Ernst-Abbe-Hochschule Jena
University of Applied Sciences

Instrumental Analysis Group

# Optimization of a photochemical gold nanoparticle synthesis

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# outline



workgroup instrumental analysis

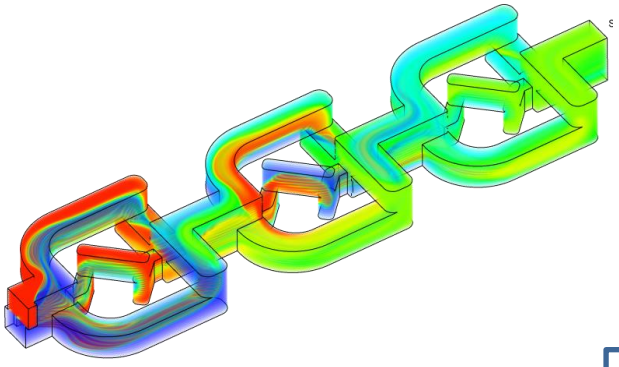
motivation

photochemical synthesis of gold nanoparticle

pre optimization – DoE I

optimization – DoE II

comparison experiment and simulation; outlook



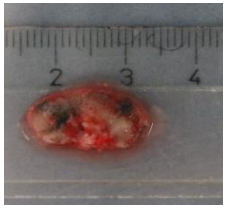
optimization tasks

simulation

experimental

biological

chemical



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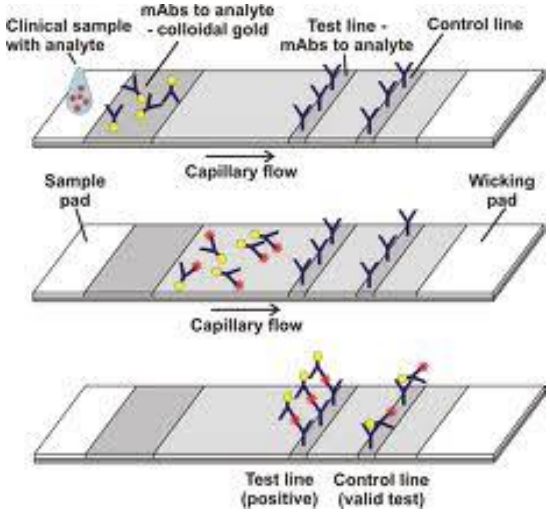
# motivation

- nanoparticle are ingredients in products of “daily” use
- color and intensity must be constant

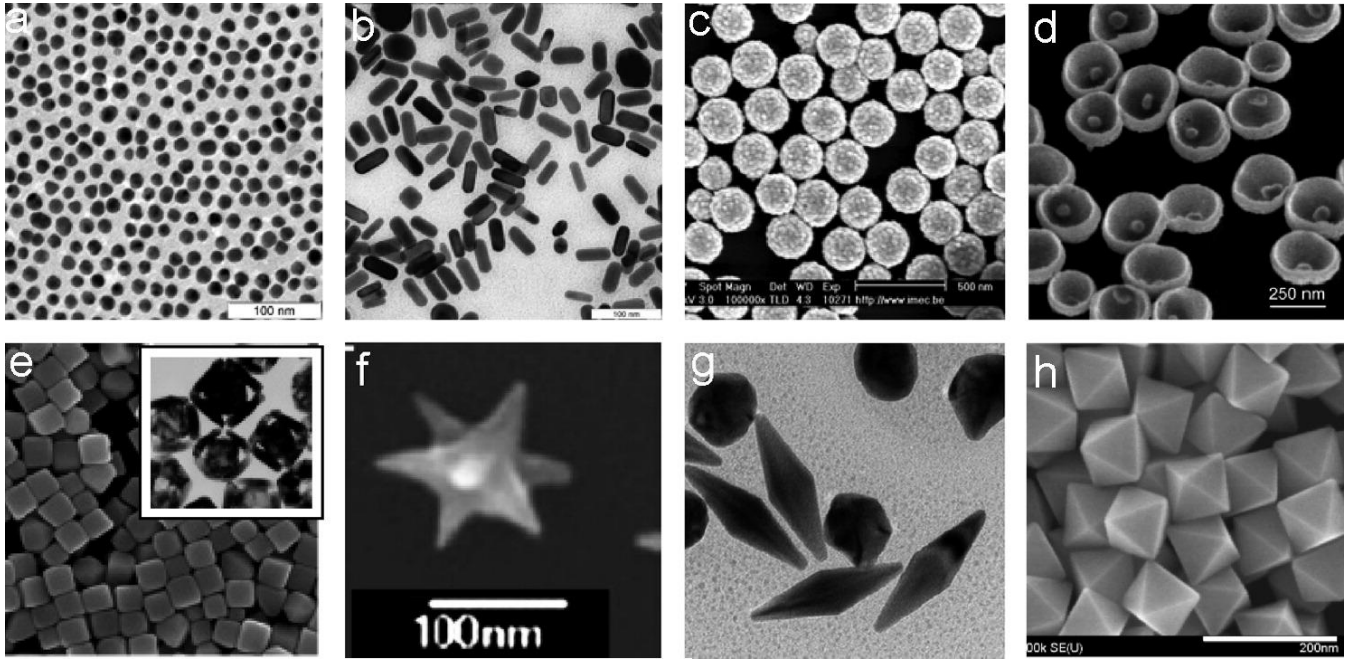




# What are Nanoparticles?

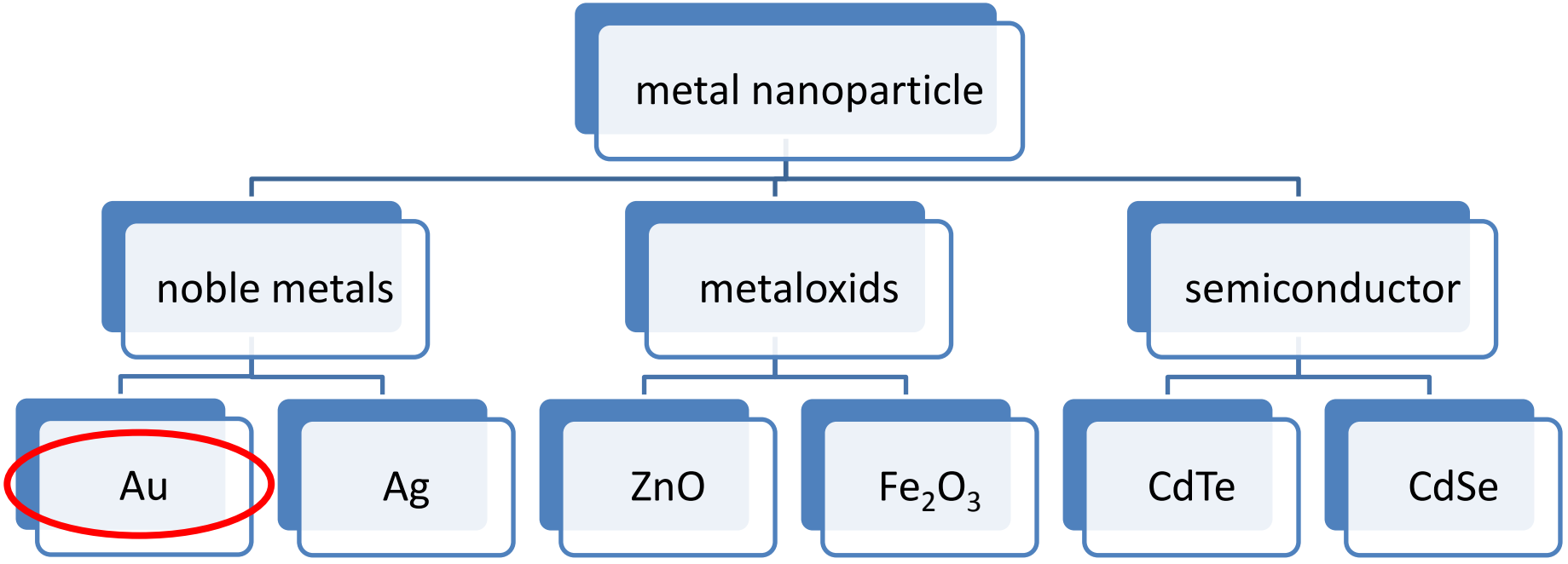


- particle size: 1 – 100 nm
- mostly artificial origin
- first usage stained glass




Khlebtsov, N. G. and L. A. Dykman (2010). "Optical properties and biomedical applications of plasmonic nanoparticles." Journal of Quantitative Spectroscopy and Radiative Transfer **111**(1): 1-35.

# nanoparticle material



# Surface Plasmon Resonance Spectra

- Nanoparticles have specific colors
  - Surface Plasmon resonance is size and charge dependent
    - different particles have a huge shift in color
    - amount of particle change color intensity

samples of different Gold- Nanoparticle sizes with specific color changes

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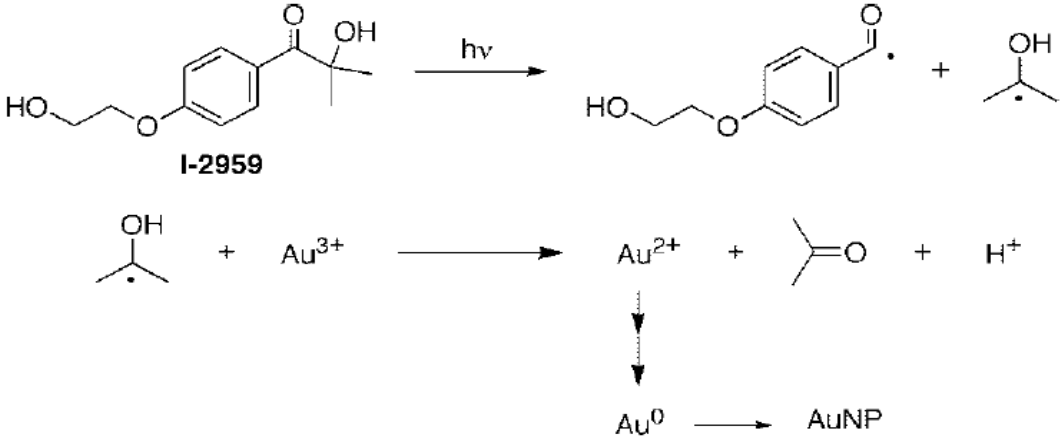
# photochemical synthesis



- photoinitiator cleavages radicals under light- irradiation
  - light intensity controls reaction
    - needs high energy (UV-region of spectra)
  - reaction is easily stoppable
  - microfluidic set up can increase yield

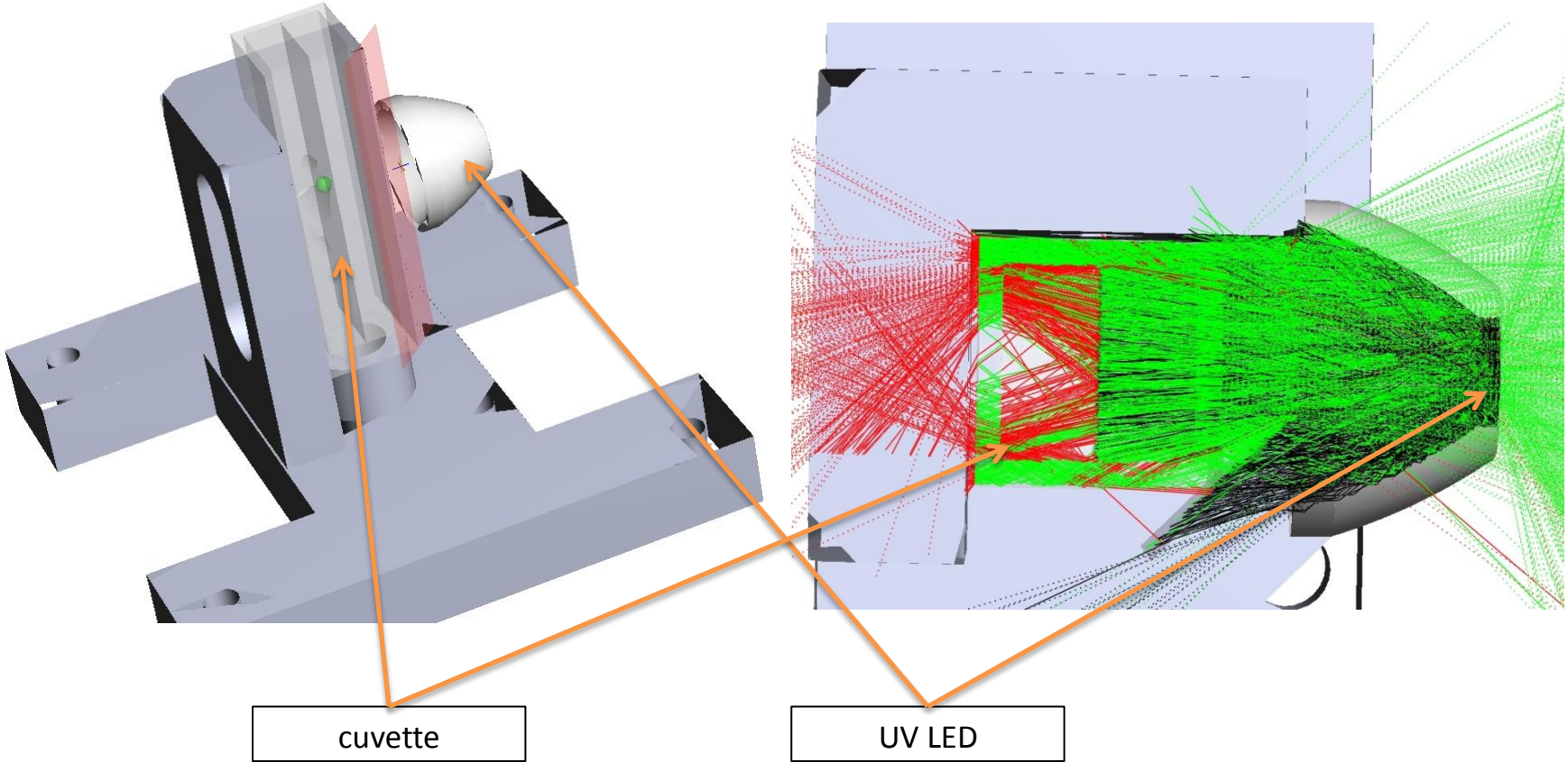
- radicals reduce Au ions
  - colloidal gold is produced




Martin et. al, 2008

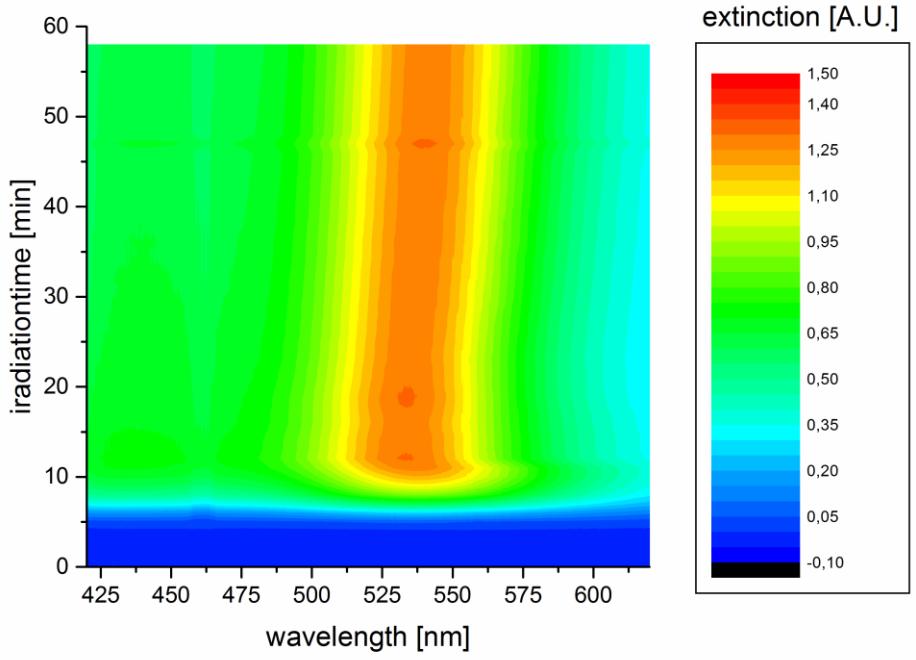
# setup with optimized optical irradiation

- raytracing simulation of set up



# time resolved experiment

- NP- synthesis take around 5 min to start
  - size of particles changes with reaction time and reactant concentration




Time dependent uv-vis spectra of NP-synthesis with I-2959

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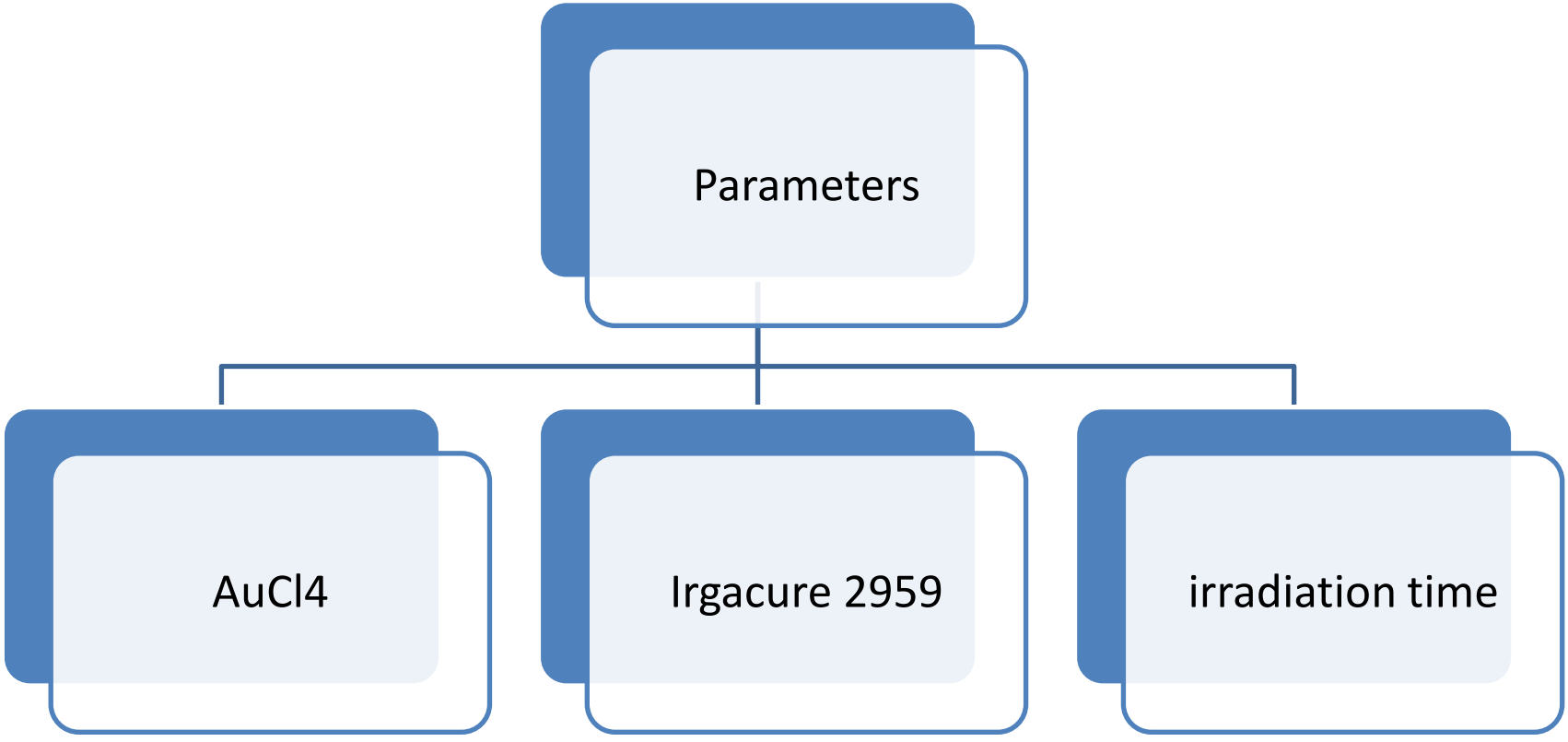
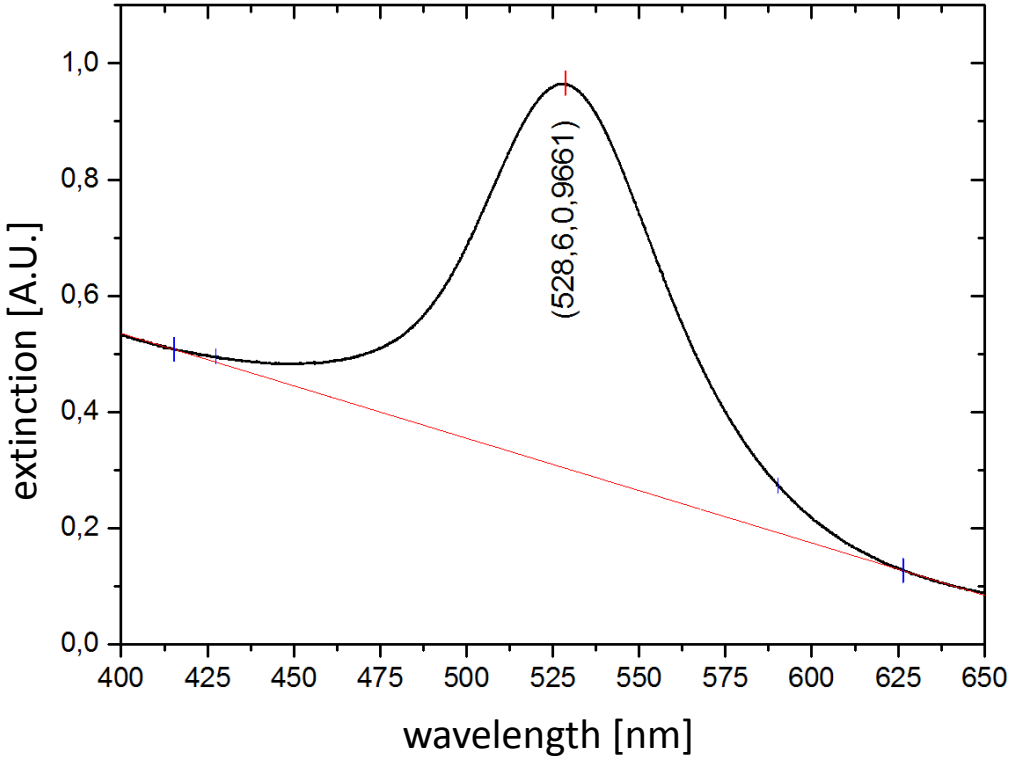
# parameters



- UV-VIS spectra
  - peak height [A.U.] = particle amount
  - wavelength [nm] = size
  - full width half maximum (FWHM) [nm] = size distribution



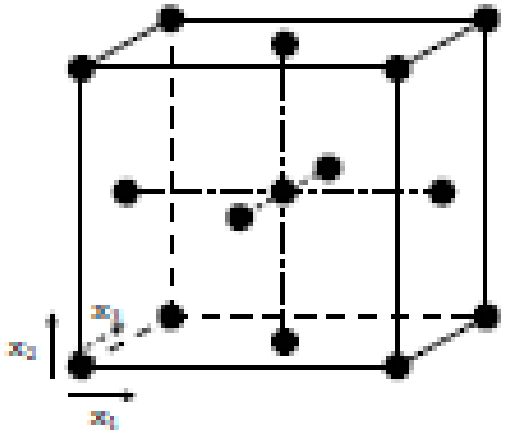
procedure

- perform first experiments to get an idea for the:
  - input factors
    - controllable
    - non controllable: collect every possible measured values!
  - output factors

- design a first design of experiments to:
  - verify the factors and factor levels
  - get a first idea of the system behavior
  - detect regions in design space with failed designs

- second design of experiment with the aim:
  - move design space to regions without failed designs
  - to verify model of the system
  - to increase dataset in the volume of interest

- Central-Composite-Design
  - method of choice for discrete input parameters with 2-3 factor levels
  - easy to extend
  - robust against failed designs
  - information concentrates to the boundary of n-dimensional hypercube
  - linear and  quadratic approximation functions useable
  - no random experiments



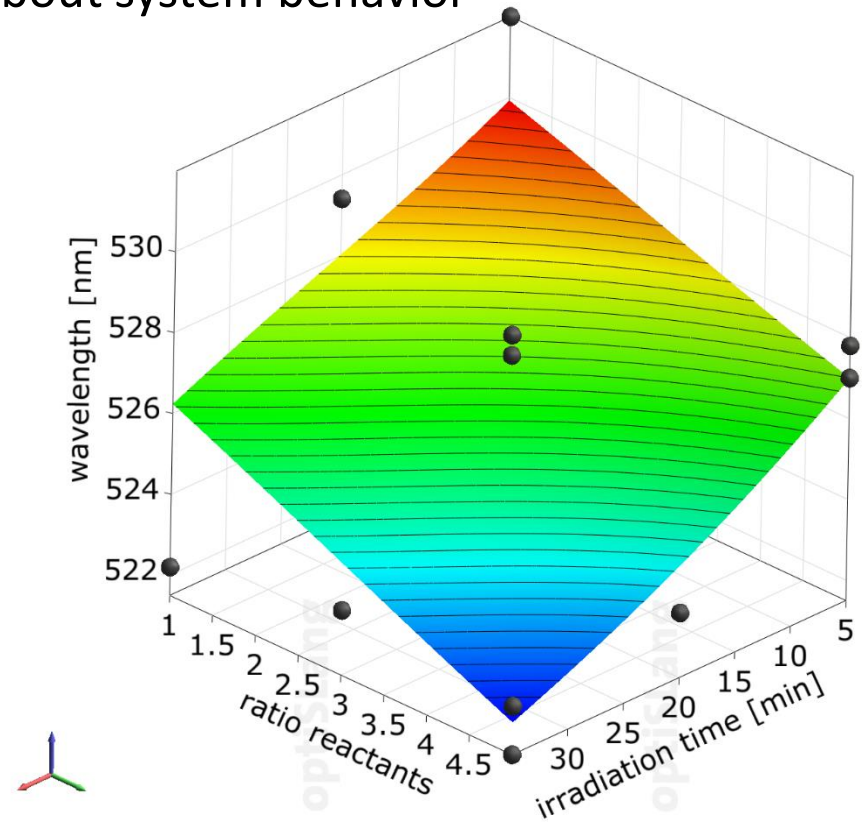
Central- Composite- DoE scheme

optiSLang Documentation

# preoptimized system



- 3 ary Central Composite Design with 15 experiments (13 succeeded)
  - gives a hint about system behavior

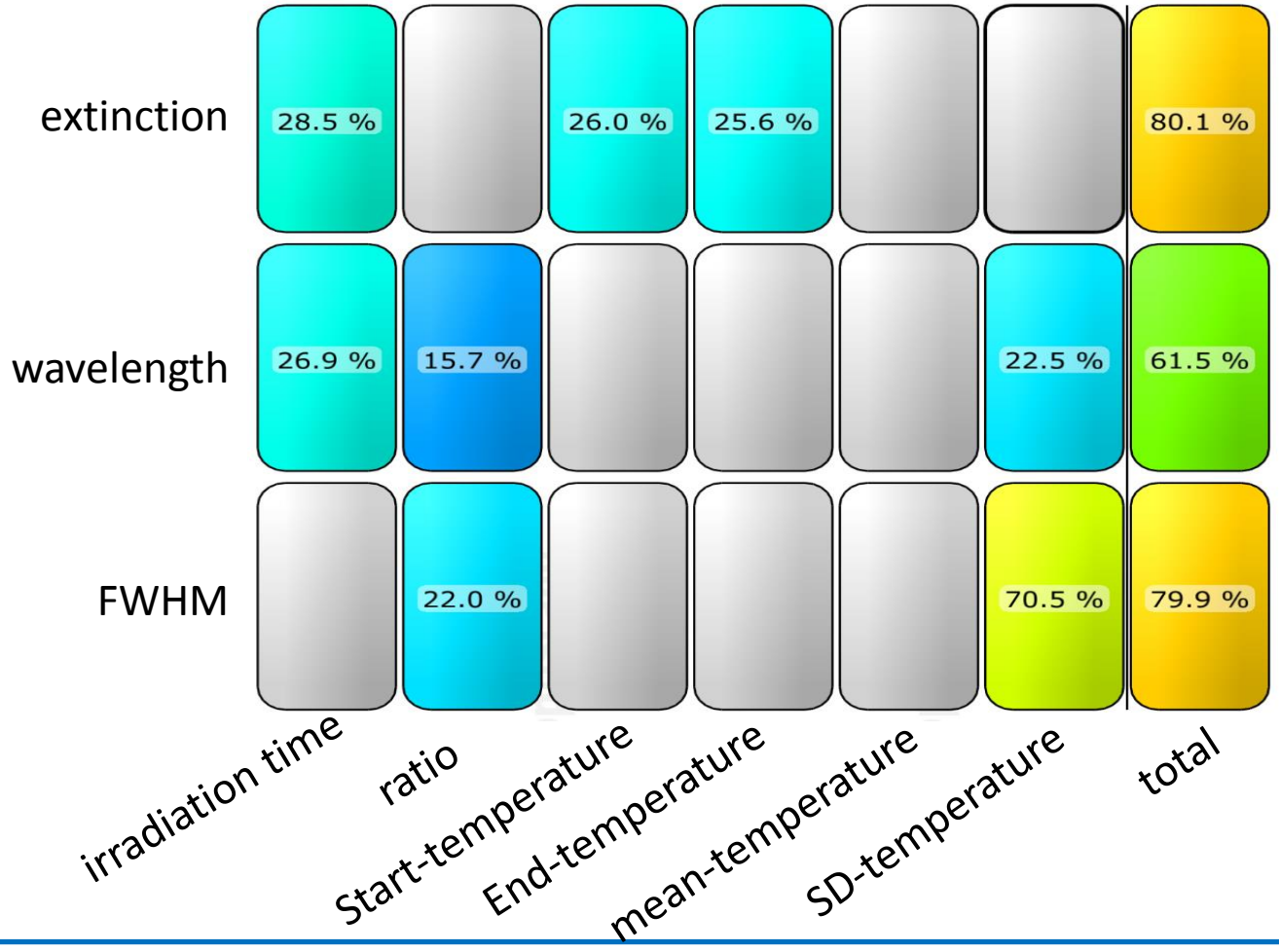



Visualization of dependency between NP-size and input parameters (CoP ≈ 60 %)

# preoptimized system II



- temperature dependency's difficult to interpret

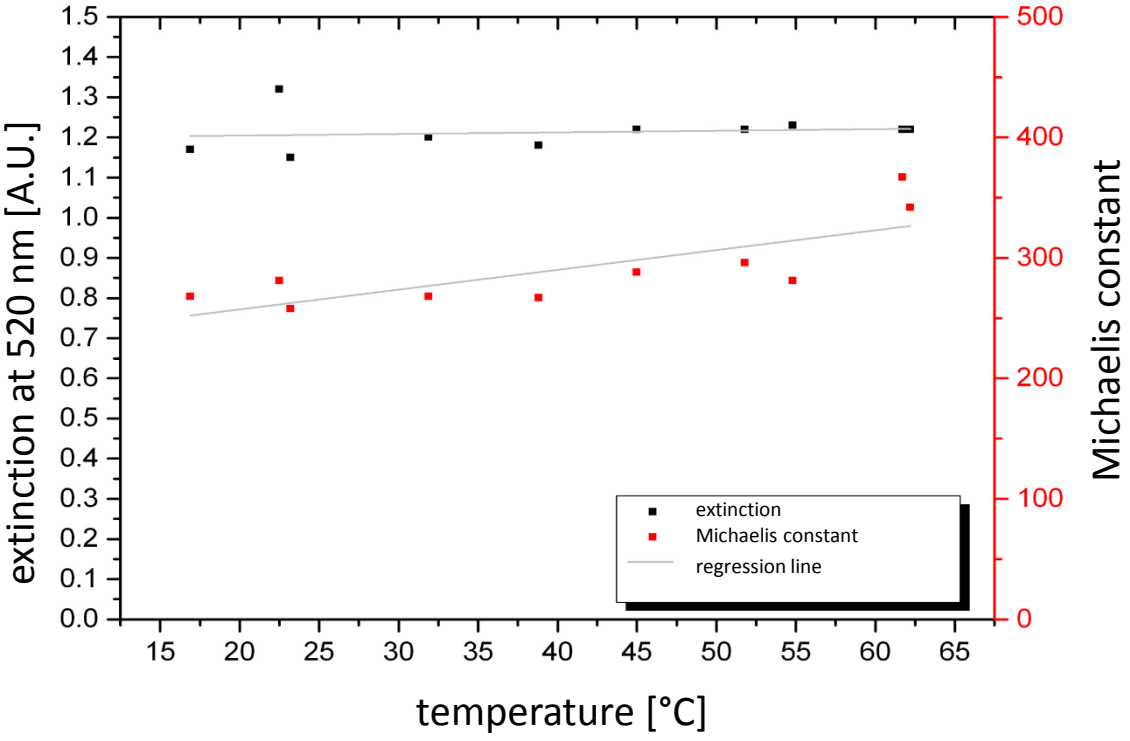



CoP- matrix for DoE I

# temperature dependency



- test reactions are a result of better system understanding
- synthesis yield independent from temperature
- reaction kinetics increases with temperature
  - contradictory to chemical reaction kinetics



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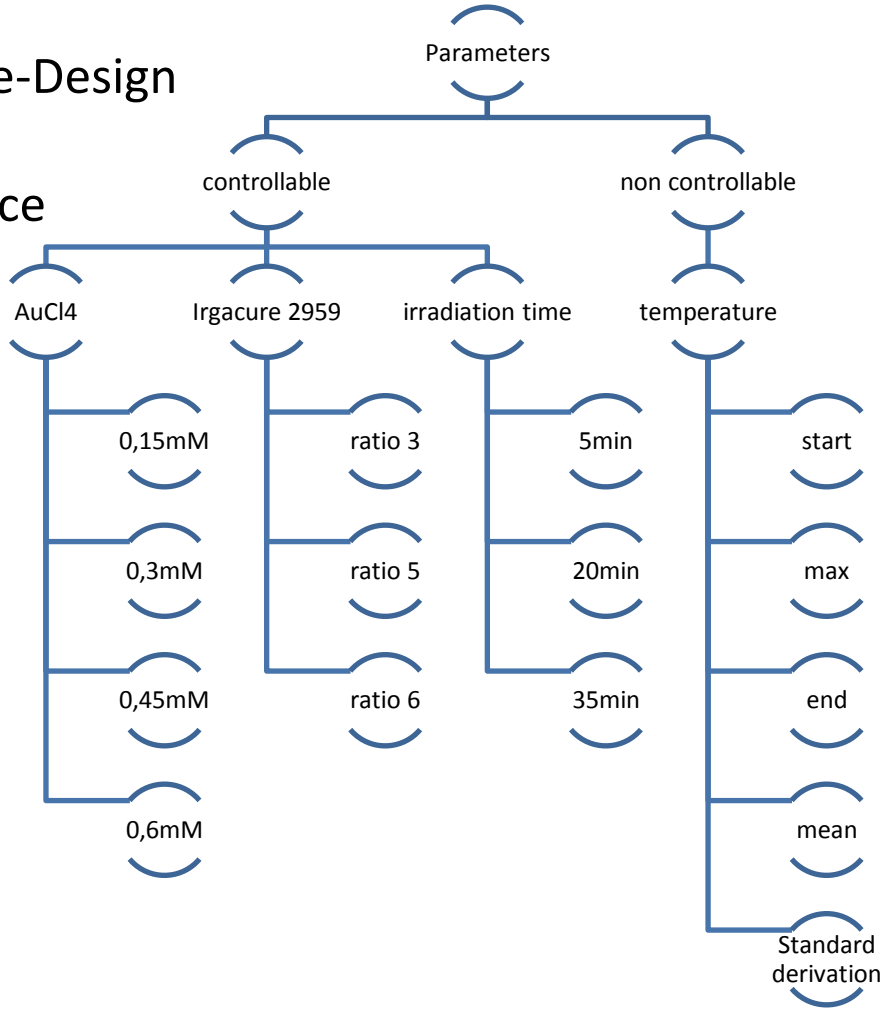
# Design of Experiment II

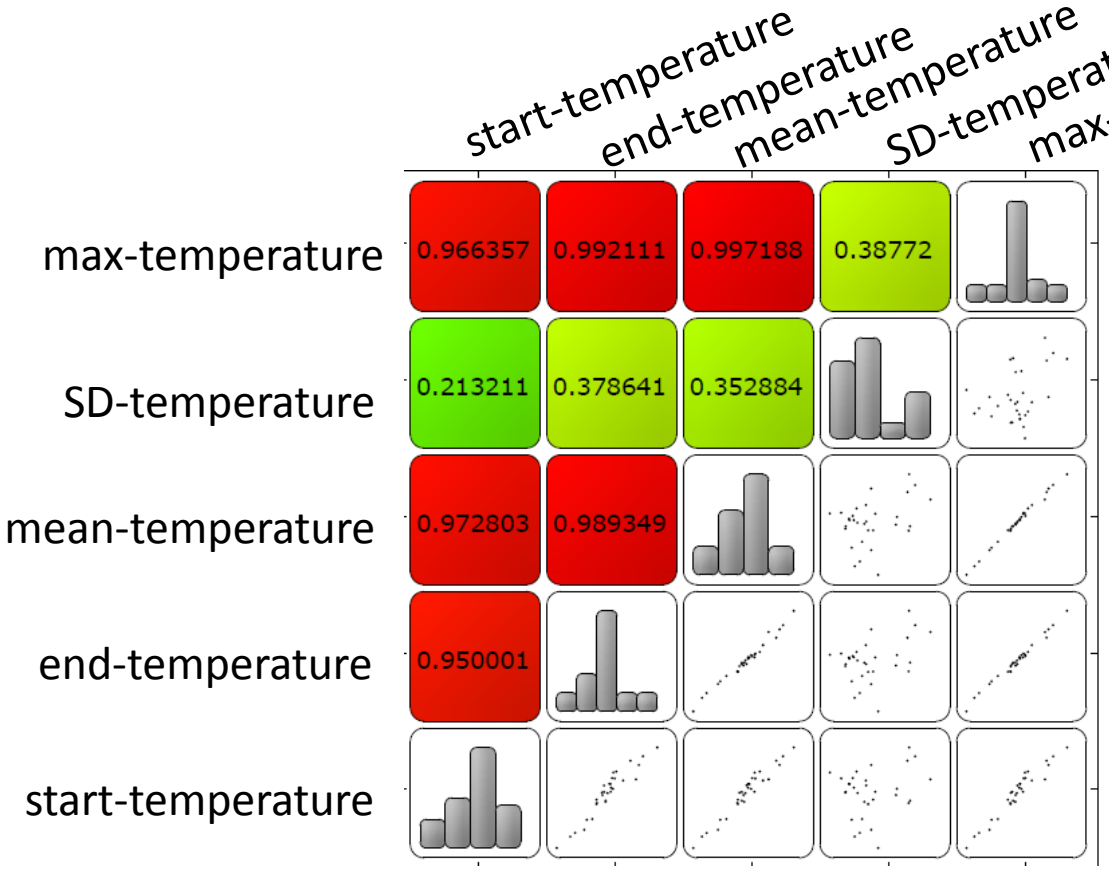


- Central-Composite-Design
- 33 experiments
- moved design space




input parameters with levels

Should more than one of the temperature parameters be used?




Correlation matrix for temperature input parameter

No, input-correlation between these parameters are to high

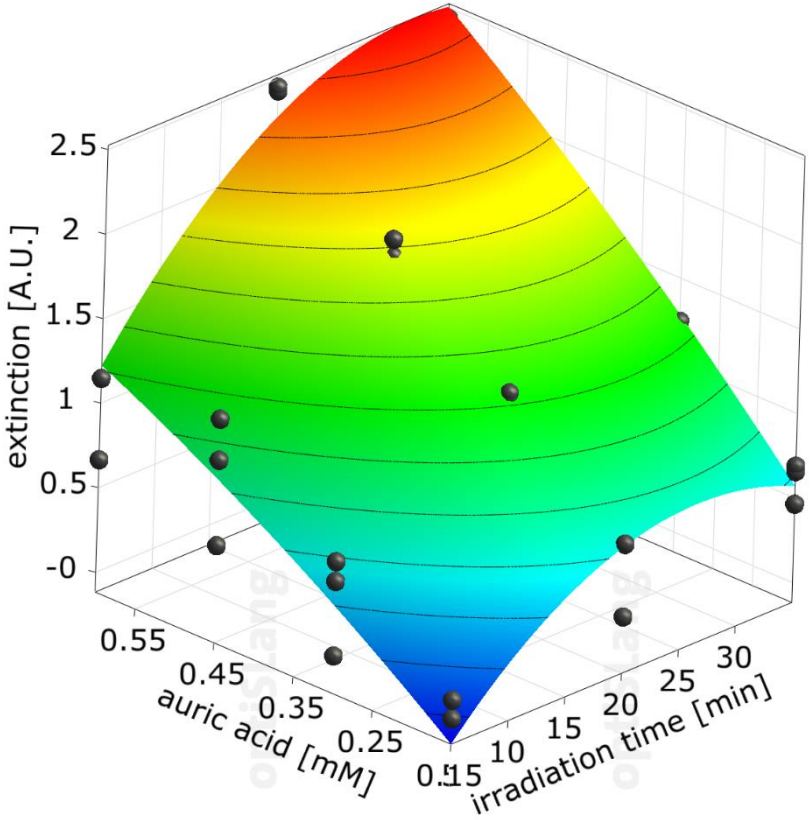
- Meta-Model-of-optimal Prognosis
  - Which input parameter should be used?

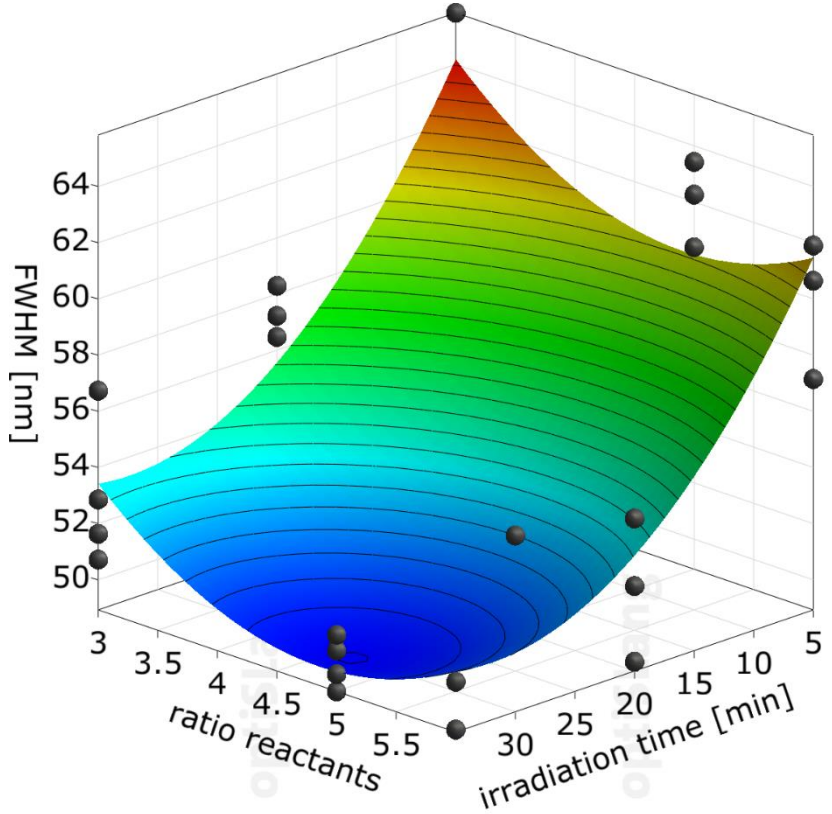
| temperature parameter | Wavelength [nm] particle size | Full Width Half Maximum [nm] Size distribution | Extinction [A.U.] Particle amount |
|---|---|---|---|
| none | 83,0 | 87,9 | 94,8 |
| all | 73,1 | 72,5 | 92,8 |
| start | 78,9 | 88,3 | 93,6 |
| max | 80,2 | 88,2 | 93,7 |
| end | 79,4 | 87,0 | 92,6 |
| mean | 80,2 | 88,2 | 93,7 |
| standard derivation | 79,6 | 81,0 | 94,5 |

COP- values in dependence of different temperature input parameter

# meta modelling

- meta models with high quality can be generated
- behavior of system can be read out of the approximations



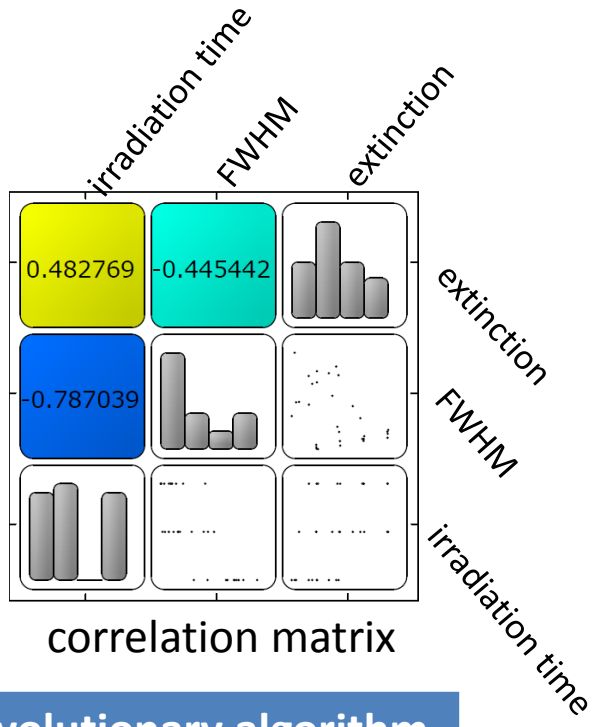



# optimization process

objectives

- size distribution -> min
- particle amount -> max
- irradiation time -> min

- different optimization algorithms possible
  - huge differences in computational effort




correlation matrix

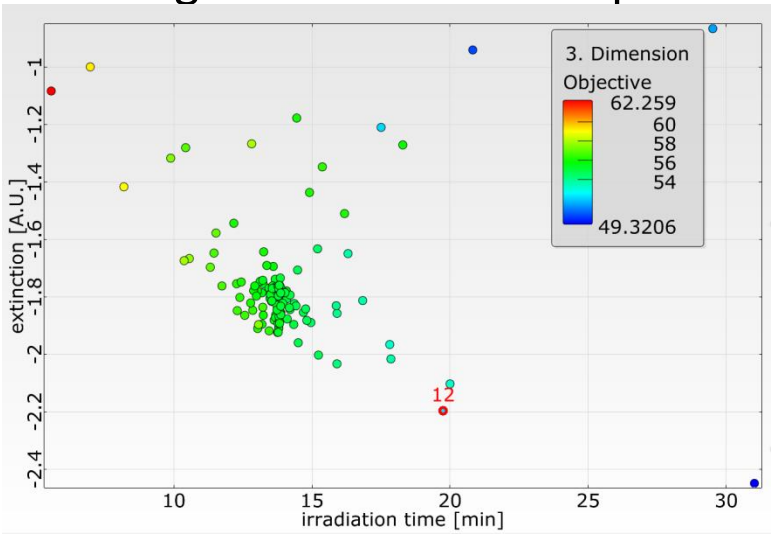
| | Particle swarm optimization | evolutionary algorithm |
|---|---|---|
| population size: | 10 | 1000 |
| Minimum generations: | 5 | 5 |
| Maximum generations: | 20 | 90 |

comparison parameter for optimization algorithms

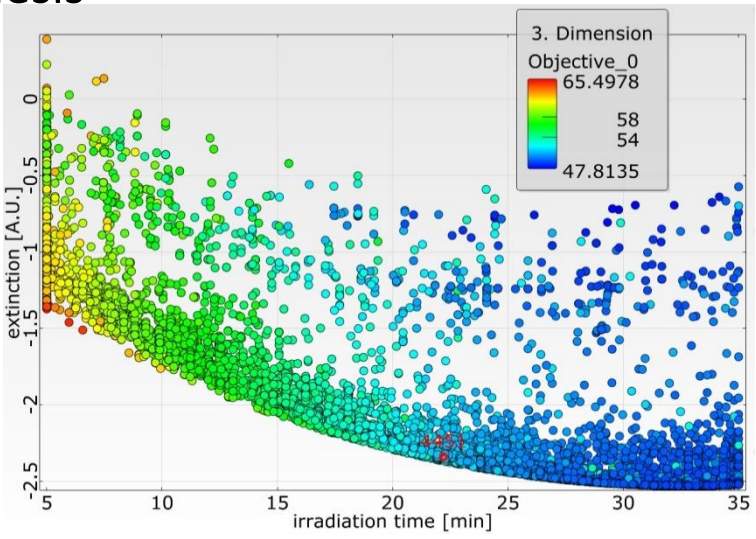
# evaluation of optimal synthesis



- evolutionary algorithm needs more data points
  - slight differences in “optimal” synthesis




Pareto-front PSO-algorithm

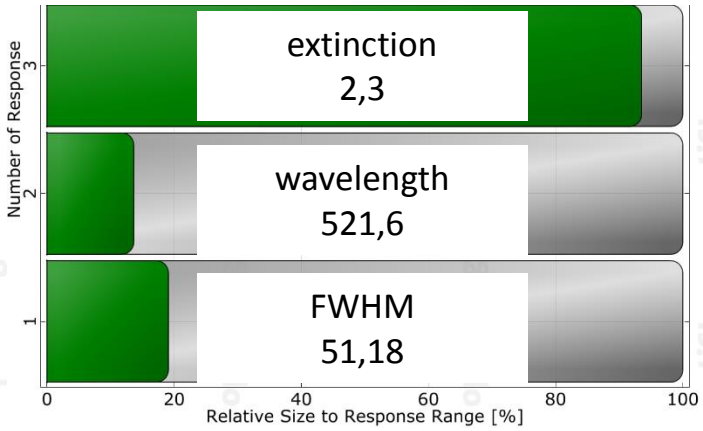



Pareto-Front EA-algorithm

| | Particle swarm optimization | evolutionary algorithm |
|---|---|---|
| irradiation time [min] | 19 | 22 |
| Concentration Auric acid [mM] | 0,58 | 0,6 |
| ratio auric acid and photoinitiator | 4,3 | 4,8 |

# evaluation of optimal synthesis

- evaluation shows stable system
- acceptable deviations to prediction
  - except of wavelength /size




Parameter bounds for EA-algorithm

| | | Particle swarm optimization | | evolutionary algorithm | |
|---|---|---|---|---|---|
| | | prediction | evaluation | prediction | evaluation |
| Extinction [A. U.] | particle amount | 2,2 | 2,3 | 2,8 | 2,53 ± 0,12 |
| wavelength [nm] | Size | 522,3 | 521,1 ± 0,38 | 523 | 521,6 ± 0,26 |
| Full Width Half Maximum [nm] | size distribution | 52,3 | 53,1 ± 0,12 | 53 | 53,57 ± 0,12 |

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# experiments: summary and particularities

procedure for experimental data

- perform first experiments to get an idea for the:
  - input factors
    - controllable
    - non controllable: collect every possible measured values!
  - output factors

- design a first design of experiments to:
  - verify the factors and factor levels
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- second design of experiment with the aim:
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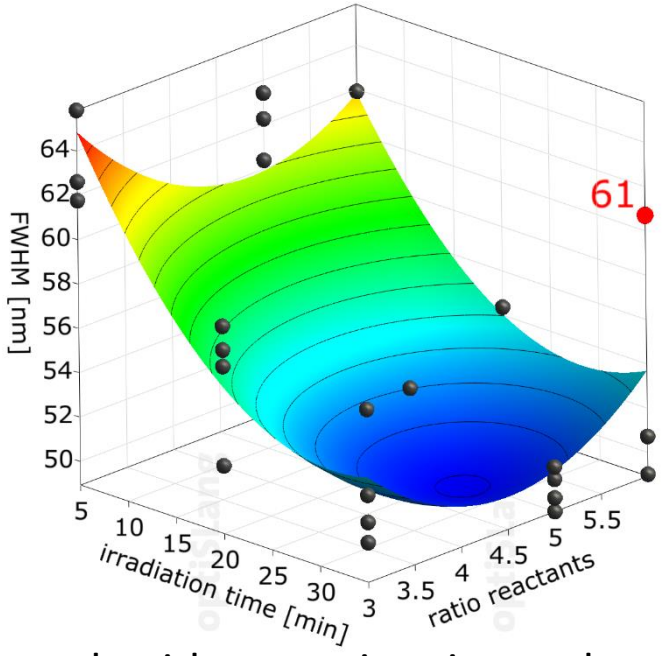
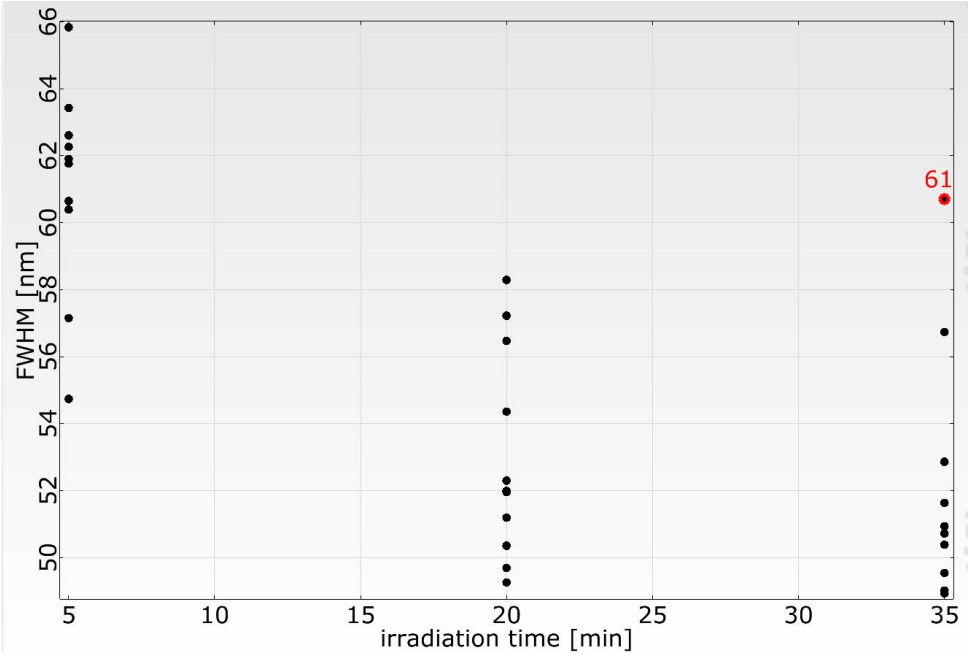
# outlier detection

- outlier detection: important to maintain quality of optimization
  - MOP- solver to test approximation quality (compare input (experimental) data with prediction of meta-model-of-optimal-prognosis)
  - compare anthill plots or 3D approximation plots




3D- graph with approximation and marked outlier




Anthill plot with marked outlier

# outlook

- Transfer synthesis into an microfluidic set-up
- Improve prediction of nanoparticle size

# Acknowledgements



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