

Optical Spectroscopy – Analysis of Complex Mixtures in Aquatic Milieu

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Content

- Possibilities of optical spectroscopy
- Qualitative and quantitative analysis
- Examples of practise
- Perspectives

Objective and methods

- Rapid information concerning variance in water quality
- Characterisation of components causing variances

- Tools: Optical Spectroscopy
 - UV/VIS-Absorption
 - UV/VIS-Fluorescence
 - Infrared

UV/VIS Absorption

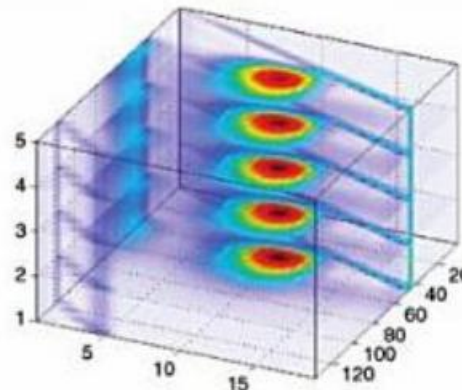
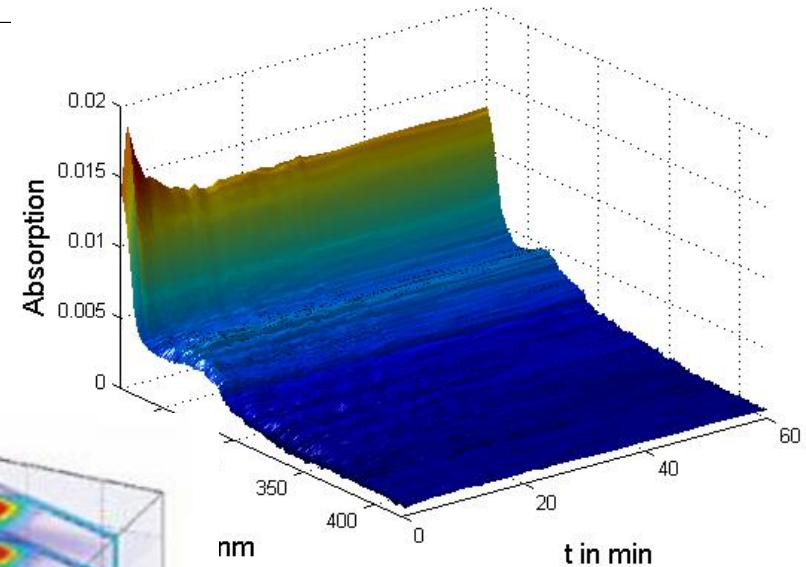
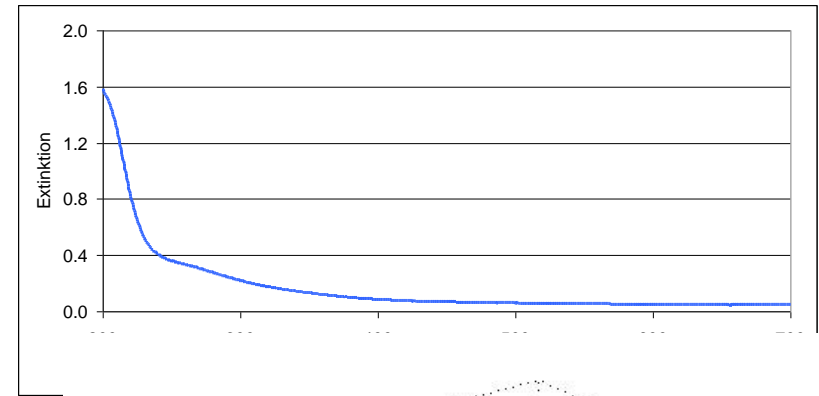
- Components
 - Anions (e.g. nitrate, nitrite, sulfate)
 - Humic compounds (UV_{254})
 - Algogenic compounds
 - Oxidations-/Disinfection agents ($HOCl/OCl^-$, ClO_2 , O_3)

Fluorescence

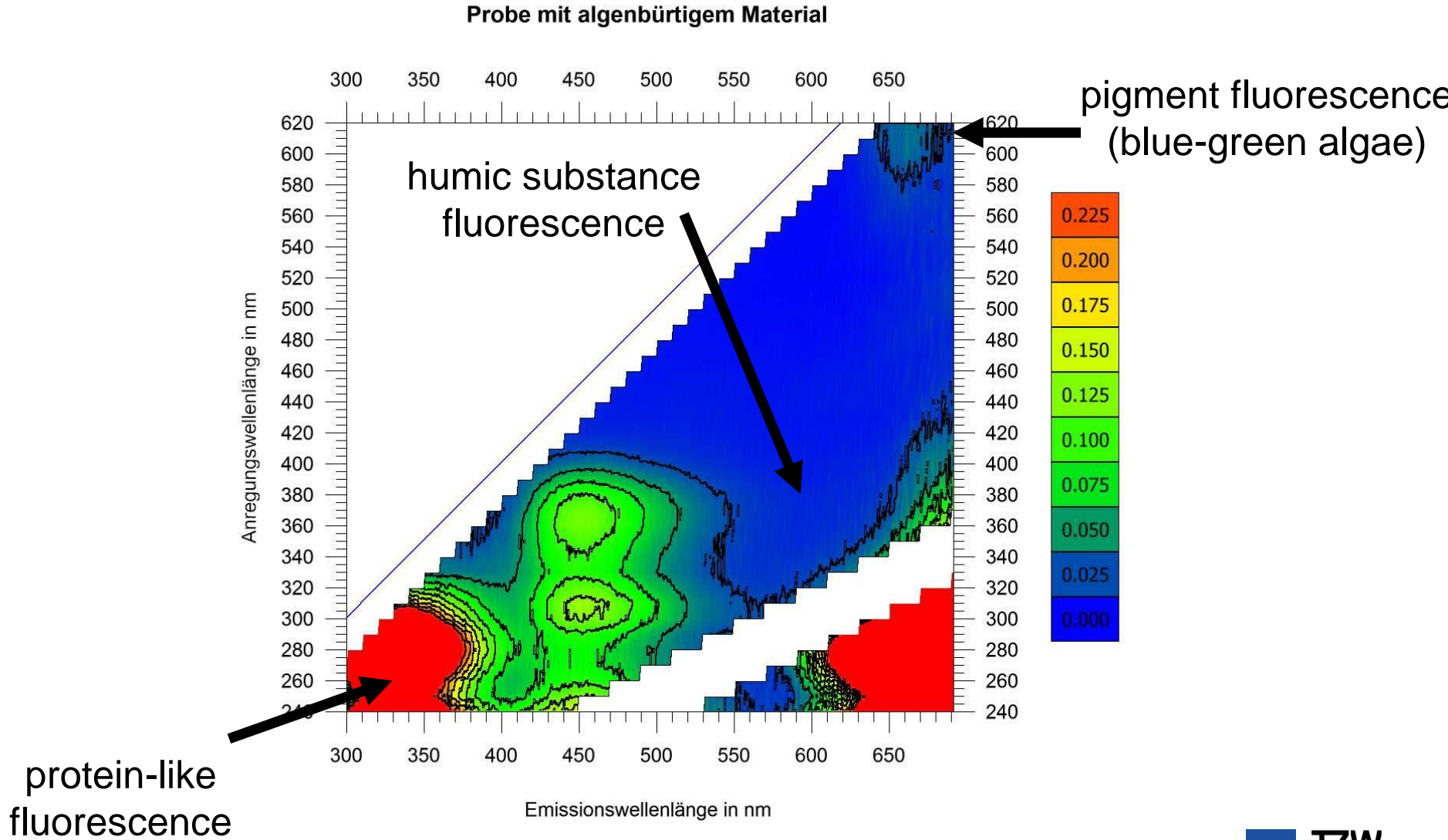
- Components
 - Humic and fulvic acids
 - Algogenic compounds (proteins, peptides, amino acids)
 - Microorganisms (EPS)

Analysis: The more data– The better !

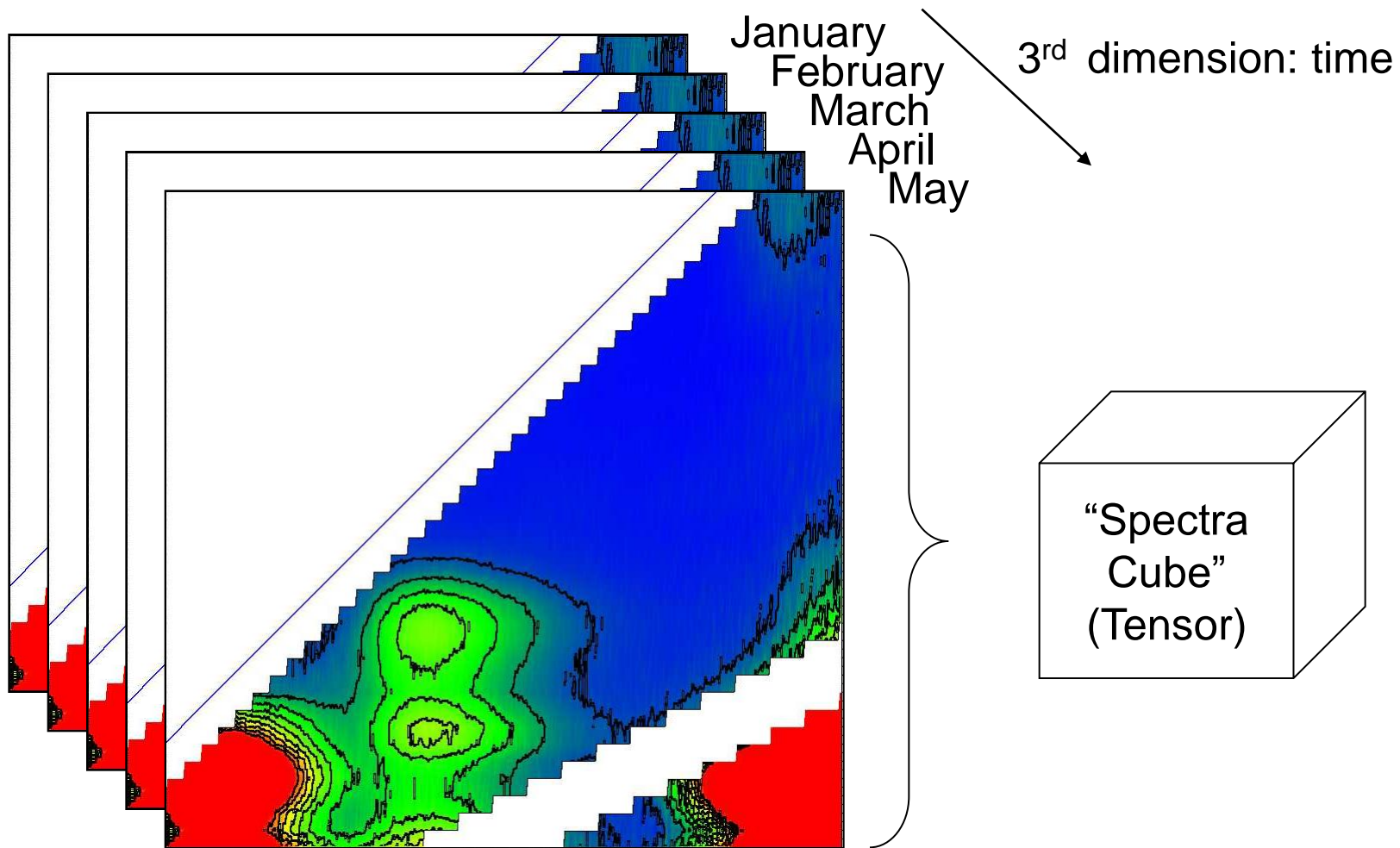
- 1 D-Spectra: $E = f(\lambda)$
- 2 D-Spectra: $E = f(\lambda, t)$
 - UV-Online
 - UV-Chromatography
- 3 D-Spectra: $E = f(\lambda, t, \text{place})$
 - UV-online at different treatment steps
 - Monitoring: reservoir
- n D-Spectra: $E = f(\lambda_{\text{ex}}, \lambda_{\text{em}}, t, \text{place})$
 - “Complex” monitoring



Fluorescence: 2D-Spectra ($F = f(\lambda_{ex}, \lambda_{em})$)



Fluorescence: 3D-Spectrum, $F = f(\lambda_{\text{ex}}, \lambda_{\text{em}}, t)$



Qualitative und Quantitative Spectra Analysis

	Qualitative Analysis	Quantitative Analysis
Aim	Identification of components by spectra decomposition	Concentration of components
Methods	Non-Negative Matrix-Factorization (NMF) ⇒ Application in 2D-Spectra	Principle Component Regression (PCR)
	Non-Negative Tensor-Factorization (NTF) ⇒ Application in 3D-Spectra	Partial Least Squares Regression (PLSR) Multiple Linear Regression with reference spectra (MLR)

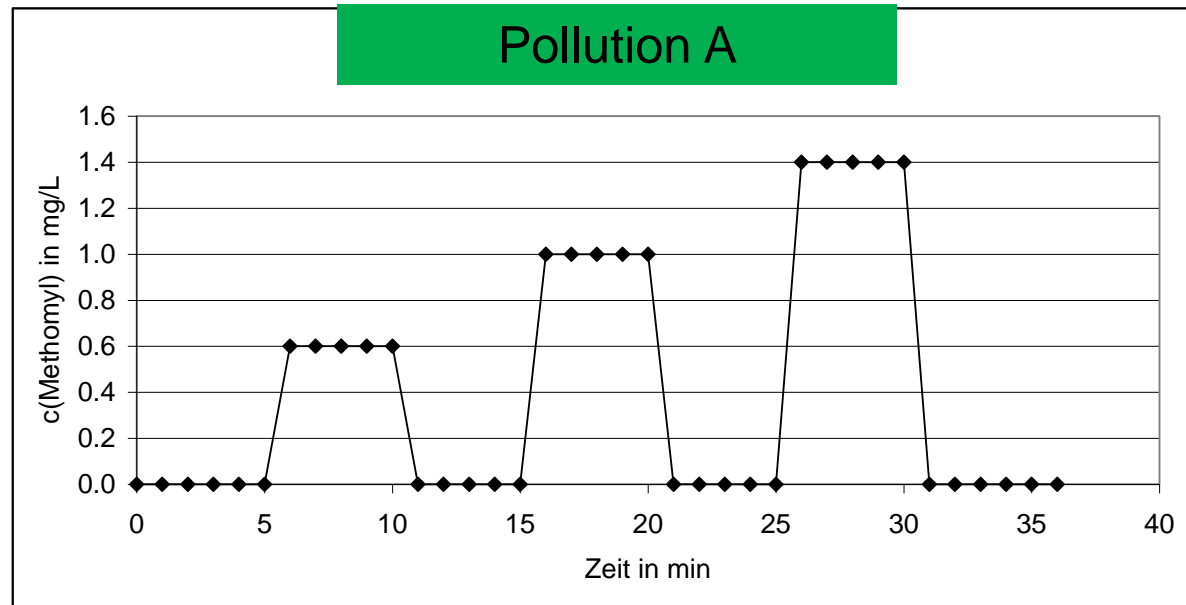
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Pollution: Component A

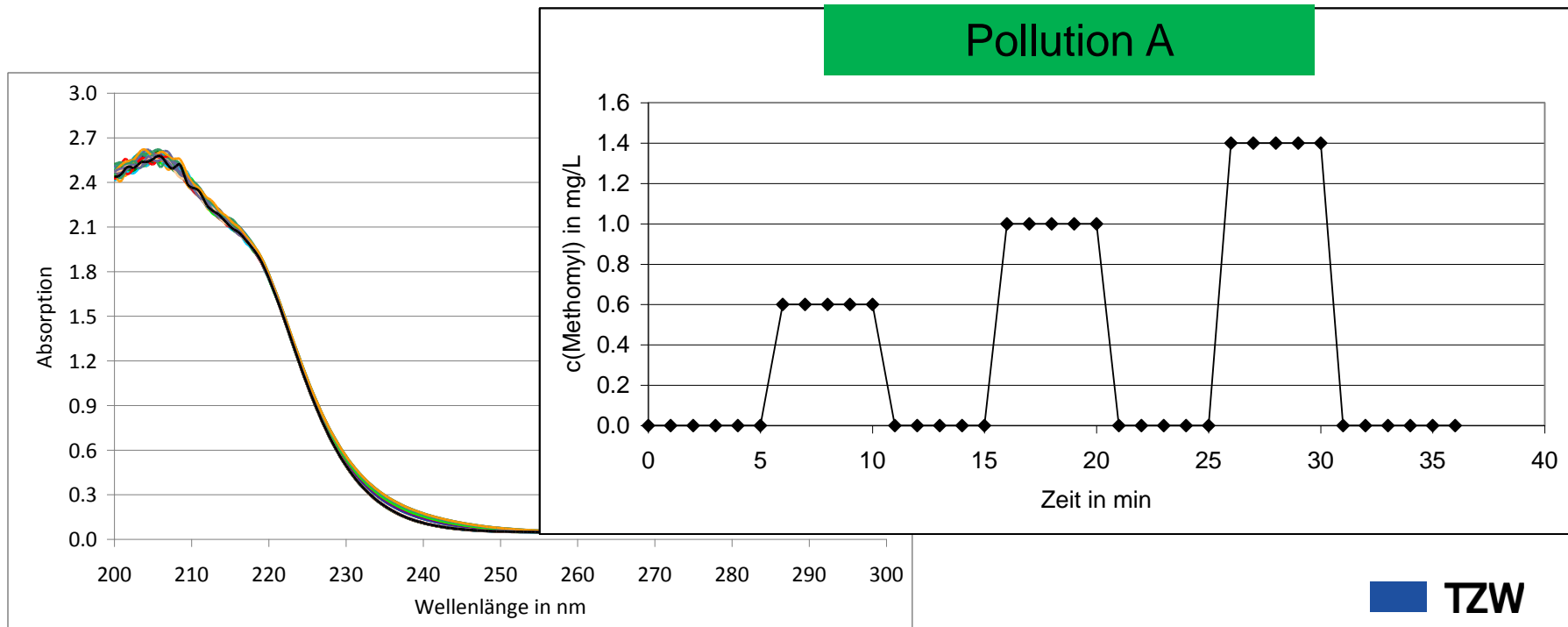
Example: Qualitative Spectra analysis (NMF)

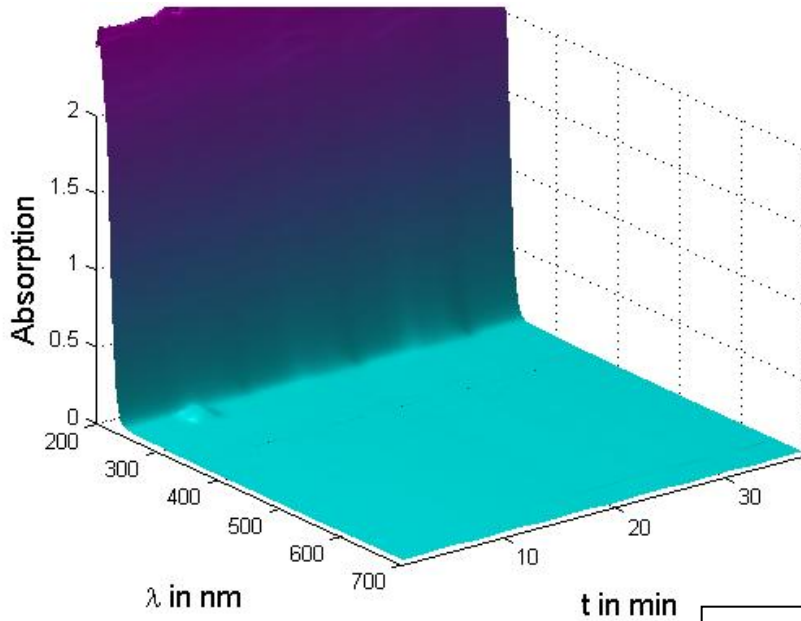
- Sequential spiking of component “A” to drinking water
- Online flow measurement of UV-VIS absorption
- Application of NMF



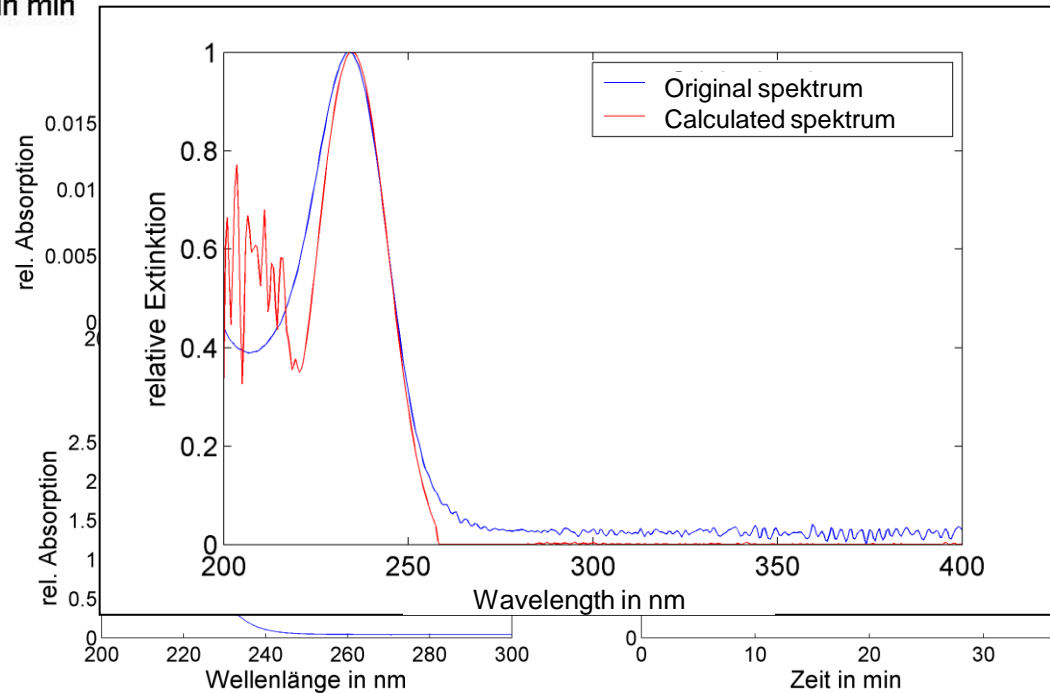
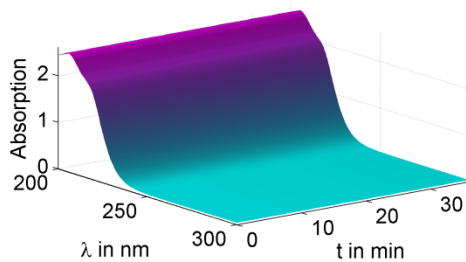
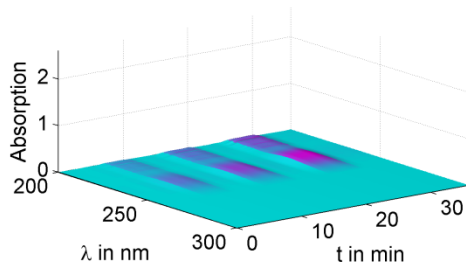
Example: Qualitative Spectra analysis (NMF)

- Sequential spiking of component “A” to drinking water
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Simulation of drinking water monitoring
 → substance in real water probe
 → decomposition with mathematical method
 (NMF = non-negative matrix factorization)



Qualitative und Quantitative Spectra analysis

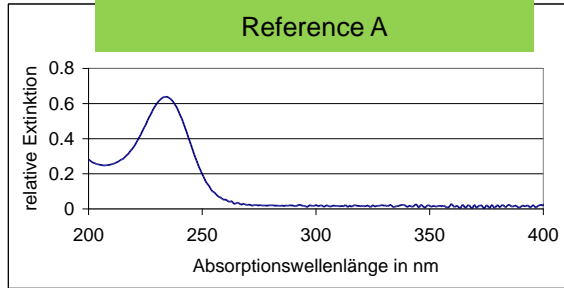
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Qualitative und Quantitative Spectra analysis

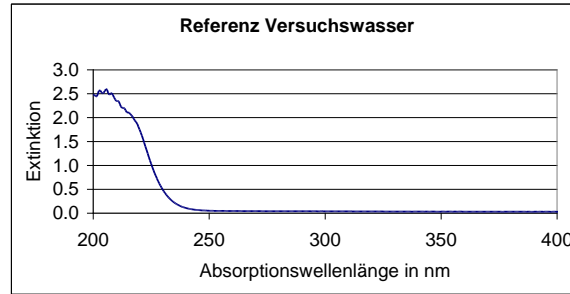
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Quantitative Analyse: Component "A"

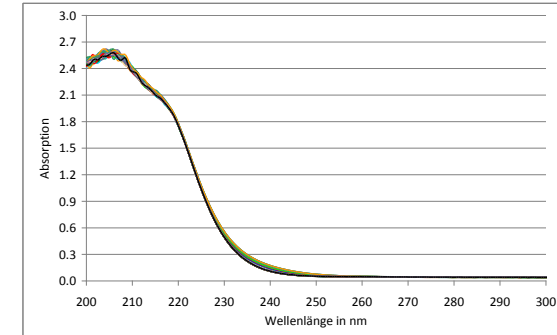
Multiple lineare Regression:



+



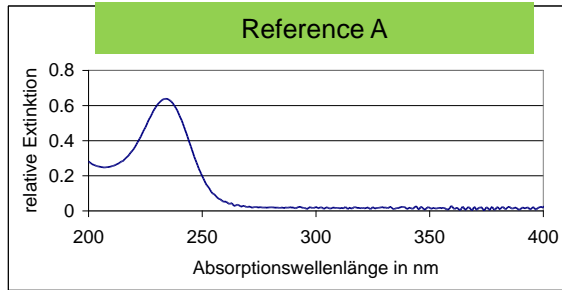
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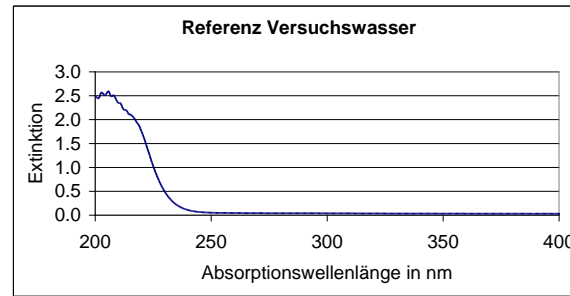
spiked and calculated concentration

Quantitative Analyse: Component "A"

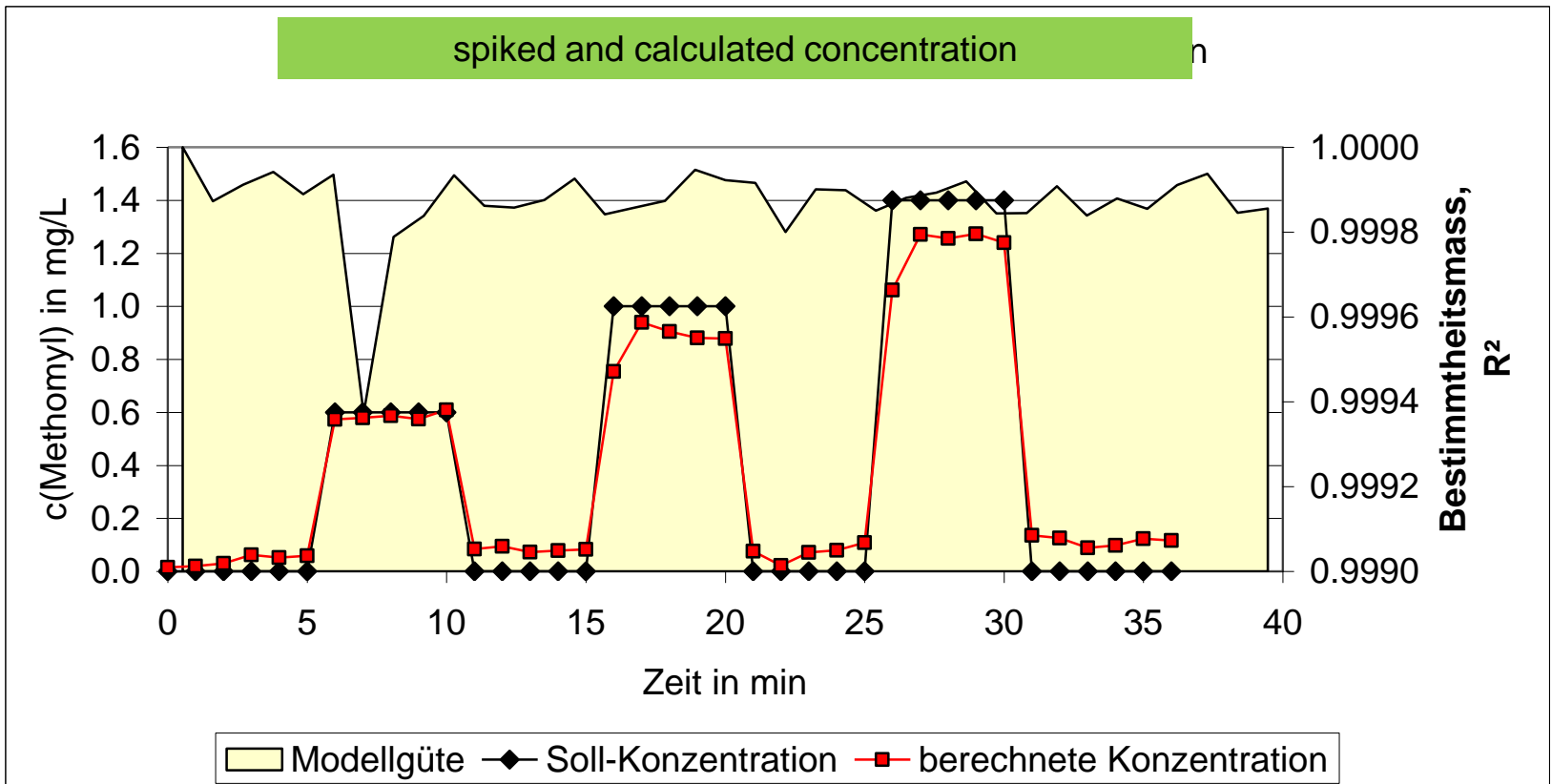
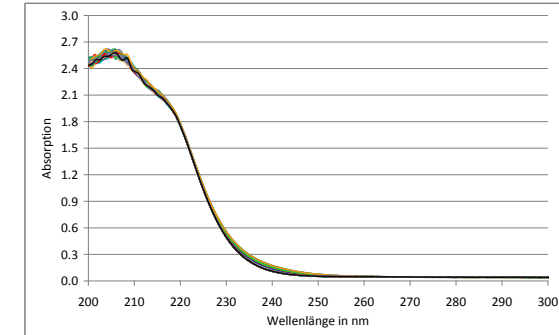
Multiple linear Regression:



+



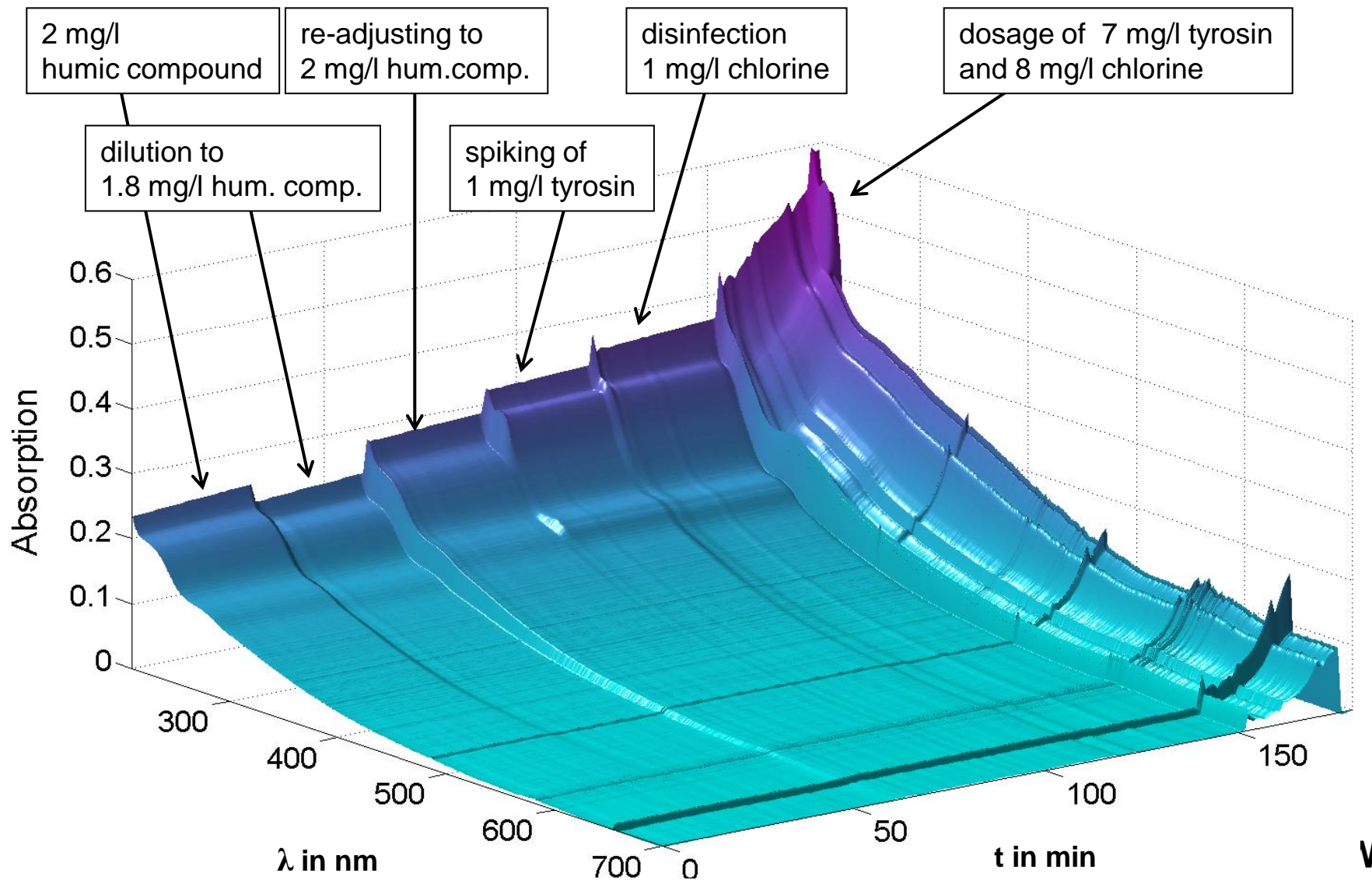
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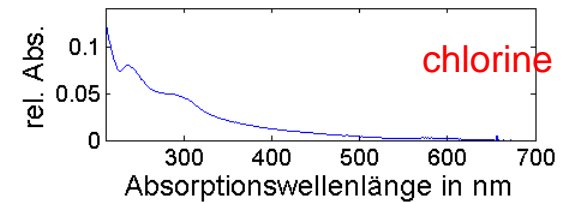
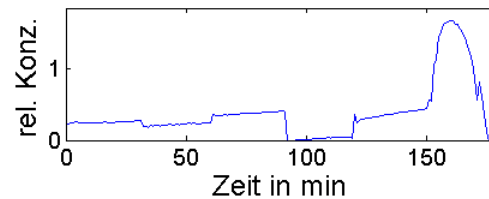
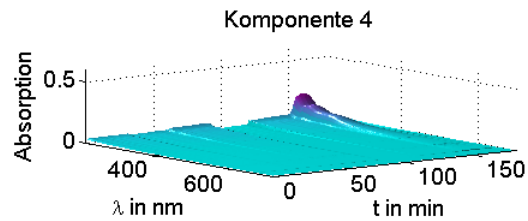
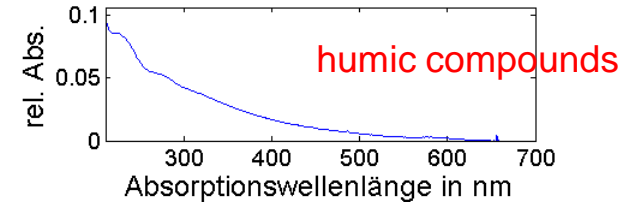
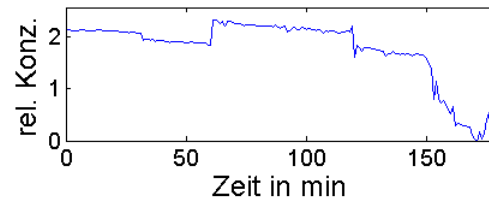
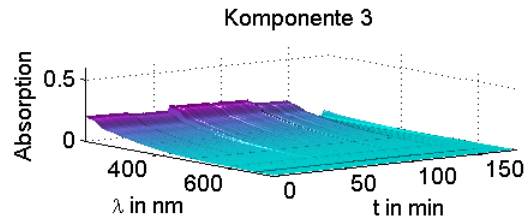
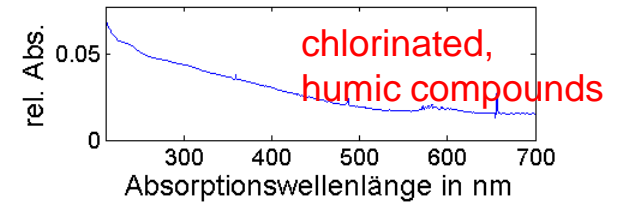
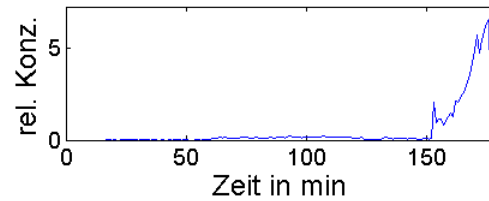
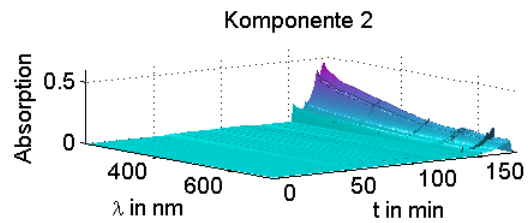
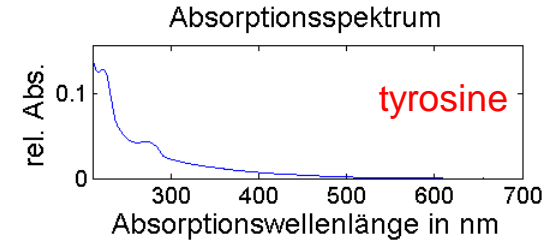
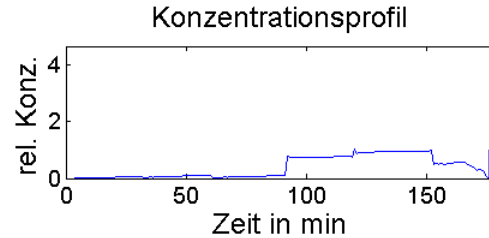
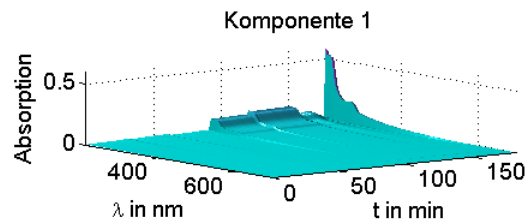
Simulation:

- **Change in natural OM**
- **Bacterial pollution**
- **Disinfection**
- **Waste water pollution and disinfection**

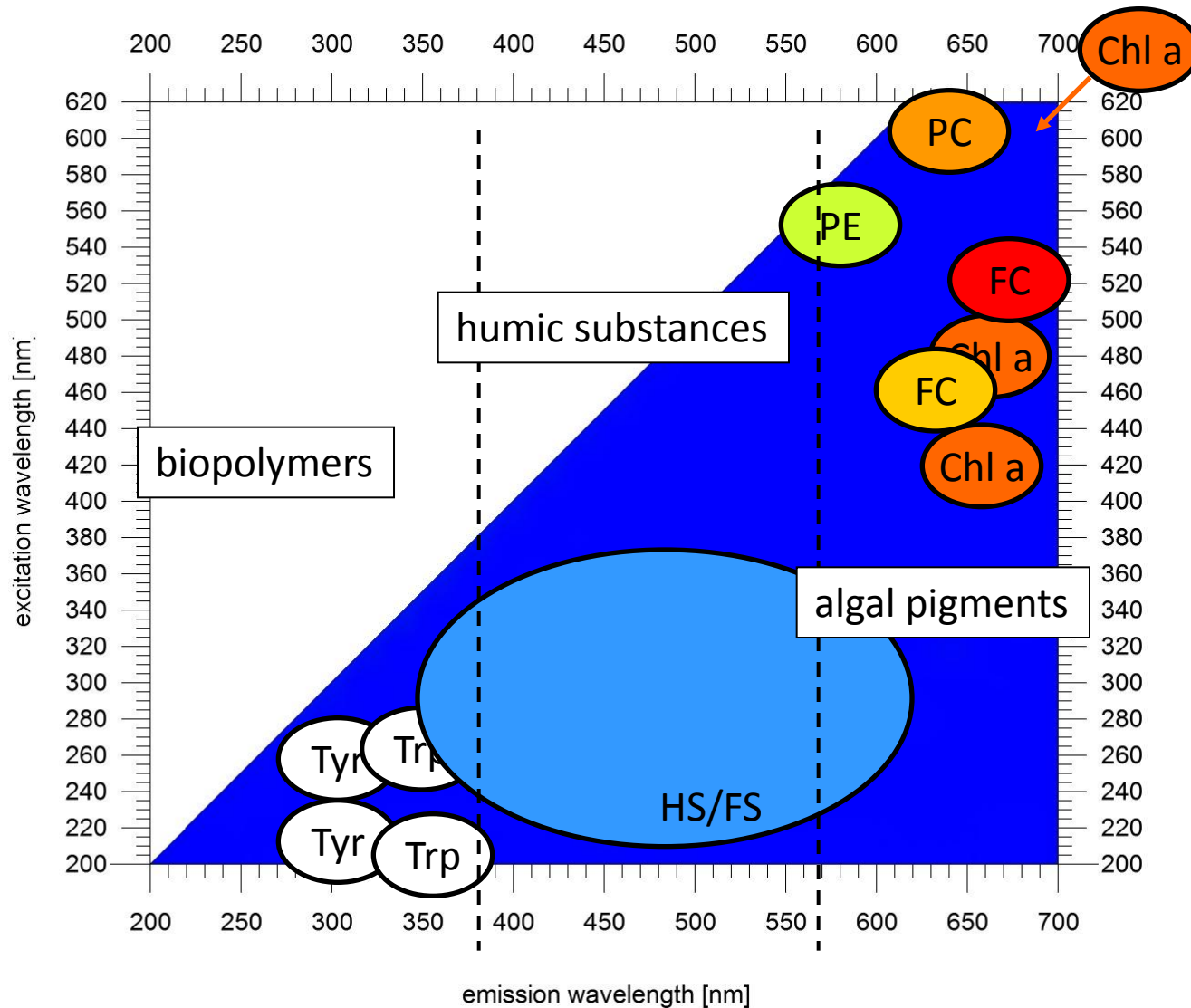
Simulation of drinking water pollution: Application of NMF



Results of NMF-calculation

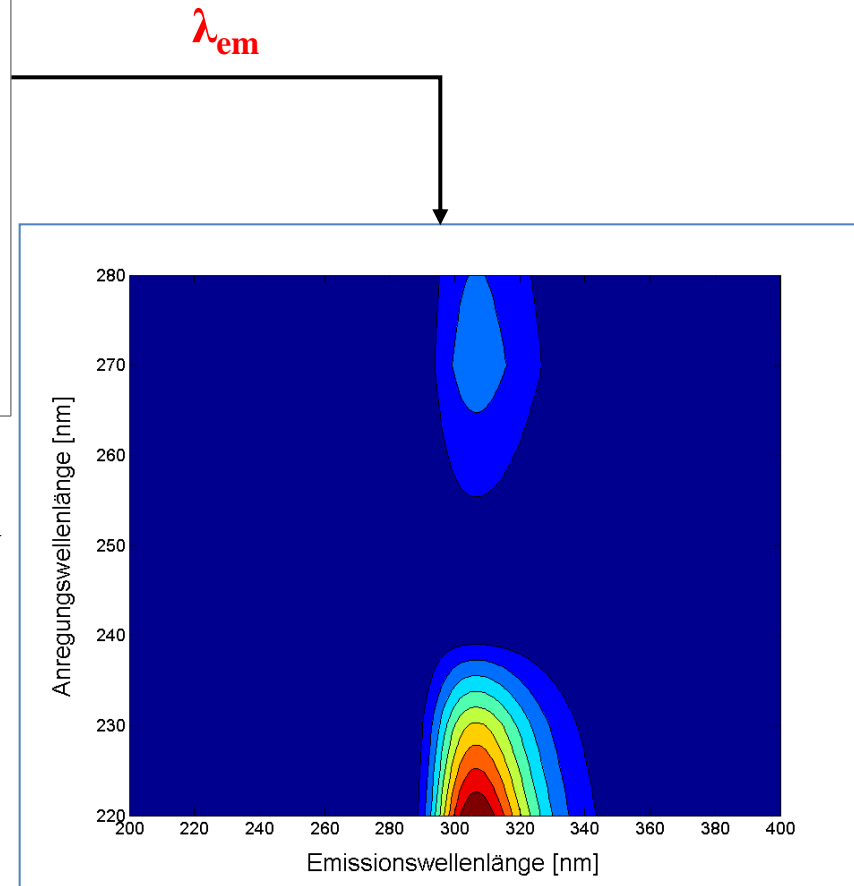
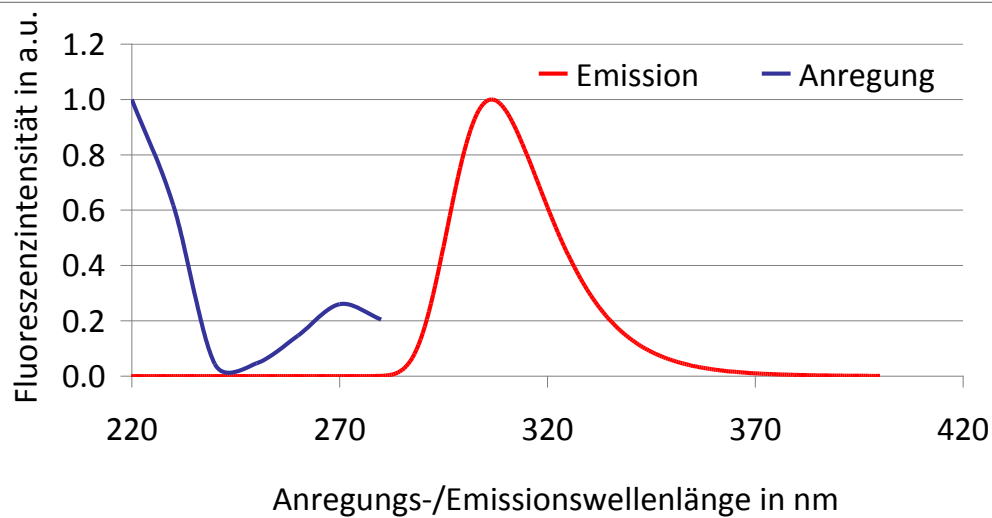


TOC-Characterization by Fluorescence



Fluorescence means one dimension more !

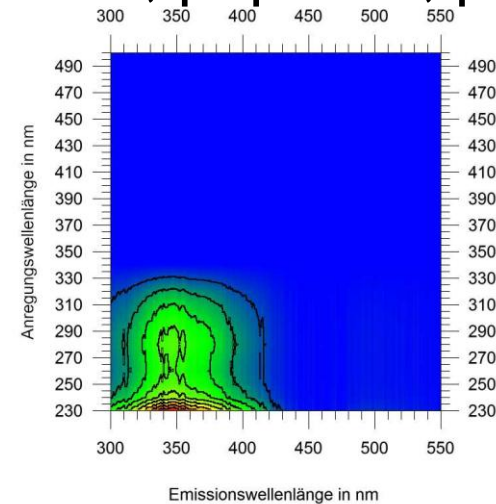
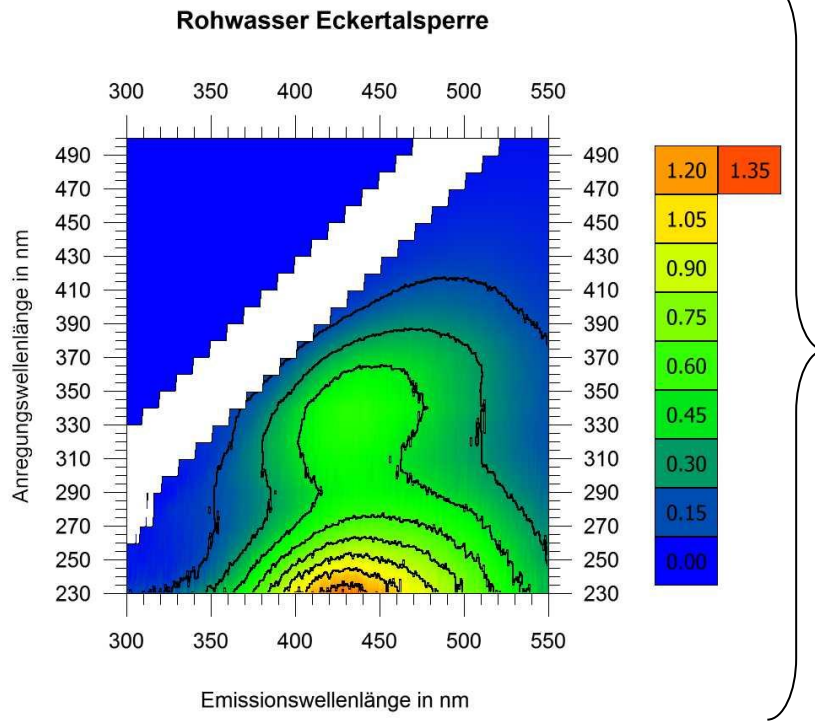
- Excitation and Emission



Application of NTF (PARAFAC Method)

- Component analysis of drinking water:

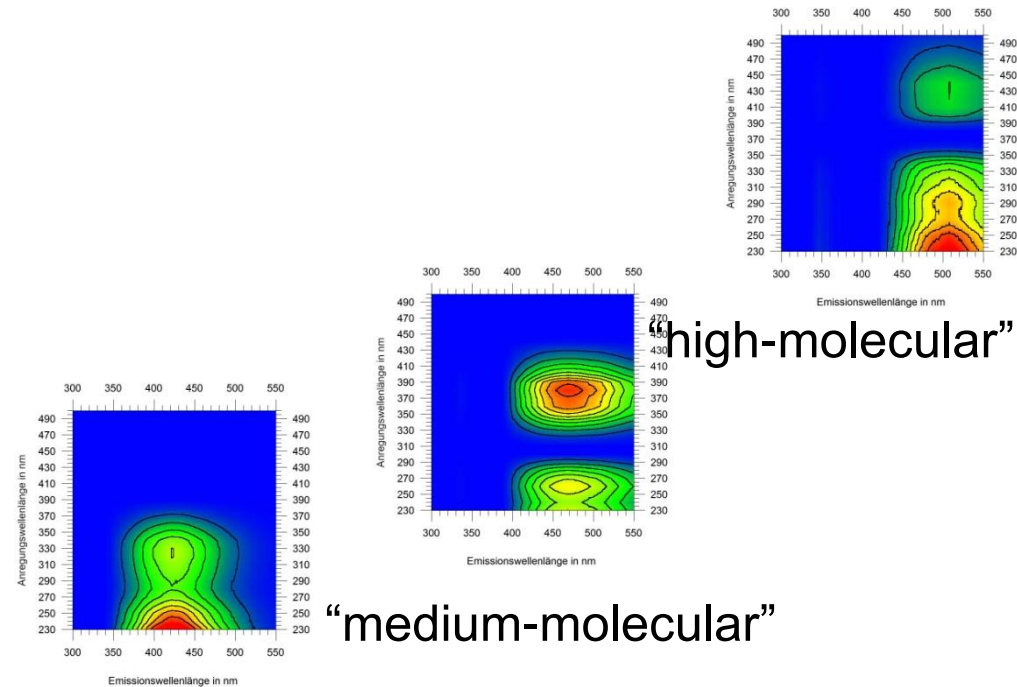
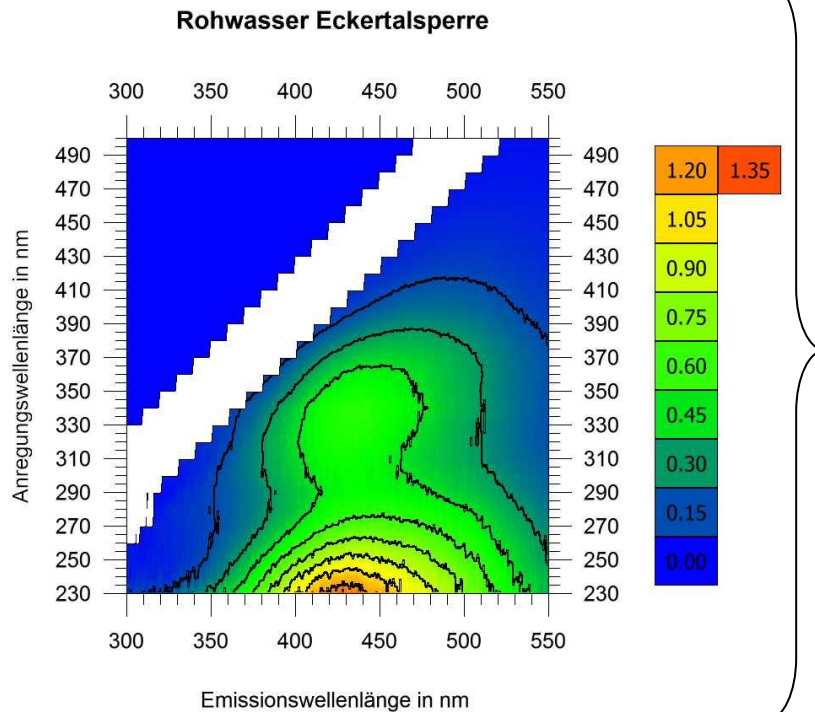
biopolymer-like fluorescence
(amino acids, peptides, proteins)



Application of NTF (PARAFAC Method)

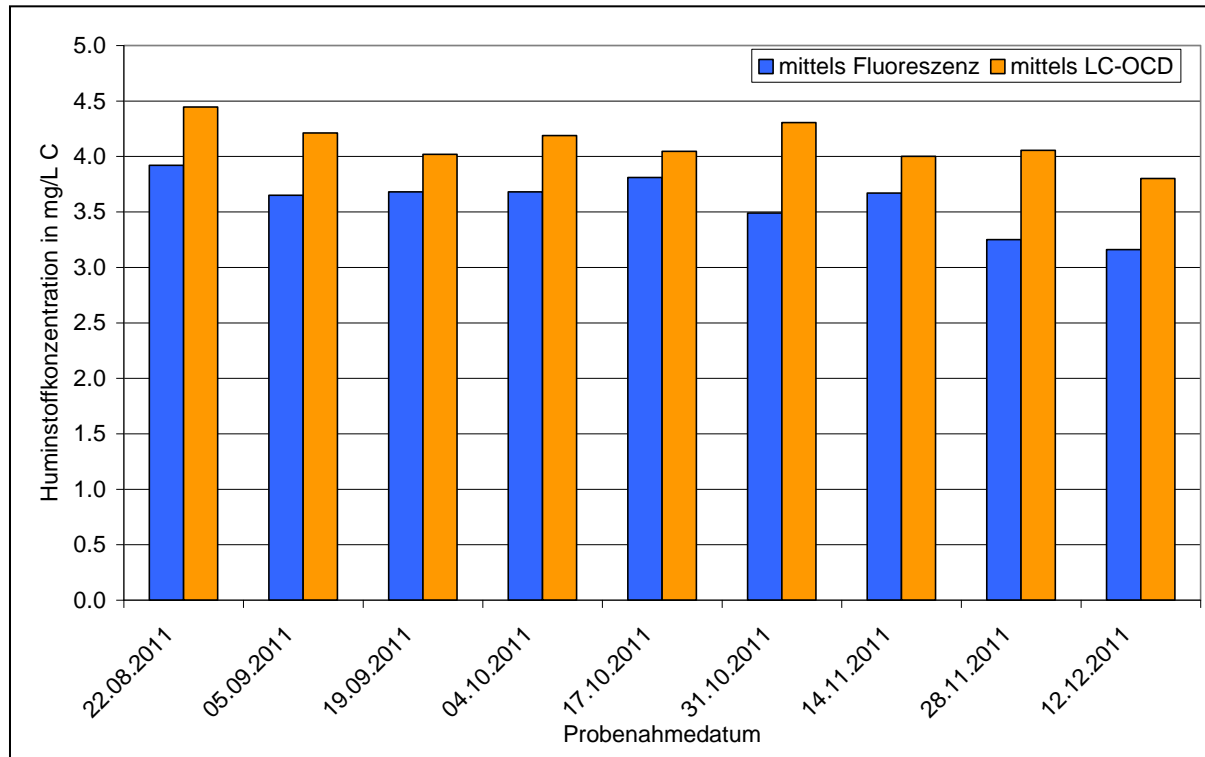
- Component analysis of drinking water:

3 fractions of humic compounds



“low-molecular”

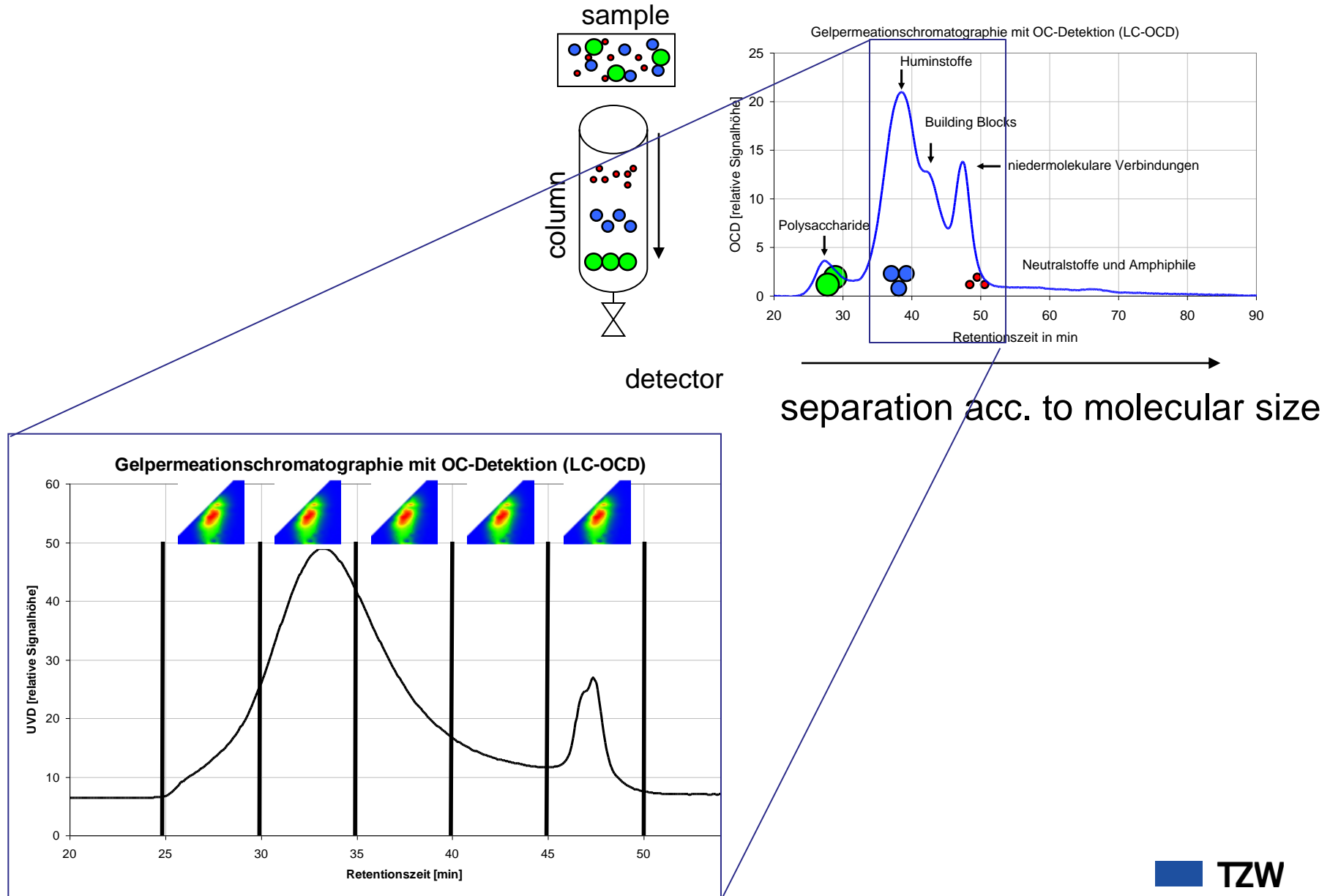
Comparison between results of the DOC analyzer - and Fluorecence



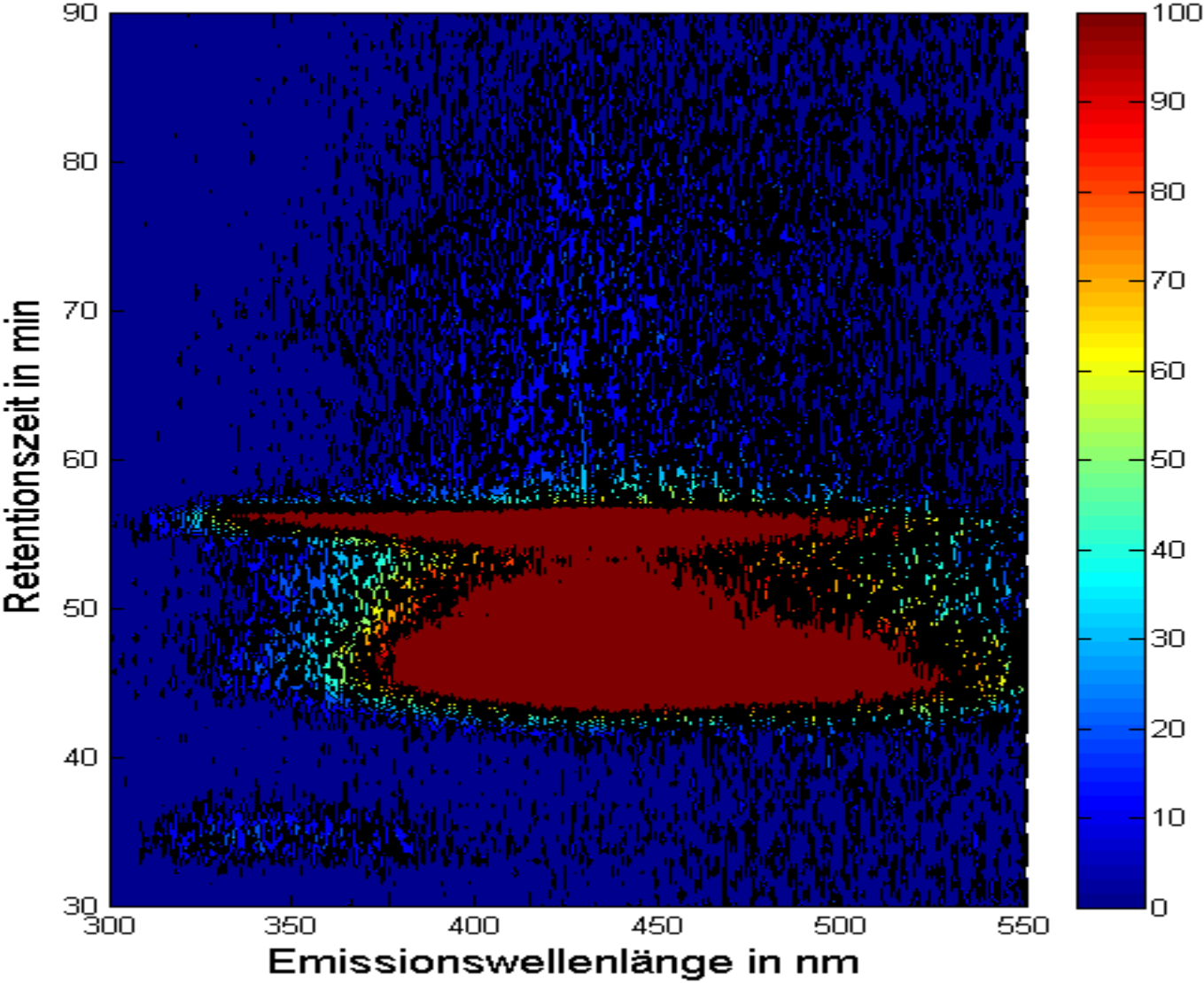
Raising of Dimensions for Fluorescence (3D→ 3+D)

- **Online measurement at different places**
 - more equipment is needed
 - makes no sense if the differences in water quality at different places are interesting !
- **Chromatographic-like separation of OM fractions**

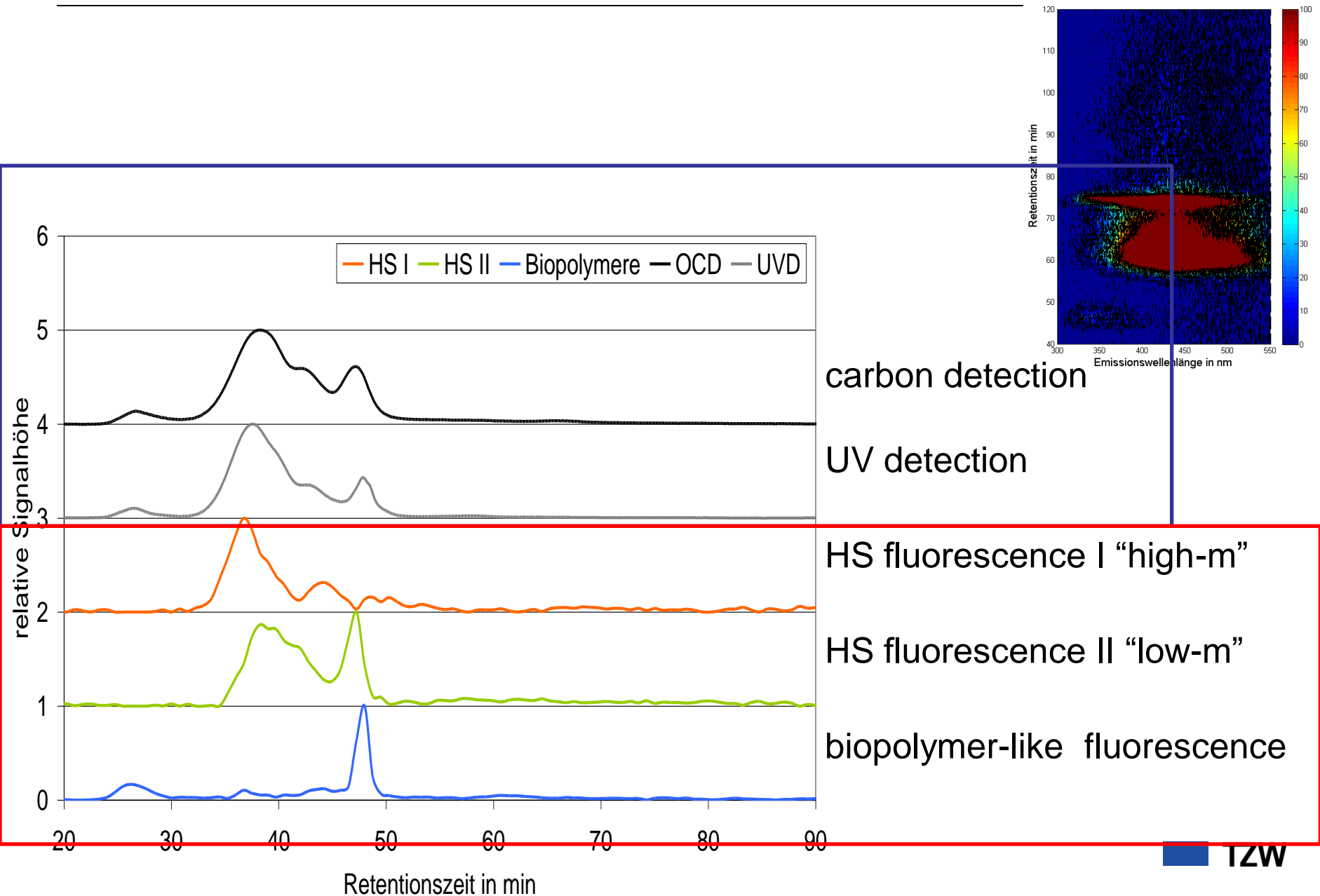
Raising of Dimensions for Fluorescence (3D → 3+D)



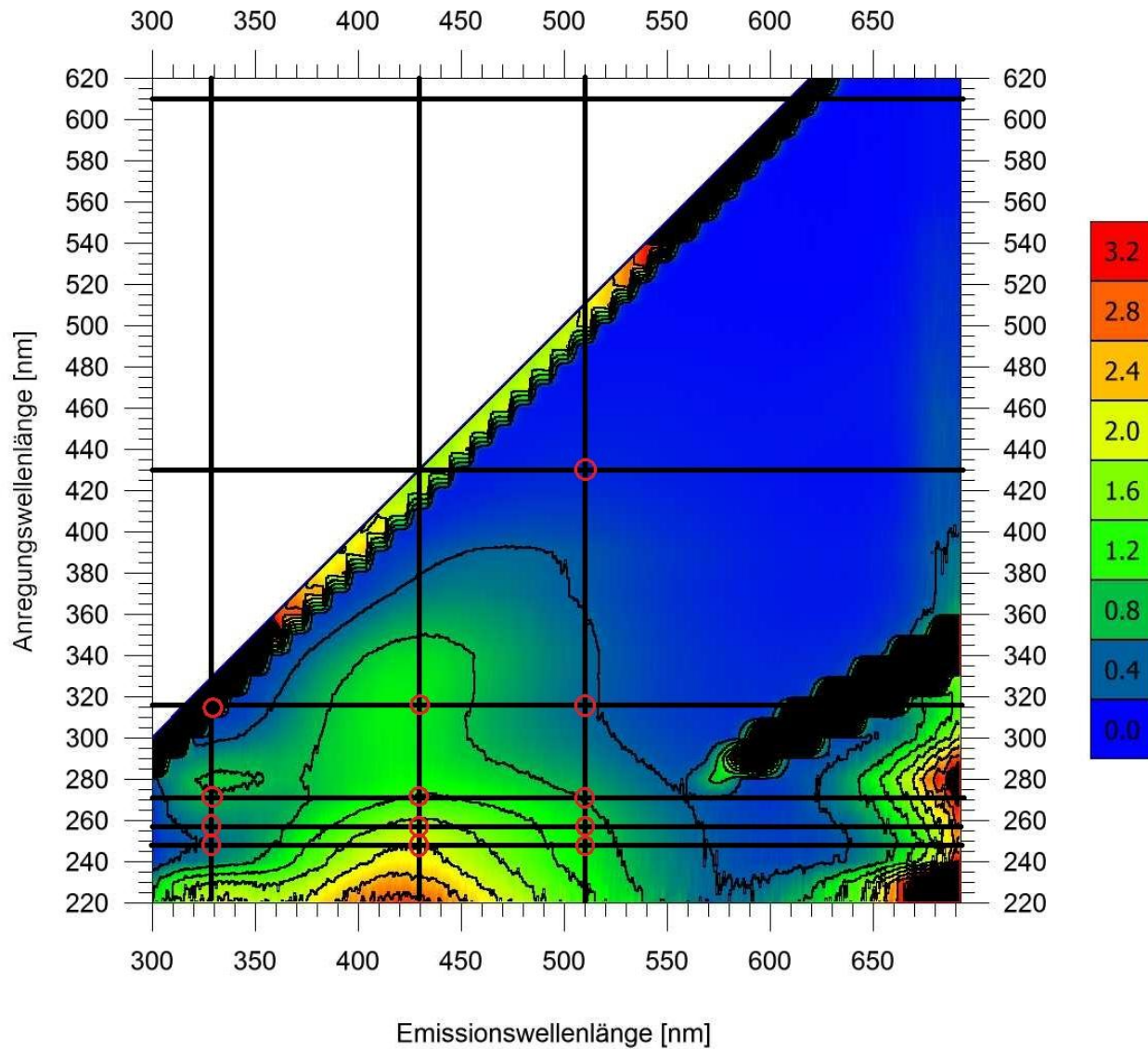
River Elbe water; Excitation 280 nm; Emission 300-550



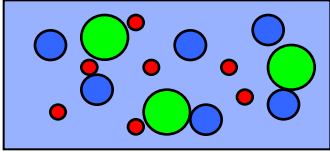
Characterization of Biopolymers and Humic Compounds



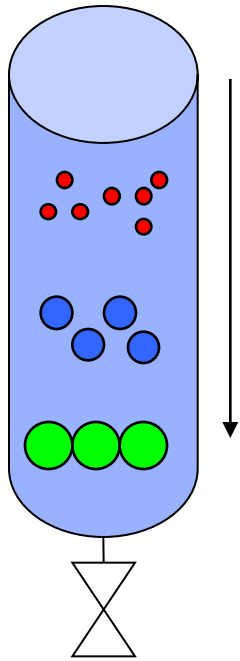
Online Fluorescence: The Problem



sample

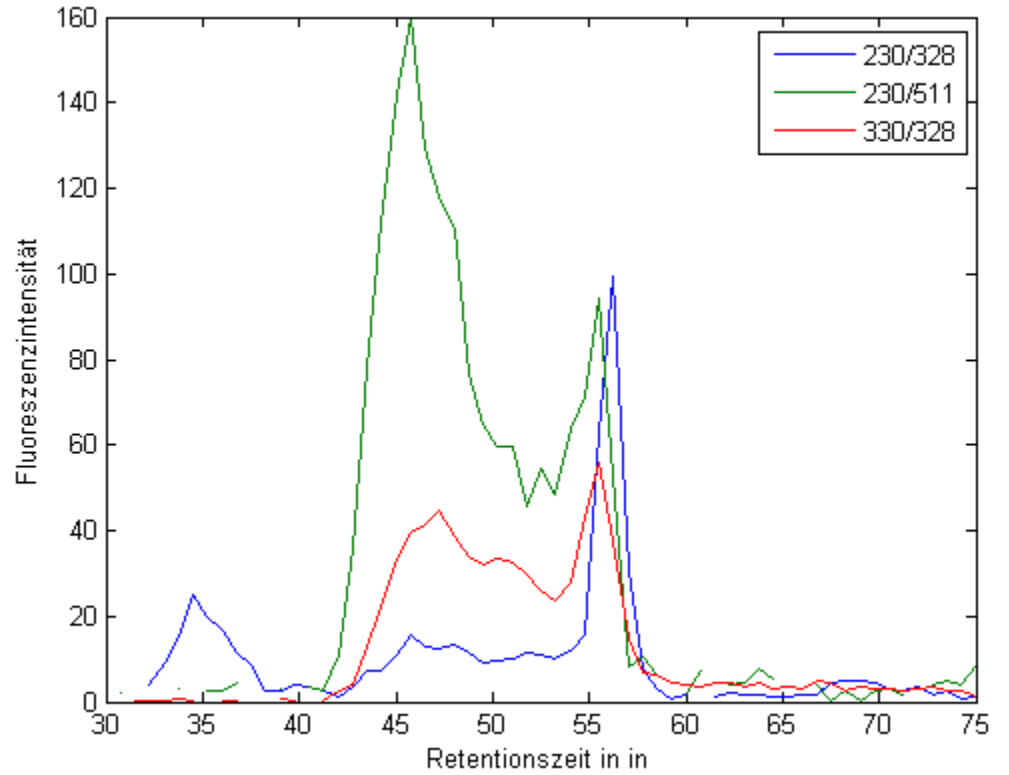
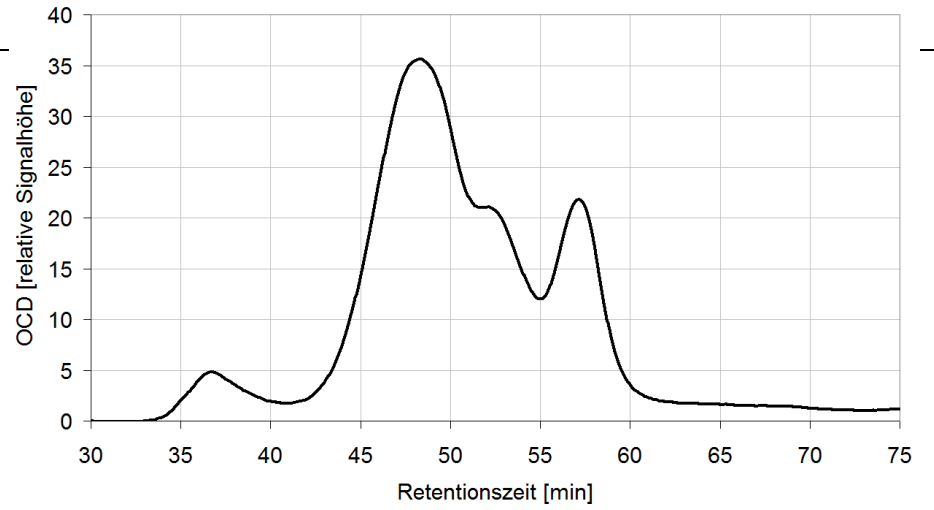


column



sensor

Gelpermeationschromatographie mit OC-Detektion (LC-OCD)



Conlusions

issue	chromatography	absorption	fluorescence	different combinations
online ?	✘	✓	✓	✓
costs	high	low	low	?
selectivity	✓✓✓	✓	✓	✓✓✓
accuracy	✓✓✓	✓✓	✓✓	✓✓
sensitivity	✓✓✓	✓	✓✓	✓✓✓

For online measurements: optimization is urgent

**Many Thanks to:
DVGW
ATT**

**Martin Wagner
Camilla Jähn**

Weißlichtanregung

Probe mit algenbürtigem Material

Alle
Wellenlängen
gleichzeitig

