Institute for Electromagnetic
Sensing of the Environment

National Research
Council of Italy

Optical spectroscopic sensor for on-line water monitoring

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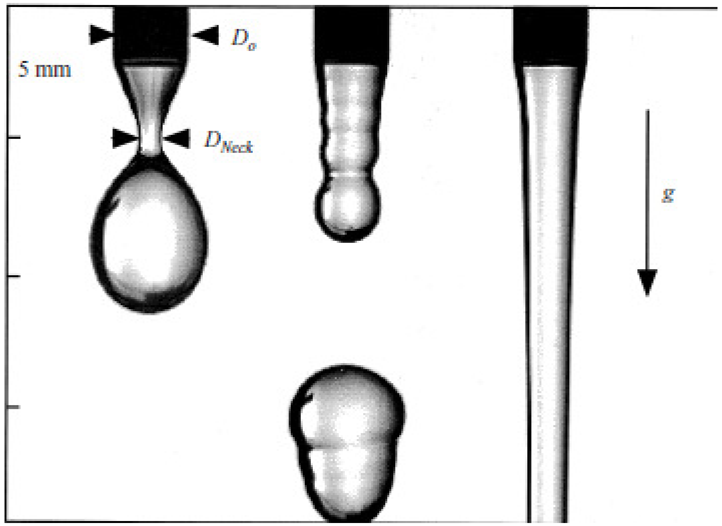
Summary

1. **Optofluidic approach → jet waveguides**
2. **Non specific detection - Jet waveguides approach for UV fluorescence spectroscopy**
3. **Specific detection - Jet waveguides approach for Raman spectroscopy**

Liquid jet



CLANET et al.J. Fluid Mech. (1999), vol. 383, pp. 307-326

Liquid jet formation

The process of a liquid jet formation is related to the magnitude of surface tension forces and to the momentum of the jet.

The dynamic behavior is characterized by the Weber number We:

$$We = \rho v^2 \frac{r}{\sigma}$$

inertial forces → ρv^2

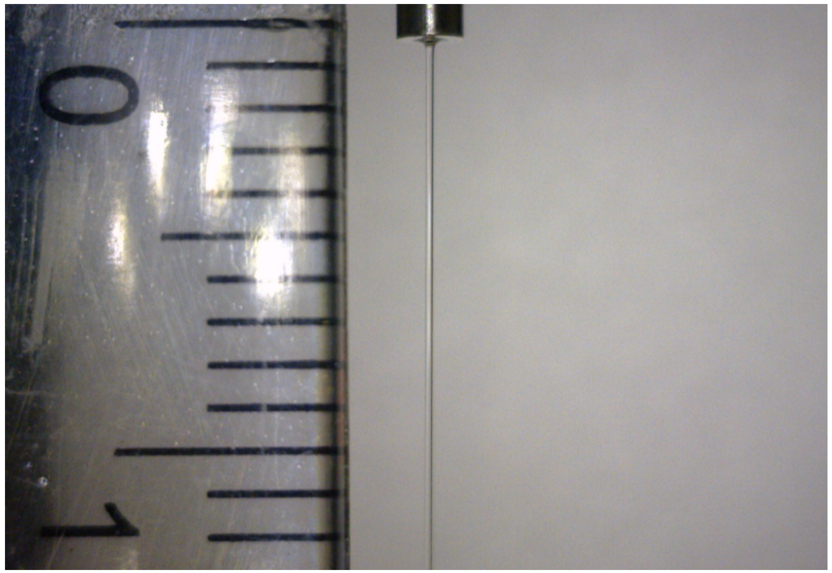
surface tension forces σ / r

where ρ is the liquid density, v is the jet velocity, r is the local radius of curvature, and σ is and the surface tension of the liquid.

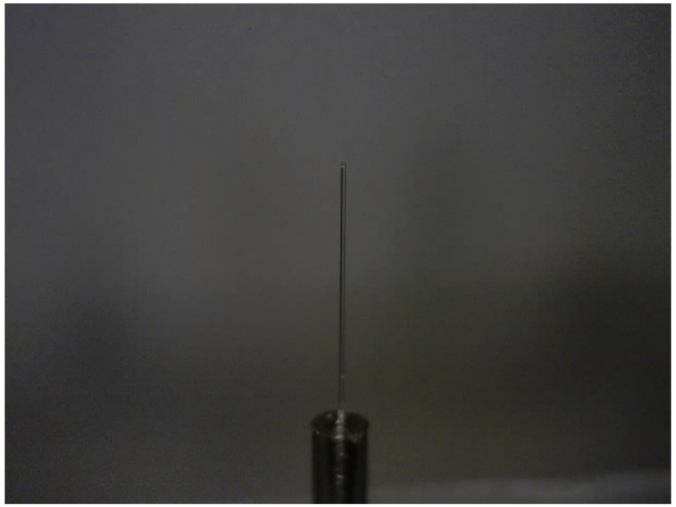
When v is sufficiently large, such that the kinetic energy overcomes the surface energy, a continuous liquid jet is formed up to a certain length (breakup length), and then it breaks up into drops.

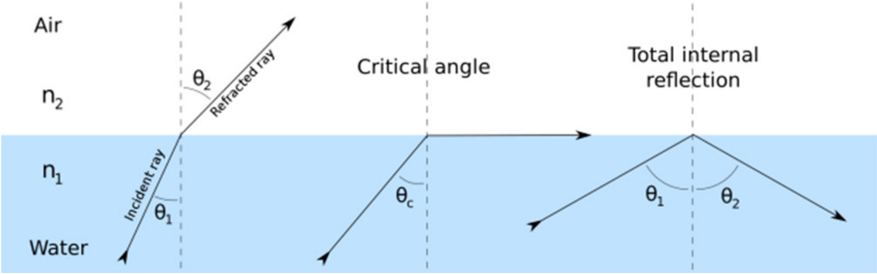
$$We = \rho v^2 \frac{r}{\sigma} < \mathbf{4}$$ dripping regime

$$We = \rho v^2 \frac{r}{\sigma} > \mathbf{4}$$ jetting regime

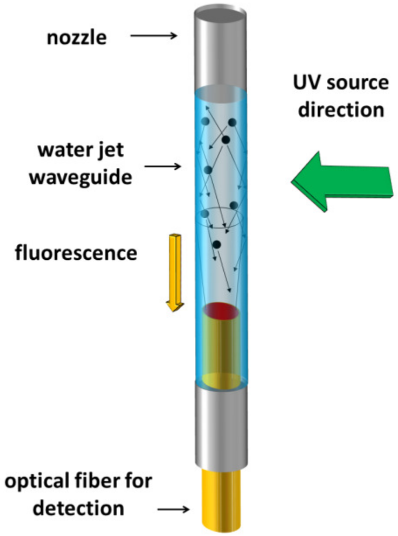


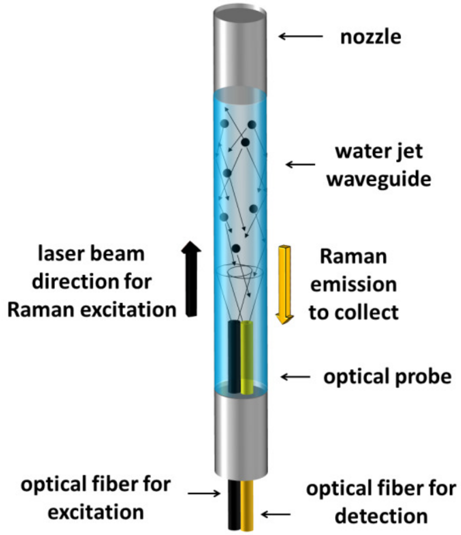
Liquid jets as waveguides





The guidance effect is based on total internal reflection (**TIR**).





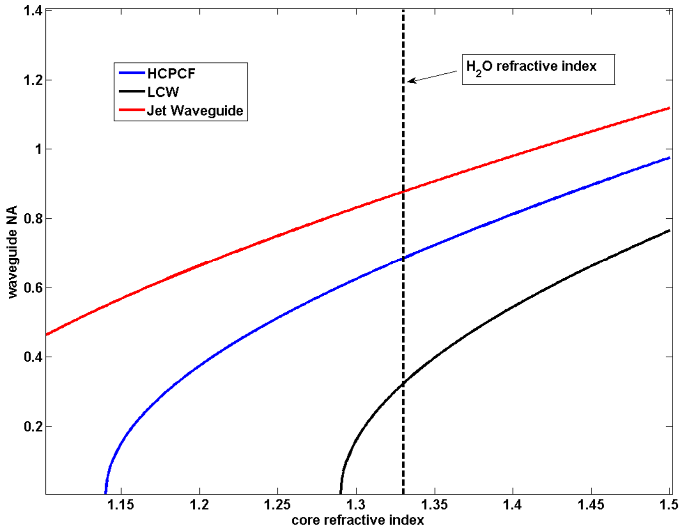
Non specific sensor based on UV autofluorescence: an UV source excites natural fluorescence of compounds in solution and is collected by means **TIR**

Specific sensor based on Raman spectroscopy:
An optical fiber is used to excite the solution, the guide exploits **TIR** to collect the signal which is transmitted to the coupling fiber.
The whole jet is excited → enhancement in the detected signal

Non specific sensor: UV autofluorescence + jet waveguide

Only the fraction of the light falling within the waveguide critical angle will be coupled and collected through **TIR** propagation.

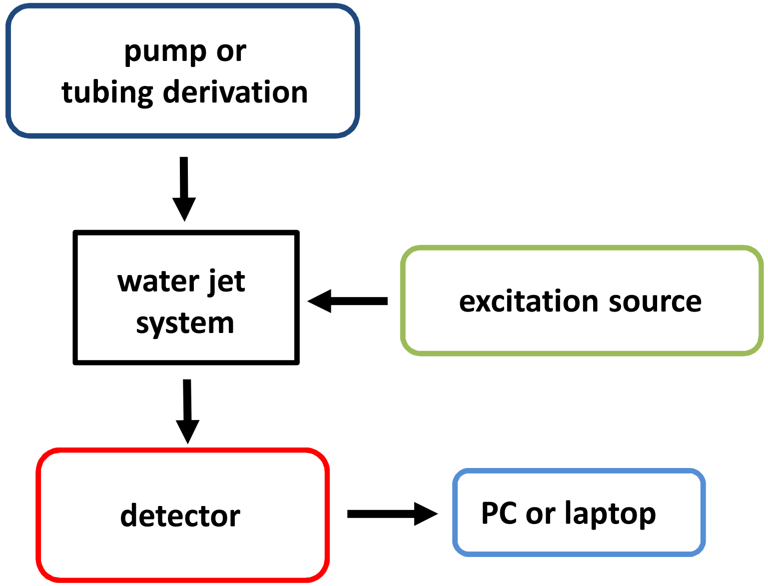
$$I \propto NA = \sqrt{n^2{}_{core} - n^2{}_{cladding}}$$



Jet waveguide NA comparison with respect liquid core waveguide (**LCW**) and Hollow core photonic crystal fiber (**HCPCF**).

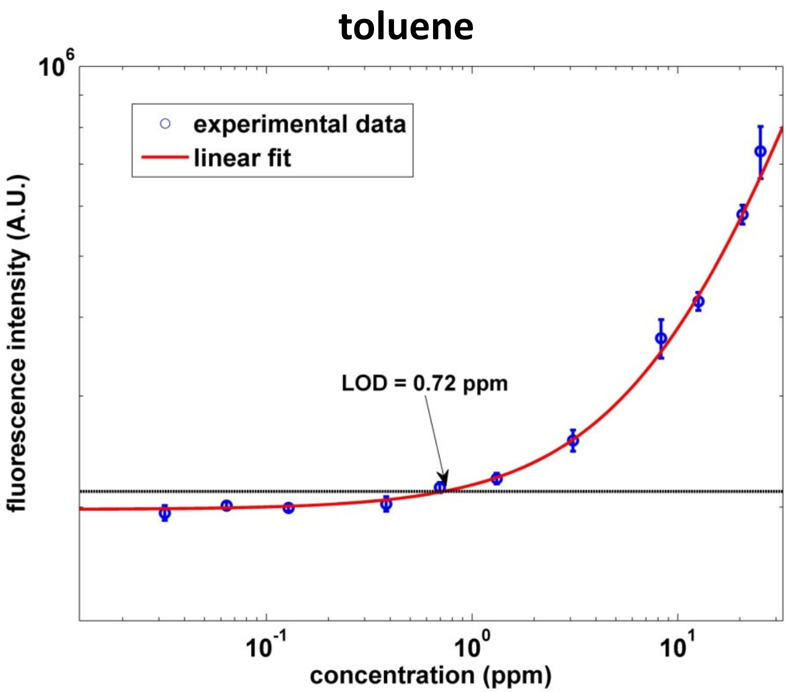
	LCW	HCPCF*	Jet Waveguide
$n_{cladding}$	1.29	1.14-1.17	1

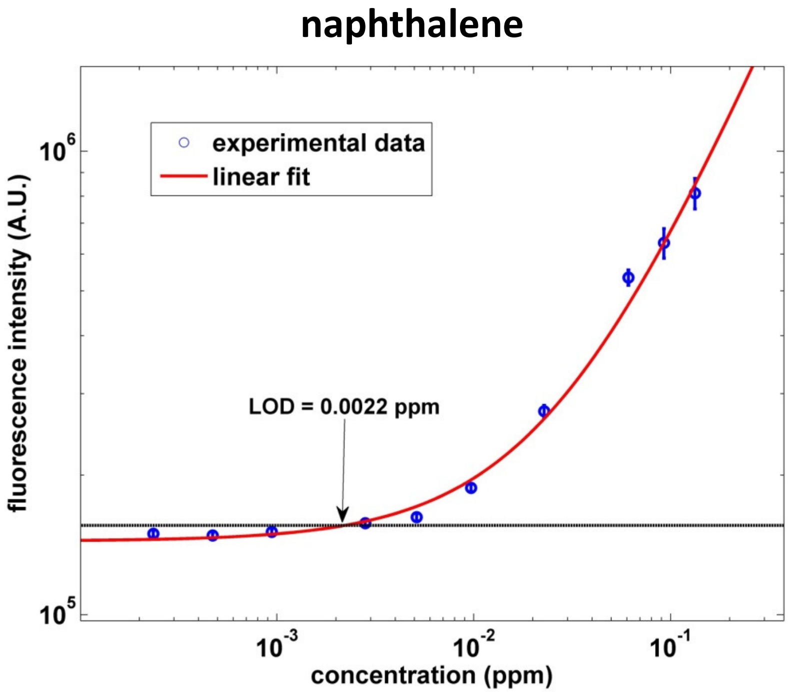
*Eftekhary et al. J. Appl Phys, 109, 113104 (2011)



- High detection efficiency.
- Minimization of the source contribution in the detected signal.
- Absence of solution container (no fluorescence, no cleaning required).
- Simple configuration (self-aligning).
- Possible on-line monitoring (no sample pre-treatment).
- Low cost technology.

Hydrocarbon detection: UV autofluorescence + jet waveguide





Hydrocarbons exhibit high fluorescence after UV excitation.

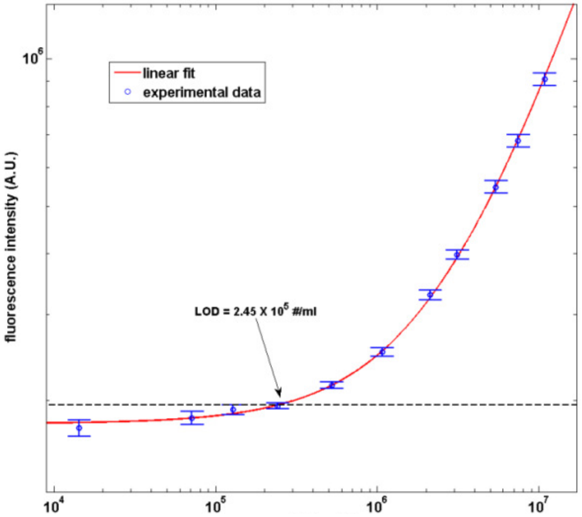
excited volume ≈ 5.73µl
jet length = 16 mm
jet Ø ≈ 955 µm
v=1.4 m/s
integration time=5s (40 repeated measurements)

Pollutant	Limit of detection (LOD)	Maximum Contaminant Level (EPA)
Benzene	1.94 ppm	5 ppb
Toluene	0.72 ppm	1 ppm
o-Xylene	0.1 ppm	10 ppm (total Xylenes)
Naphthalene	2.2 ppb	-

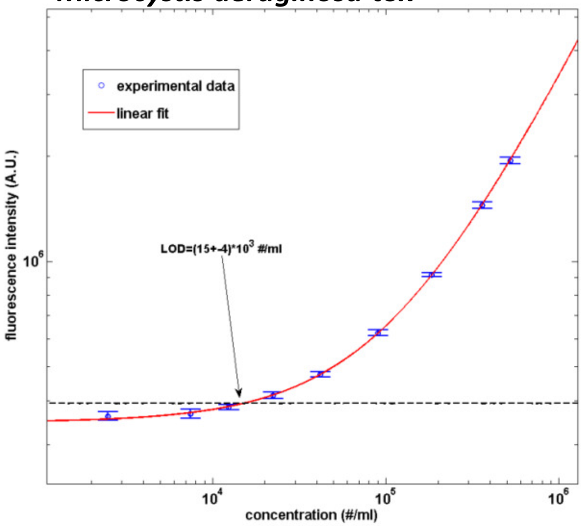
G. Persichetti et al. ”High sensitivity UV fluorescence spec-troscopy based on an optofluidic jet waveguide” *Opt. Express* **21** 24219–24230 (2013) .

Bacterial detection: UV autofluorescence + jet waveguide

Bacillus Clausii



***Microcystis aeruginosa* tox**



The same approach has been used also in detection of bacteria, that are fluorescent due to the presence of specific amino acids, nucleic acids and coenzymes

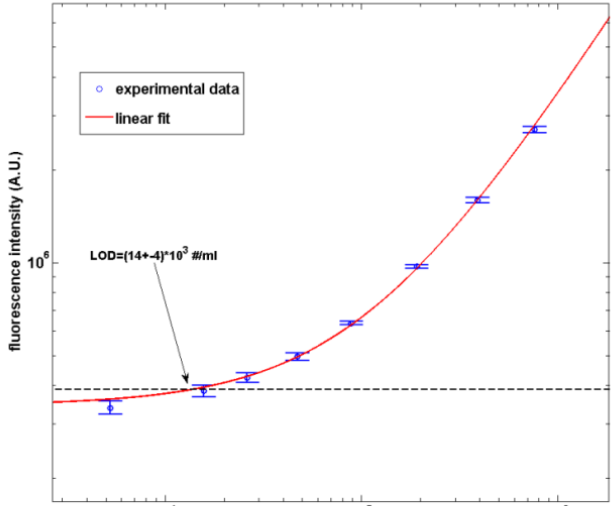
bacteria	LOD (#/ml)
Bacillus Clausii	$2.45*10^5$
Microcystis aeruginosa (non tox)[1]	$1.4*10^4$
Microcystis aeruginosa (tox) [1]	$1.5*10^4$

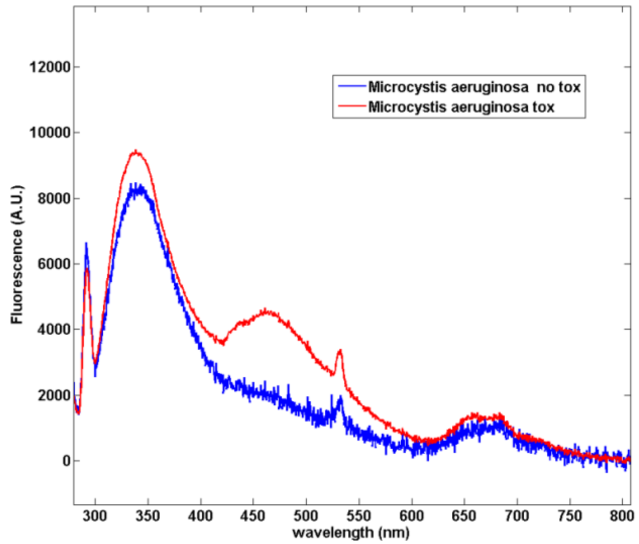
[1] Samples provided by *Algares srl* within the project **ACQUASENSE**

Microcystis aeruginosa → eutrophication

The detected spectra of the 2 types of bacteria (*Microcystis aeruginosa* tox e non tox) show different spectral characteristics that may be related to the presence of the toxin.

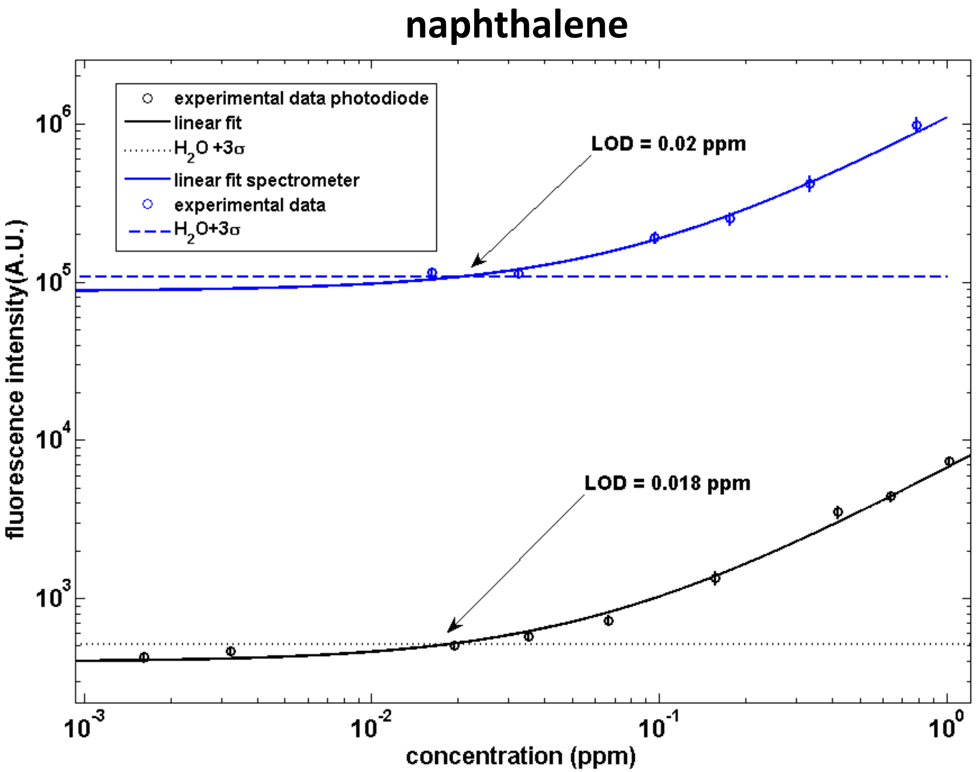
***Microcystis aeruginosa* non tox**



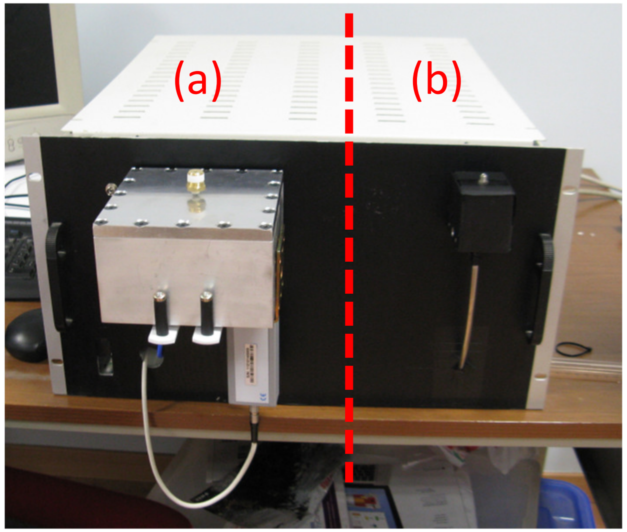


UV autofluorescence + jet waveguide: low-cost approach

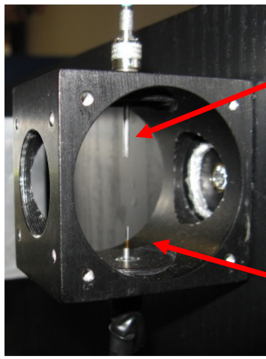
Within the framework of the ACQUASENSE project it was evaluated the possibility to also use a low-cost instrumentation: a **UV LED** as an *excitation source* and a **photodiode** as a *detector*.



The experimental results show that using **photodiode** as detector and **UV LEDs** of adequate power, it is possible to achieve results similar to those that use spectrometers and laser sources.



(b) Portable UV autofluorescence sensor prototype based on jet waveguide (right side) developed in the framework of the national project **ACQUASENSE**

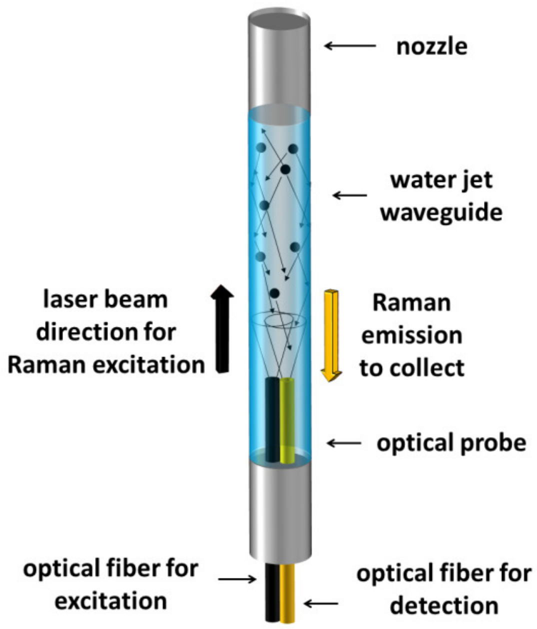


stainless steel capillary for jet ejection

UV LED (265nm)
P ≈ 3 mW

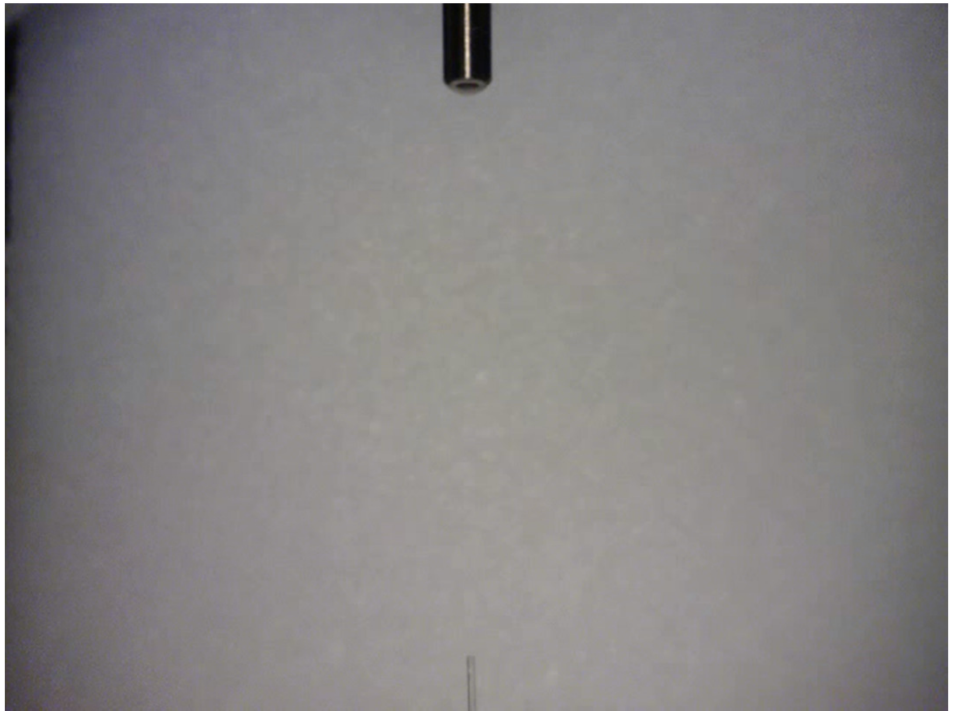
optical fiber used to deliver the signals to the photodiode

Specific sensor: Raman spectroscopy+ jet waveguide

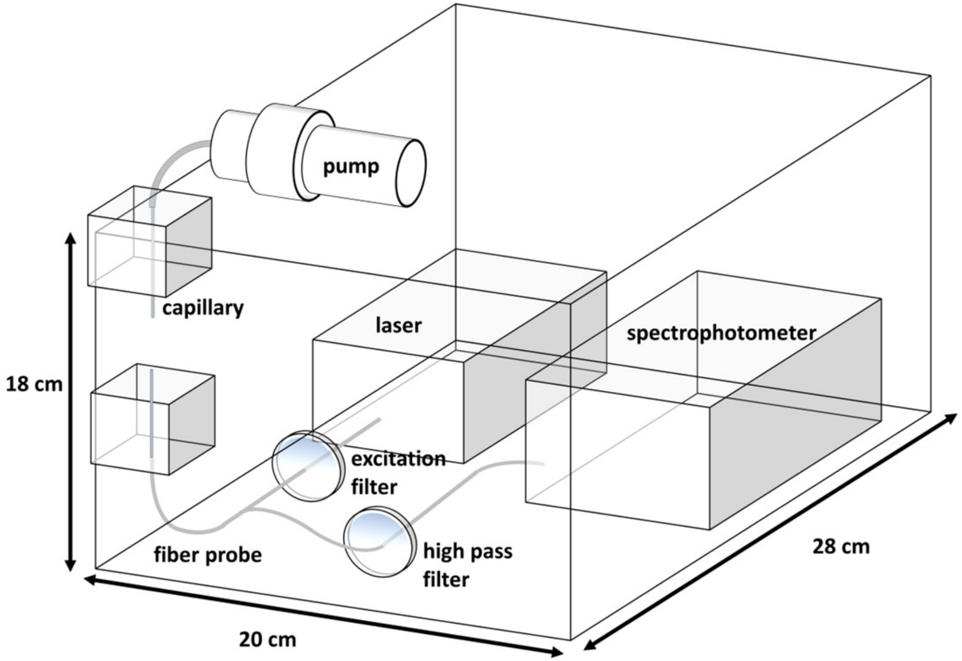


Raman spectroscopy system: a fiber is used for the excitation of the solution, the liquid guide collects the Raman signal by means of TIR and send it to the collection fiber.
It is excited the whole jet with consequent increase of the detected signal.

- High efficiency of excitation / collection
- Specificity (specific Raman spectrum of the substance)
- Absence of fluorescence due to the containment of the solution
- Simple configuration
- Possible use in online monitoring (not necessary solution pretreatment)



Portable device for Raman spectroscopy



2 fiber probe:
excitation fiber - diameter 200 µm and NA=0.22
detection fiber - diameter 600 µm and NA=0.39

source: diode laser emitting at 785 nm
Pmax = 500 mW
(output power at sample level: 120 mW)

detector: spectrophotometer with NA=0.39
1625 lines per mm holographic grating
slit width: 50 µm
resolution: 10 cm^{-1} at 810 nm

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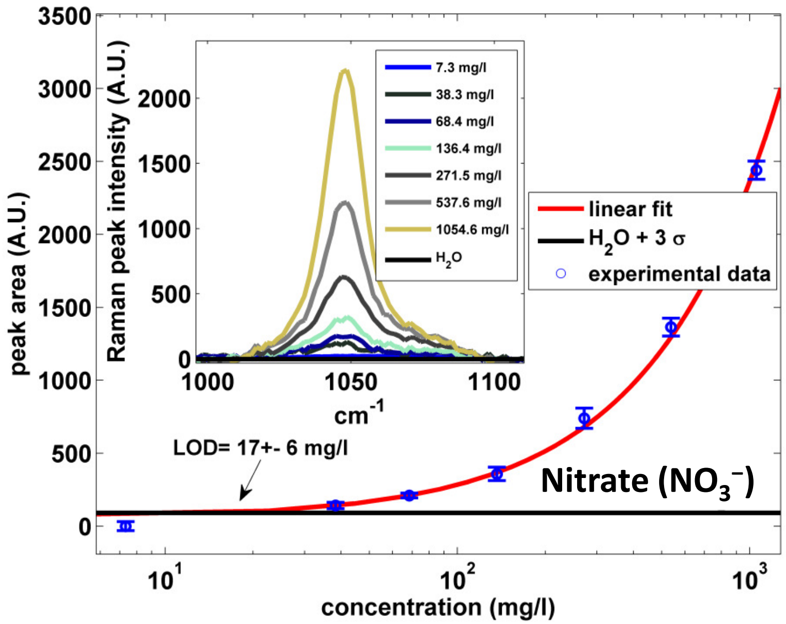
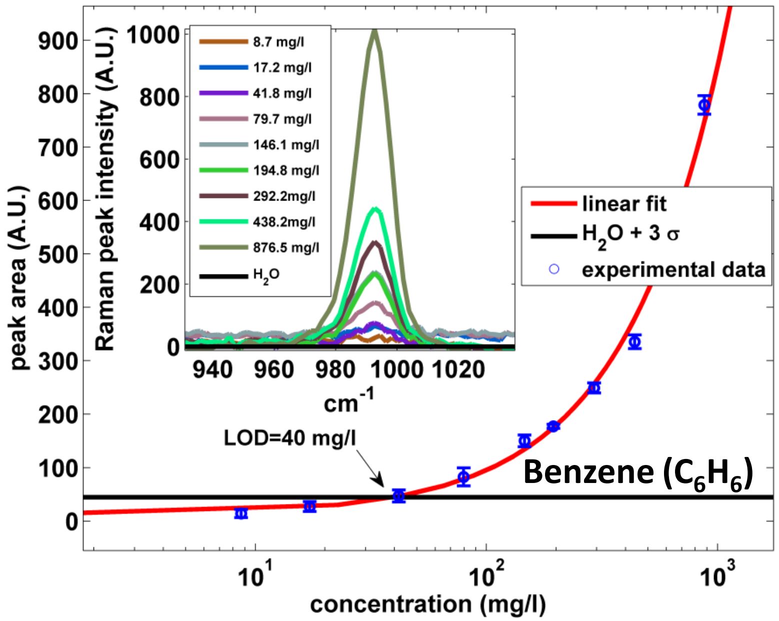
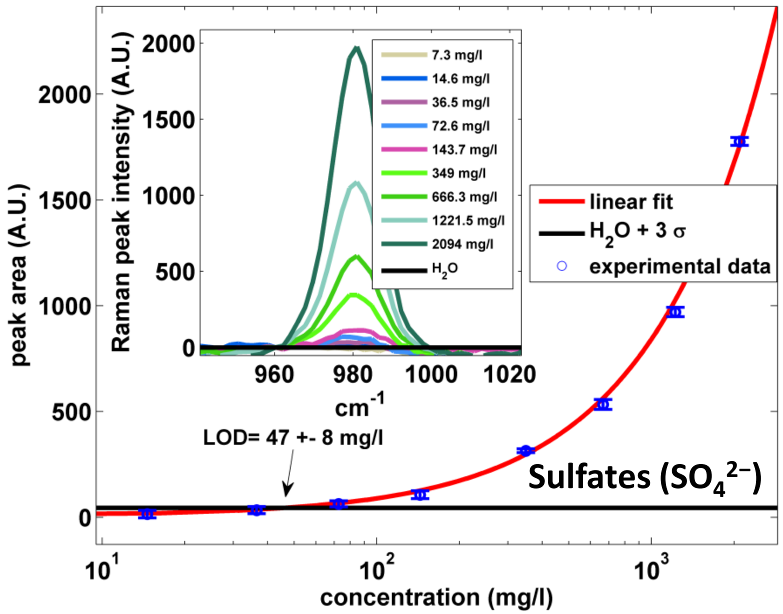
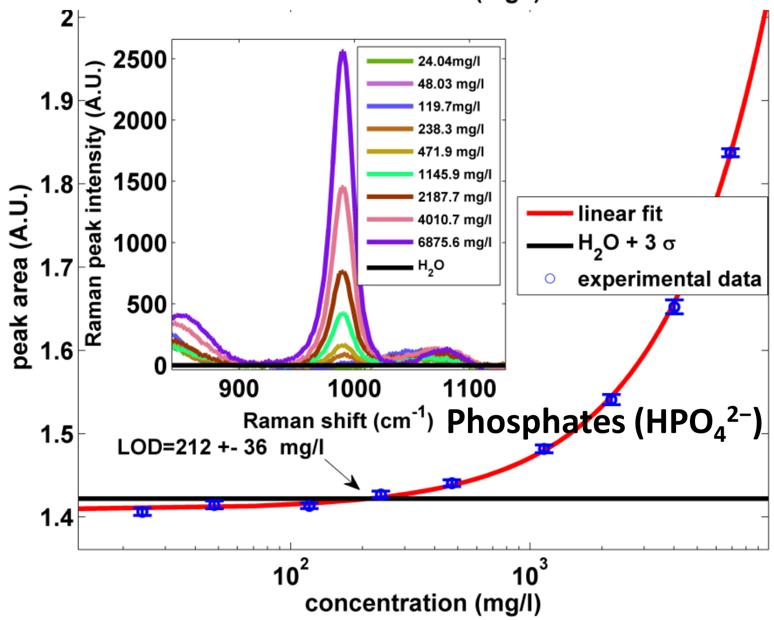
Raman spectroscopy measurements

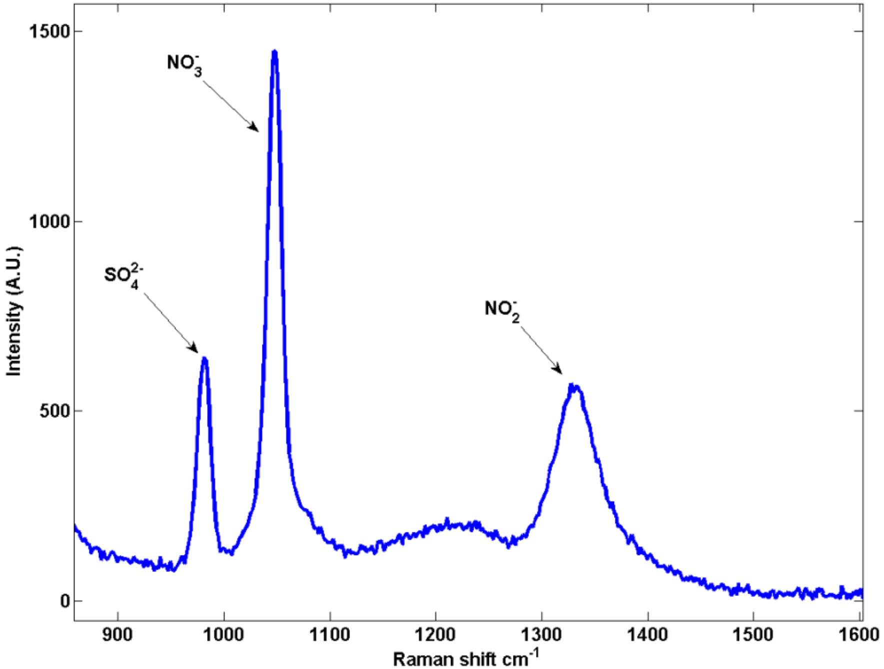








Raman spectroscopy measurements



The Maximum Contaminant Level (**MCL**) allowed in in drinking water is very highly demanding.

Raman spectroscopy is based on a low sensitive effect.

Despite jet waveguide approach offers the possibility of high excitation/collection efficiency, the detection at trace level is precluded for most of the water pollutant.

Contaminant	Maximum contaminant level (EU)	Limit of detection (LOD)
Nitrate (NO_3^-)	50 ppm	20 ppm
Nitrite (NO_2^-)	0.5 ppm	180 ppm
Solfate (SO_4^-)	250 ppm	50 ppm
Phosphate (HPO_4^{2-})	-	200 ppm
Benzene (C_6H_6)	-	40 ppm

possible detection below MCL

G. Persichetti, R.Bernini " Water monitoring by optofluidic Raman spectroscopy for in situ applications" *Talanta* **155** (2016) 145–152.

Conclusions

Jet waveguide approach results a suitable strategy in water monitoring:

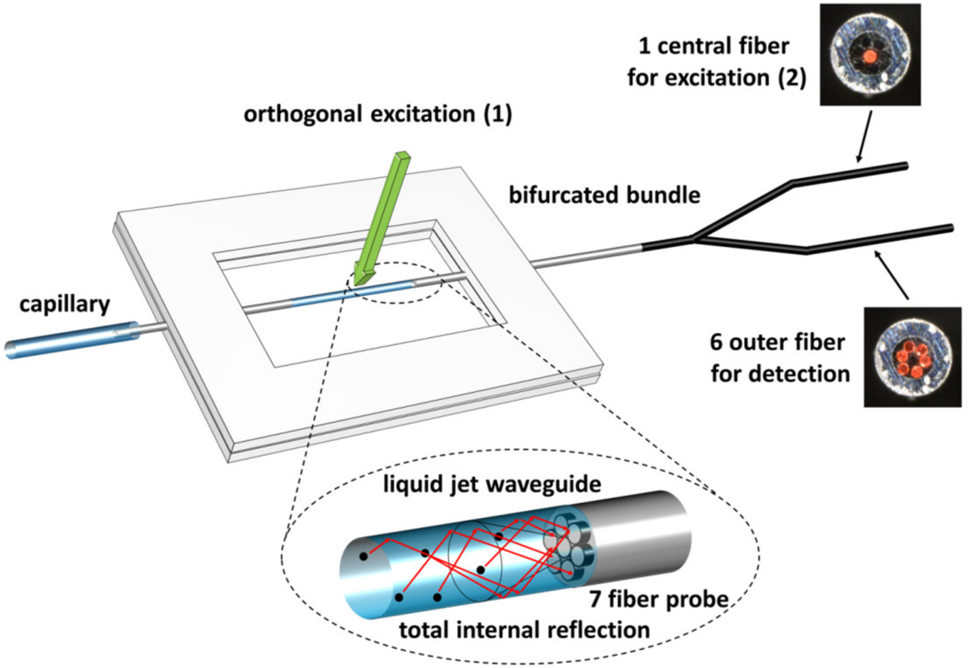
- **UV autofluorescence spectroscopy → non-specific and high sensitive detection**
- **Raman spectroscopy → highly selective detection**

Jet waveguide – miniaturization

Advantages of on-chip platform

high flexibility: the same on-chip sensor can exploit two different excitation approaches

high versatility: applicable to both Raman and fluorescence spectroscopy

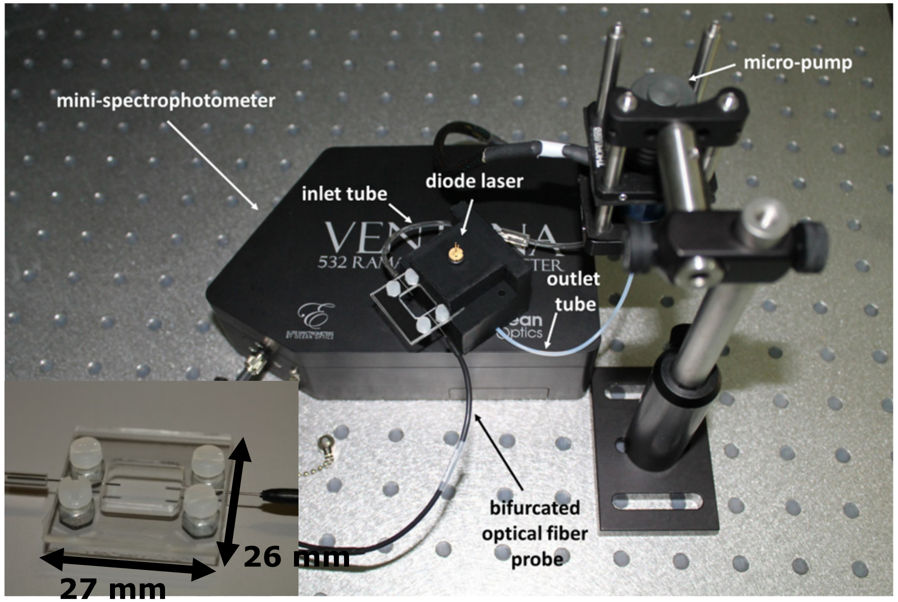


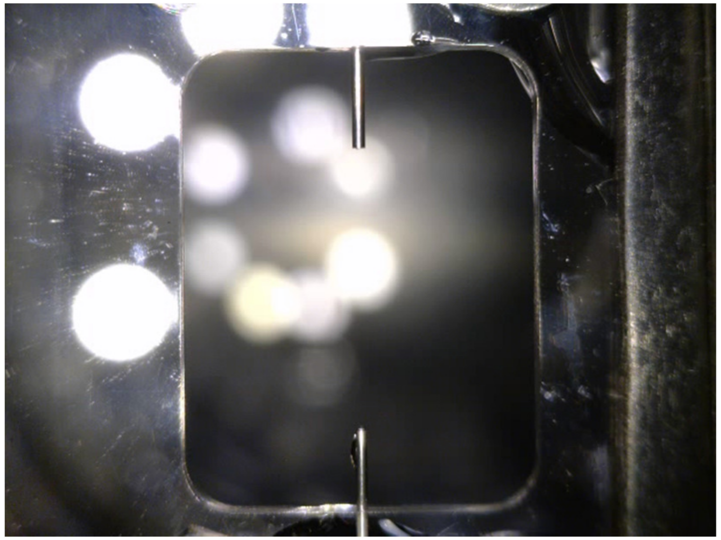
jet diameter: 150 µm
jet length: 7 mm

7 fiber probe:
1 excitation fiber - diameter 50 µm and NA=0.56
6 detection fiber - diameter 50 µm and NA=0.56

detector: spectrophotometer with NA=0.39
1600 lines per mm grating
slit width: 50 µm resolution: 20 cm^{-1}

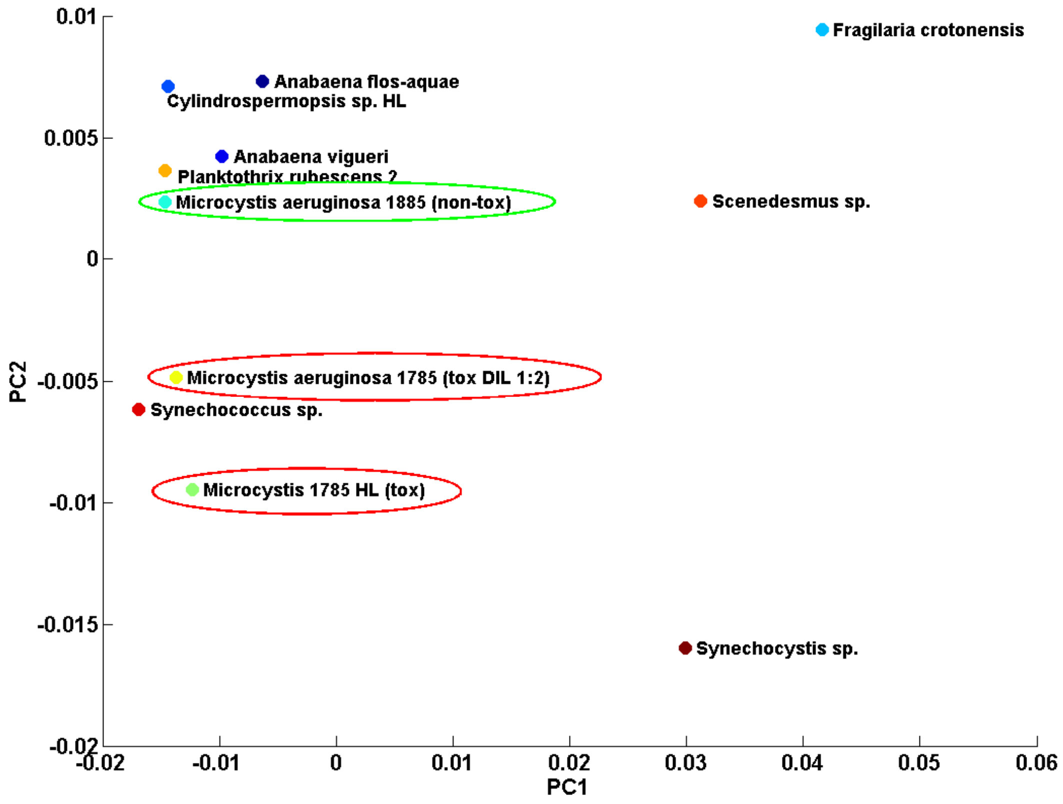
Experimental setup

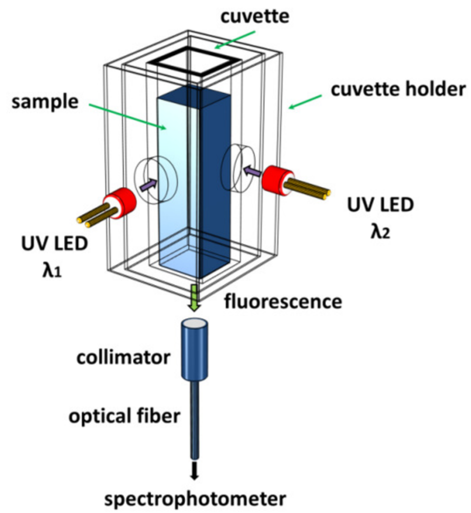




UV autofluorescence for specific detection: cyanobacteria

Use of fluorescence fingerprints for the estimation of cyanobacteria. Principal Component Analysis (PCA) is a multivariate data analysis technique that is used to approximate a large data matrix through observed patterns. Approximation of the data patterns is achieved by obtaining new, mutually independent, variables that are mathematically represented by linear combinations of the original variables.





Experimental data are obtained with single excitation wavelength.

- The use of different excitation wavelength could help in further discrimination of cyanobacteria.
- The jet waveguide approach could further increase sensitivity and decrease time measurements.

M. Bresciani *et al.*, Caratterizzazione e analisi delle proprietà ottiche dei cianobatteri lacustri ASITA 2016