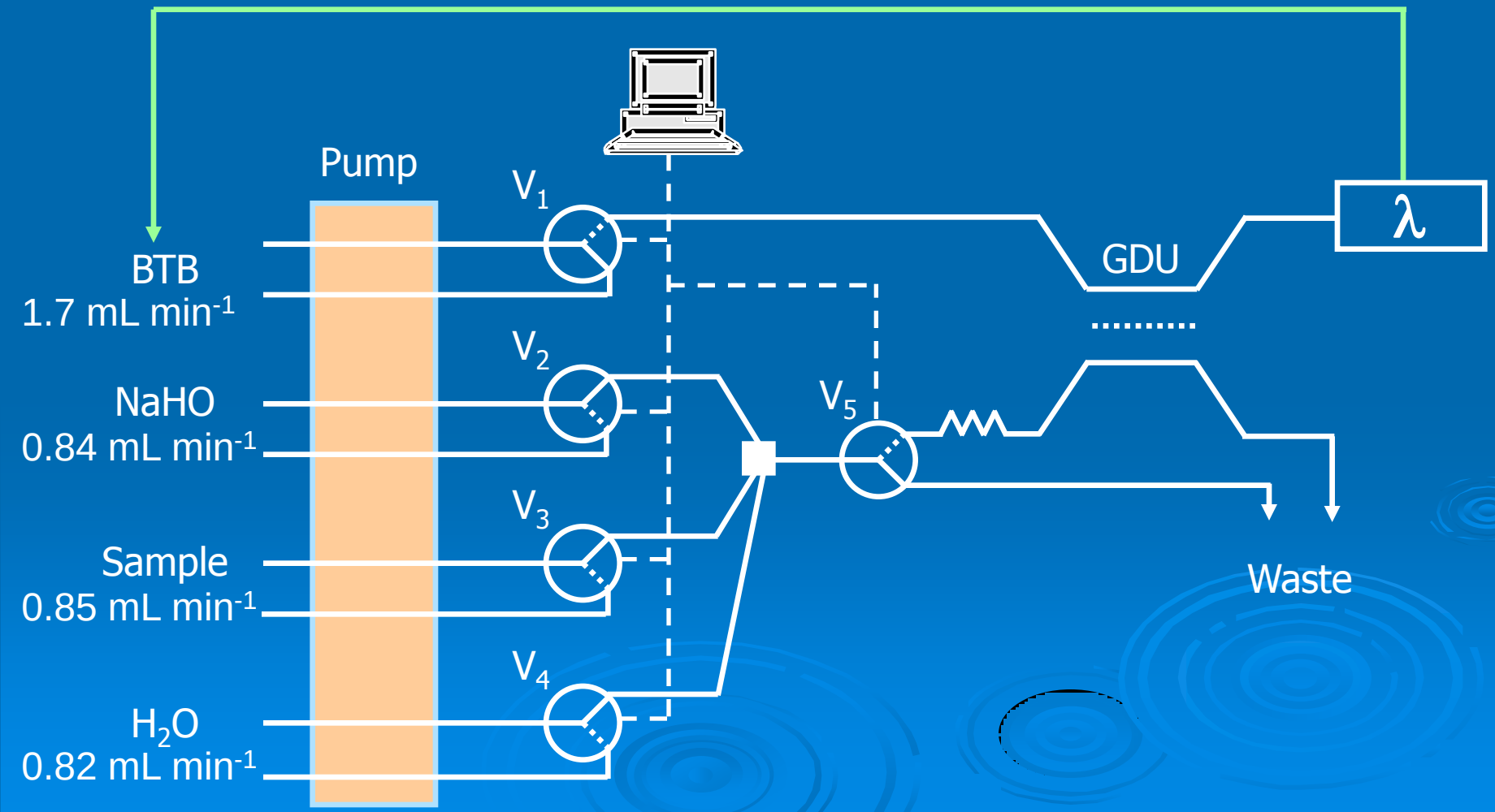
- Interferences

| Interfering ion | Concentration tested | Relative deviation / % |
|---|---|---|
| $Cu^{2+}$ | 200 μg $L^{-1}$ | -0.61 |
| $Zn^{2+}$ | 200 μg $L^{-1}$ | -3.64 |
| $Fe^{2+}$ | 200 μg $L^{-1}$ | 4.5 |
| $Ca^{2+}$ | 200 μg $L^{-1}$ | -4.15 |
| $Mg^{2+}$ | 200 μg $L^{-1}$ | -4.15 |
| $Al^{3+}$ | 200 μg $L^{-1}$ | 2.75 |
| $HCO_3^-$ | 10 mg $L^{-1}$ | -2.47 |

$NH_4^+$ concentration = 100 μg $L^{-1}$

# Development of the flow system

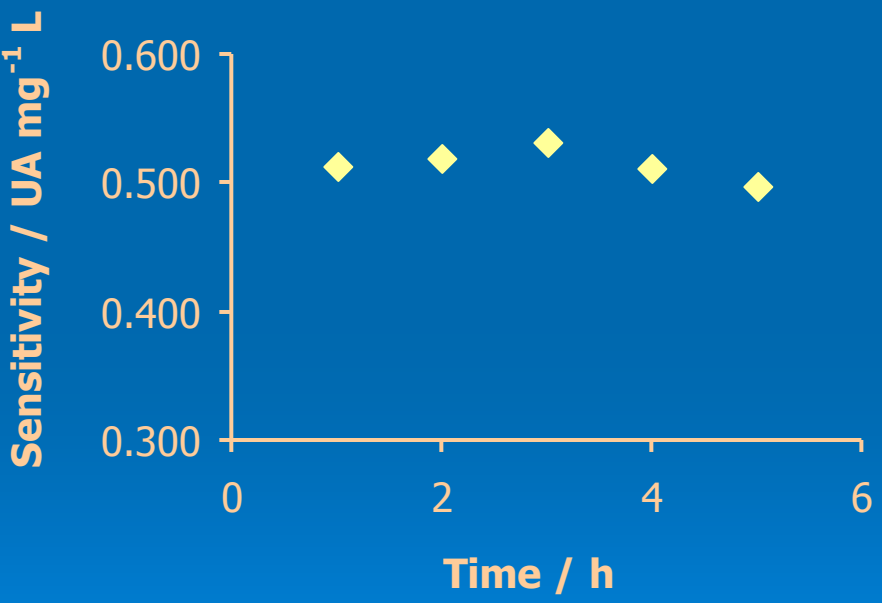
- Multicommuted manifold with BTB recirculation



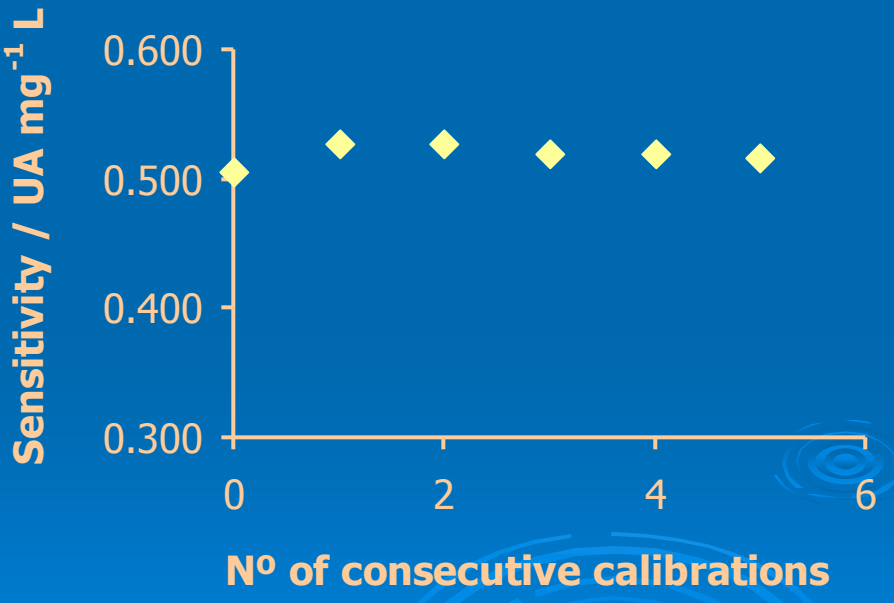
# Development of the flow system

- Possibility of BTB recycling

No recycling




With recirculation




**There is no statistical difference between both graphs**
**t- test: $|t|_{calculated} = 0.77 < t_{critical} = 2.26$**

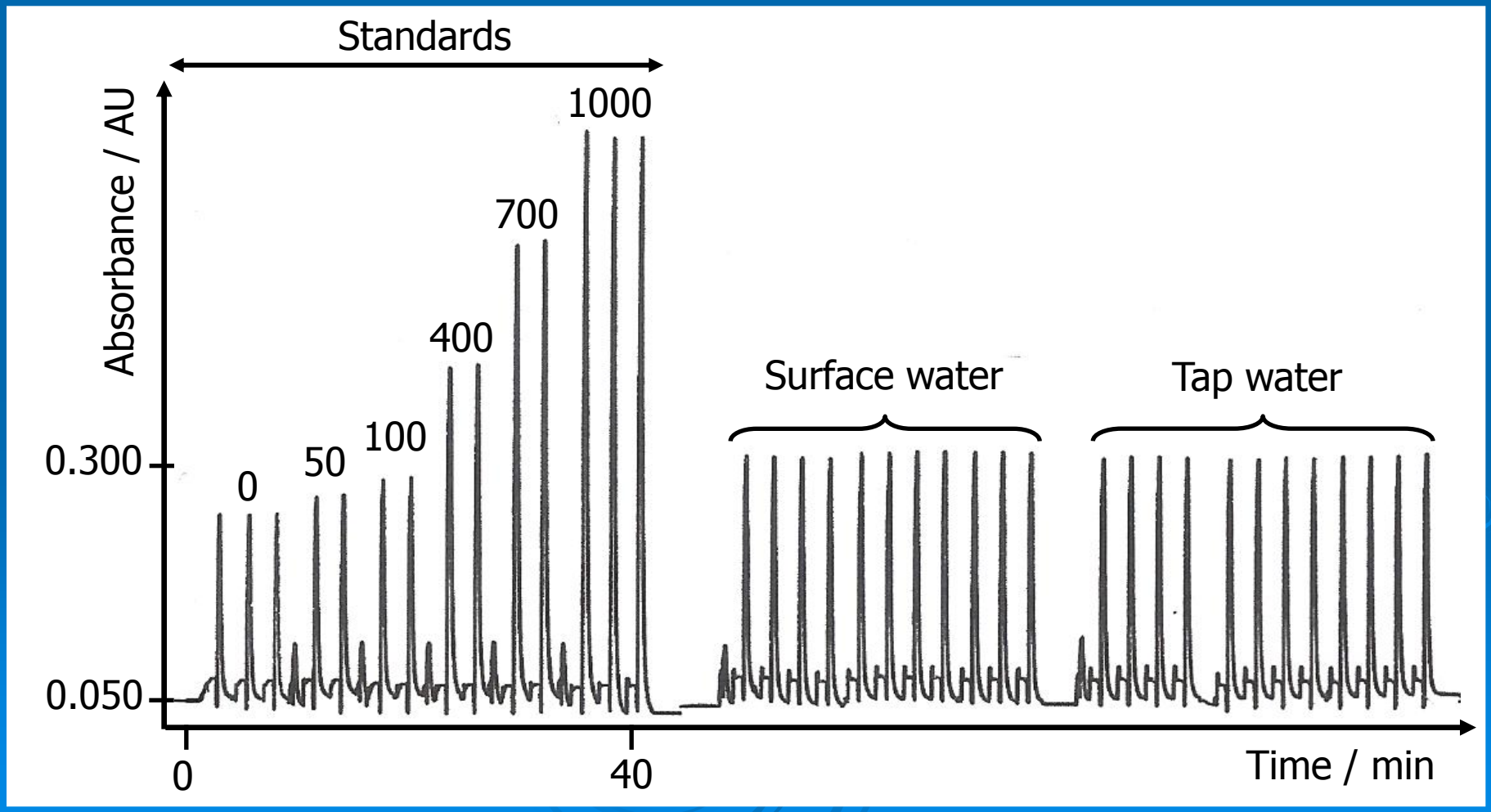
# Development of the flow system

- Figures of merit

| | |
|---|---|
| Concentration range / $\mu g\ L^{-1}$ | 50 – 1000 |
| Sensitivity / AU $mg^{-1}\ L$ | $0.519 \pm 0.008$ |
| Quantification limit / $\mu g\ L^{-1}$ | 42 |
| Detection limit / $\mu g\ L^{-1}$ | 27 |
| Relative standard deviation / % (n = 10) | <1.6 |
| Determination rate / $h^{-1}$ | 20 |
| Effluent volume per determination / mL | 3.2 |

# Development of the flow system

- Calibration curve ($|NH_4^+|$ expressed in $\mu g\ L^{-1}$)



# Application to water samples

- Recovery studies

| $\lvert NH_4^+ \rvert$ added / $\mu g\ L^{-1}$ | Recovery % | | |
|---|---|---|---|
| | Surface water 1 | Surface water 2 | Tap water |
| 0 | ----- | ----- | ----- |
| 50 | 120±13 | 99.0±3.2 | 98.3±2.2 |
| 200 | 102±2 | 95.1±1.3 | 100±1 |
| 500 | 99.2±0.8 | 97.5±1.9 | 99.0±0.7 |
| 800 | 102±2 | 99.3±1.7 | 100±1 |

n = 9

# Application to water samples

- Certified sample (VKI QC RW1)

| | \|N\| / μg $L^{-1}$ | SD | Concentration range |
|---|---|---|---|
| Certified values | 100.9 | 1.26 | 100.2 – 101.5 |

| | | \|N\| / μg $L^{-1}$ | SD | RSD / % |
|---|---|---|---|---|
| Certified sample prepared in | Deionised water | 100.3 | 1.0 | 0.96 |
| | Surface water | 100.5 | 1.6 | 1.5 |
| | Tap water | 101.0 | 1.2 | 1.2 |
| | Sea water | 100.6 | 1.2 | 1.1 |

n = 10

# Conclusions

- The proposed system configuration allowed easy manipulation of the flow procedure
  - Sample volume/analyte concentration
  - Efficiency of the diffusion process
  - Reagents recirculation
- Ammonium determination in waters
  - Certified sample results and recovery tests indicate good accuracy
  - Successful application of the system to the determination of low levels of $N\text{-}NH_4^+$ in several types of water
  - BTB recirculation reduces reagent consumption and effluent generation

# Acknowledgements

Sara Oliveira and Ildikó Tóth thank Fundação para a Ciência e a Tecnologia (FCT) and FSE (III Quadro Comunitário) for the grants SFRH/BD/23782/2005 and SFRH/BPD/5631/2001, respectively

Porto

Thank you all for your kind attention