Direct-injection detectors: a novel approach to flow analysis for water quality monitoring

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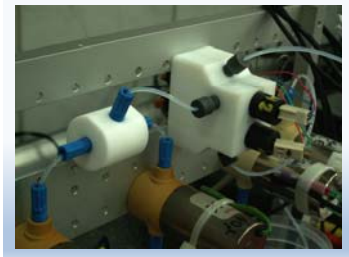
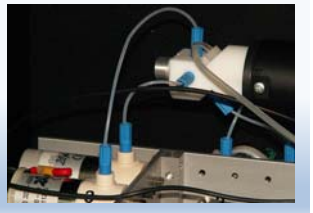
DIRECT-INJECTION DETECTORS (DID)

- They are detectors used in flow analytical methods
- They can be used in monitoring systems for quality and safety of water
- They can be used in early warning systems for water supply
- Analitical systems with this kind of detectors consume very small volume of solutions and low amount of energy
- We develop a multiparameter electrochemical direct-injection detector for recognition of unexpected water pollutions

DIRECT-INJECTION DETECTORS (DID)
EXAMPLES

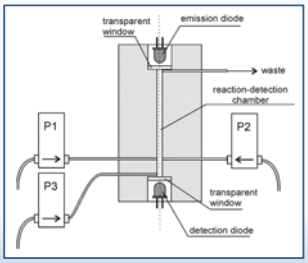
Photometric and chemiluminometric





Characteristics of the direct-injection detectors

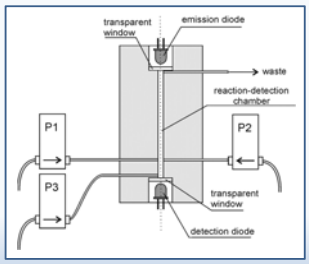
An example of a photometric detector



The detector contains a reaction-detection chamber, in which a chemical reaction and analyte detection process are carried-out.

Characteristics of the direct-injection detectors

An example of a photometric detector

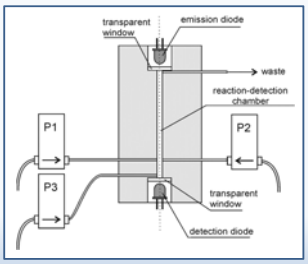


IMPORTANT

The solutions are injected in a small volume directly into the reaction-detection chamber, using solenoid pulse micropumps.

Characteristics of the direct-injection detectors

An example of a photometric detector

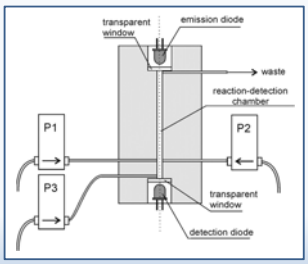


IMPORTANT

The volume of liquid in the reaction-detection chamber is fixed. Injection of any additional solution causes removal of the same volume of existing solution, usually a carrier solution.

Characteristics of the direct-injection detectors

An example of a photometric detector

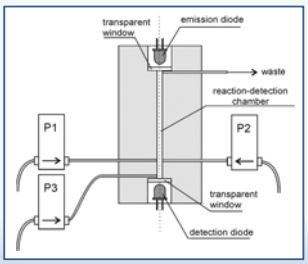


IMPORTANT

The total volume of the sample and reagents injected into the detector is lower than the volume of the reaction-detection chamber. These solutions do not escape from the chamber after injection.

Characteristics of the direct-injection detectors

An example of a photometric detector

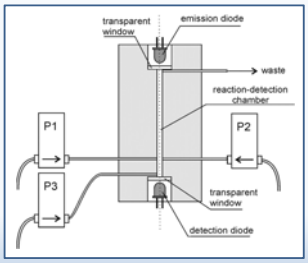


IMPORTANT

Analytical signal is recorded in the stop-flow mode. The signal is more stable and noises are lower than in typical, continuous flow mode.

Characteristics of the direct-injection detectors

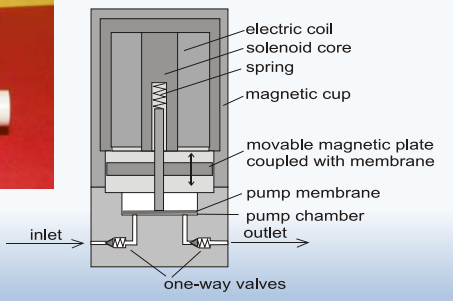
An example of a photometric detector



IMPORTANT

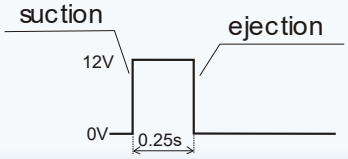
The sample and reagents are injected in the countercurrent mode. The solutions are rapidly mixed. Time of analysis is mainly dependent on kinetics of the reaction.

Solenoid pulse micro-pump



Solenoid pulse micro-pump

Fixed volume, typically
10µL, 20µL, 40µL, 50µL …



Supply voltage:

- ✓ 12V – for laboratory applications and portable instruments (current consumption 300-400 mA)
- ✓ 24V – for industrial applications

Homogenization of the solution inside the reaction-detection chamber

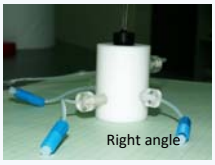
Not required	Required
Photometric Chemiluminometric Fluorimetric	Potentiometric Amperometric Voltammetric Mikrogravimetric

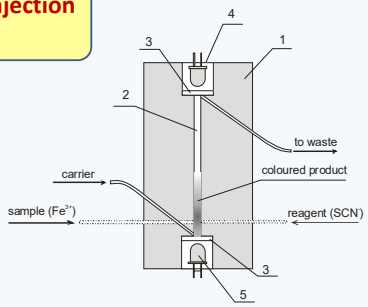
Why it is not necessary to **homogenize** the solution?

Spectrophotometric DID – all absorbing melecules are present on the light path

Chemiluminometric and fluorimeric DID – all shining molecules are „visible" by the photodetector

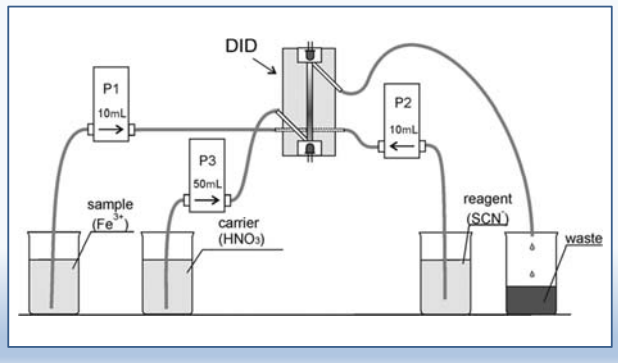
Photometric direct-injection detector



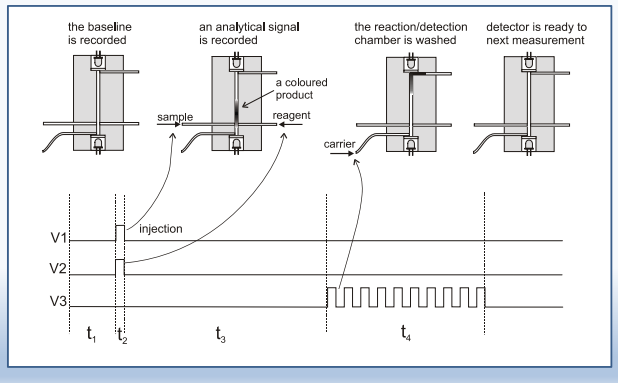


1 – detector trunk
2 – reaction-detection chamber
3 – glass windows
4 – emission LED
5 – detection diode

SIMPLE FLOW SYSTEM FOR DETERMINATION OF IRON(III)



WORKING PRINCIPLE OF THE PHOTOMETRIC DID

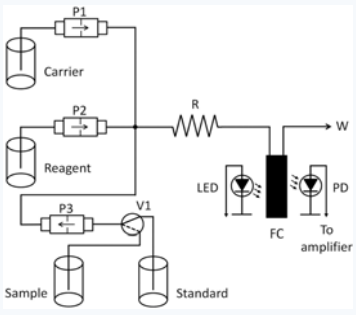


FLOW ANALYTICAL SYSTEM FOR DETERMINATION OF PHOSPHATES (Non-DID system)

Flow system: MPFS

Reagent: vanadomolybdate

Detector:
- Classical glass flow cel (length 1cm, internal volume 250 µL),
- LED 5 mm high-bright, λ_{max}= 415 nm,
- Silicon photodiode as photodetector

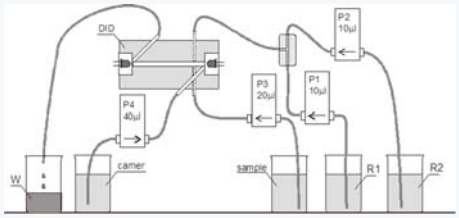


Scheme of the flow system. P1, P2, P3: solenoid pulse micropumps (20ul). V1: three-way solenoid valve. R: reaction coil. FC: flow detector. LED: emission diode, PD: photodiode*

*González P. , Pérez N., Knochen M., *Low cost analyzer for the determination of phosphorus based on open-source hardware and pulsed flow.* Quim. Nova 39 (2016) 305-309.

Determination of phosphates with the molibdenum blue method

Flow system: MPFS

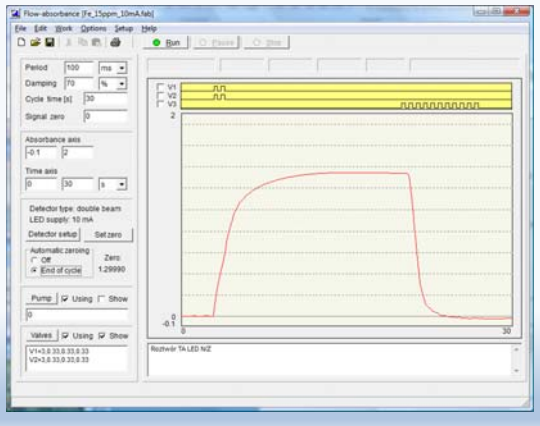


DID – direct-injection photometric detector, optical path length 20 mm, volume of the reaction-detection chamber 60 µL

This method was applied for determination of phosphates in treated wastewater from a wastewater treatment plant. Recovery was in a range from 96 to 106 %.

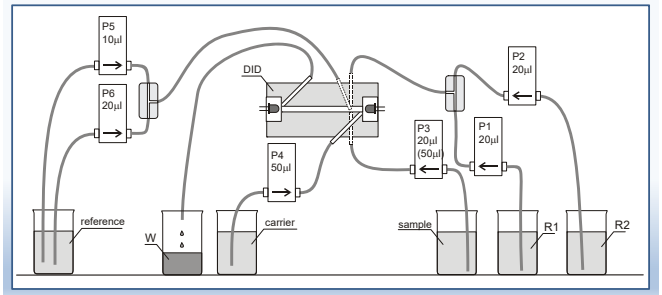
*S. Koronkiewicz, M. Trifescu, L. Smoczynski, H. Ratnaweera, S. Kalinowski, A novel automatic flow method with direct-injection, photometric detector for determination of dissolved reactive phosphorus in wastewater and freshwater samples, Environ. Monit. Assess (2018) 190: 133

Window of the program used for controlling the analytical system

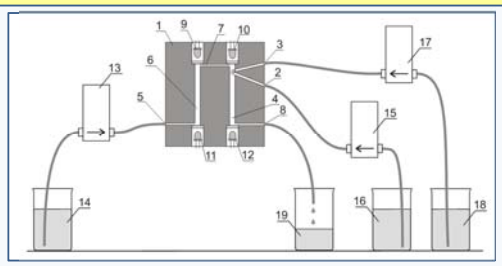


System for determination of phosphates with internal callibration

Additional pulse micropumps P5 i P6 are used for internal callibration system:
- they can inject the reference solution with volume 10, 20 or 30 µl,
- they can be applied for creation of characteristics of the detector (reference graph),
- thy can be applied for the reference addition callibration method (partially elimination of the matrix influence).

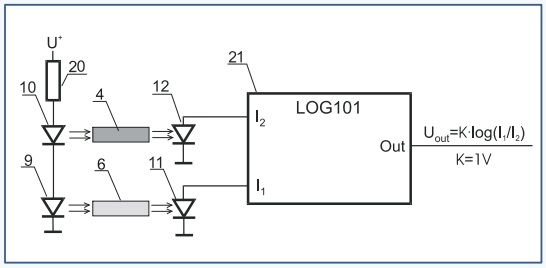


Flow system with the double-beam photometric DID



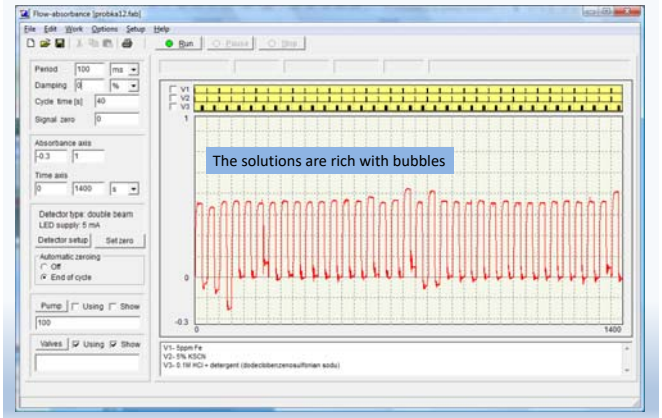
1 – detector trunk
2 – inlet of the sample
3 – inlet of the reagent
4 – reaction-detection chamber
5 – inlet of the carrier solution
6 – reference chamber
7 – inner channel
8,19 – outlet and wastes
9,10 – emission LEDs
11,12 – detection LEDs
13,15,17 – pulse pumps
14 – carrier solution
16 – sample solution
18 – reagent solution

Electronic part of the double-beam detector

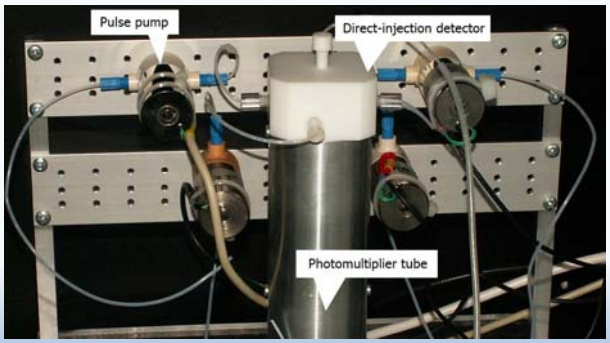


4 – reaction-detection chamber
6 – reference chamber
9,10 – emission LEDs
11,12 – detection LEDs
20 – resistor setting the emission LED's current
21 – the log amplifier

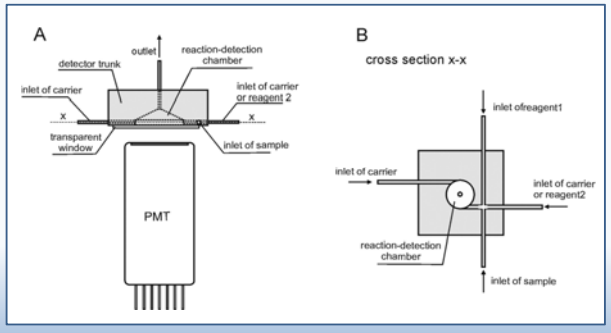
Example of analytical signal for solutions rich in bubbles



Direct-injection chemiluminometric detector

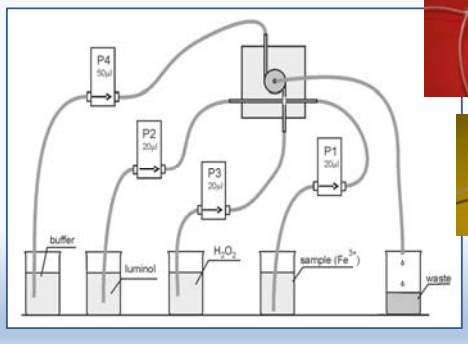


Direct-injection chemiluminometric detector

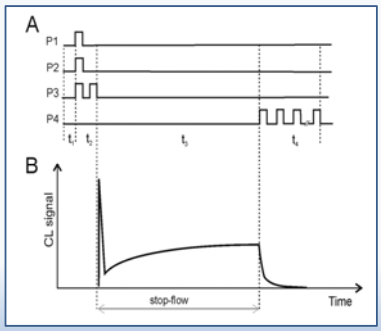


Direct-injection chemiluminometric detector

The chemiluminometric system for determination of Iron(III)

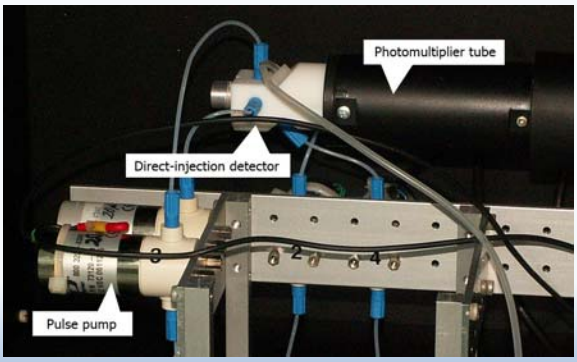


Direct-injection chemiluminometric detector

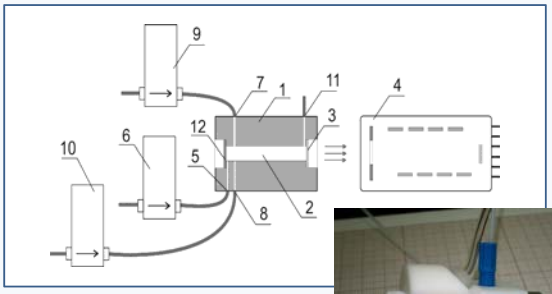


A – timetable for pumps
B – analytical signal

Torch-like chemiluminometric detector

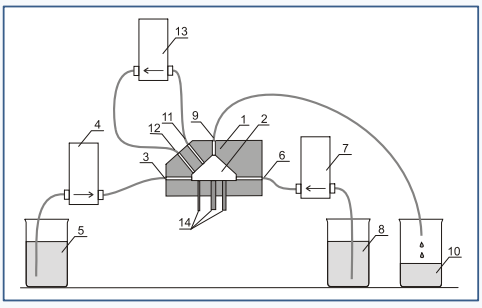


Torch-like chemiluminometric detector



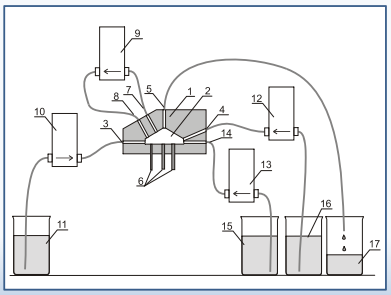
1 – detector trunk, 2 – reaction-detection chamber, 3 – glass window, 4 - photomultiplier, 5 – carrier solution inlet, 6 – pulse pump, 7 – sample inlet, 8 – pulse pump, 9 – reagent inlet, 10 – pulse pump, 11 – outlet to wastes, 12 – mirror.

Analytical system without internal callibration



1 – detector trunk
2 – reaction-detection chamber
3 – inlet of a carrier solution
4,7,13 – pulse micropumps
5 – carrier solution
6 – sample inlet
8 – sample
9,10 – outlet and wastes
11,12 – outlet and inlet of mixed solution
14 – detector electrodes

Analytical system with additional channel for reference solution



1 – detector trunk
2 – reaction-detection chamber
3 – inlet of a carrier solution
4 – inlet of a reference solution
5 – outlet of wastes
6 – detector electrodes
7 – outlet to mixing pump
8 – inlet from mixing pump
9 – mixing pump
10 – pump for carrier solution
11 – carrier solution
12 – pump for a reference solution
13 – pump for a sample solution
14 – sample inlet
15 – sample solution
16 – reference solution
17 - wastes

Advantages of the direct-injection detectors in the flow analysis

- simplification of the flow analytical system
- reduction of volume of solutions
- reduction of time of analysis
- reduction of power consumption
- reduction of size of the flow analytical system
- increasing the reliability
- simple optimization of the measurement system
- reduction of the maintenance time
- excellent properties for monitoring systems

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