Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

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MICROFLUIDIC PLATFORM AND FLUORESCENT SENSOR PARTICLES FOR THE DETECTION OF THE HERBICIDE 2,4-D IN WORLDWIDE SAMPLES

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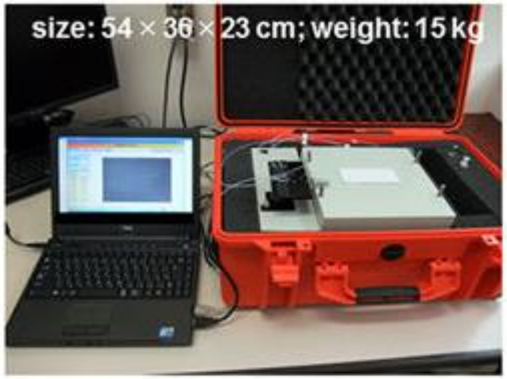
Introduction

New analytical tools

- High sensitivity and selectivity
- Reliable and robust
- Embedded system
- Low or reasonable cost



Picture from: Scientific Reports
doi:10.1038/s41598-017-03293-9

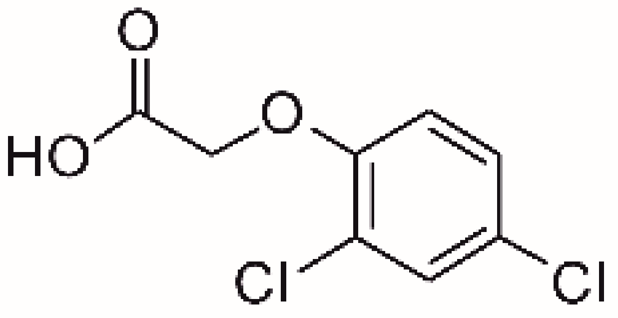
An ideal sensor system is a combination of a selective receptor, an effective transducer and a sensitive detector

Fluorescent probe + Opto-microfluidics + Imprinted polymer

Introduction

Model analyte: 2,4-Dichlorophenoxyacetic acid (2,4-D)

- Small organic molecule soluble in water
- Active ingredient of over 1,500 herbicide products
- Endocrine disruptor
- Representative of emerging pollutants:
  - **Carboxylic acid** function
  - **Aromatic** unit with chlorines
  - Medium **solubility in water**
  - **Worldwide** distribution

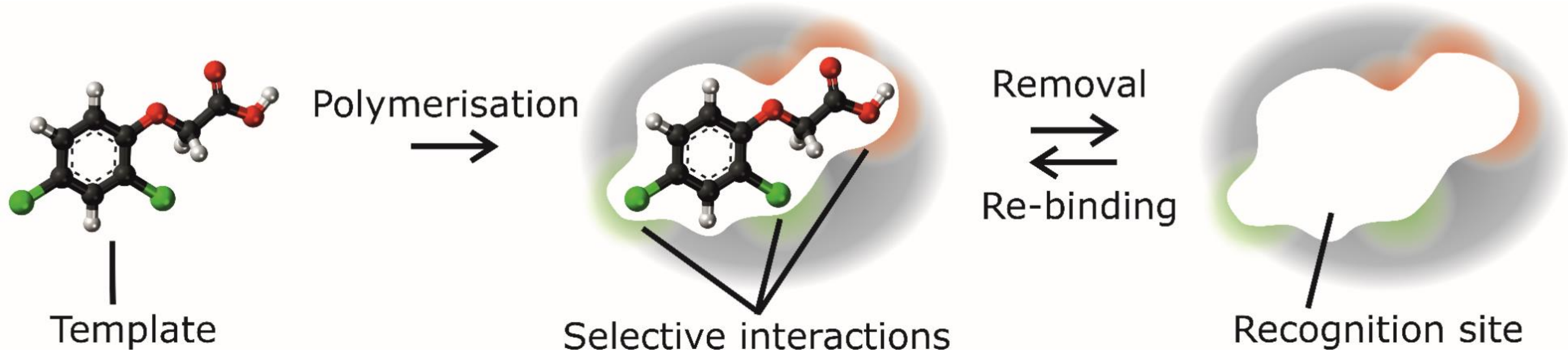


2,4-D

Introduction

Molecularly imprinted polymers (MIP)

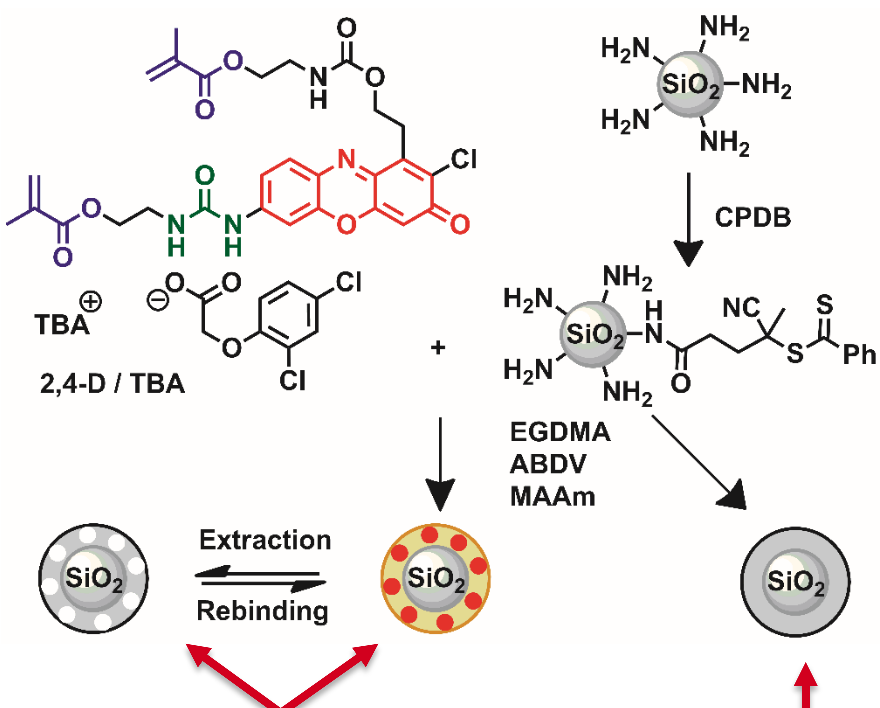
- Plastic antibodies
- Recognition based on chemical interactions and shapes
- Versatile technology
- Reversible and robust
- Possible combination with fluorescent molecular probes



➔ Ideal for extraction and detection of small organic molecules in aqueous samples

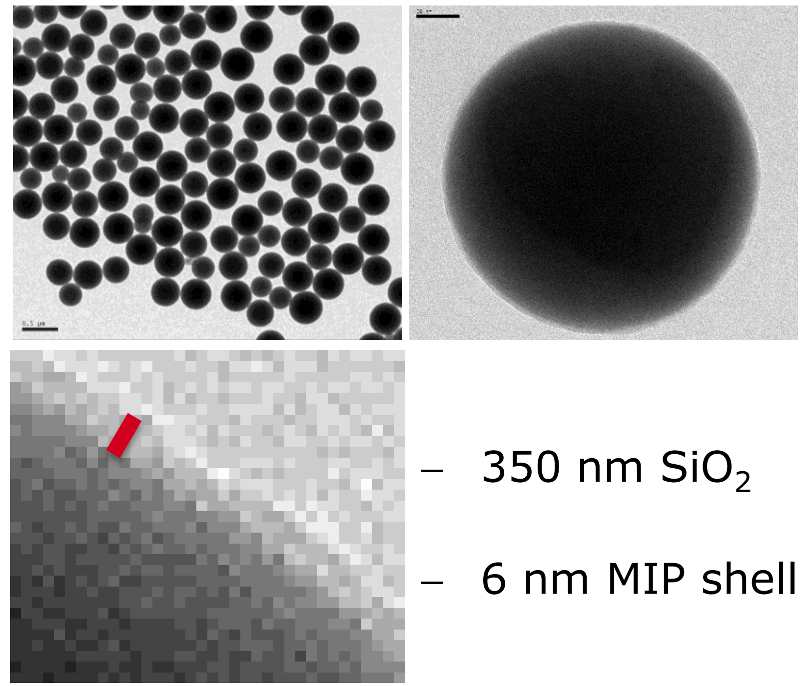
Core/shell SiO_2-MIP particles

Phenoxazinone cross-linker integrated in a polymer shell



MIP

Non imprinted polymer (NIP)

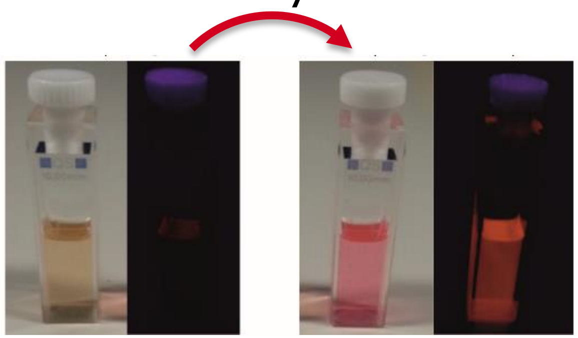


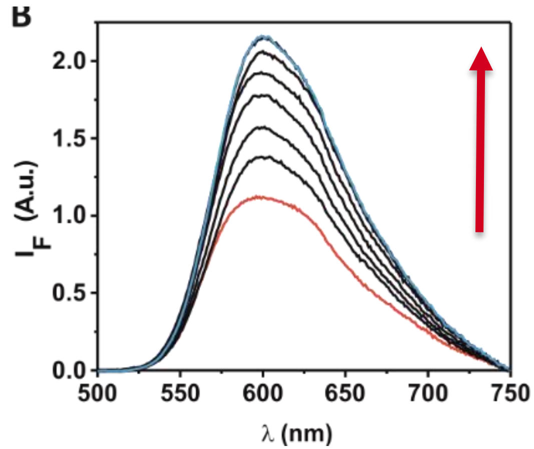
- 350 nm SiO_2
- 6 nm MIP shell

Core/shell SiO_2-MIP particles

Fluorescence response

Analyte

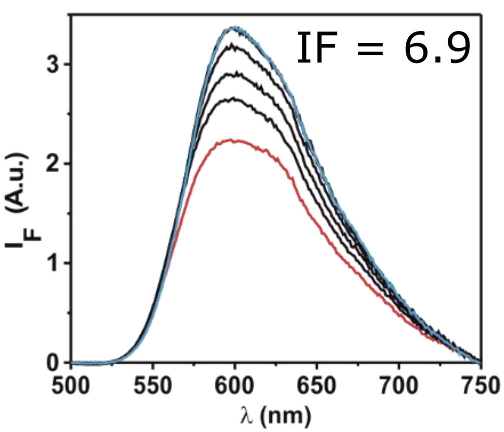


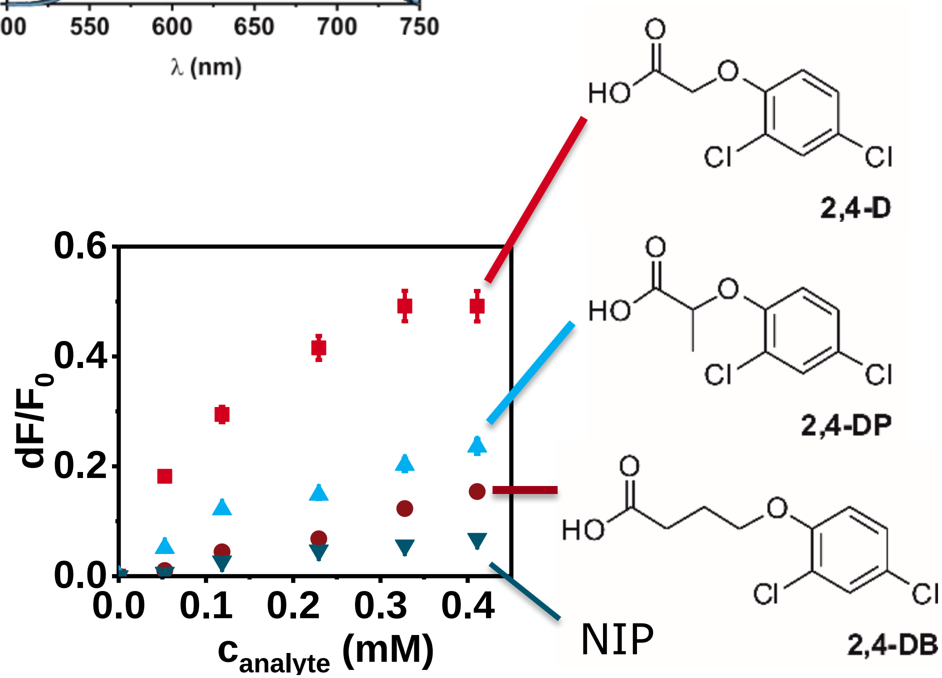


Imprinting factor:

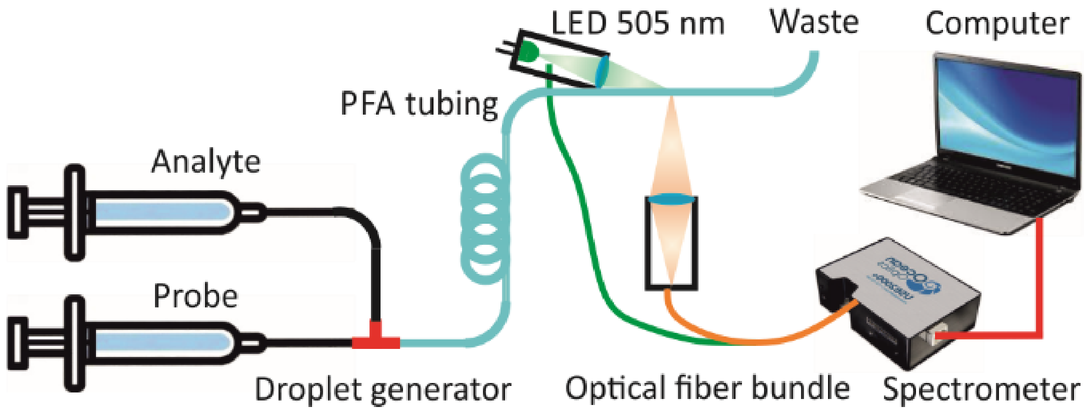
$$\frac{Response\ MIP}{Response\ NIP} = 4.9$$

Extraction assays



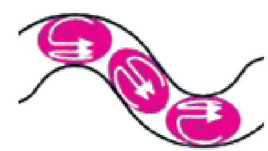


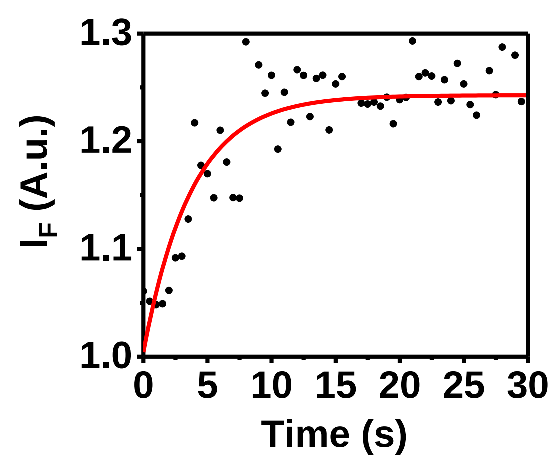
Integration in a modular microfluidic system



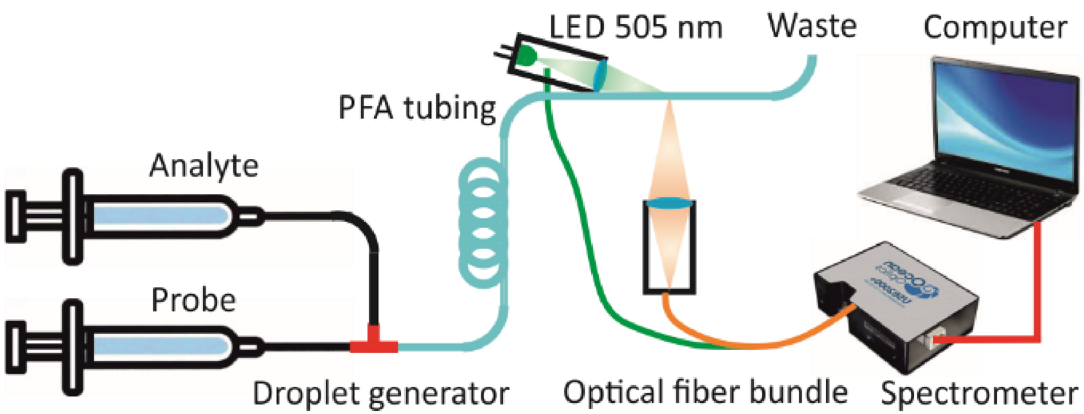
- Two inlets:
  - Analyte / water at 20 µL/min
  - MIP / chloroform at 10 µL/min
- Modular tubing system (PFA)
- Droplet generator:

  Low pressure T-connector
- Mixing by chaotic advection (30 s)

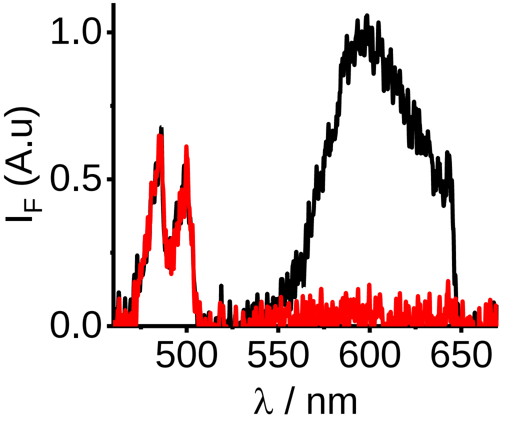




Integration in a modular microfluidic system



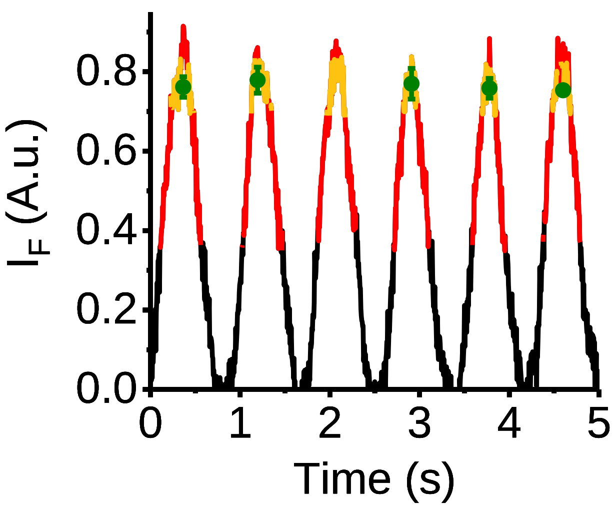
- Optomechanical cube
- Excitation: LED + filter
- Emission: USB spectrometer + filter + fiber bundle
- Recorded signals:
  - S_{LED}: 470-505 nm
  - S_{MIP}: 535-650 nm



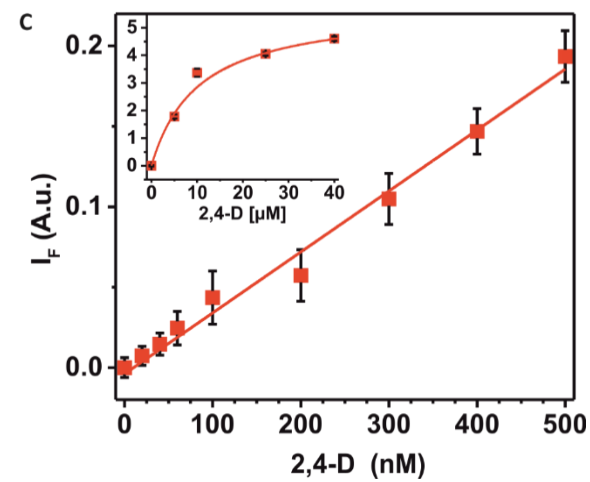
Integration in a modular microfluidic system

Automation of the signal analysis

- Consecutive logical equations
- Can be replaced by electronic or algorithmic operations



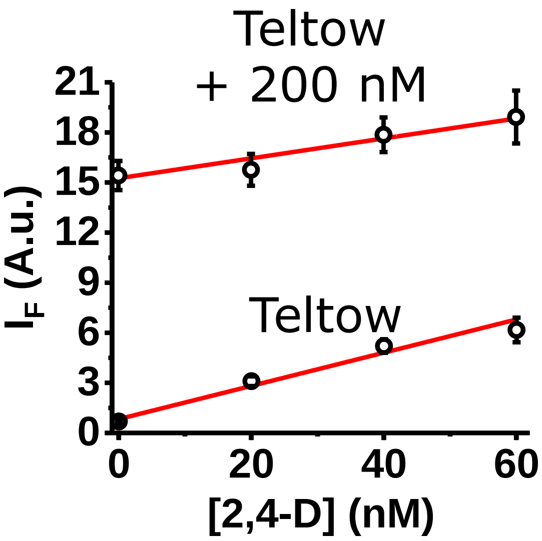
1. Organic phase
2. Droplets
3. Final



- 5 – 10 droplets (10 s) to get an acceptable standard deviation
- Error: 1.5% (Milli-Q water)
- Dynamic range: 20 nM – 5 µM

Surface water analyses

- Water from the Teltow Canal, Berlin, Germany
- No pre-treatment
- Standard addition method (spiking from 0 – 60 nM)
- Simulated concentrated sample (+ 200 nM)



- Slight matrix effects:
  - Error of 5%
  - Over estimation
- Comparable dynamic range
- Detection of concentrated sample

Surface water analyses

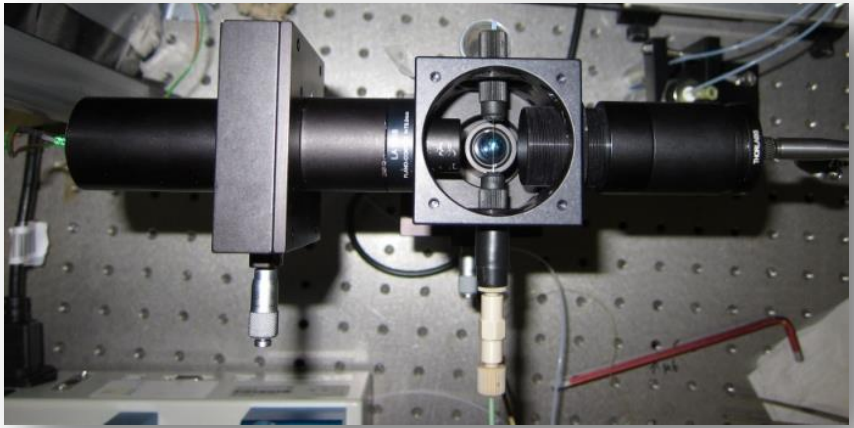
Water samples	Concentrations (nM)		
	Found	Corrected	ELISA
Santa Fe River, USA	**< 20**	-	-
Mississippi, USA	**< 20**	-	-
Hàn River, VNM	**22.3 ± 0.3**	-	-
Lake Nghệ An, VNM	**26.0 ± 0.4**	-	13.7 ± 5.8
Teltow Canal, DEU	**< 20**	-	-
Teltow Canal, DEU + 200 nM	**239.4 ± 13.6**	194 ± 11.6	-
Rio Paranapanema, BRA	**27.6 ± 0.1**	17.8 ± 0.8	18.4 ± 2.3

Maximum acceptable concentration:

– EU: 0.1 µg/L = 0.5 nM (surrogate zero)
– WHO: 30 µg/L = 136 nM
– EPA: 70 µg/L = 317 nM

Conclusion

- Preparation of sensory **SiO_2-MIP Core/shell** microparticles
- **Modular** opto-microfluidic system with sensitive and selective **fluorescence response**
- Dynamic range for 2,4-D: **20 nM – 5 µM**
- Only **traces of 2,4-D** found in all samples
- Miniaturized laboratory prototype:



Conclusion

BAM

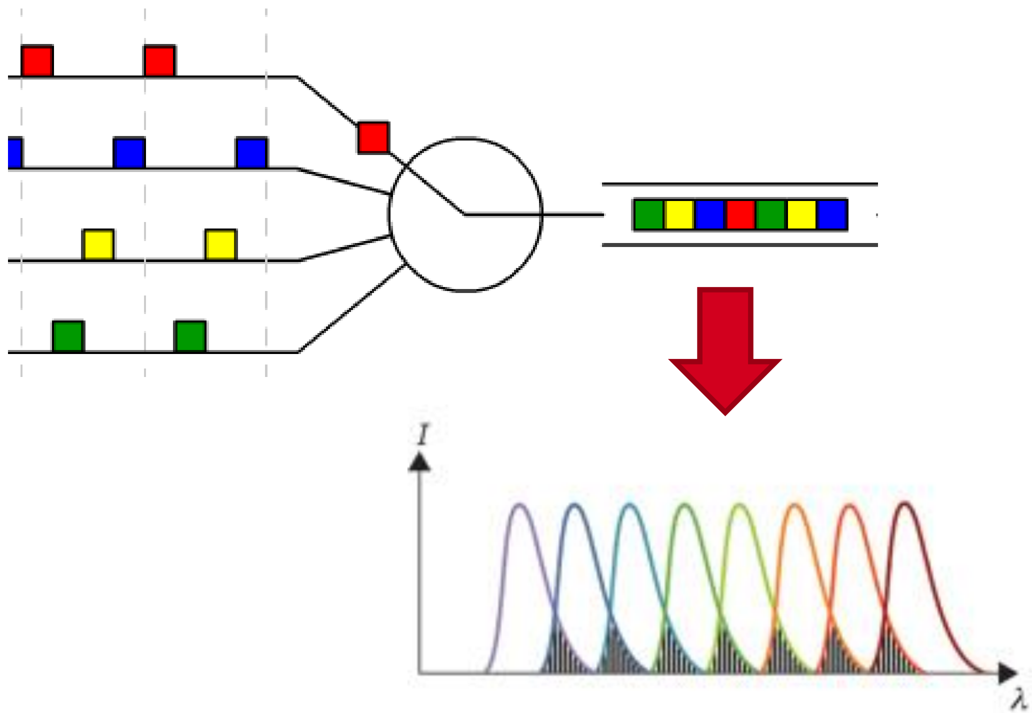
- Potential adaption for other small organic molecules of **environmental** but also **pharmaceutical, food, chemical, biochemical or medical** interest.
- Multiplexing possibilities:

Carbamazepine

Ibuprofen

Diclofenac

Caffeine



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