Application of the Laser-Induced Fluorescence (LIF) for single-compound analysis in PAH mixtures

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Overview and aim

Aim : Adapt and combine existent fluorescent method for the measurement of single-PAH in gasification and pyrolysis processes

Liquid phase

Spectroscopy analysis of pure compounds and samples
Qualitative and quantitative aspects

- Analysis and combination of different LIF sub-techniques (delayed fluorescence, EEM, synchronous fluorescence)
- Database of PAH spectra / influence of the solvent
- Comparison and validation of the data
- Creation of a methodology for PAH measurements
- Determination of optimal conditions for quantification
- Comparison of the results with other systems (GC-MS, GC-FID)

Gas phase

Analysis of pure compounds
Qualitative aspects

- Adapt the techniques used in liquid phase to gas phase
- Determine the possible limitations of these techniques (effects of temperature and oxygen content)
- \`Database‘ of PAH spectra in gas phase

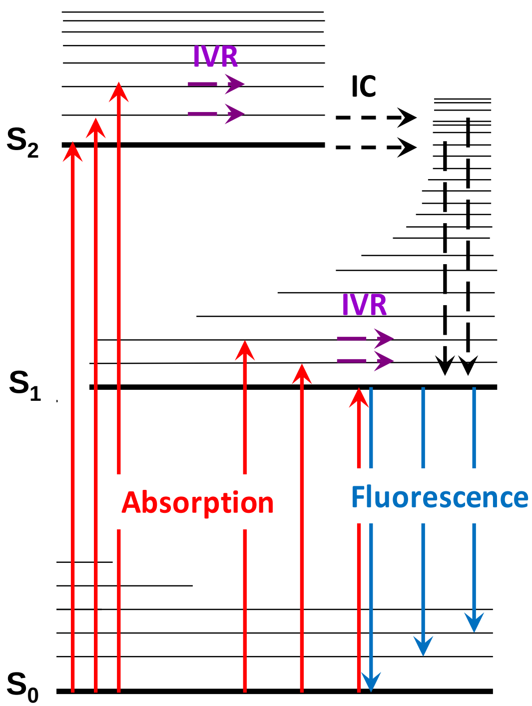
Context – Spectroscopy as a tool for PAH measurements

Pros and cons:

Absorption	Fluorescence
- Cheap	- Expensive
- Rather simple to set-up and apply	- Quite complex set-up / requires several conditions to be proportional to the concentration
- Works for many compounds	- Works for fluorescence compounds
- Low sensitivity in its single-path application	- High sensitivity
- Quite bad selectivity in UV-visible range. More suited for mixtures of few known components	- Higher selectivity which can be good enough for measurement in some mixtures

Principle of Laser Induced Fluorescence

Two steps process

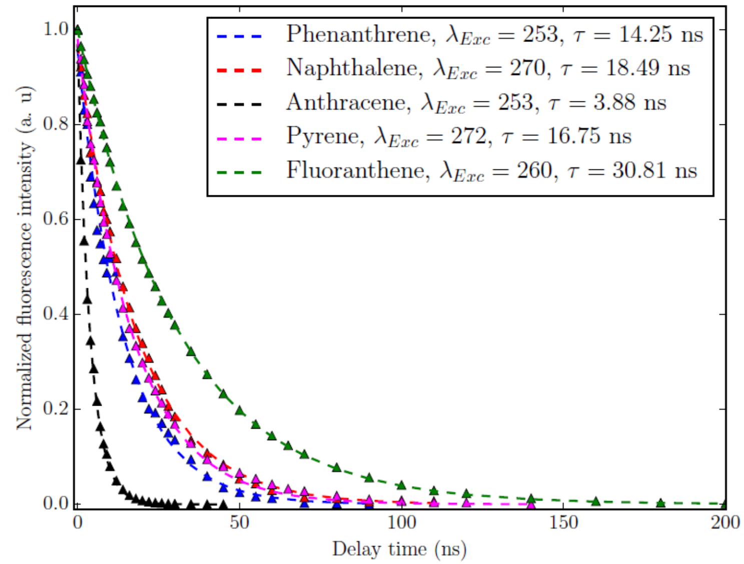


Absorption step → Fluorescence excitation spectrum

Fluorescence step → Fluorescence emission spectrum

⇨ **Double selectivity**

Time-dependent process



Lifetime of PAHs dissolved in cyclohexane

⇨ **Lifetime can be taken into consideration for selectivity** (use of a camera as detector)

Access to laser excitation wavelengths

Most commonly used UV excitation wavelength for fluorescence spectroscopy :

266nm - 355nm (Nd:YAG laser)

351nm – 364nm (Ar laser)

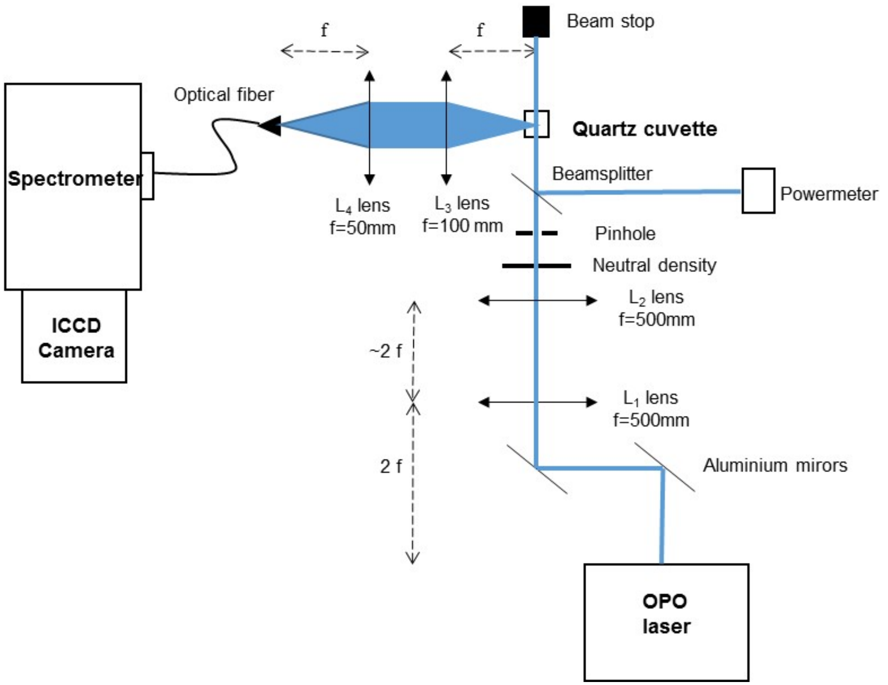
To be more selective : use of dye laser

- CMR compounds
- Has to be dissolved / accurate concentration for optimization
- small range of accessible wavelenths~10-20 nm
- Low energy output
- Quite unstable (1 month up to 1 week)

Optical Parametric Oscillator (OPO) laser

- Easy to use
- Higher energy
- Wide range of wavelengths available (225-2200nm)

Experimental set-up for liquid phase measurements



Equipment

- **OPO laser**
- Lenses and pinhole (size and homogeneity of the beam)
- Neutral density filters (ensure linearity with energy
- Beamsplitter/**powermeter** (correction of laser fluctuations)
- **Quartz cuvette** – 700 µL (minimize photon re-absorption)
- Optical fiber and lens doublet (collection)
- **Spectrometer and camera**

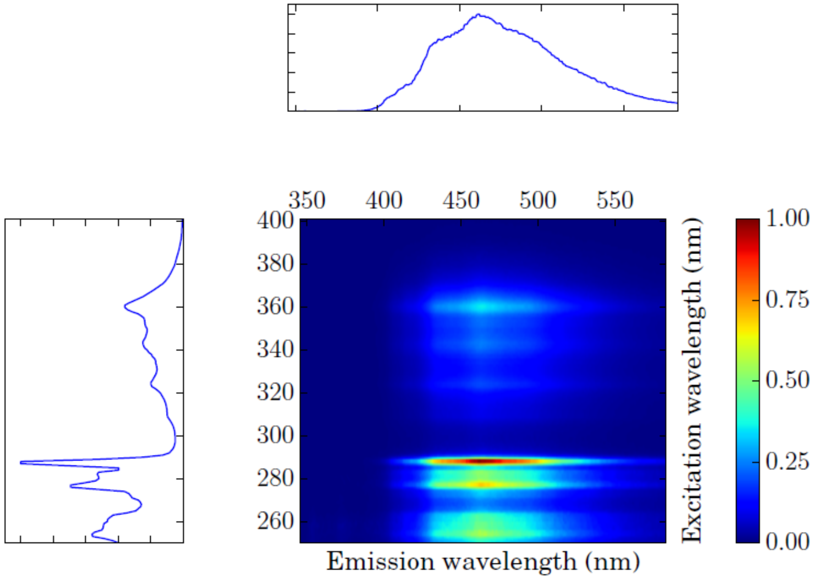
Operating conditions

- Linear range of signal with fluence and concentration
- [PAH]<10^{-4} mol/L (avoid saturation effect, self-absorption, excimere formation)
- Acquirement of fluorescence spectra (300-580 nm range, suited for light to medium PAHs)
- Analysis of 5 PAHs : naphthalene, anthracene, phenanthrene pyrene and fluoranthene
- 2 solvents: cyclohexane (spectroscopy) and isopropanol (samples with water content)
- Access to the fluorescence spectra for all excitation wavelengths in the range of 250-400nm
- Prompt-LIF and delayed measurements

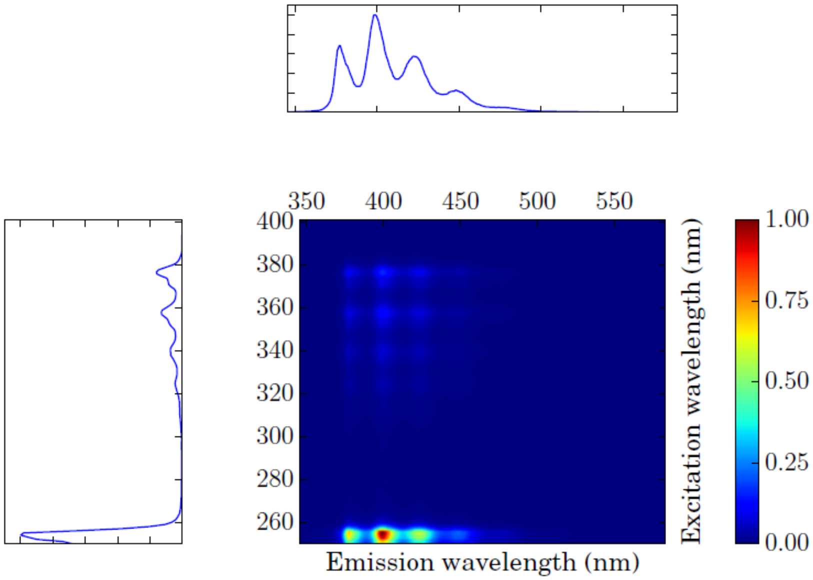
Excitation-Emission Matrix (EEM)

- 3D-isocolor diagram
- Obtained by combining the fluorescence spectra obtained for different excitation wavelengths
- Equivalent to the ‘fingerprint‘ a molecule

Fluoranthene in cyclohexane



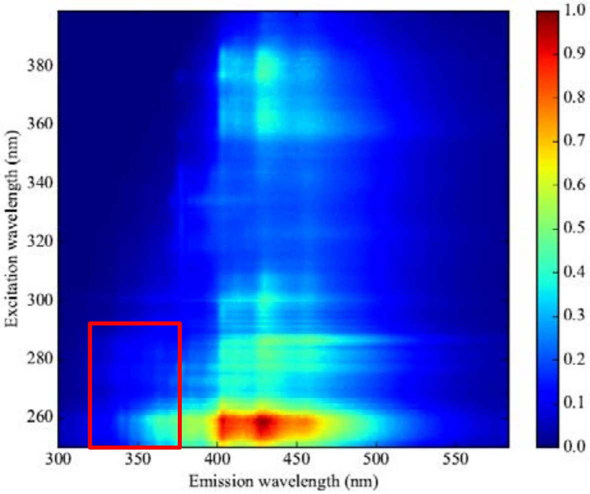
Anthracene in cyclohexane



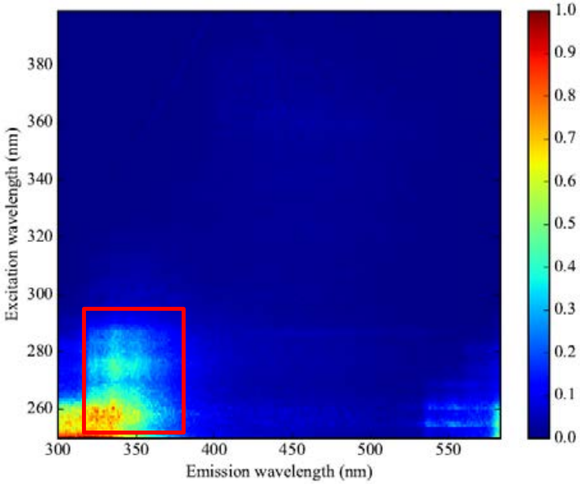
Excitation-Emission Matrix (EEM)

Can provide information on evolution of mixtures during a process by spectral comparison

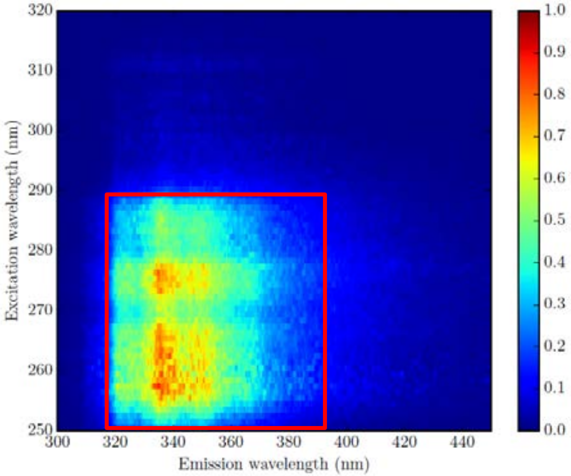
Ex: gasification sample (in isopropanol) before and after the gas cleaning system (quenche + ESP)



Before



After

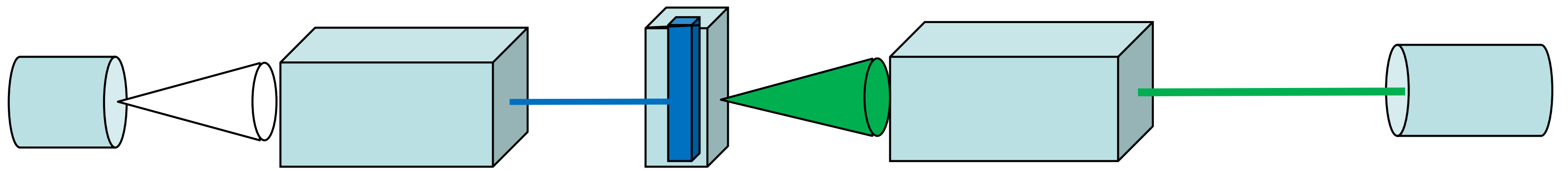


Pure naphthalene in isopropanol

➡ However, hard to get quantitative information on single-compounds if many different components

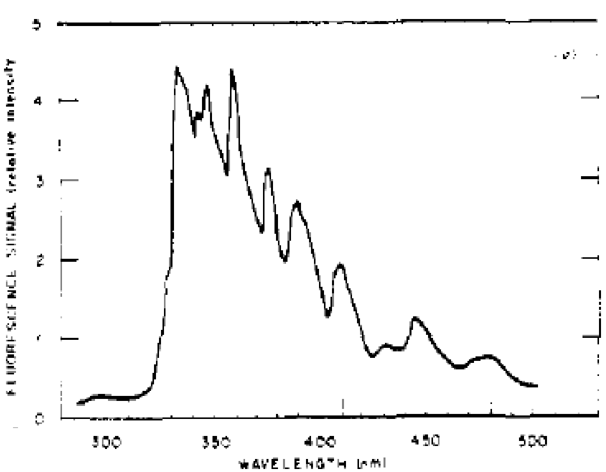
Synchronous-LIF

1978 : T. Vo-Dinh* : Synchronous Luminescence spectrometry

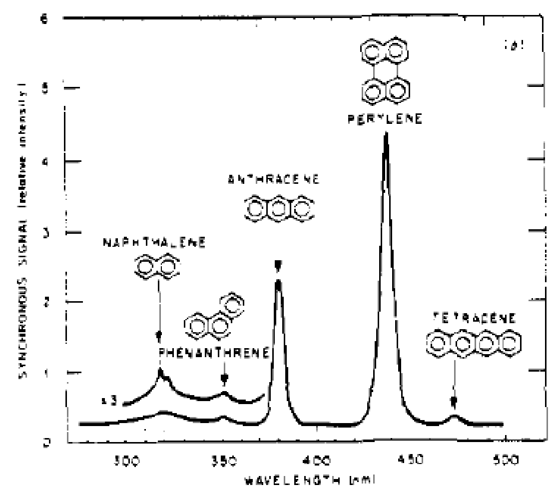


λ_{exc} λ_{em}

$\Delta\lambda = \lambda_{em} - \lambda_{exc}$



Conventional fluorescence spectrum, λ_{exc}= 258 nm*



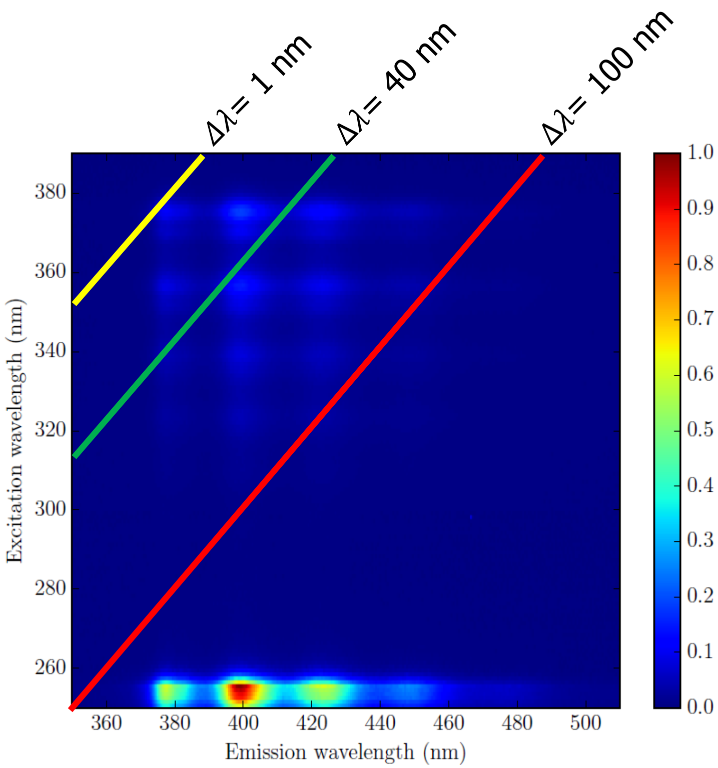
Synchronous spectrum, $\Delta\lambda$= 3 nm*

- Only measured in liquid phase
- 1 experimental = 1 spectrum (1 value of $\Delta\lambda$)
- No delayed fluorescence

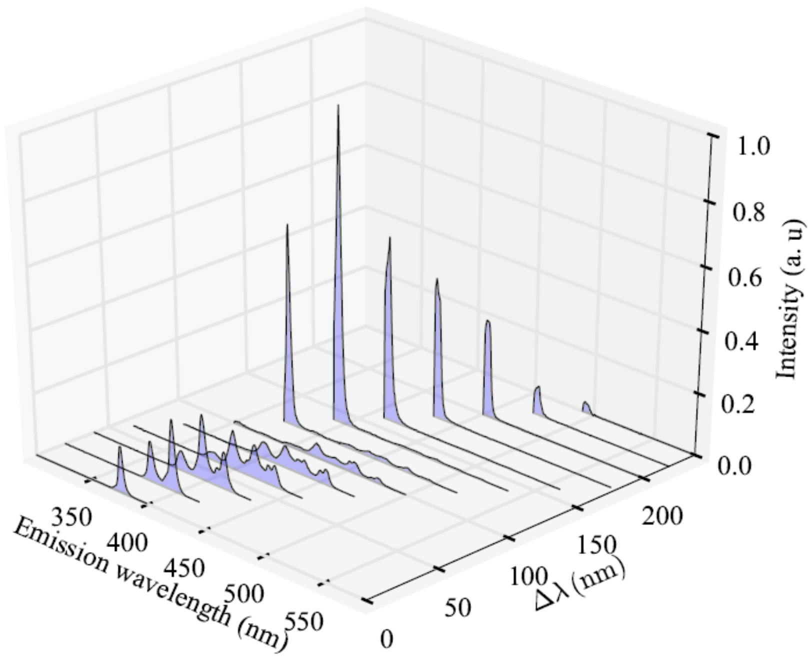
Synchronous-LIF

Idea : generate the synchronous spectra from the experimental EEM

- Access to all $\Delta\lambda$ values with 1 EEM
- Combined with fluorescence lifetime for multicomponent mixtures



EEM of anthracene in isopropanol

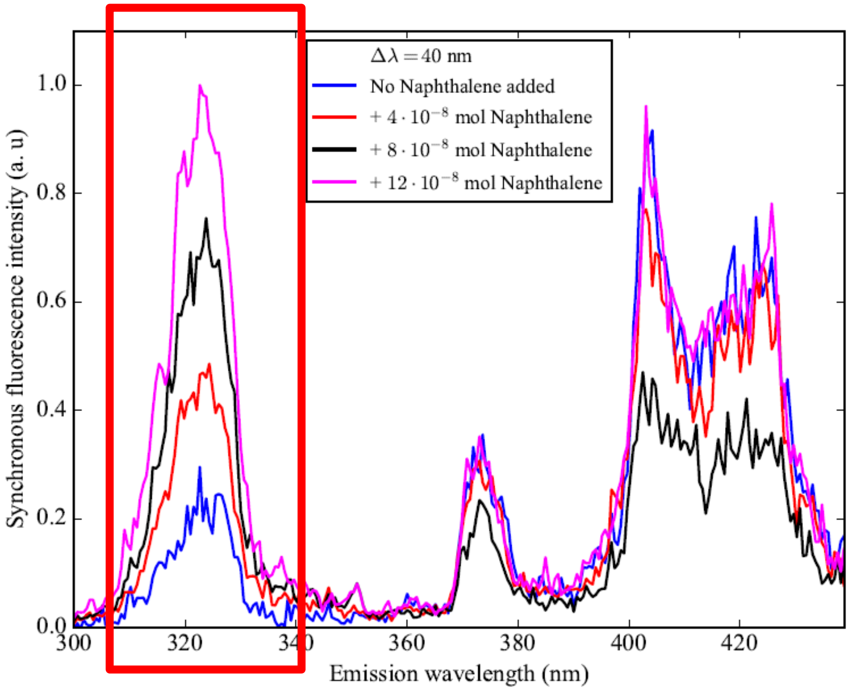


Synchronous spectra of anthracene in isopropanol (0< $\Delta\lambda$<250nm)

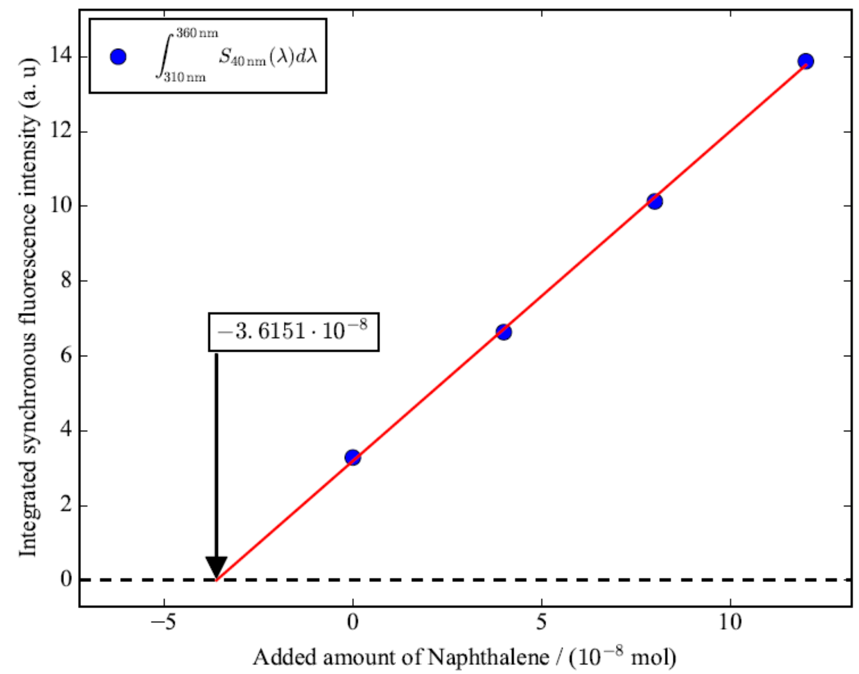
Quantification of pure compounds in mixtures

LIF measurements doesn‘t directly give concentration → **Standard addition method** for calibration

Ex: Naphthalene quantification in liquid sample from ethylene pyrolysis (LM-22)



Synchronous spectra of the mixtures with added amounts of naphthalene



Calibration curve for naphtahlene quantification

Results and comparison to gc-measurements

Preliminary results from liquid sample from ethylene pyrolysis
Measurement campaign at PSI, Switzerland, 26th-27th October 2016

Example of results for the sample LM-22

Compounds	LIF*	GC-FID
Naphthalene	$1.8.10^{-3}$	$1.9.10^{-3}$
Anthracene	$< 6.5.10^{-5}$	-
Phenanthrene	$2.1 - 2.8.10^{-4}$	$1.4.10^{-4}$
Pyrene	$9.7.10^{-5}$	$8.7.10^{-5}$
Fluoranthene	$1.1.10^{-4}$	$1.1.10^{-4}$

Concentration are given in $mol.L^{-1}$.
*Original sample diluted by 100.

What will we still do this year?

- Apply the approaches presented again to the gas phase
- Examine the applicability and its limits in the gas phase
- Publish the main findings

Thank you for your interest !

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