Sizing with on-line Methods

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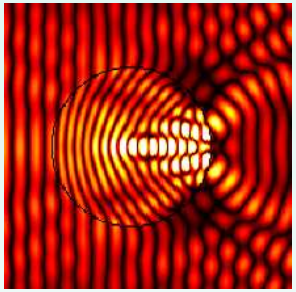
On-line analysis of particle size and concentration of gypsum slurry by ultrasonic extinction

SYMPATEC

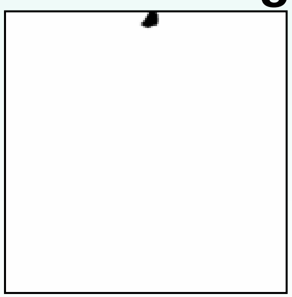
Measuring Methods

Laser Diffraction (LD)



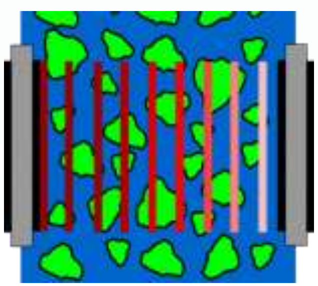
- ✓ absolute method
- ✓ wide size range:
  ~ 0.1 µm – 10 mm
- ✓ highest reproducibility

Dynamic Image Analysis (DIA)



- ✓ absolute method
- ✓ wide size range:
  ~ 1 µm – 20 mm
- ✓ shape information

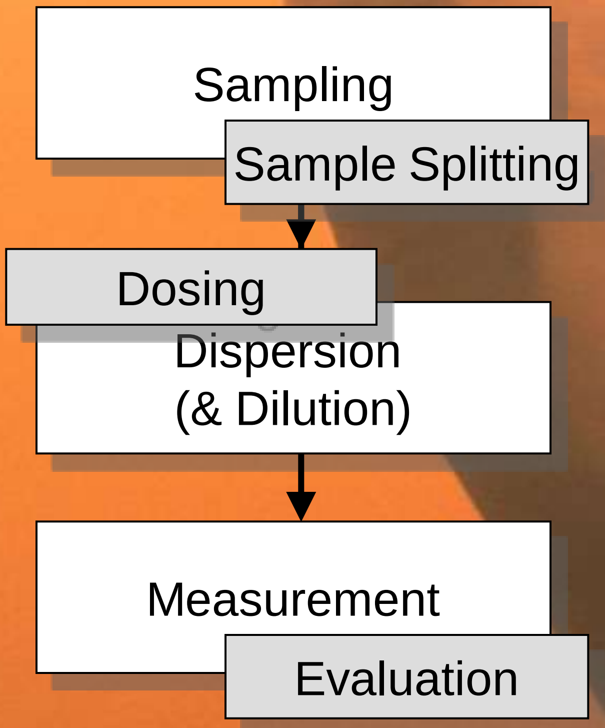
Ultrasonic Extinction (UE)



- ✓ wide size range:
  ~ 100 nm – 3 mm
- ✓ very robust method
- ✓ no dilution necessary

Introduction

Particle characterization
usually comprises 3 steps



<u>Contributions of Errors</u>

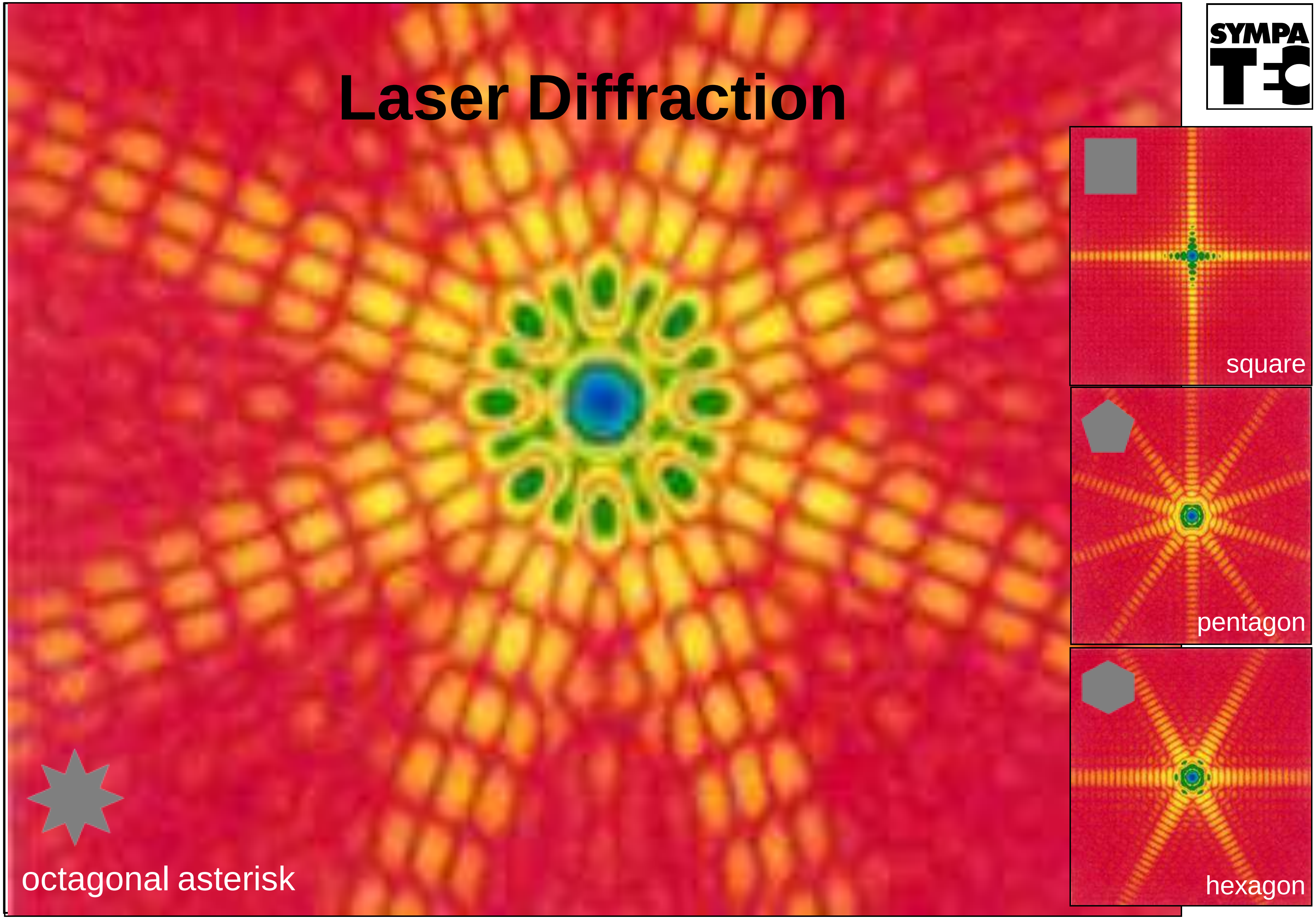
often *dominating*
(σ ~ 10 – 50 %)

large
(σ ~ 5 – 20 %)

very *small*

σ < 0.1%	laser diffraction
σ < 1%	dynamic image analysis
σ < 3%	ultrasonic extinction

Laser Diffraction



Combined System MYTOS & TWISTER

Advantages

- ✓ the partial flow remains inside the process pipe → *inner pressure does not influence* the sampling
- ✓ space saving 90° elbows are avoided → *reduced ware*
- ✓ no moving gaskets → bellows enable *use in hazardous areas*
- ✓ small moving masses → *small drive unit*
- ✓ all parts in contact with the particles allow for wide mechanical tolerances → *hardened materials* (e.g. ceramic)
- ✓ *adaptation to the mass flow* Φ by the diameter d of the inlet cap
- ✓ adaptation to different *diameters of the process pipe* D by the length of the sampling pipe
- ✓ as d is selected smaller than the subsequent stages: ‚*safety sieve*'
- ✓ all parts are at the same temperature → *no problems with condensation*

Application Types

Definition

- ★ **in-line**
  - ☆ sampling and sensor *integrated in the process pipe*
- ★ **on-line**
  - ☆ sampling in the process pipe, *sensor outside*
- ★ **at-line**
  - ☆ *automated lab application* without sampling
- ★ **off-line**
  - ☆ *manual lab application*

On-line Laser Diffraction with MYTOS & TWISTER

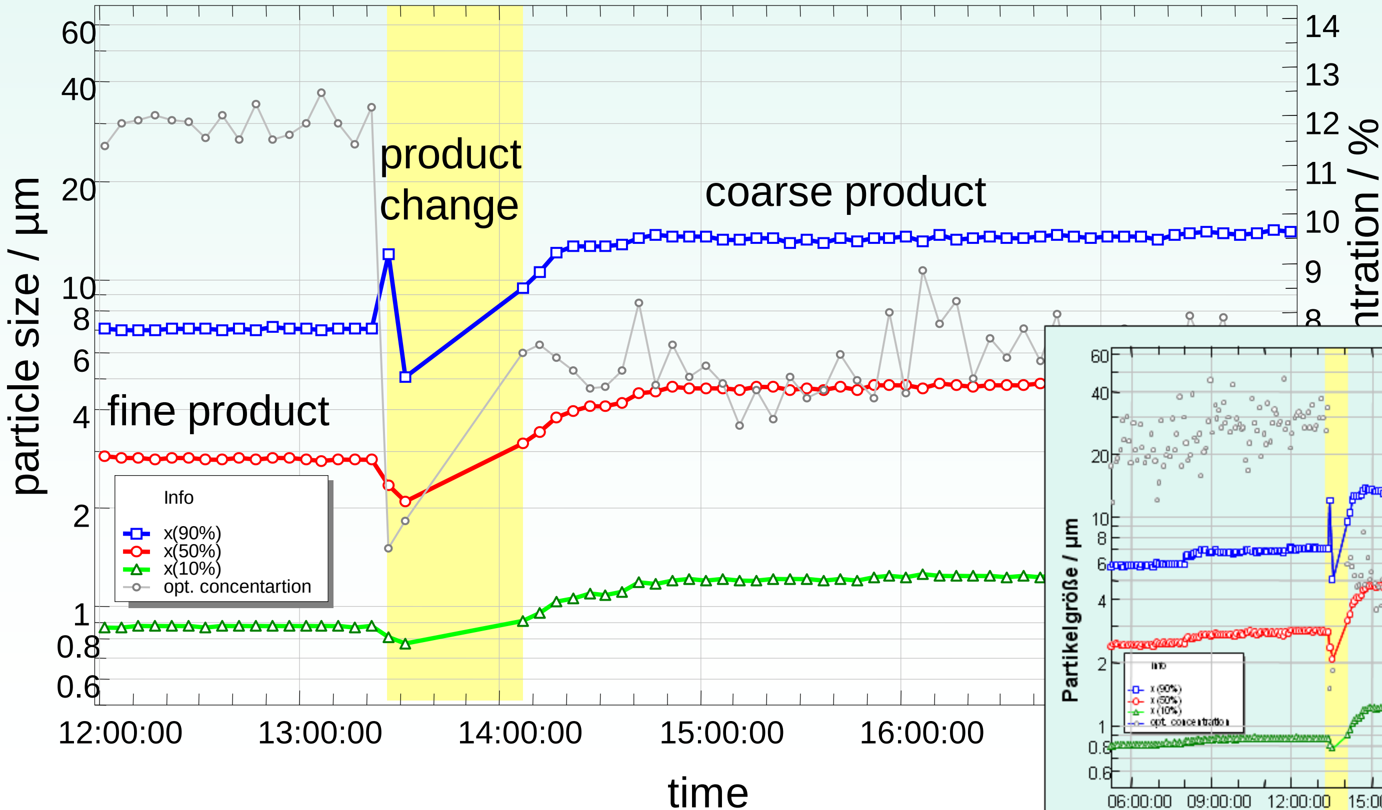
Specifications

- ★ pipe diameter — DN 440 mm
- ★ orientation — horizontally

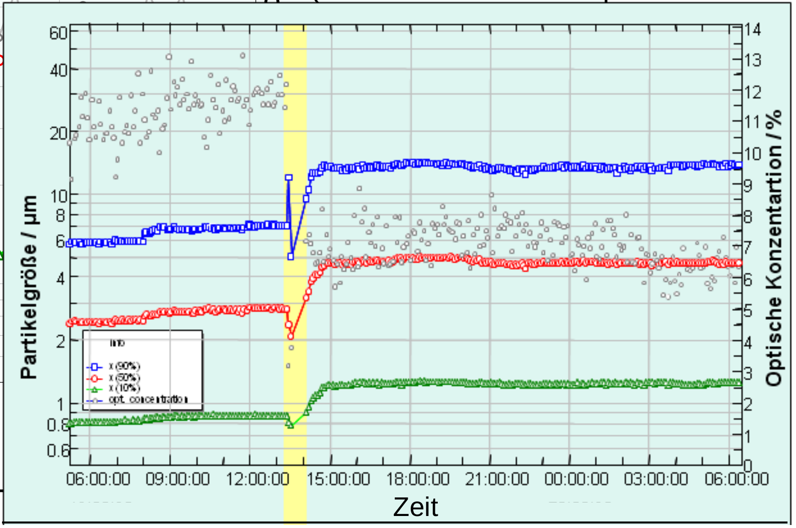
Results (Laser Diffraction)

Measurements in a production of polymer (Ex area)

- ★ measurements are possible with *high statistical relevance*
- ★ the change of product is *monitored* and *controlled very well*

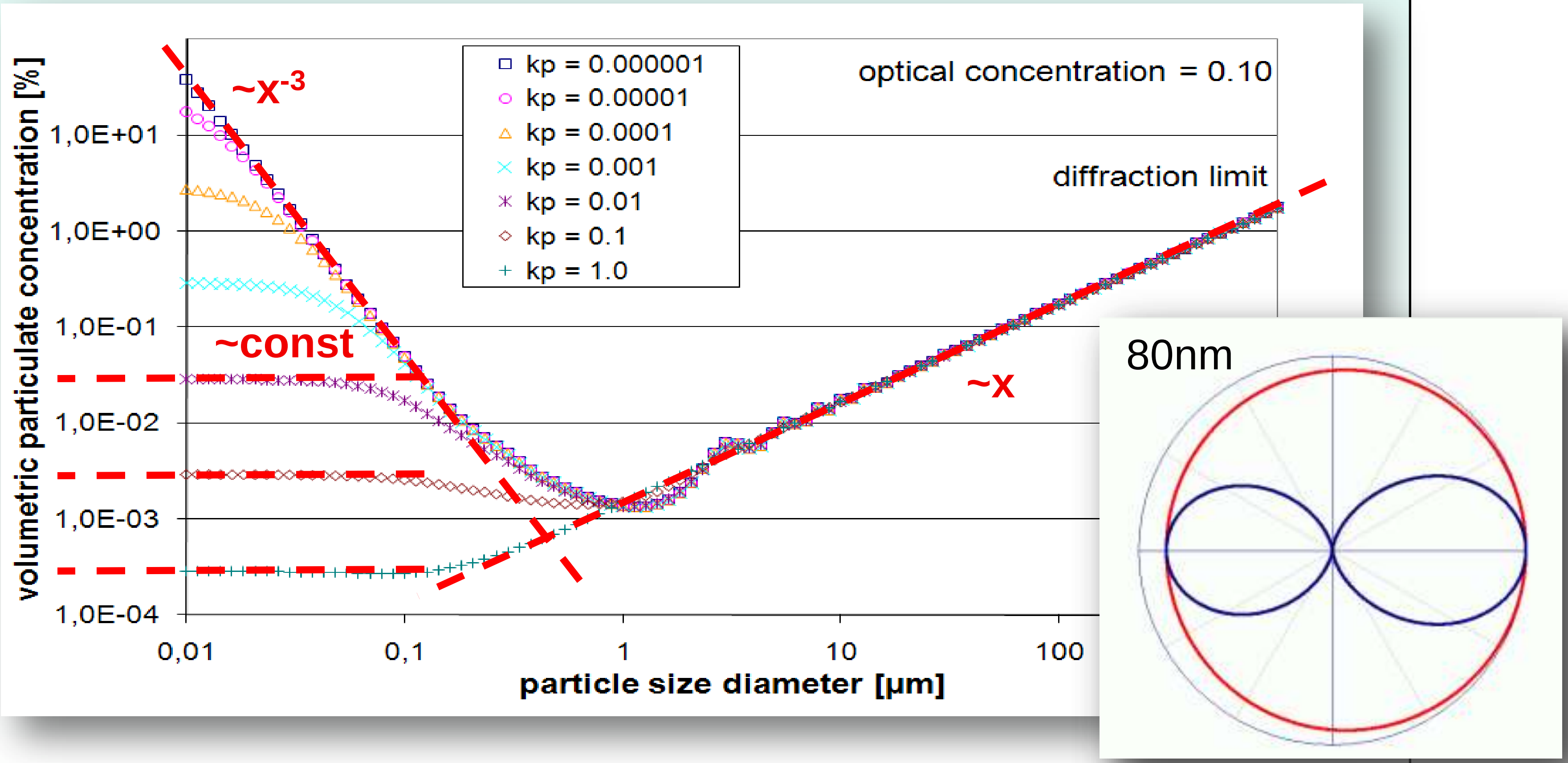


trend over 1 day



Lower Size Limit of Laser Diffraction?

Calculation of volume concentration by Mie-Theory



For x < 1µm strong dependency on optical parameters!

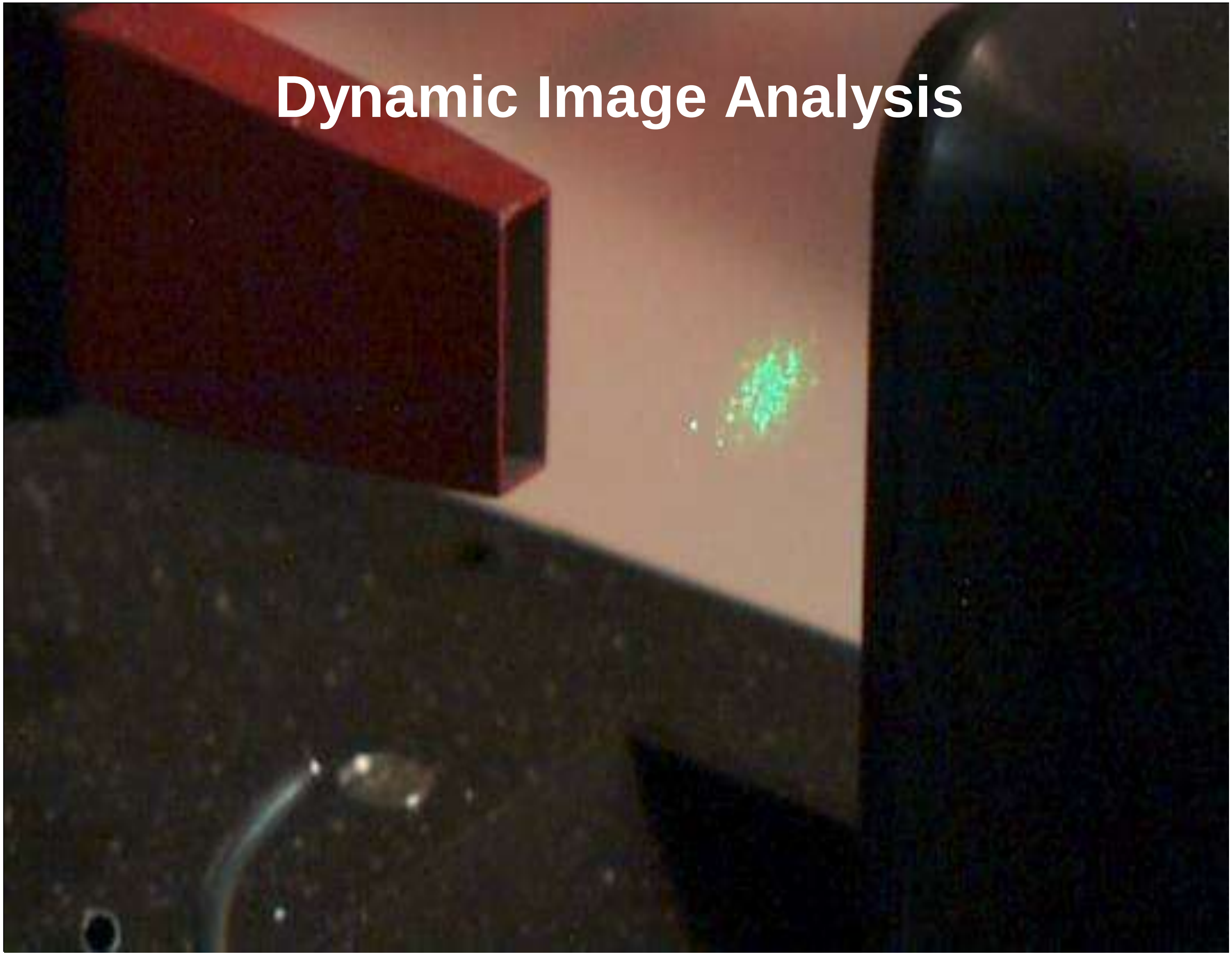
Conclusions: Laser Diffraction

Laser diffraction is currently the dominating technique in the field of particle size analysis in the process environment

- ✓ *absolute method*, free of parameters in case of Fraunhofer approximation
- ✓ wide size range (0.1 µm up to > 8 mm)
- ✓ *arbitrary PSD functions*
- ✓ applicable for *dry, wet dispersion* and sprays
- ✓ *laboratory* and *process* environment
- ✓ *high reproducibility* of the results
- ✓ *fast* (up to 2000 PSD/s)
- ✓ well established

Characterization of nano-particles limited to > 100 nm

Dynamic Image Analysis

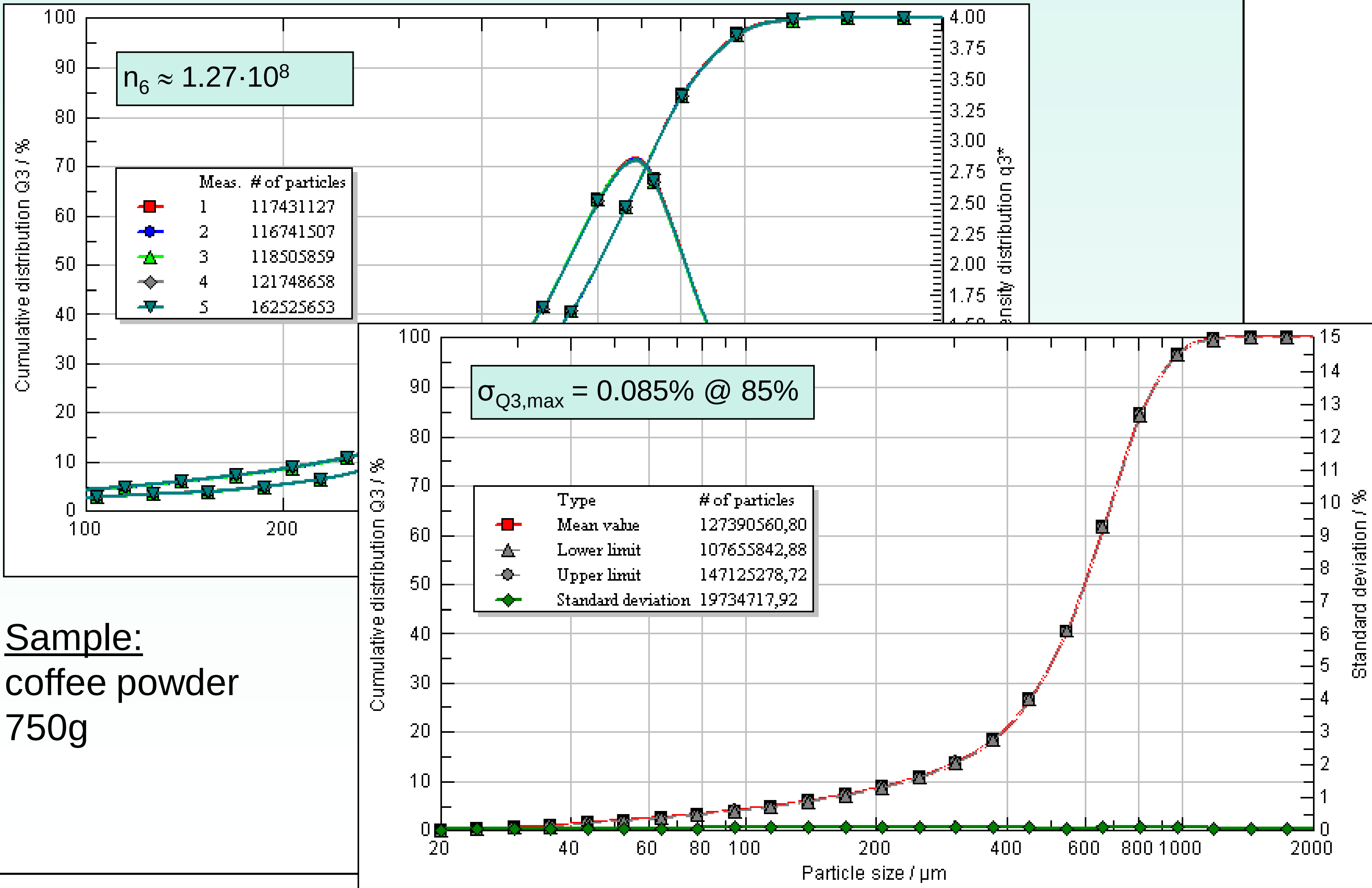


High Speed Image Analysis

Measurements with QICPIC and dry disperser RODOS/L

1. *introduction* of the sample in the hopper of the feeder
2. *constant feed* into the hopper of the dry disperser
3. *image capture* at the dispersed aerosol beam with 500 1ns flashes per second
4. *presentation* of the particle images

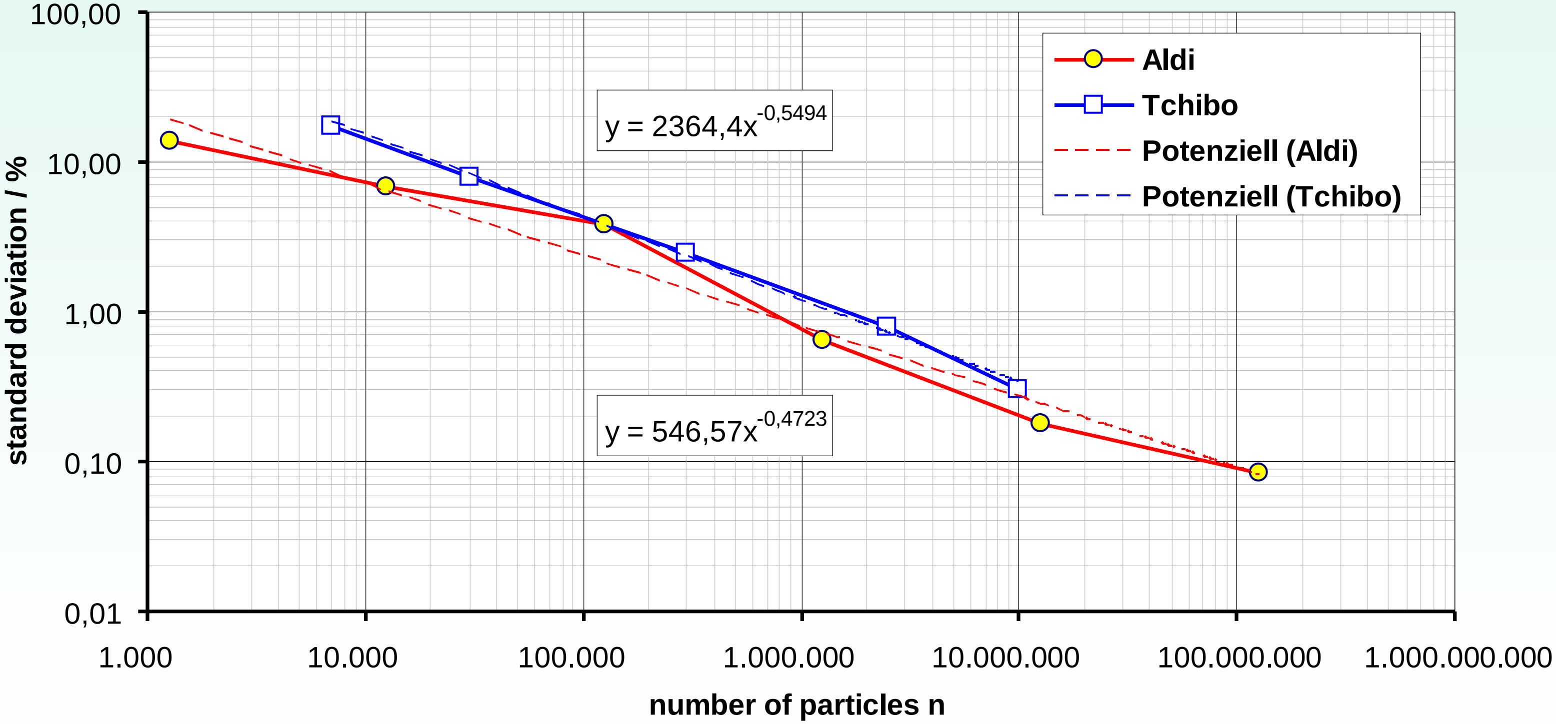
Other Improvements (# of Particles)



Sample:
coffee powder
750g

Result

Comparison of the *experimentally* evaluated standard deviations σ_{Q3} for different coffee brands vs. number of particles



$\sigma_{Q3,max} \sim 1/\sqrt{n}$

n > 1.000.000 particles necessary for $\sigma_{Q3,max} \leq 1\%$

Particle Gallery of Coffee Powder

Selection of individual shape information via filter conditions

- ★ *60 flocks* are found in **2,464,034 particles** with 1000 µm < x < 3000 µm and aspect ratio of < 0.4
- ★ *back-traceability* to the original image

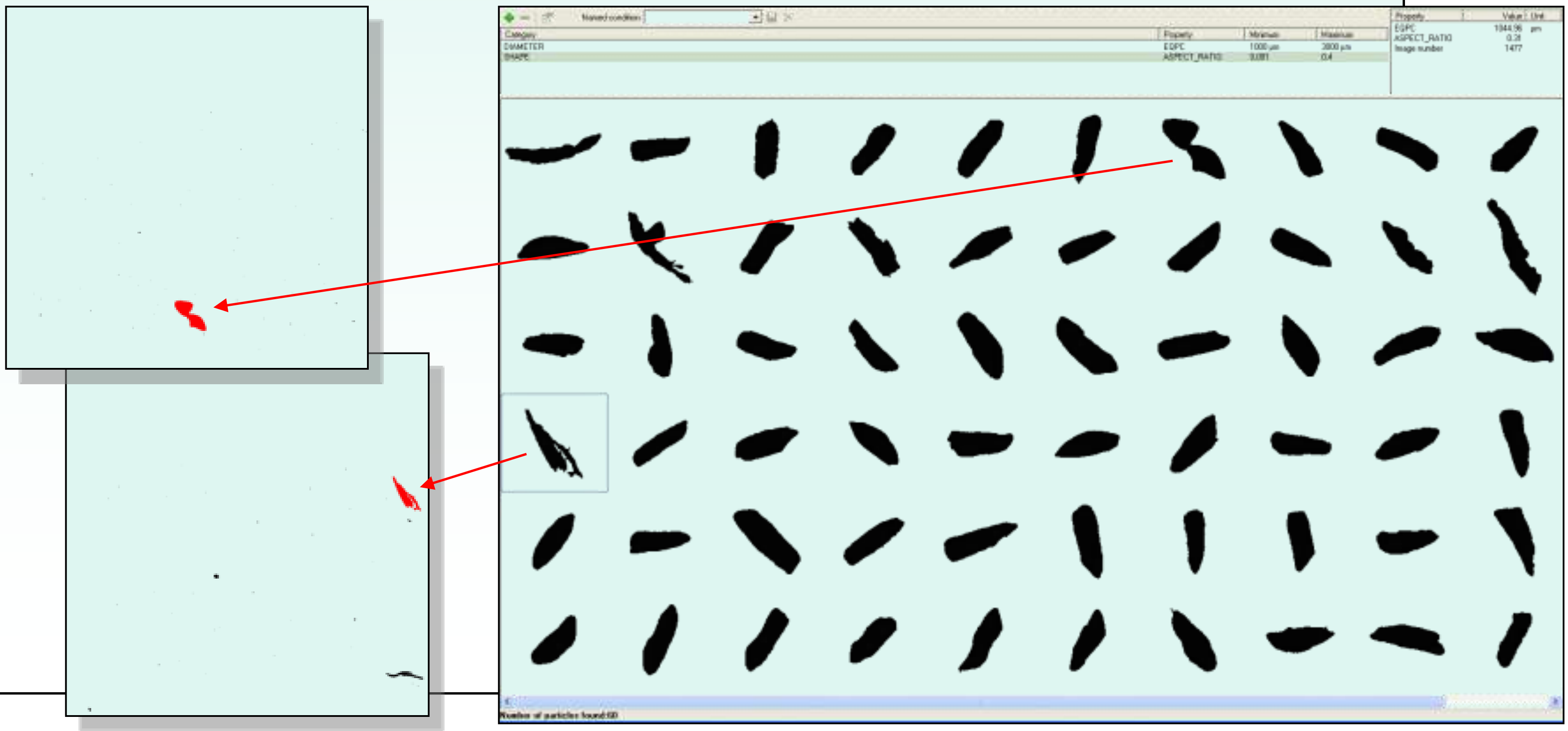
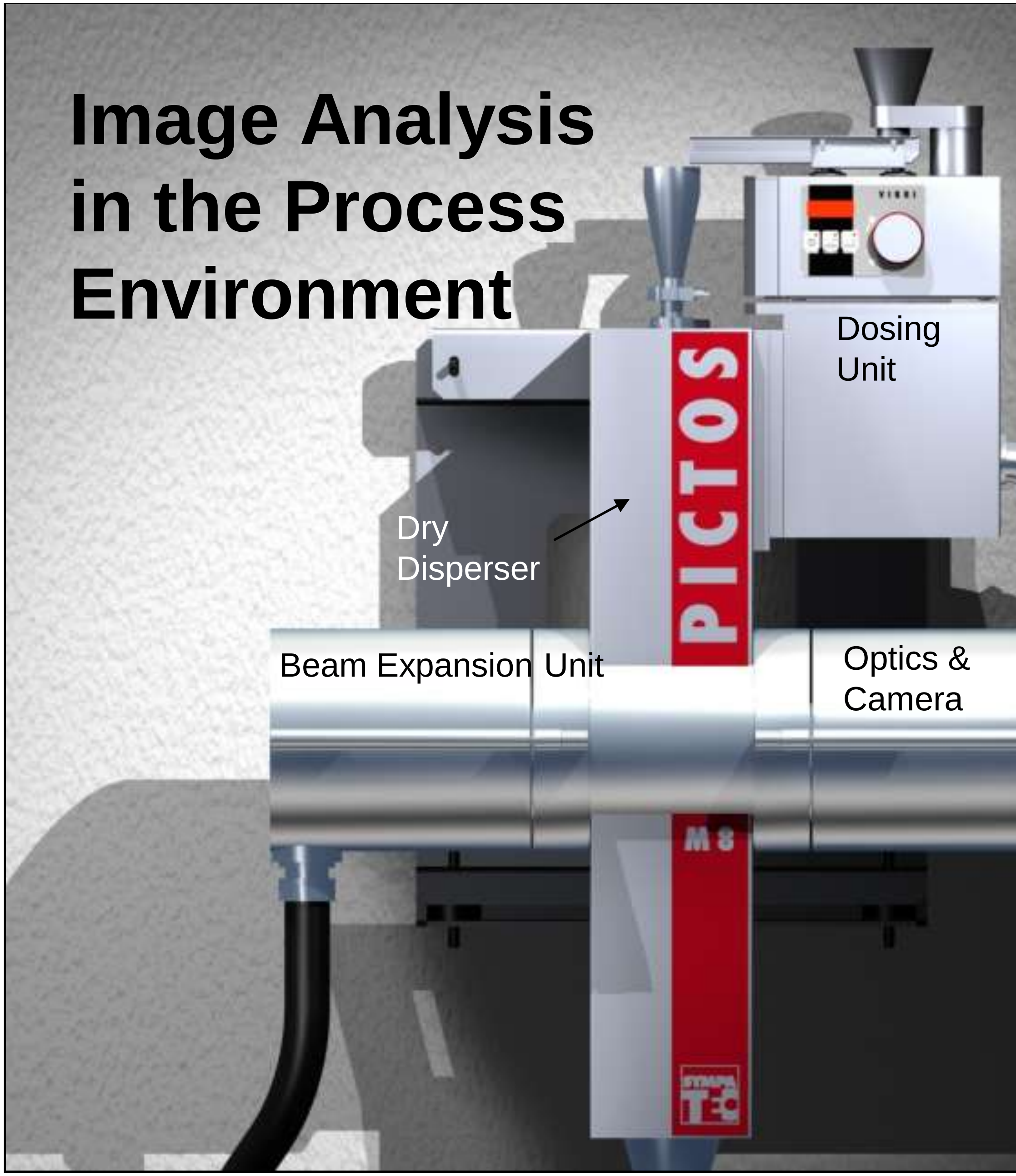
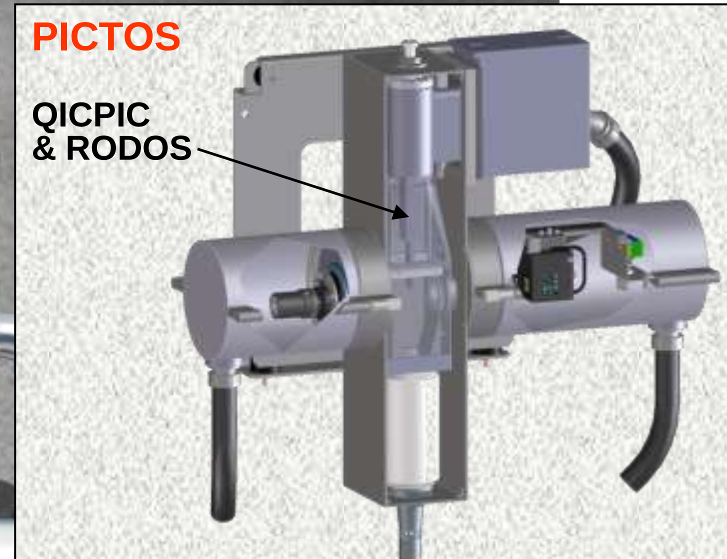
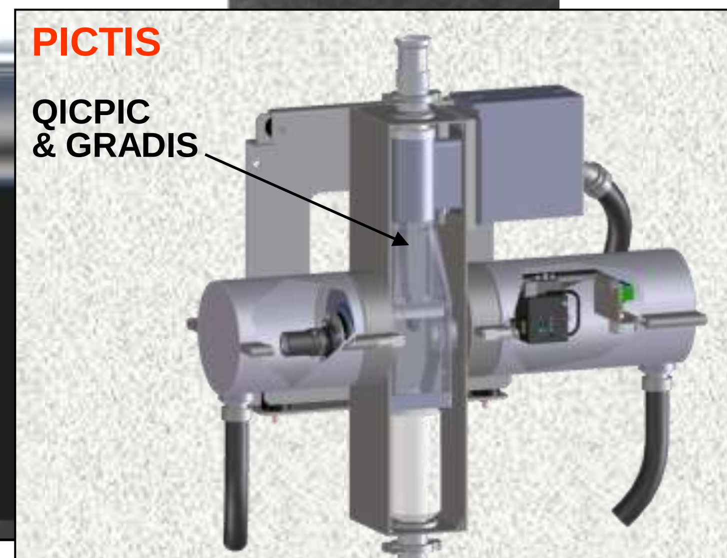


Image Analysis in the Process Environment

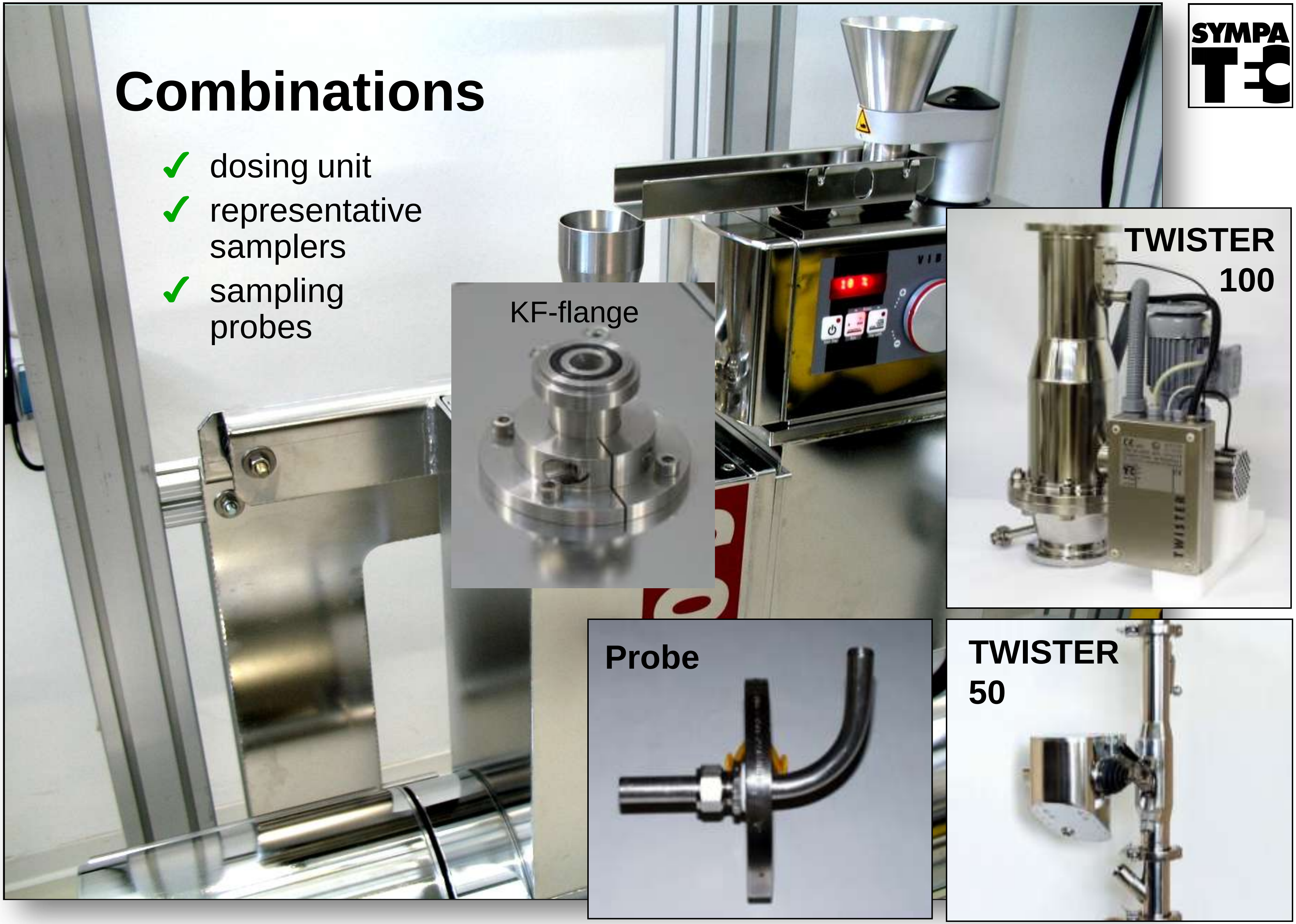






Combinations

- ✓ dosing unit
- ✓ representative samplers
- ✓ sampling probes



Recently in our Test House ...

On-line
Image Analysis

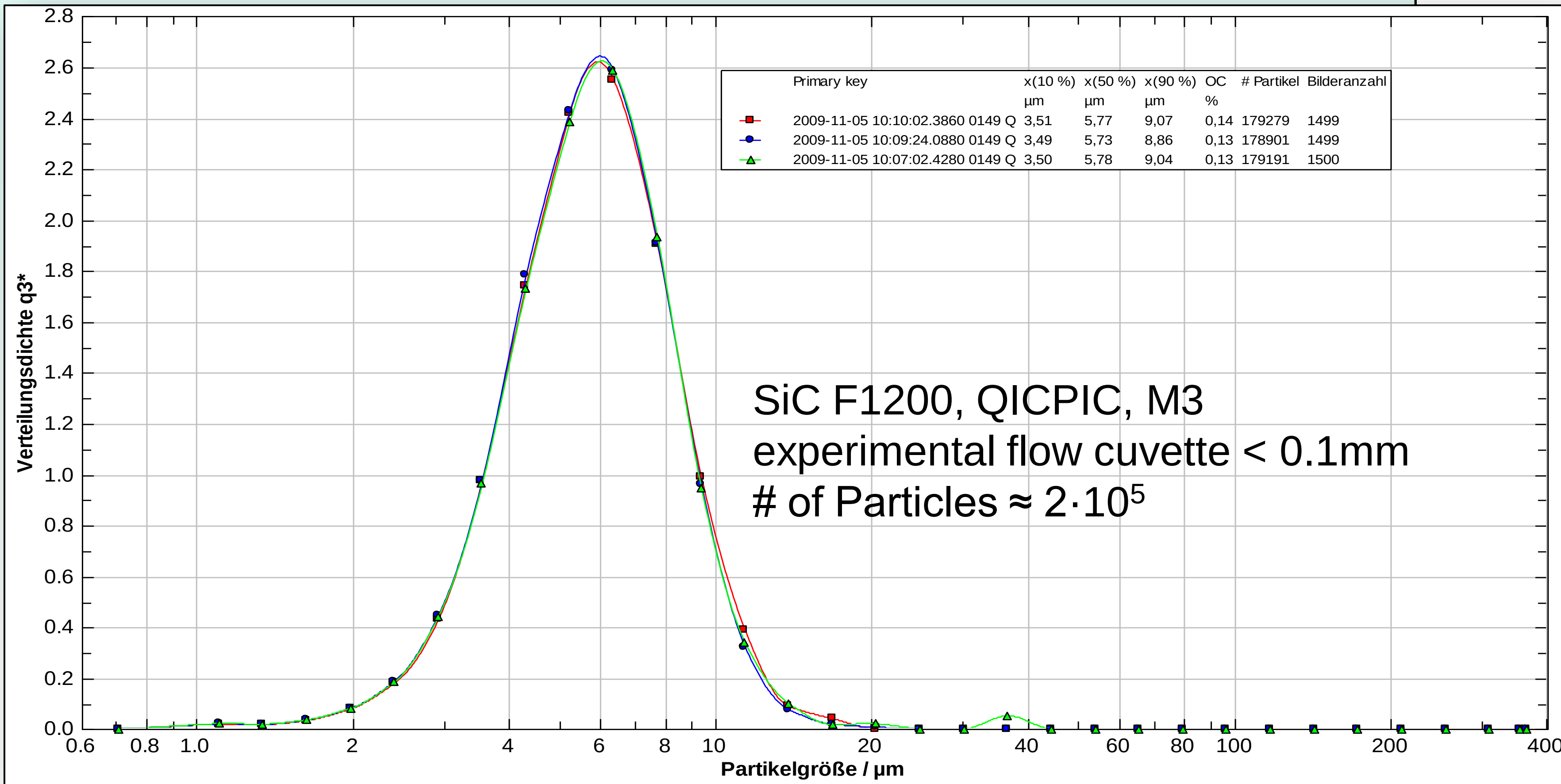
★ 5 TWISTERs in combination with
★ 1 PICTOS

✓ sequential IA for up to 5 production lines

✓ very fast cycle times < 1 minute / line

✓ real time evaluation
- ☆ Pentium-M (measurement)
- ☆ Core-2-duo (control)
- ☆ Core-2-quad (evaluation)
- ☆ 1.5 TByte disk capacity
- ☆ network-wide presentation

Current Limits of DIA



➠ Particle sizing down to ≈1µm is possible

Conclusions: Dynamic Image Analysis

Dynamic Image Analysis is currently the dominating technique for particle size and shape analysis in the process environment

- ✓ *absolute method*, free of parameters
- ✓ *large size range* (≅ 1 µm to above 10 mm)
- ✓ *arbitrary PSD functions*
- ✓ applicable for *dry and wet* dispersions
- ✓ for *laboratory* and *process* environment
- ✓ *good reproducibility* for high particle counts
- ✓ *high resolution*
- ✓ *single particle analysis*
- ✓ *well established*

Characterization of particles limited to > 1000 nm

Ultrasonic Extinction

Ultrasonic Extinction

Particle Wave Interaction:

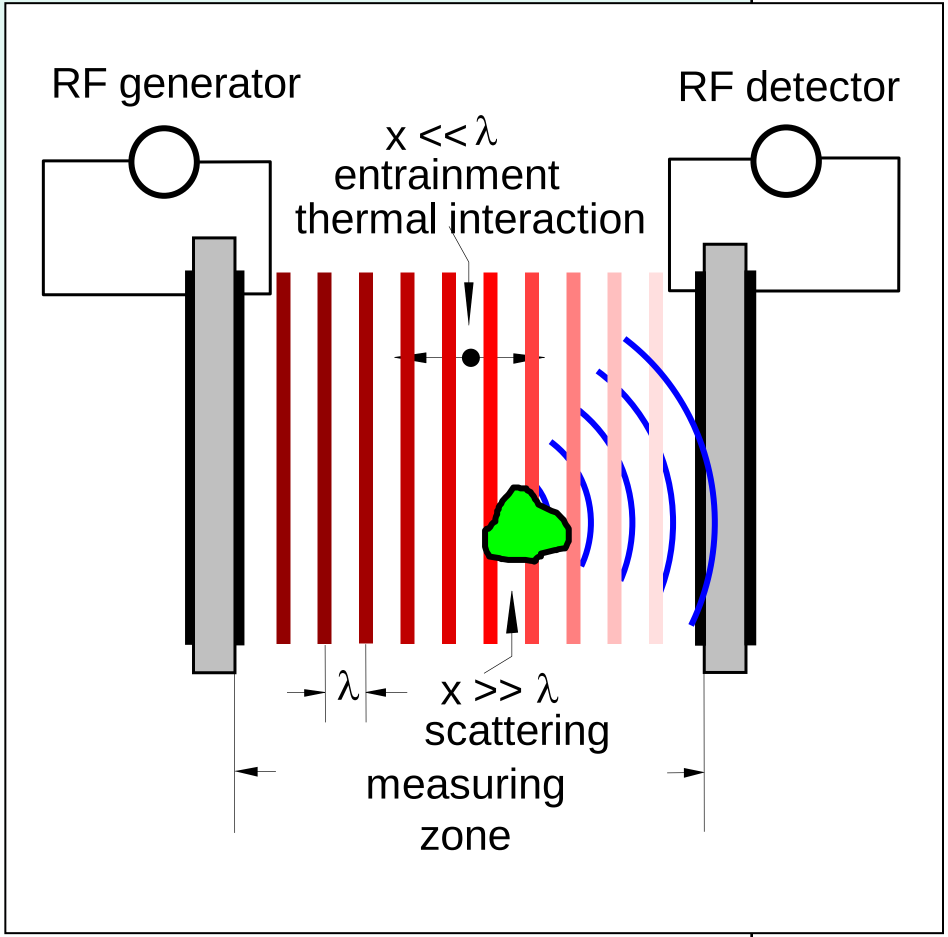
x << λ : *entrainment*
(high density difference)
thermal interactions
(low density difference)

x ≈ λ : *resonances*

x >> λ : *scattering*

The Sympatec Solution:

- ★ wide frequency range *0.1 – 200 MHz*
- ★ dynamic range up to *160 dB*
- ★ an *empirical* solution is used for evaluation in addition to the calculated *extinction function* basing on model calculations

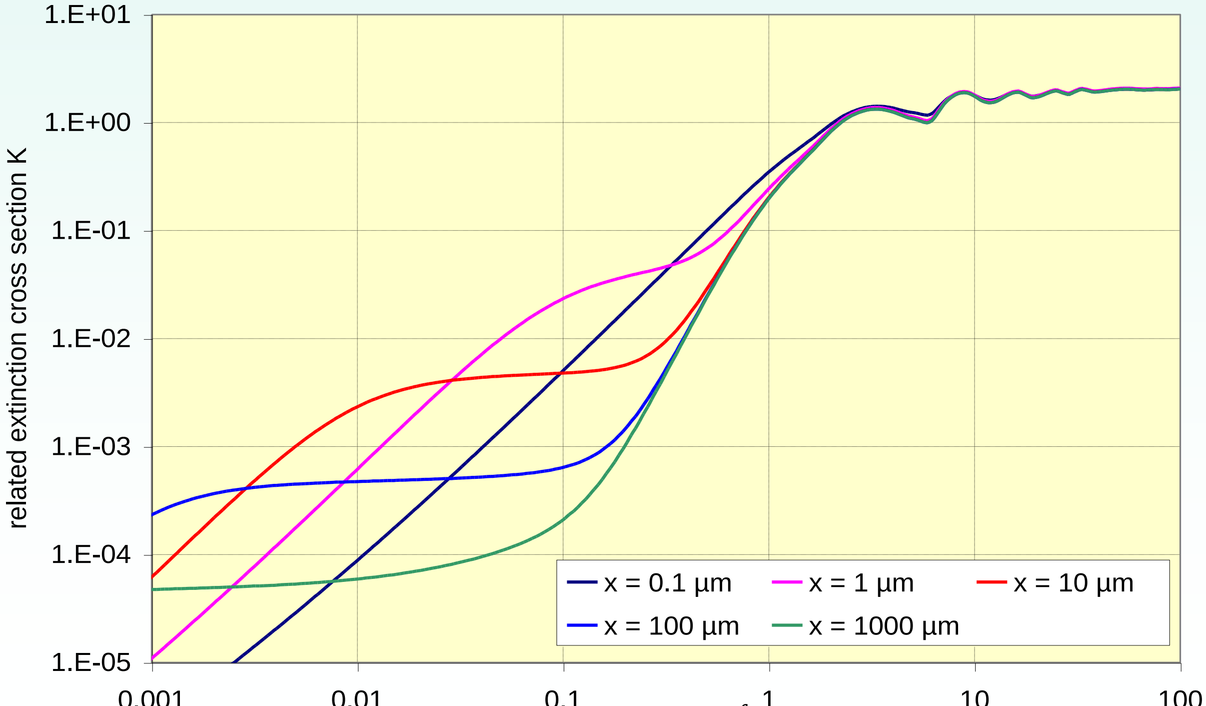


Mathematical Treatment

Law of *Lambert-Beer*, adapted to particle size distributions:

$$-\ln\left(\frac{I}{I_0}\right)_{f_i} = \Delta l \cdot c_{PF} \cdot \int_{x_{\min}}^{x_{\max}} K(f_i, x) \cdot q_2(x)\, dx$$

★ main parameter: related extinction cross section K, material specific

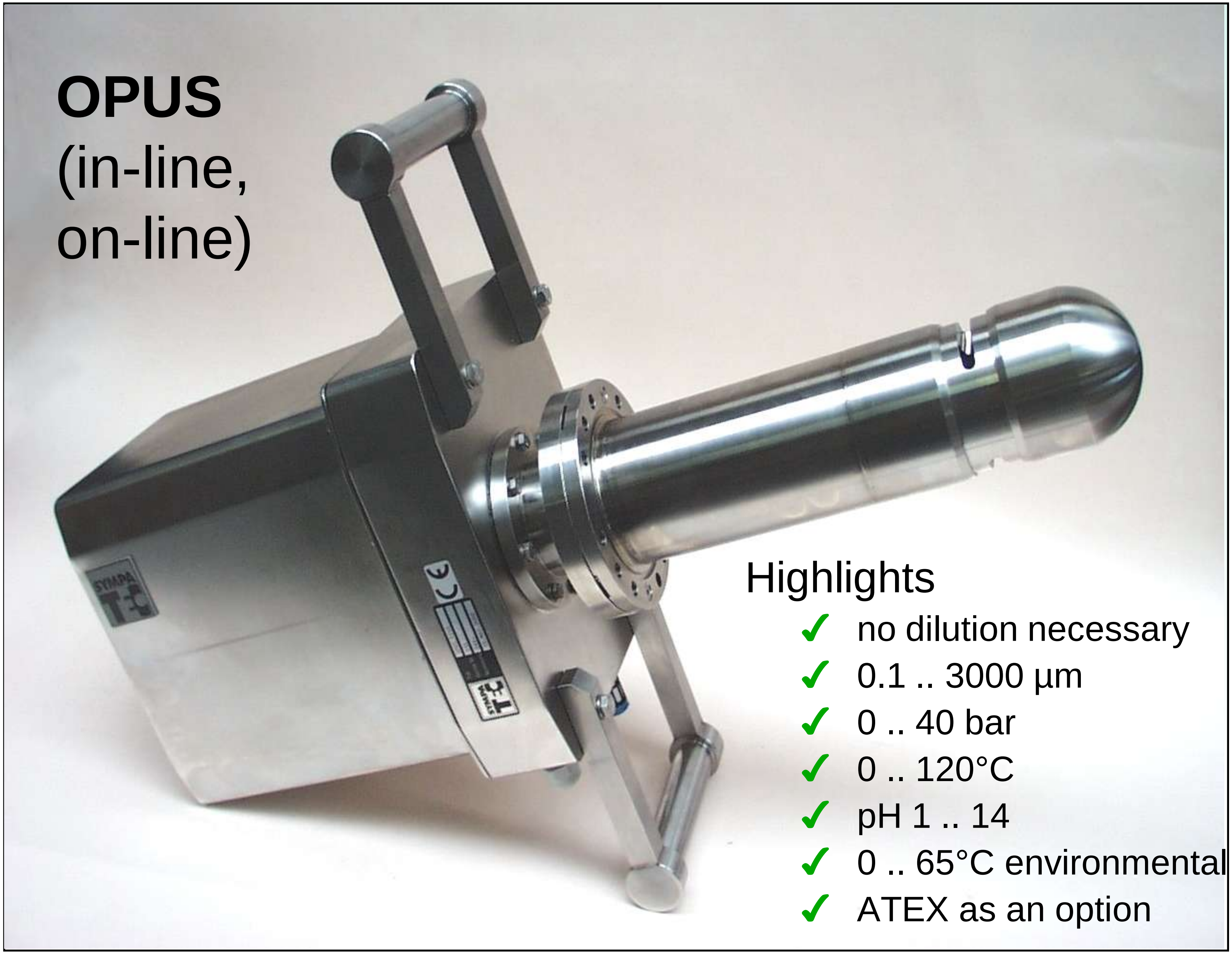


$$\sigma = \frac{\pi \cdot x}{\lambda} = \frac{\pi \cdot x \cdot f}{c}$$

legend

- $-\ln\left(\frac{I}{I_0}\right)$: ultrasonic extinction
- c : speed of sound
- c_{PF} : projection area concentration
- *f* : ultrasonic frequency
- *x* : particle size
- Δl : width of measurement gap
- λ : wave length
- σ : dimensionless size parameter (SP)

OPUS
(in-line,
on-line)

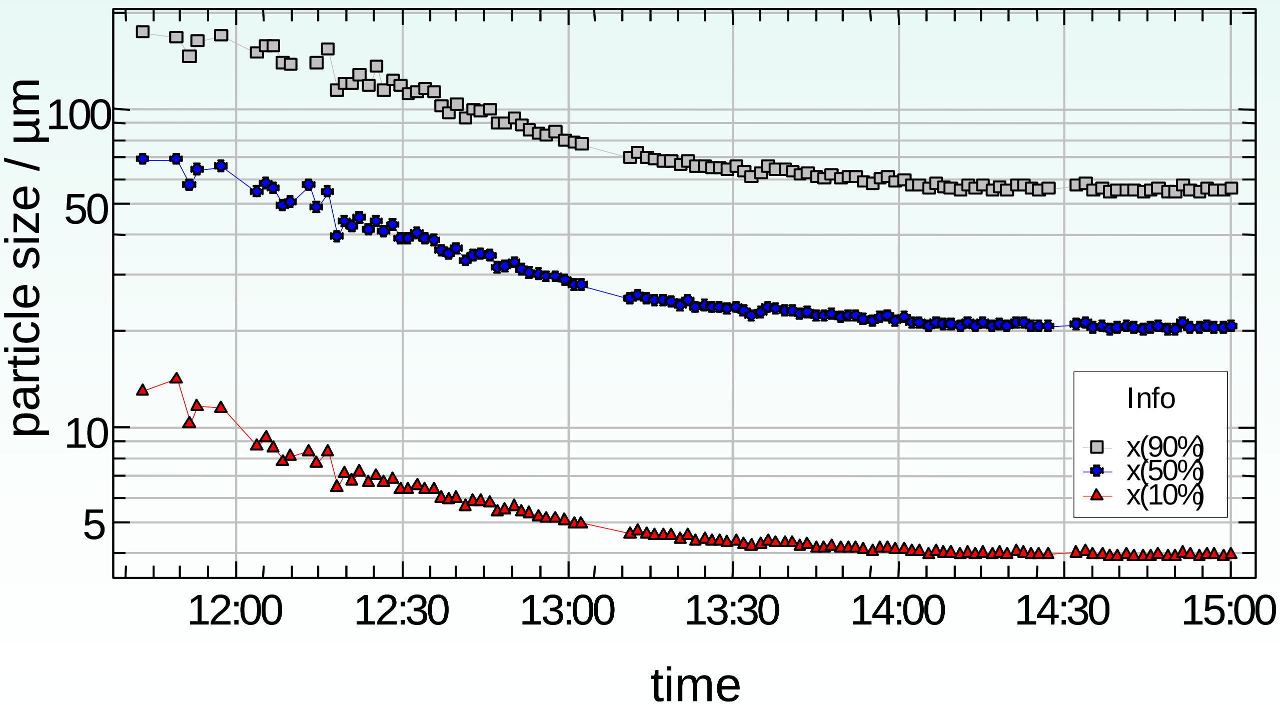


Highlights

- ✓ no dilution necessary
- ✓ 0.1 .. 3000 µm
- ✓ 0 .. 40 bar
- ✓ 0 .. 120°C
- ✓ pH 1 .. 14
- ✓ 0 .. 65°C environmental
- ✓ ATEX as an option

Results (Ultrasonic Extinction)

Trend diagram of a milling application for aluminum pigments in benzene

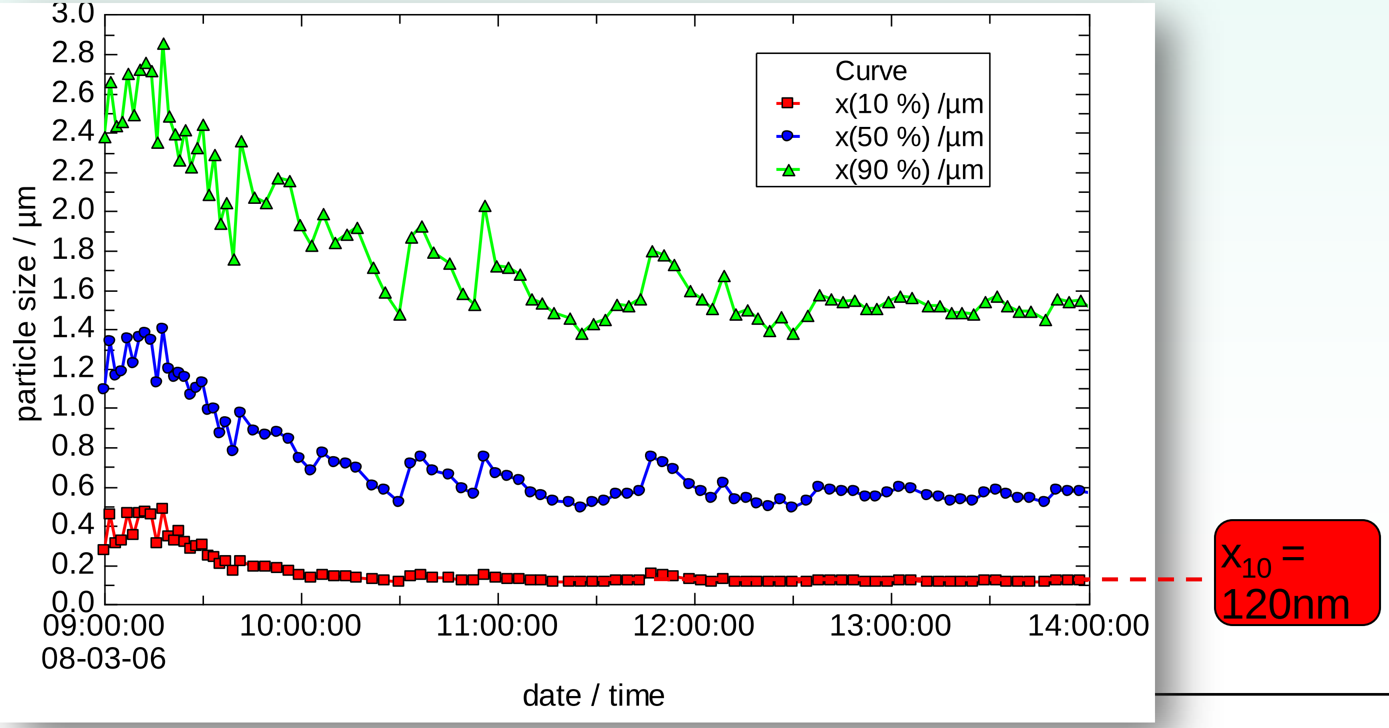


OPUS &
FT 25 Adapter

OPUS Nano Application

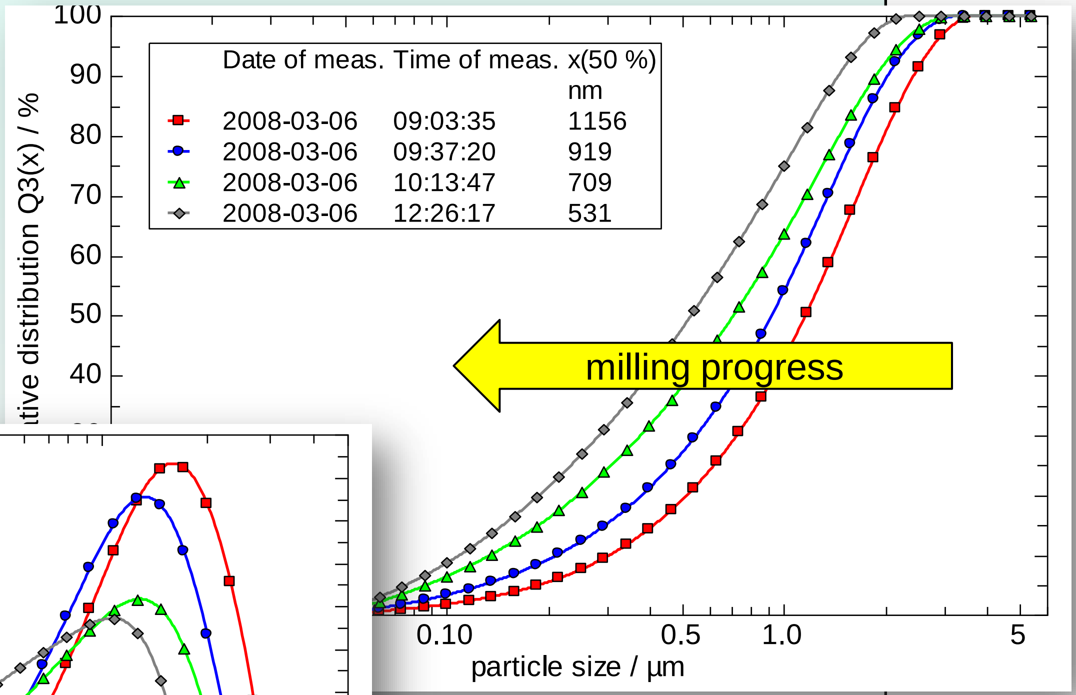
TiO_2 milling process

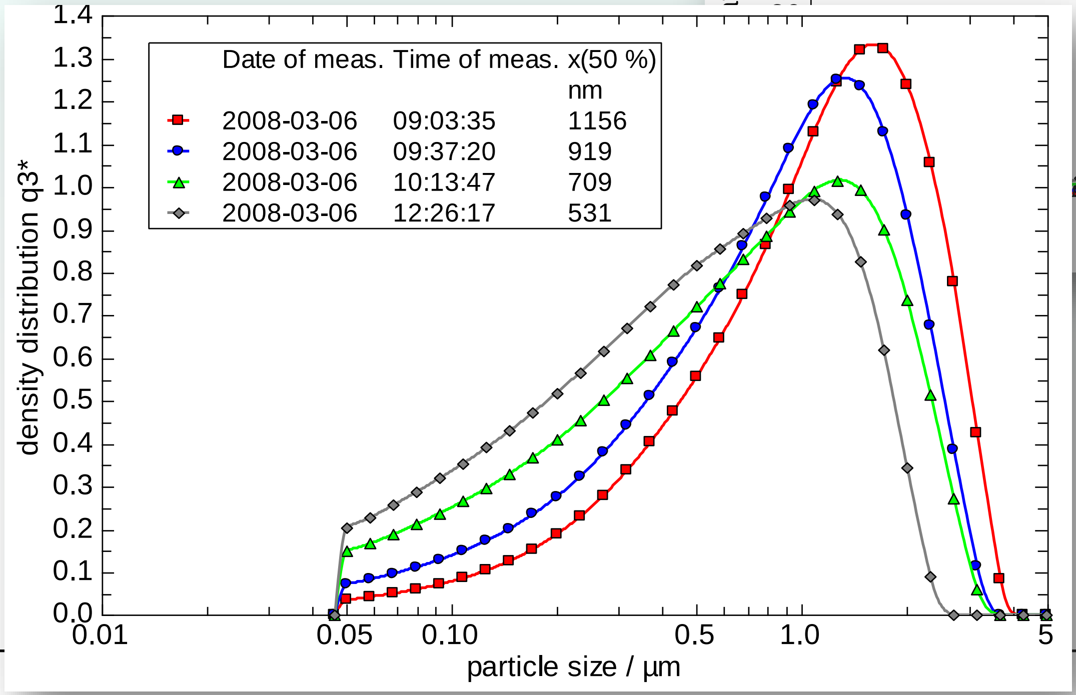
- ★ suspension liquid: water
- ★ product concentration: 6 – 18 $\%_{vol.}$
- ★ PSD range: 0.01 µm – 10 µm
- ★ particle density: 4.15 g/cm³



OPUS Nano Application

TiO_2 milling process





Conclusions: Ultrasonic Extinction

Ultrasonic Extinction has a high potential for particle size analysis in the regime of wet process applications

- ✓ *wide size range* (<100 nm to ≅ 3 mm)
- ✓ wide range of concentrations *1% to > 70% C_{vol}*
  ➠ no dilution necessary (ideal e.g. for crystallisation)
- ✓ very *robust method*, 0 - 120°C, 0 - 40 bar, pH 1 - 14.
- ✓ *quite fast* (about 1/minute)
- ✓ *large measuring volume*
- ✓ well *reproducible results*
- ✓ equivalent diameter similar to sieve analysis
- ☆ for suspensions & emulsions
- ☆ but ➠ *reference method* for suspensions required

Characterization of nano-particles down to < 100 nm

Today's Status

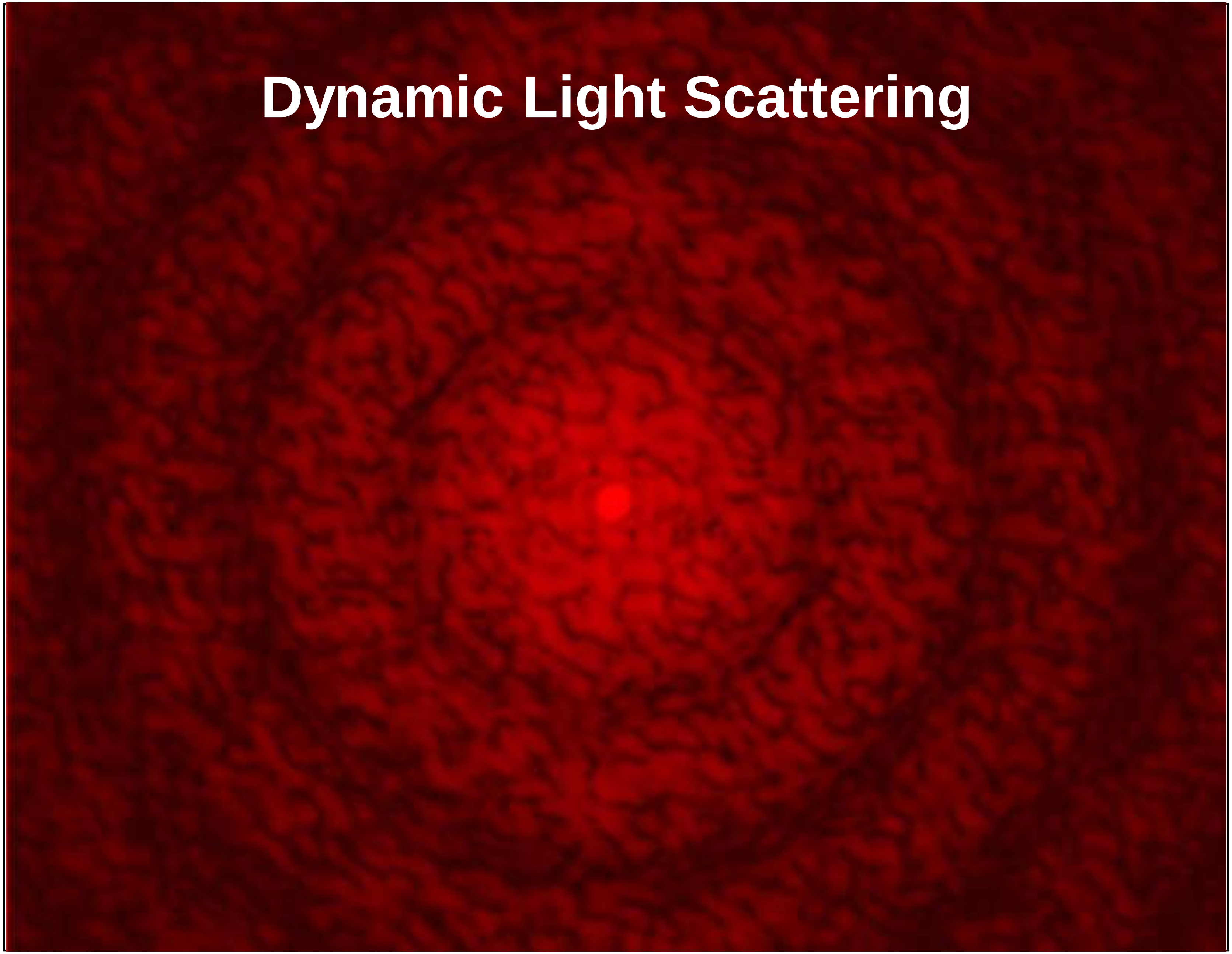
A selection of *samplers*, *dispersers* and **in-line** or **on-line sensors** is combined for the *optimum adaptation* to the application

Systems for Process Environment

… in all fields ...

… but typically above 100 nm!

Dynamic Light Scattering



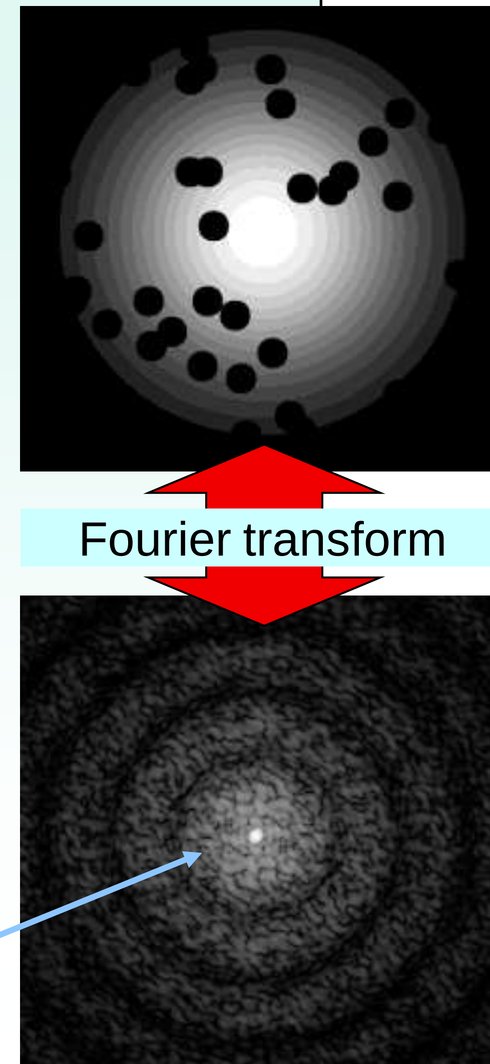
Dynamic Light Scattering

Photon Cross-Correlation Spectroscopy (PCCS)

- ★ *dynamic light scattering* as with photon correlation spectrometry (PCS)
- ★ measuring range *1 .. 10 000 nm*

But:

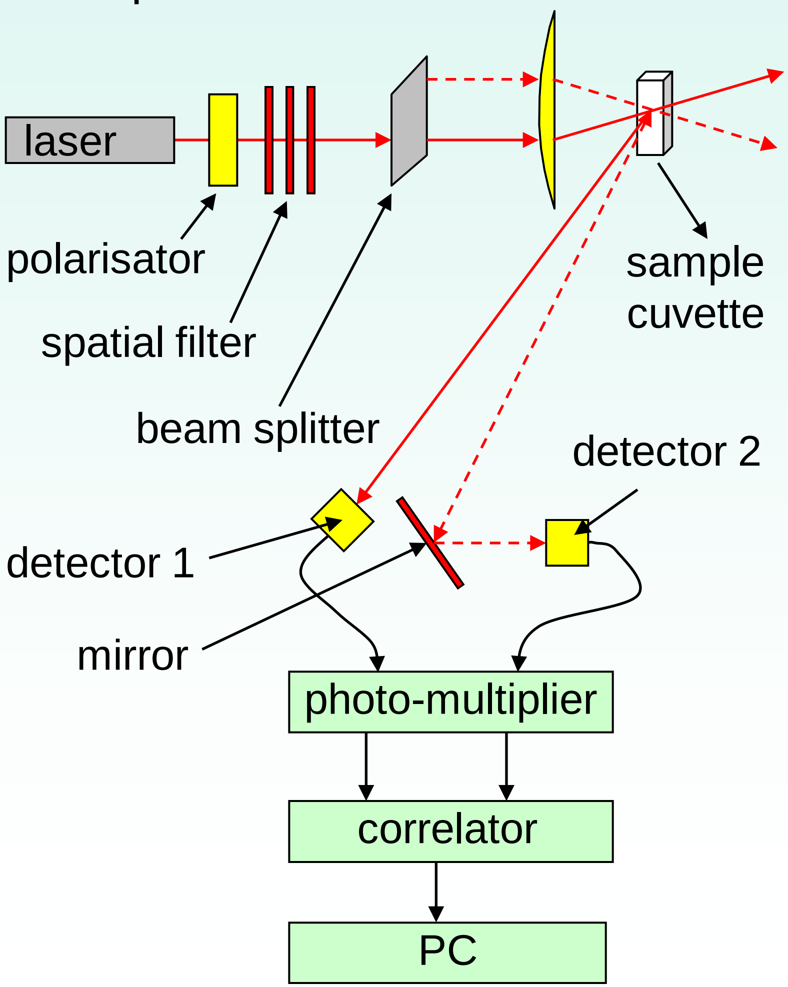
- ✓ *complete suppression* of *multiple scattering* by 3D cross-correlation
  - ✓ *high concentrations* possible
  - ✓ *short measuring times* due to high count rates
  - ✓ *clean room environment* is *not required*



PCS and PCCS evaluates the intensity fluctuations caused by the Brownian molecular movement

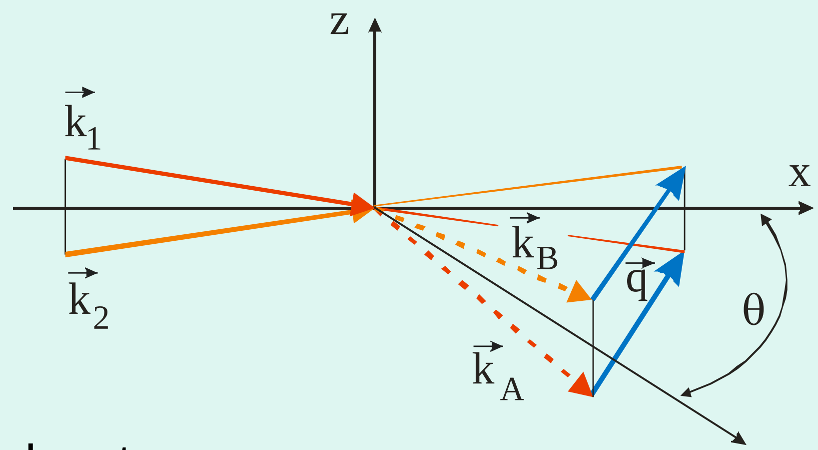
PCCS-Setup

Principle



Challenges

- ☆ the *scattering vectors* have to be identical in magnitude and direction
- ☆ the *scattering volume* (≈ 320 µm² x 50 µm) has to be identical



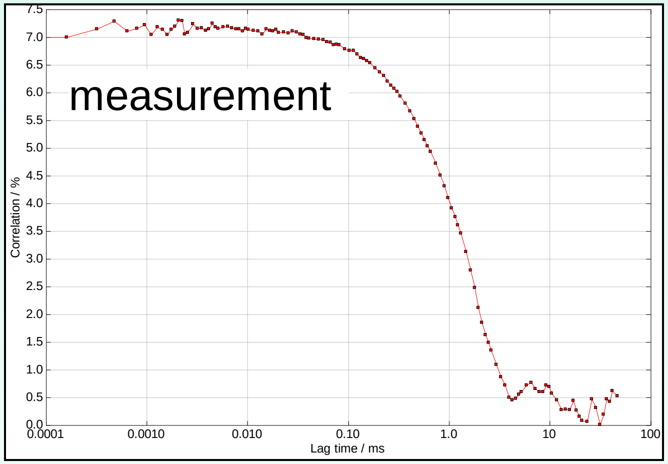
Advantages

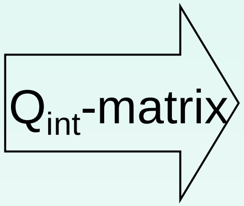
- ☆ The cross-correlation function *G2(τ)* suppresses the multiple scatters fractions → it acts as a “filter“
- ☆ the slope of *ln(G2(τ) –1)* ∝ diffusion function *D(x)* ∝ 1/x

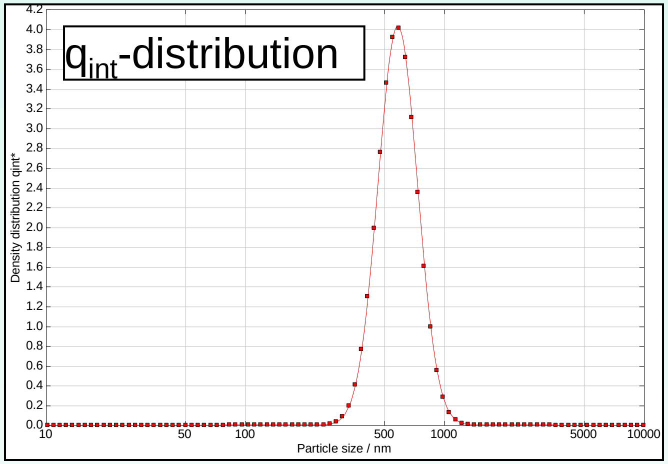
NANOPHOX

Sympatecs PCCS system

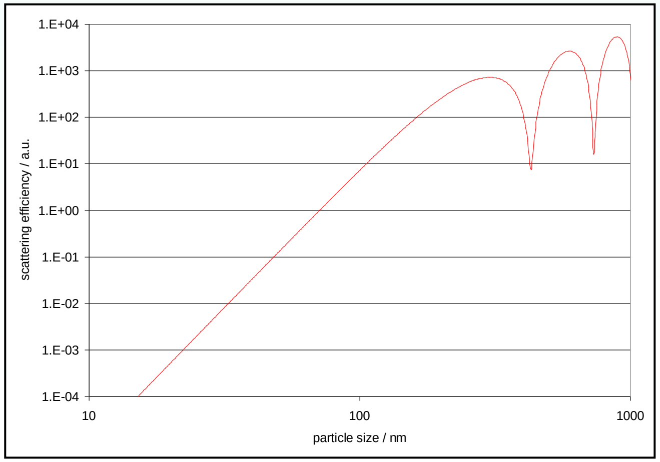
Evaluation with Q_{int}-Matrix

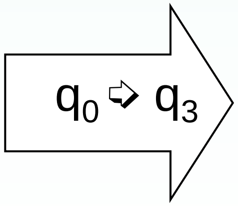




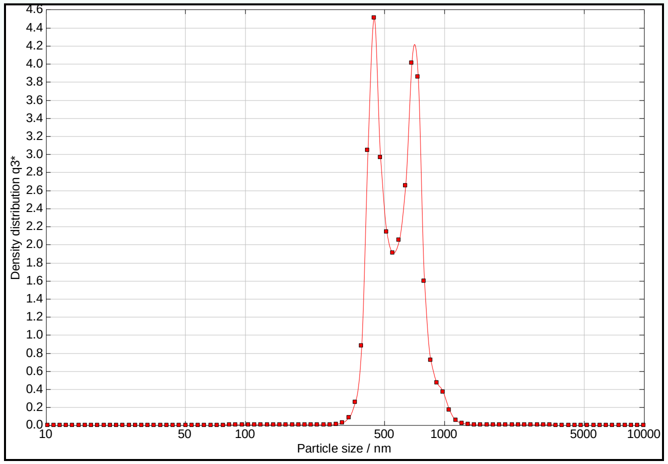


weighing factors q_{int} ⇨ q_0

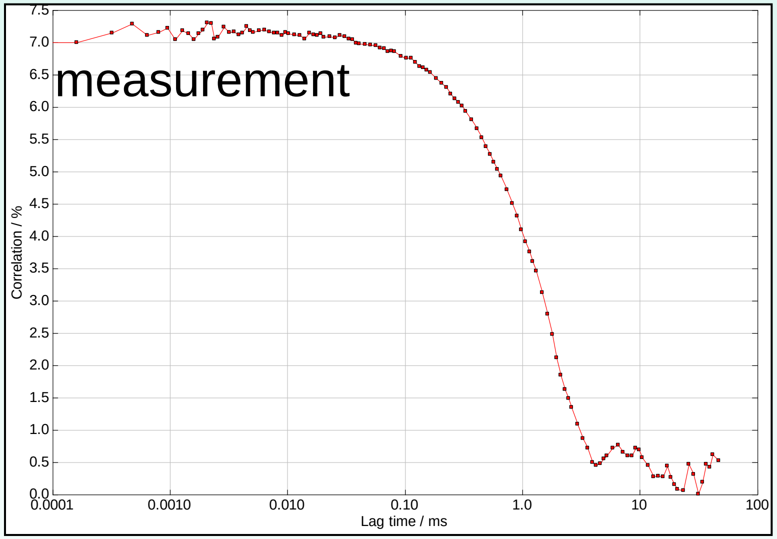




unrealistic q_3-result



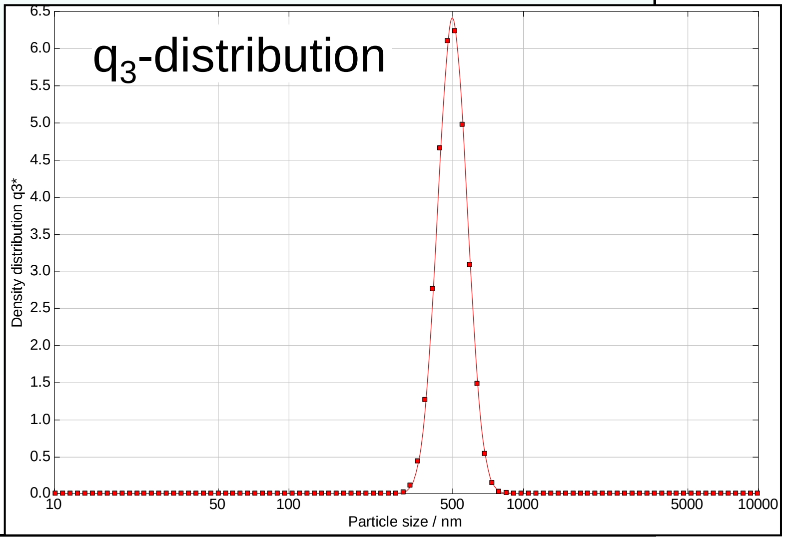
Evaluation with Q_3-Matrix



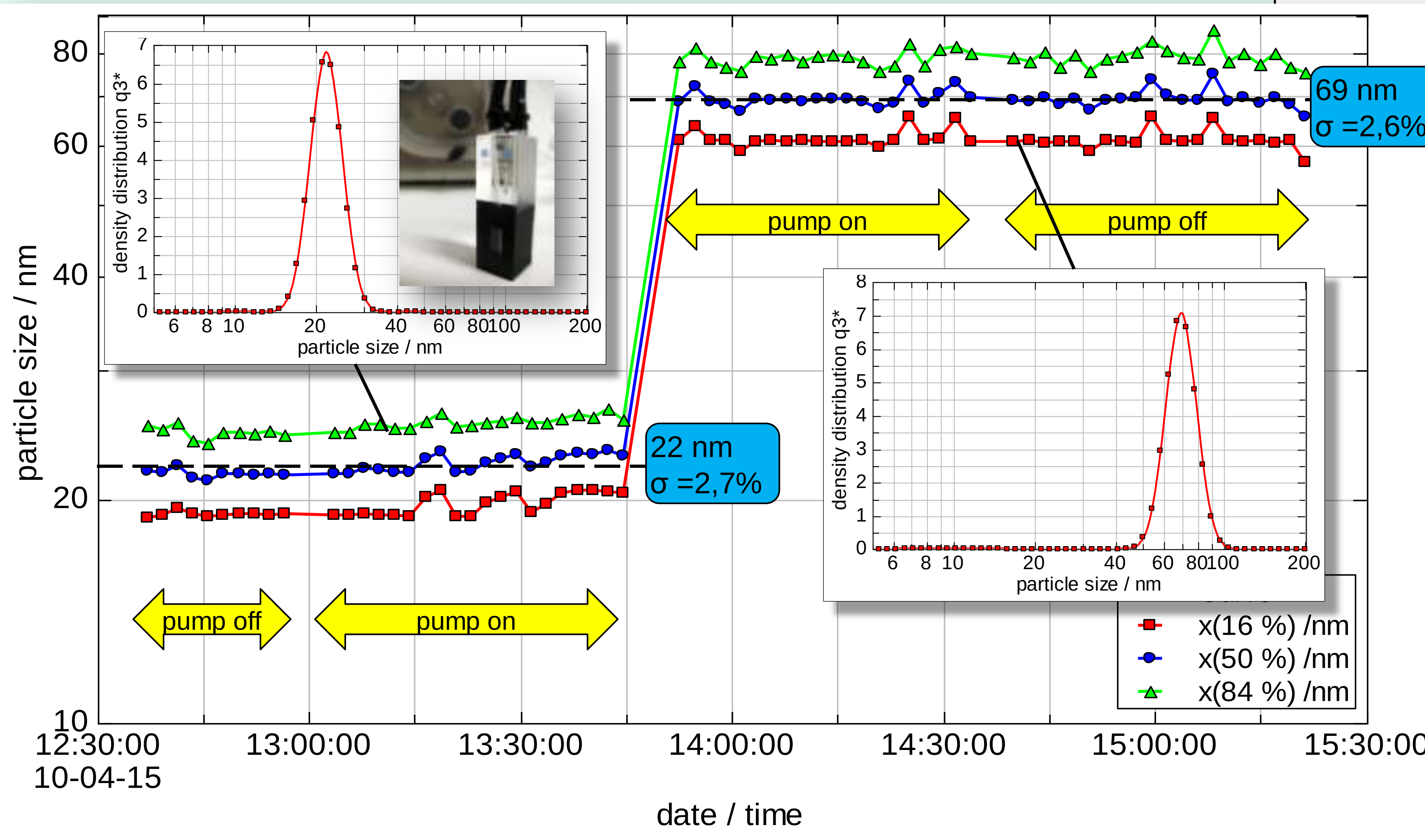
Q_3-matrix

- ✓ constraint „*smooth distribution*“ is *plausible*
- ✓ result *directly comparable* to other measurement techniques

- ✓ *avoids* the *calculation artefacts* of q_{int} to q_3 conversion
- ✗ complex *index of refraction* is needed for the calculation
- ✗ *condition* of Q_3-matrix is *poor* compared to Q_{int}-matrix
  - ↳ requires a *demanding inversion algorithm*



NANOPHOX On-Line Application



Conclusions PCCS

Photon Cross-Correlation Spectroscopy (PCCS) is an improvement over PCS

- ✓ *absolute method*, free of parameters (for known temperature and viscosity), for Q_3 complex refractive index required
- ✓ characterizes the *hydrodynamic diameter* of the particles
- ✓ *large size range* (1 nm to ≅ 10 µm)
- ✓ mostly *no dilution* required
- ✓ for auto-NNLS *well reproducible results*
- ✓ Q_3-distribution: direct comparability with other methods
- ✓ *quite fast* (some minutes)
- ✓ *established*
- ✓ limited to suspensions and emulsions with *small distribution widths*

Characterization of the complete nano-range!

Conclusions

Sizing with on-line methods is well established and off-the-shelf available for suspensions and emulsions with particle sizes > 1 µm.

Limitations:

✓ Dynamic Image Analysis	>	1000 nm (dry & wet)
✓ Laser Diffraction	>	100 nm (dry & wet)
✓ Ultrasonic Extinction	>	100 nm (wet)

Current Outlook

✓ Dynamic Light Scattering	≅	1 nm to 10 µm (wet)
☆ SAXS	≅	1 nm to 300 nm (dry & wet)
☆ others ?		

Sizing of nano-particles with on-line methods is a real challenge today