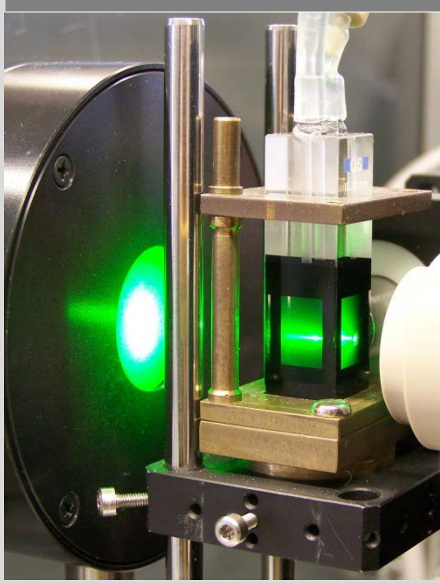
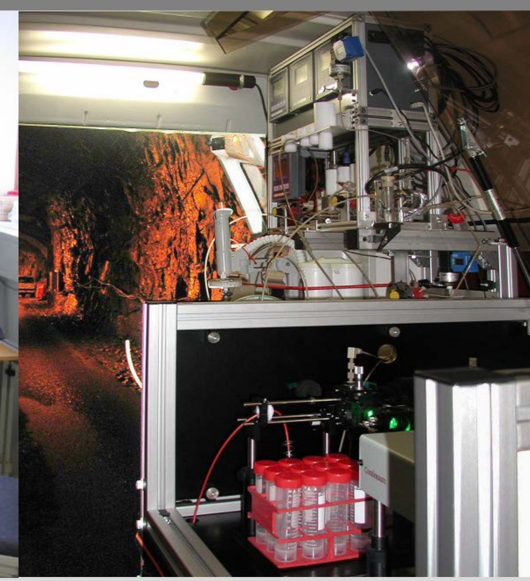
Lecture: Laser Induced Breakdown Detection (LIBD)

Thorsten Schäfer

Institute for Nuclear Waste Disposal (INE)



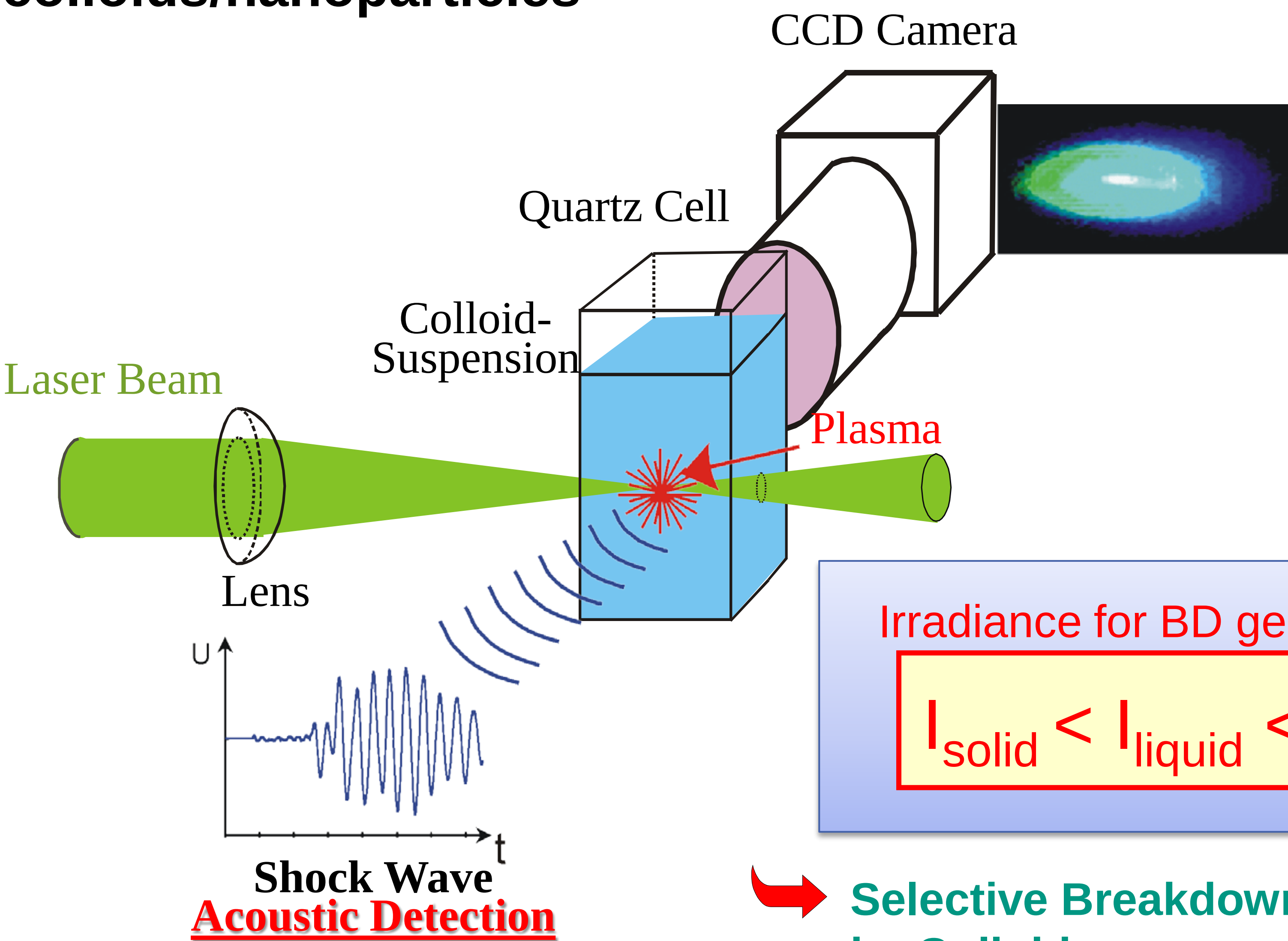


Outline

- **LIBD Technique**
  - Some Fundamentals
  - Optical system
  - Acoustic system
  - Calibration
- **Application examples**
  - Nucleation measurements
  - Solubility measurements
  - Colloid mobility in natural formations

By **LIBD, size and number density of aquatic colloids < 1000 nm** are determined down to the **ppt-concentration range (10^5 particles/ml).** The technique is based on plasma formation **by a focused pulsed (ns) laser beam** selectively when and only when a colloid is present in the focal volume. Each plasma event corresponds ideally to one single colloid and hence the relative number of events per number of laser shots gives a measure of colloid concentration.

Selective breakdown (BD) generation of colloids/nanoparticles



2D Optical detection
Plasma image

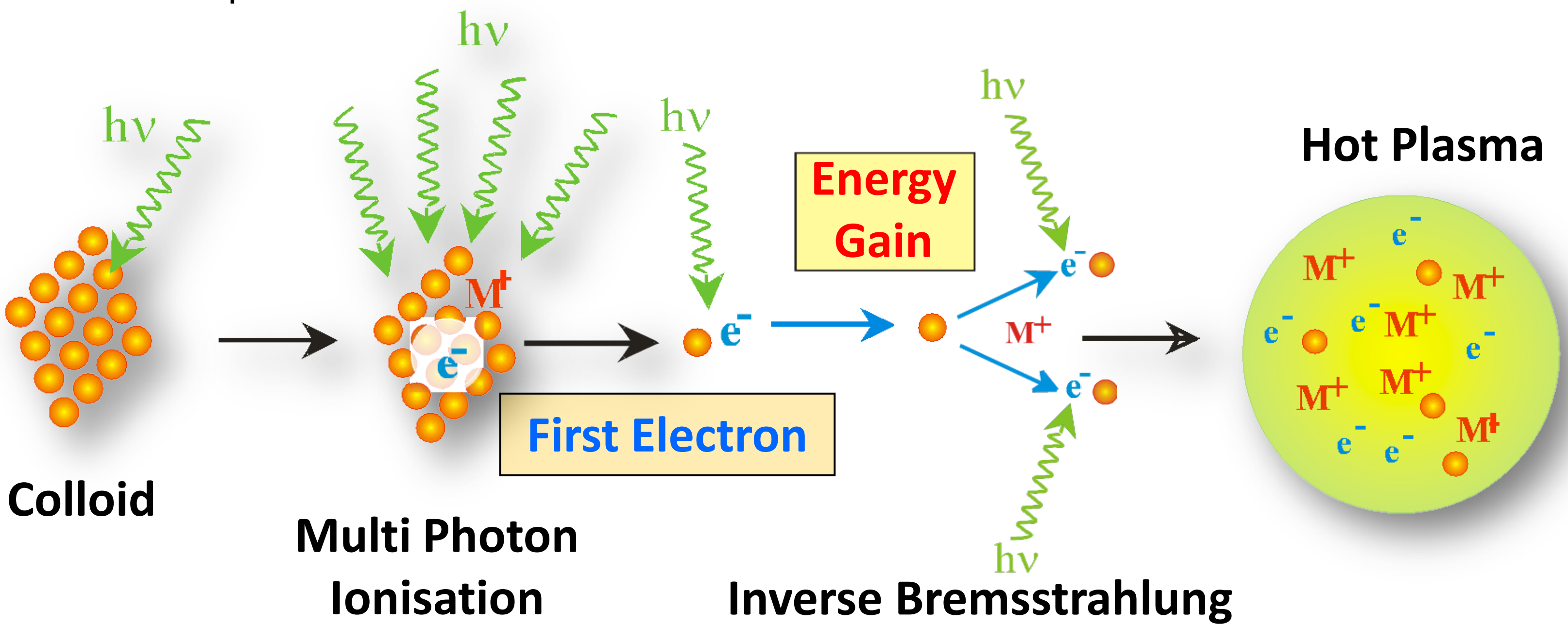
Irradiance for BD generation:

$$\boxed{I_{solid} < I_{liquid} < I_{gas}}$$

Selective Breakdown Generation by Colloids

Process of Plasma Generation

1. Pulsed laser is focused tightly into a medium and a certain pulse energy threshold is exceeded, a so called breakdown (BD) occurs.
2. In the beginning at least one atom is ionized by multi-photon ionization (MPI), resulting in a seed electron which is accelerated by inverse Bremsstrahlung in the high electric field of the laser pulse.
3. After gaining sufficient energy additional atoms are ionized by collisions, multiplying the number of electrons.
4. Hence, the density of free charge carriers increases in avalanche after a few consecutive iterations and a plasma is created.



Some theory…..

Irradiance for BD generation:

$$\boxed{I_{solid} < I_{liquid} < I_{gas}}$$

W ??

density of "targets"

MPI cross-section

order of process

$$N_{Plasma} = 1 - \exp\left\{ -\rho \iiint_V dV \int^{\tau_{CRIT}} \cdots \underbrace{\frac{\cdots}{\sqrt{\pi}\tau} e^{-\frac{t^2}{\tau^2}}}_{\text{temporal}} \underbrace{\frac{1}{\pi\sigma^2} e^{-\frac{r^2}{\sigma^2(Z)}}}_{\text{spatial}} \Big]^m \right\}$$

number of e^- produced

- Quality of measurements strongly dependent on stability of laser system
- Material dependency

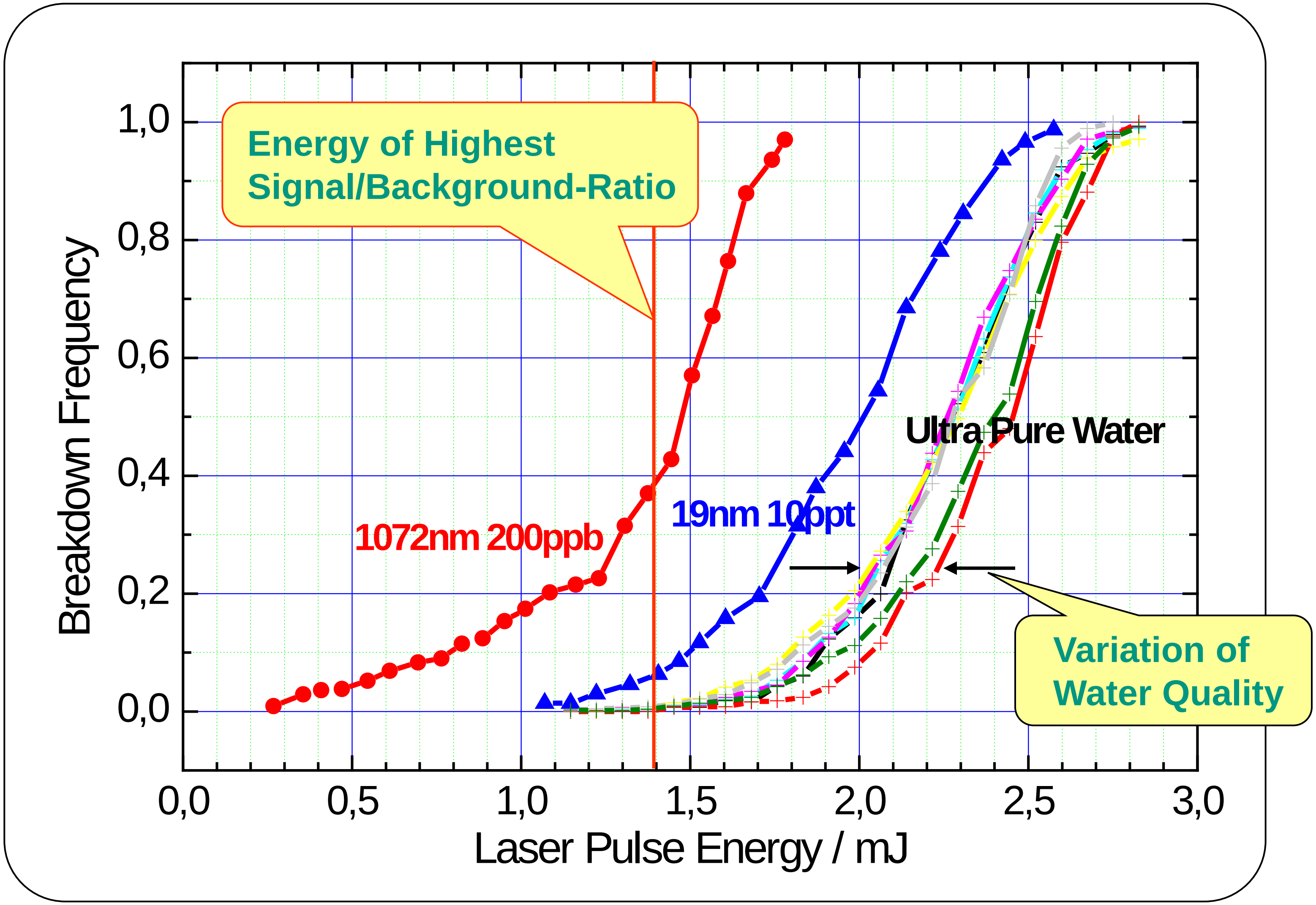
If there are N of these elec… …ng an multi-photon ionization (MPI) -cross section σ, the probability to excite o… …unbound state amounts to

$$P_{\mathrm{BD}} = N \int_0^{\Delta t} \int_{-\infty}^{\infty} \sigma(\Phi(t,\vec{x}))^n \, \mathrm{d}^3x \, \mathrm{d}t + \mathcal{O}(\sigma\Phi^n)^2$$

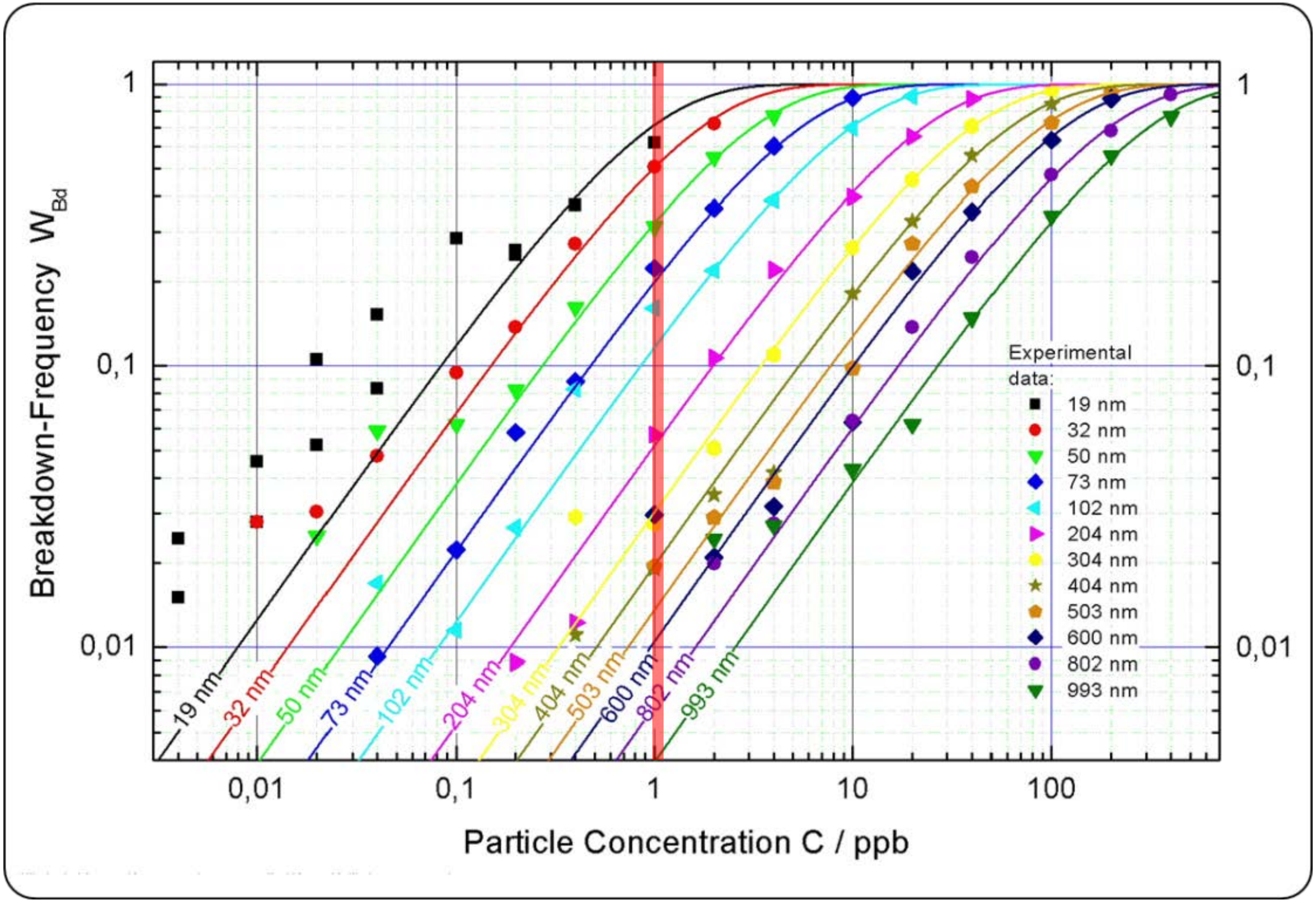
… being the photon flux density (time and space dependent), n the number of photons necessary to overcome the binding energy of an electron and Δt the laser pulse duration.

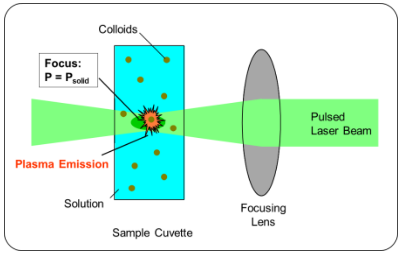
[1] Kitamori, Yokose, Suzuki, Sawada, Goshi, Japanese Journal of Applied Physics **27,** L983-L985 (1988).
[2] Walther, Bitea, Kim, Scherbaum, Nucl. Instr. Meth., B **195**: 374-388 (2002).
[3] Scherbaum, Knopp, Kim Applied Physics B-Lasers and Optics, **63(3)**, 299-306 (1996).

Breakdown-Frequency as a Function of Laser Pulse Energy



Concentration Calibration with Polystyrene Particle Standards
- Detection with <u>constant Laser Pulse Energy</u> -

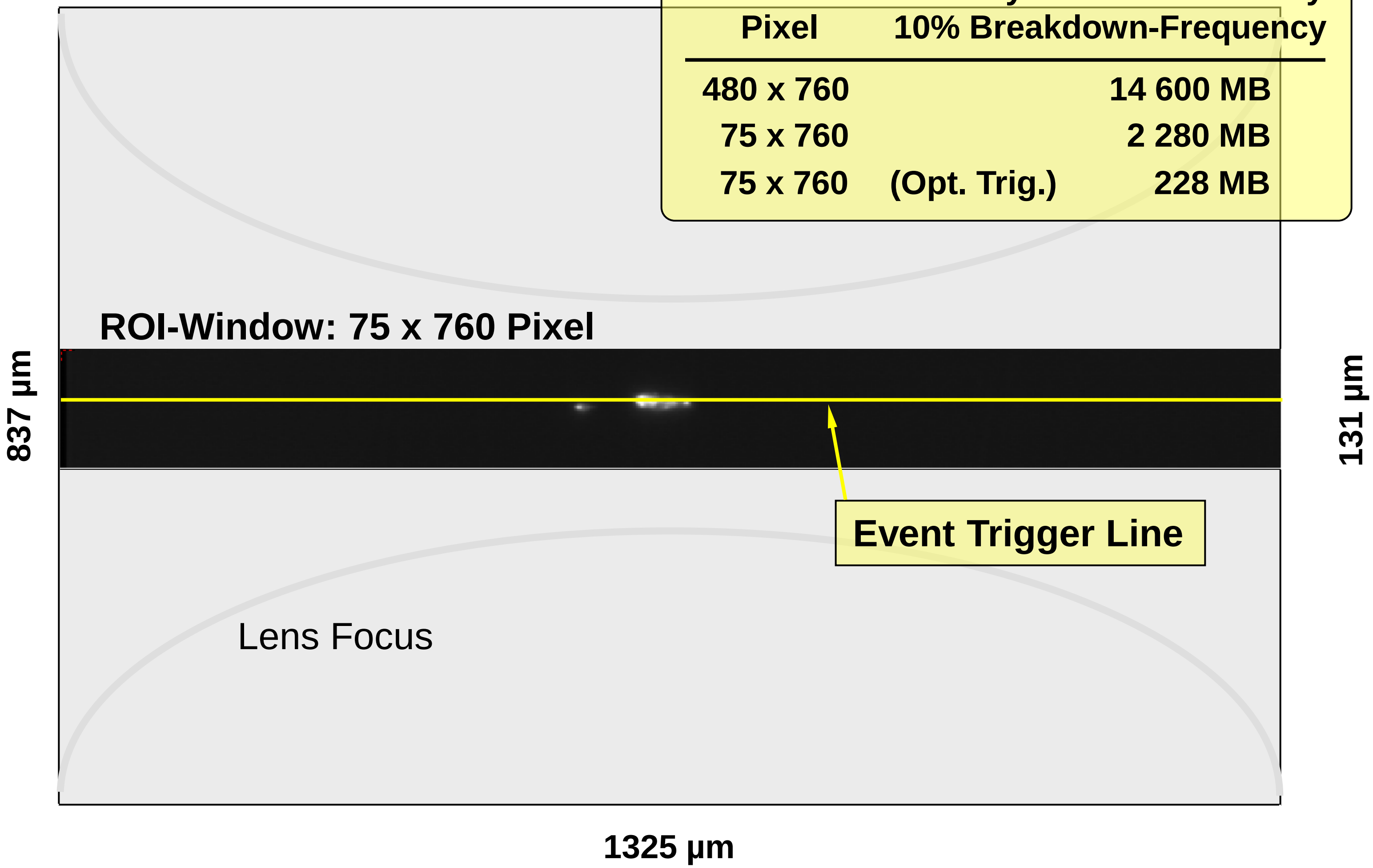




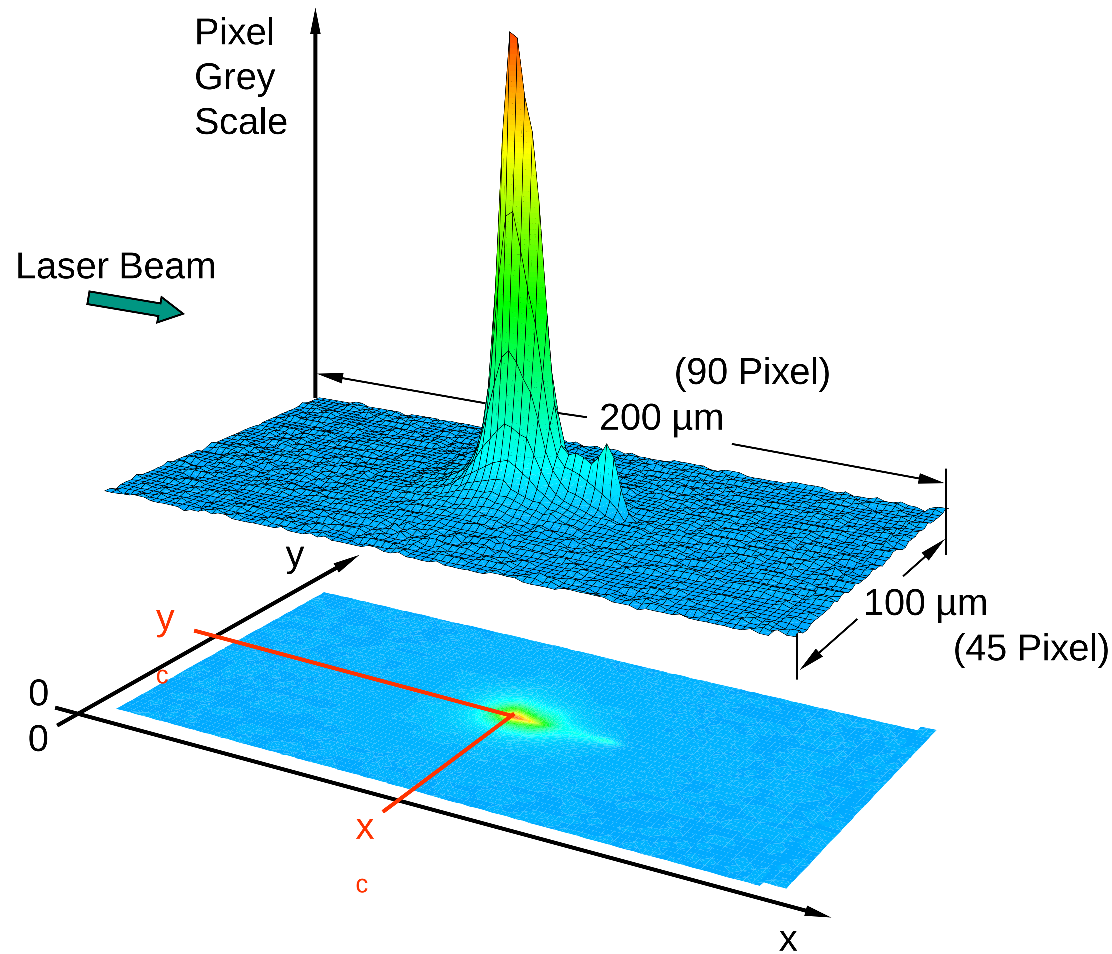
Method of Optical Detection: Definition of an Optical Event Trigger

Camera Window: 480 x 760 Pixel

Picture Size Pixel		Memory for 4000 Events by 10% Breakdown-Frequency
480 x 760		14 600 MB
75 x 760		2 280 MB
75 x 760	(Opt. Trig.)	228 MB



Coloured Grey Scale Picture of a Single Particle BD Event
- Particle Diameter: 19 nm -



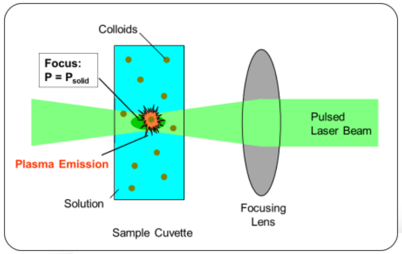
Some theory…..

Irradiance for BD generation:

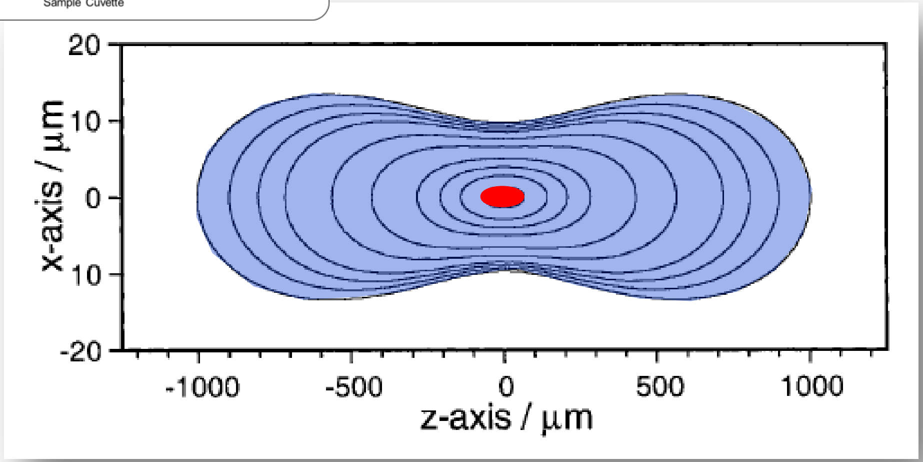
$$\boxed{I_{solid} < I_{liquid} < I_{gas}}$$

WHY????

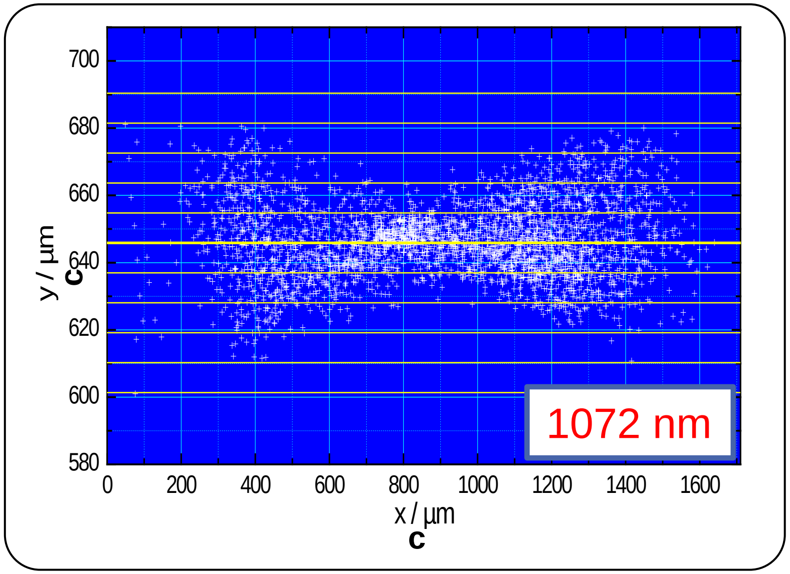
Typical ionization energies of **solids** are 6 eV < E_I < 10 eV
(**<u>lower energy</u>** for larger colloids needed)
Typical ionization energy of **water** is between 18.11-18.72 eV



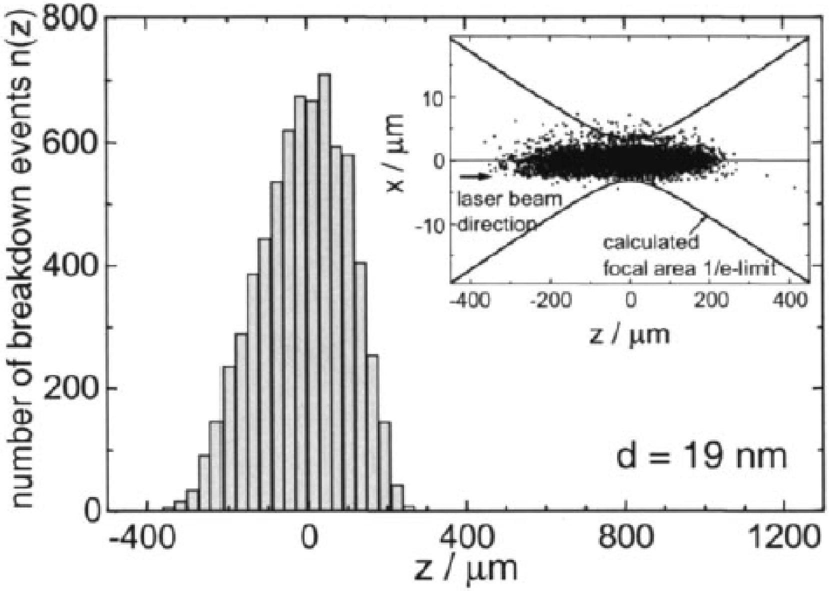
Isolines of maximum irradiance of a laser pulse in the focus range

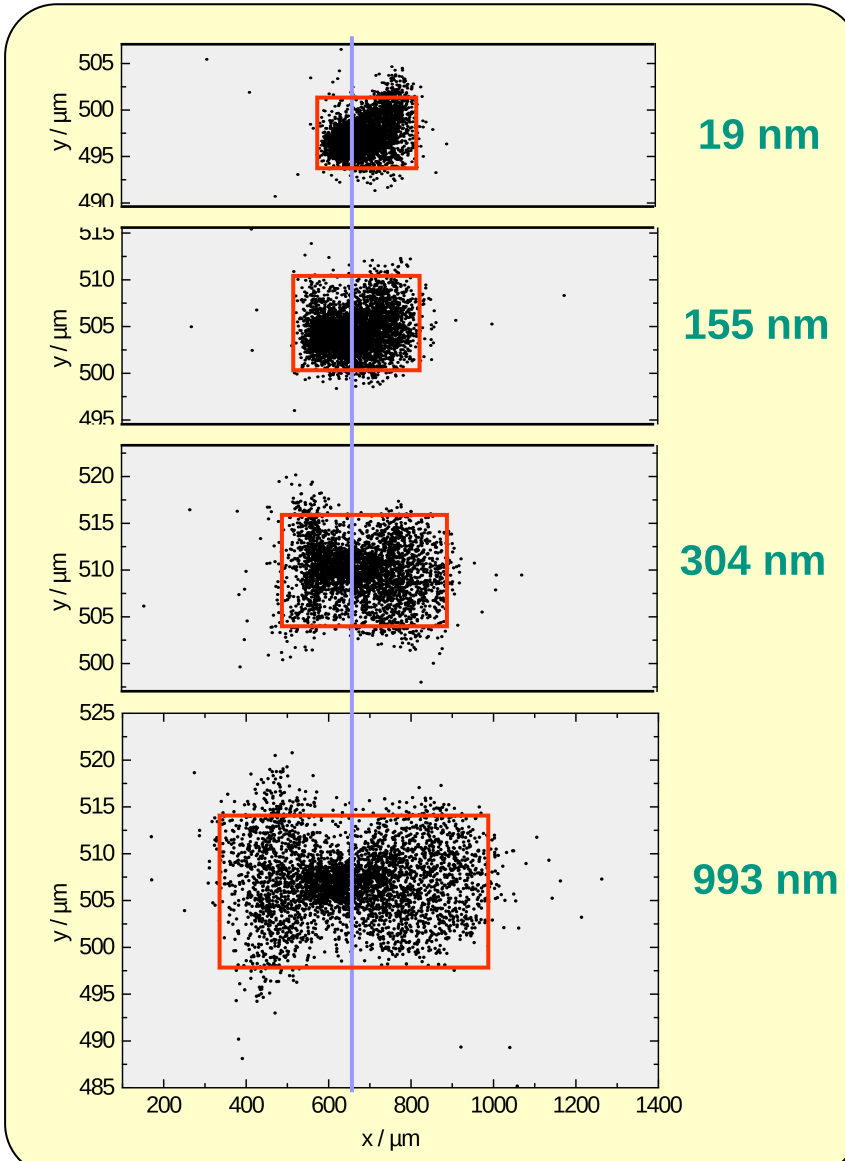


Complete ROI-Window: Coordinates of the breakdown centers



Particle Size Dependence of Breakdown Emission Centers

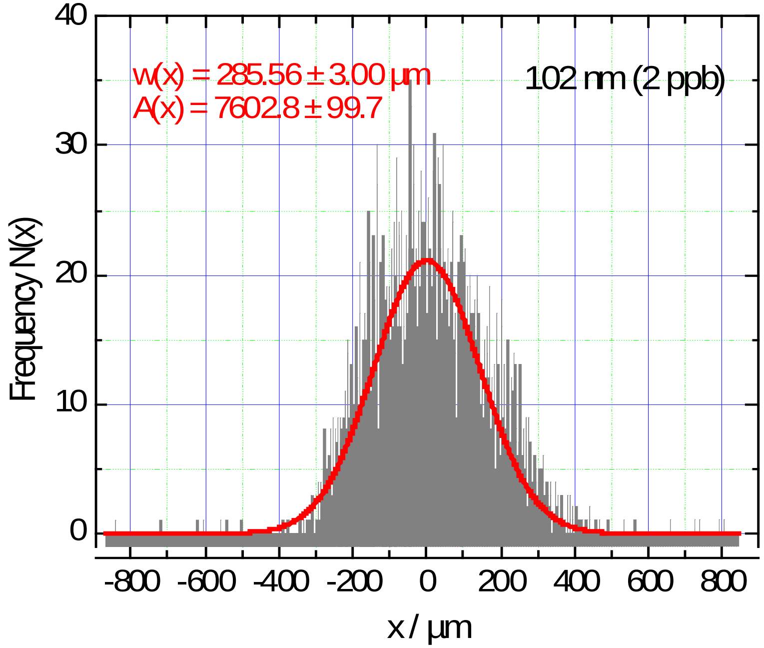




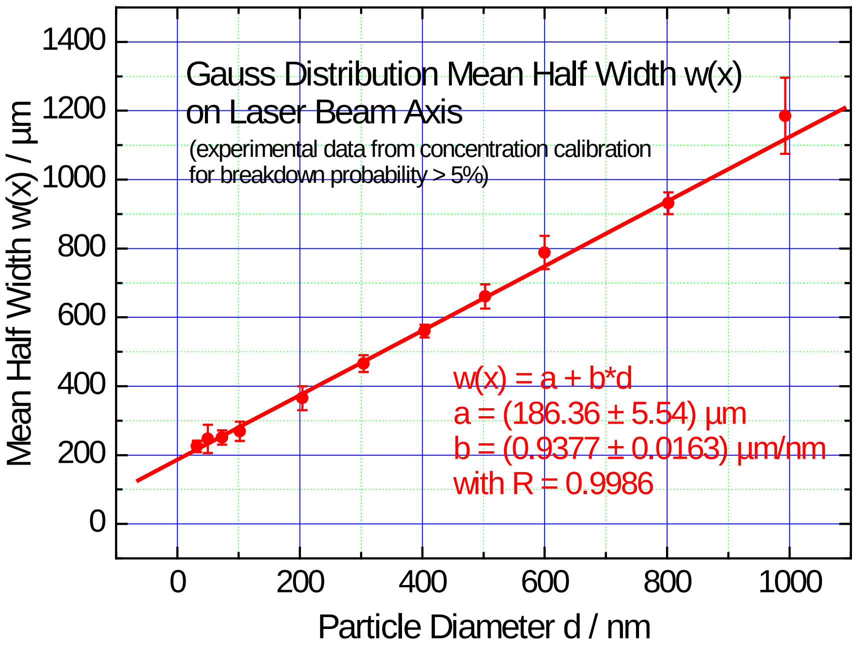
Size Calibration with Polystyrene Particle Standards of 2D optical LIBD

Gauss Distribution parallel to the Laser Beam Axis:

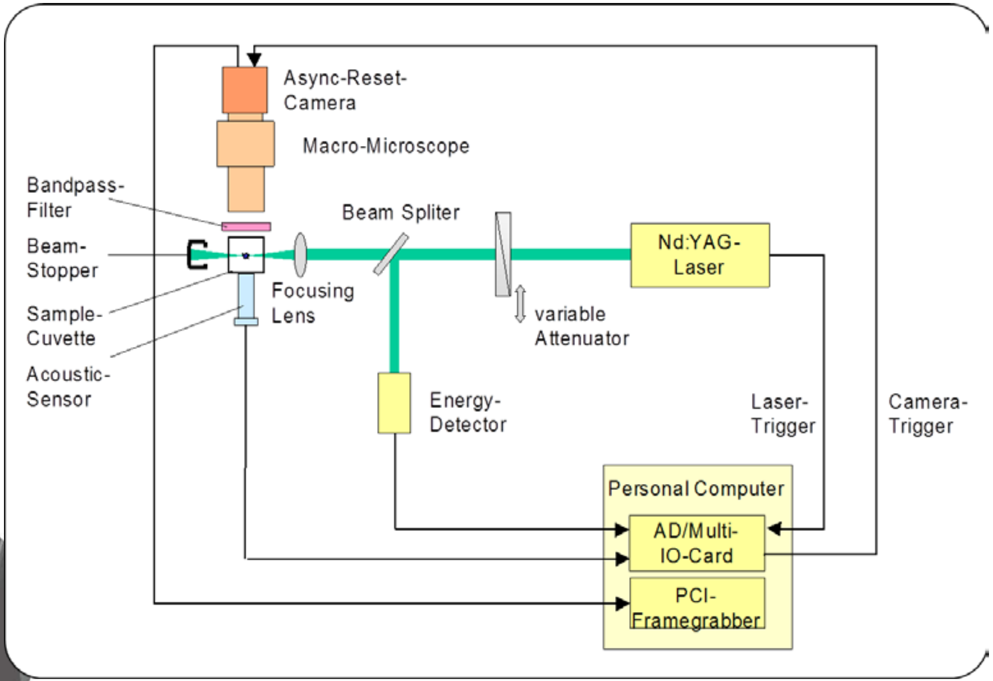
$$N(x) = A(x) / (w(x) * (\P/2)^{1/2}) * e^{-2 (x / w(x))^2}$$

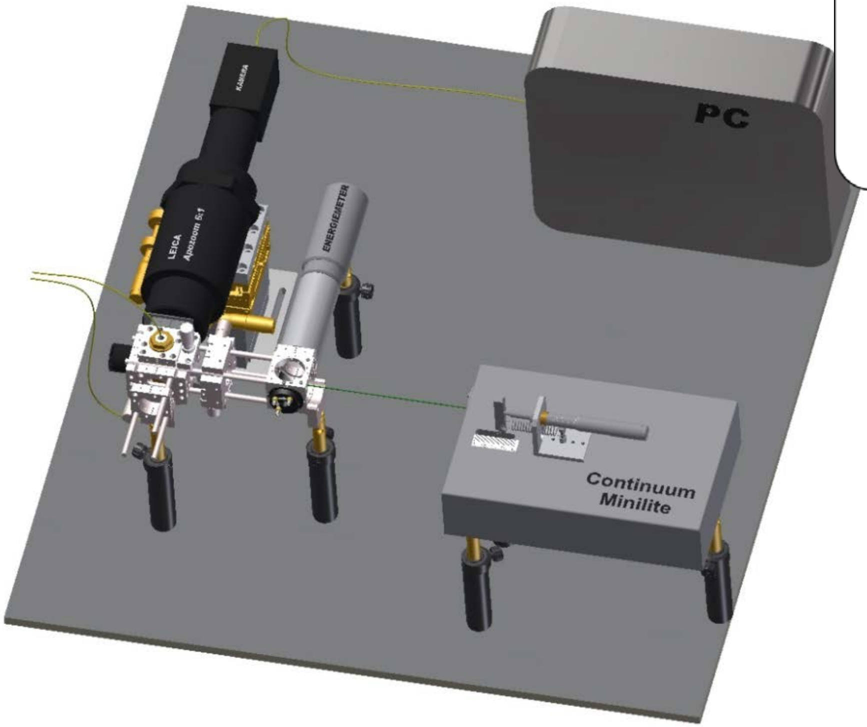


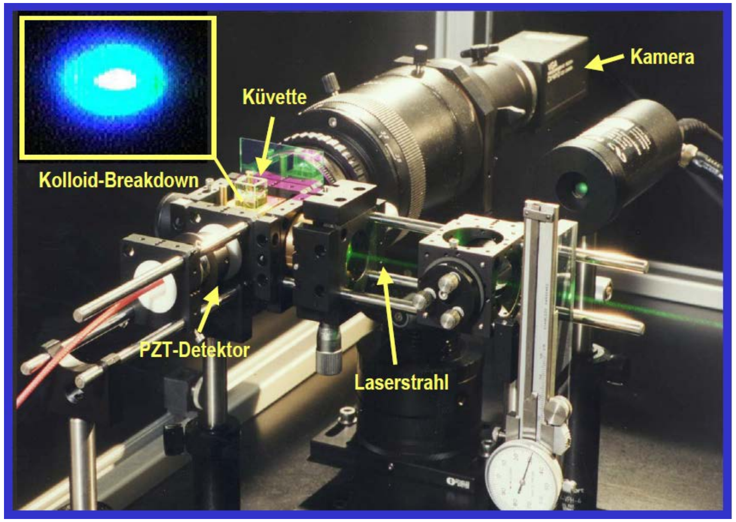
Average Mean Half Width as a Function of the Particle Diameter



2D Optical LIBD Instrumentation with Computer Controlled Picture Processing

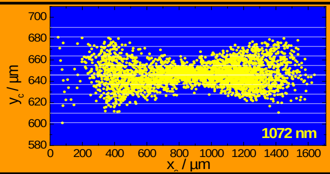






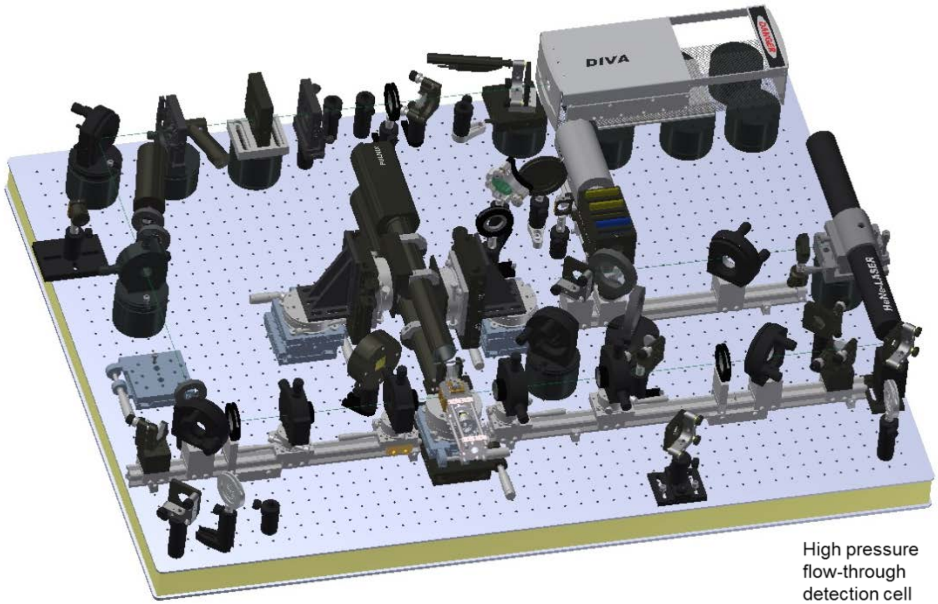
Characteristics of the INE LIBD Instruments

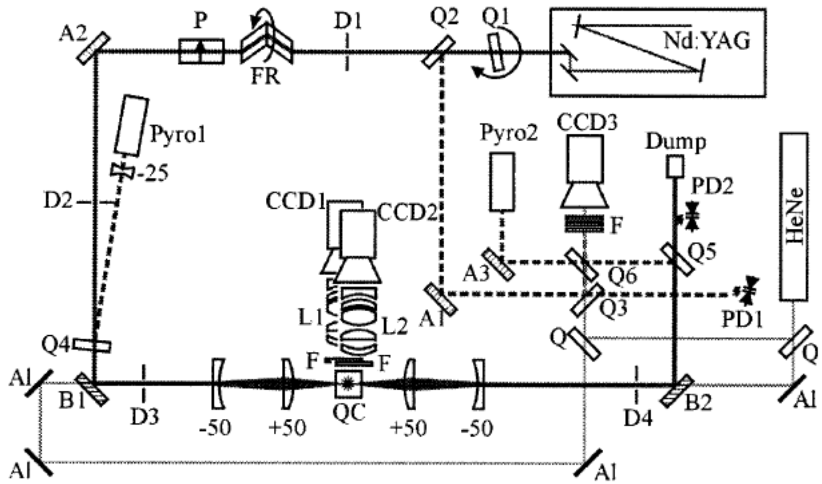
Karlsruher Institut für Technologie

	2D-Optical Detection LIBD (*) **3 Systems**
	
Application	mobile, robust system for field experiments, **long time online detection**
Breakdown Detection Method	optical detection, constant laser pulse energy (~1.3 mJ)
Special Features	pressurized (60 bar, **200°C**) flow-through detect. cells, geo-monitoring
Detection Form	online (offline evaluation)
Typical Measurement Duration	1 - 10 min., **> 50 h detection mode**
Colloid Size Detection	average particle diameter
Colloid Size Range	20 - 1000 nm
Colloid Concentration Range	ppt - ppm

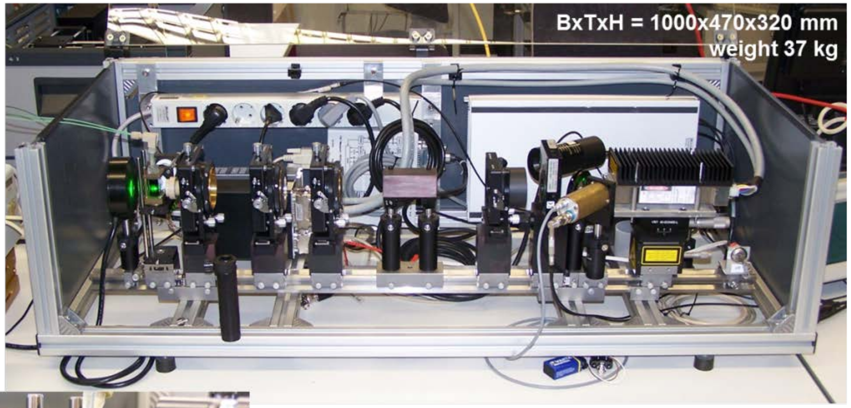
(*) Patent KIT (Forschungszentrum Karlsruhe GmbH),
Verfahren zur Bestimmung der Größe von Partikeln, Deutsches Patent DE 198 33 339.0-52 (2000)

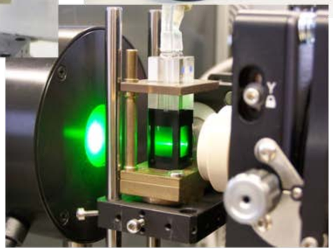
S-Curve LIBD





High pressure flow-through detection cell



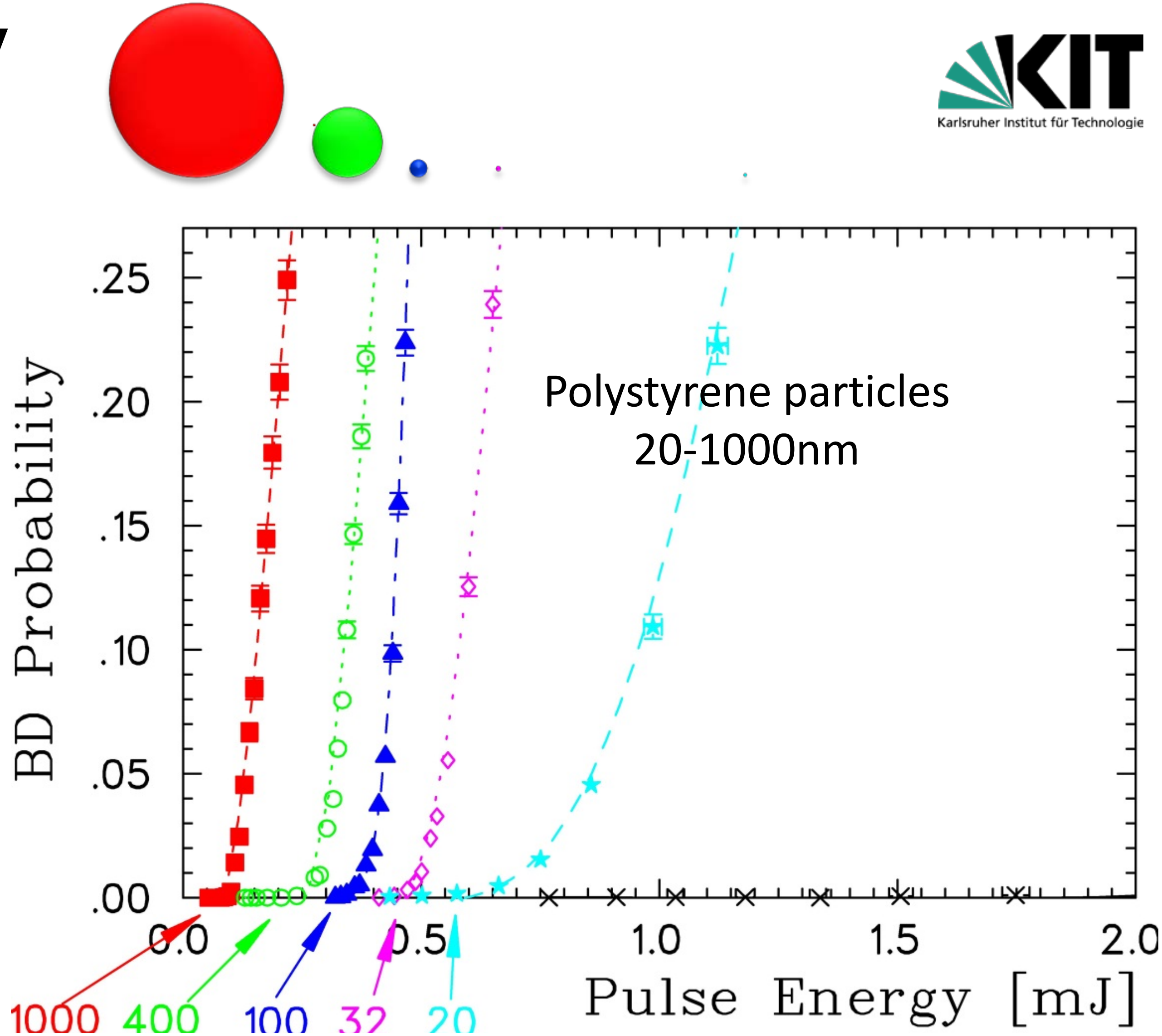


Silica flow-through detection cell (Hellma)

Innolight Flare GN

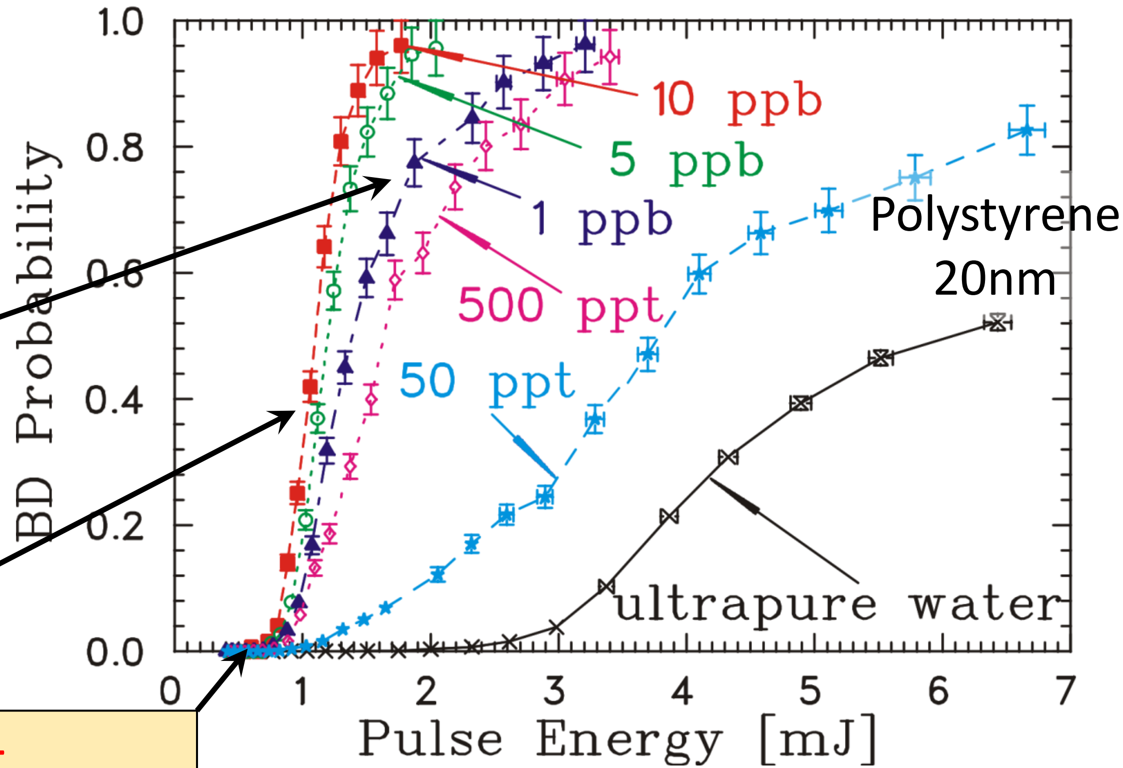
Passively Q-switched
Wavelength: 532 nm
Pulsenergy: **424 (440) µJ**
Puls duration: **2.76 ns**
Beam diameter: 0.5 mm
Pulse rep. rate: **100 Hz**
Hermetic sealing
Long-life operation

Size dependency of BDP



Breakdown threshold

Concentration dependency of BDP (20nm Polysterene)

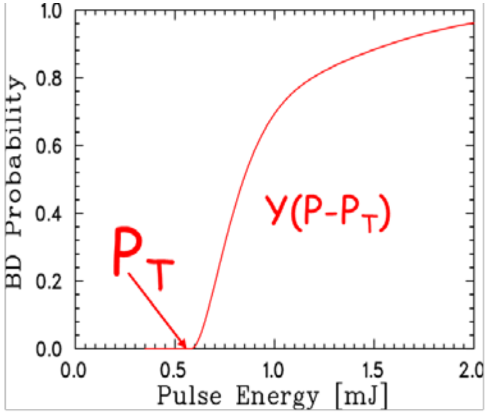


Slope corresponding to the particle number density

Constant breakdown threshold

Calculation for colloid size distribution

I

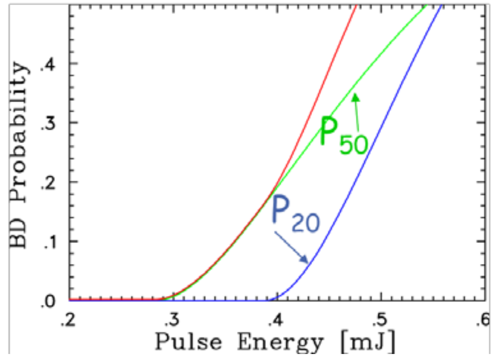


BD Probability = $Y(P, P_T, a)$

Pulse Energy — Size — Concentration

II

Summation: $P1 + P2 = 1 - \overline{P1} \bullet \overline{P2}$ Product of Antiprobabilities



"summation" of 2 s-curves

e.g.: 20nm + 50nm

$1-Y_{20}$

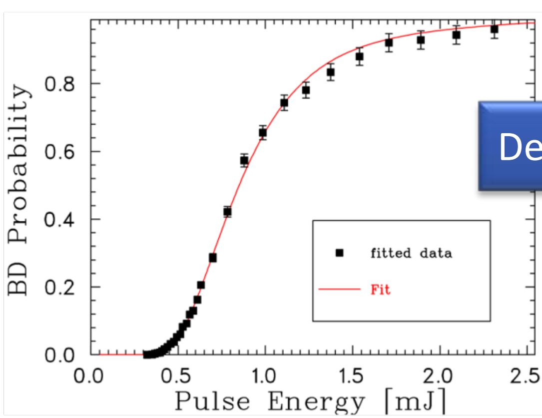
$Y_{SUM} = 1 - \overline{Y_{50}} \bullet \overline{Y_{20}}$

III

Synthetic Trimodal Sample

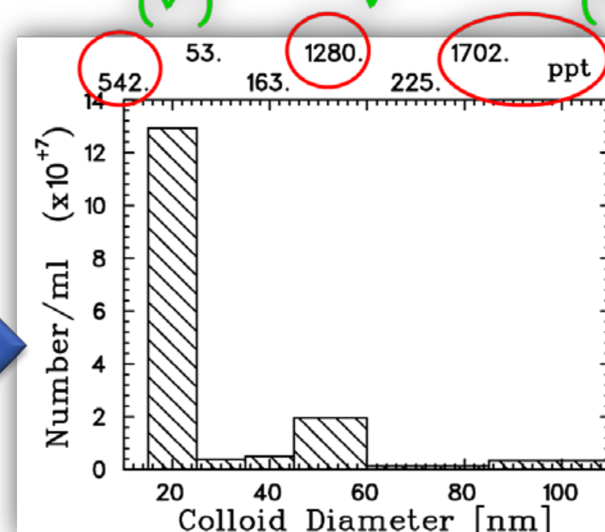
'Pareto'-like

20nm
1ppb
+
40nm
1ppb
+
70nm
1ppb



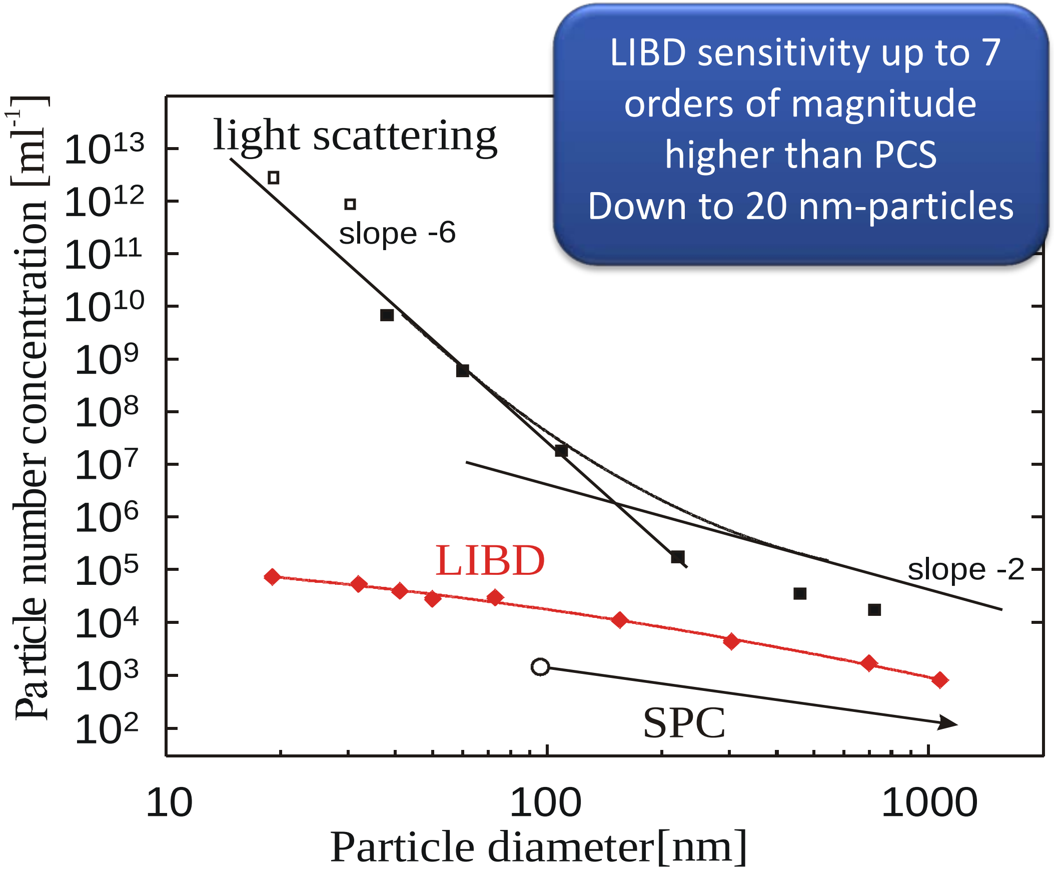
Deconvolution

(✓) ✓ (✓)



$$y = 1 - \left(1 + b_{m,n} * (x - a_n) - \frac{1}{i} * \left(b_{m,n} * (x - a_n)\right)^2 + \frac{1}{j} * \left(b_{m,n} * (x - a_n)\right)^3\right) e^{-b_{m,n}(x - a_n)}$$

Detection limits of different nanoparticle detection methods



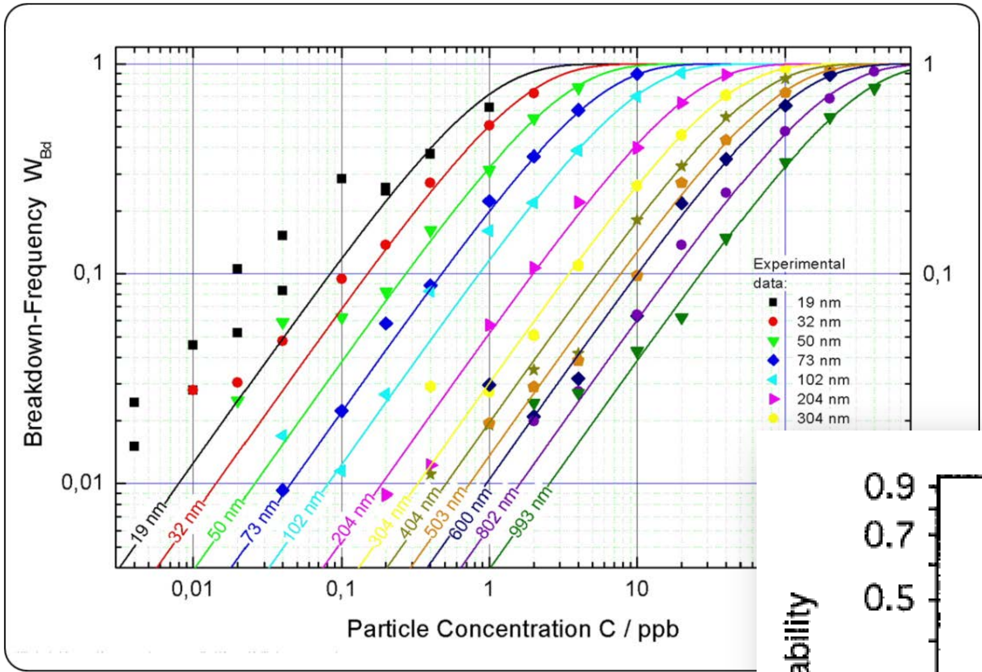
Detection limits (3σ) of LIBD in comparison with scattering light detection for monodisperse polystyrene particles

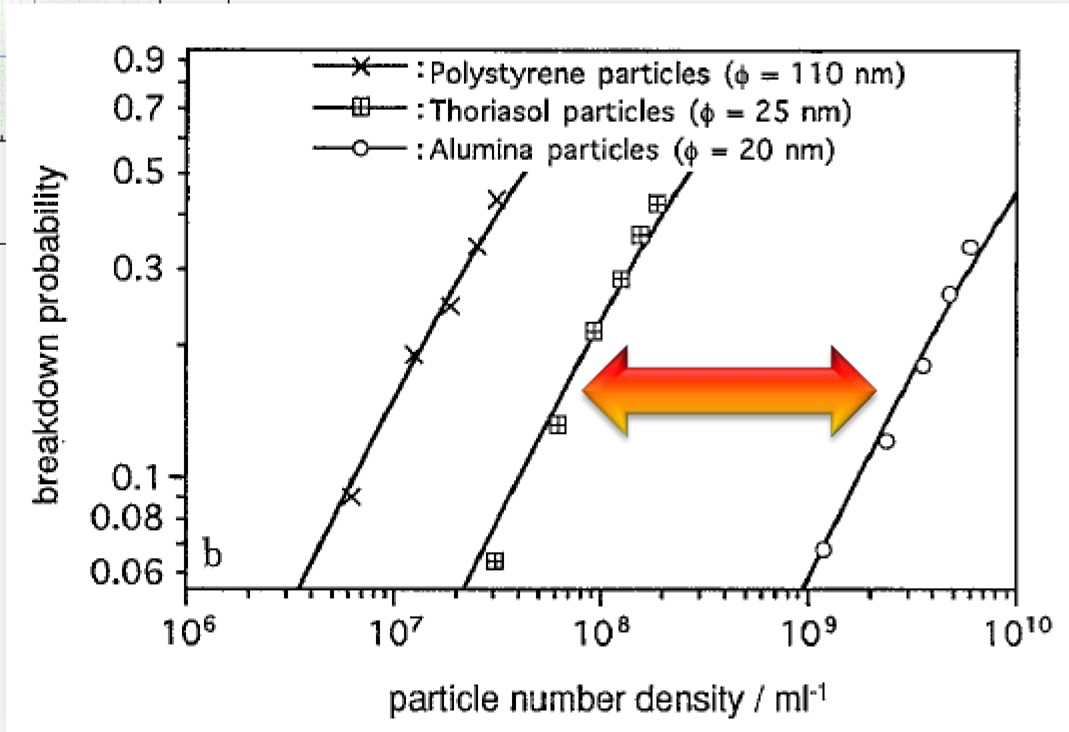
Advantages:

- Direct method
- Detection limit in the sub- ppt-range ($<10^5$ particles/ml),
- Highest sensitivity for particles <100 nm,
- suited for in situ & online detection,
- simultaneous detection of particle diameter and concentration,
- compact, mobile instrumentation
- **BUT: not suited for high concentration!**

Calibration with Polystyrene spheres

Material dependency





Scherbaum, Knopp, Kim Applied Physics B-Lasers and Optics, **63(3)**, 299-306 (1996).

Breakdown thresholds are calculated to be:
$P_{A.crit}$ (polystyrene) :
$P_{A,\ crit}$ (thoriasol) :
$P_{A.crit}$ (alumina) =
1 : 1.1 : 1.7

Outline

- **LIBD Technique**
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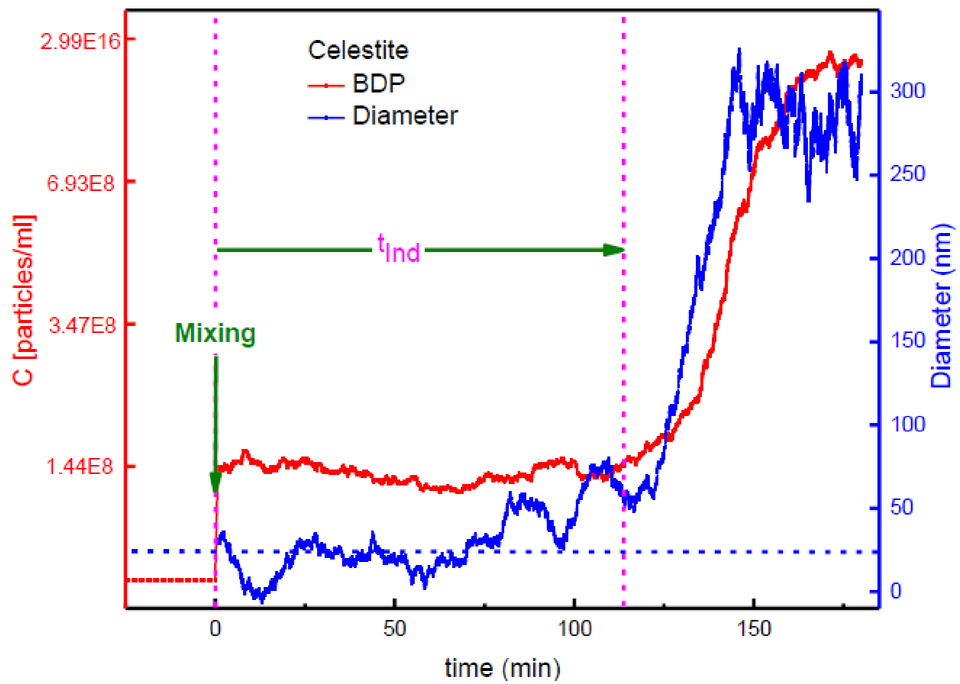
  - Optical system
  - Acoustic system
  - Calibration

- **Application examples**
  - Nucleation measurements
  - Solubility measurements
  - Colloid mobility in natural formations

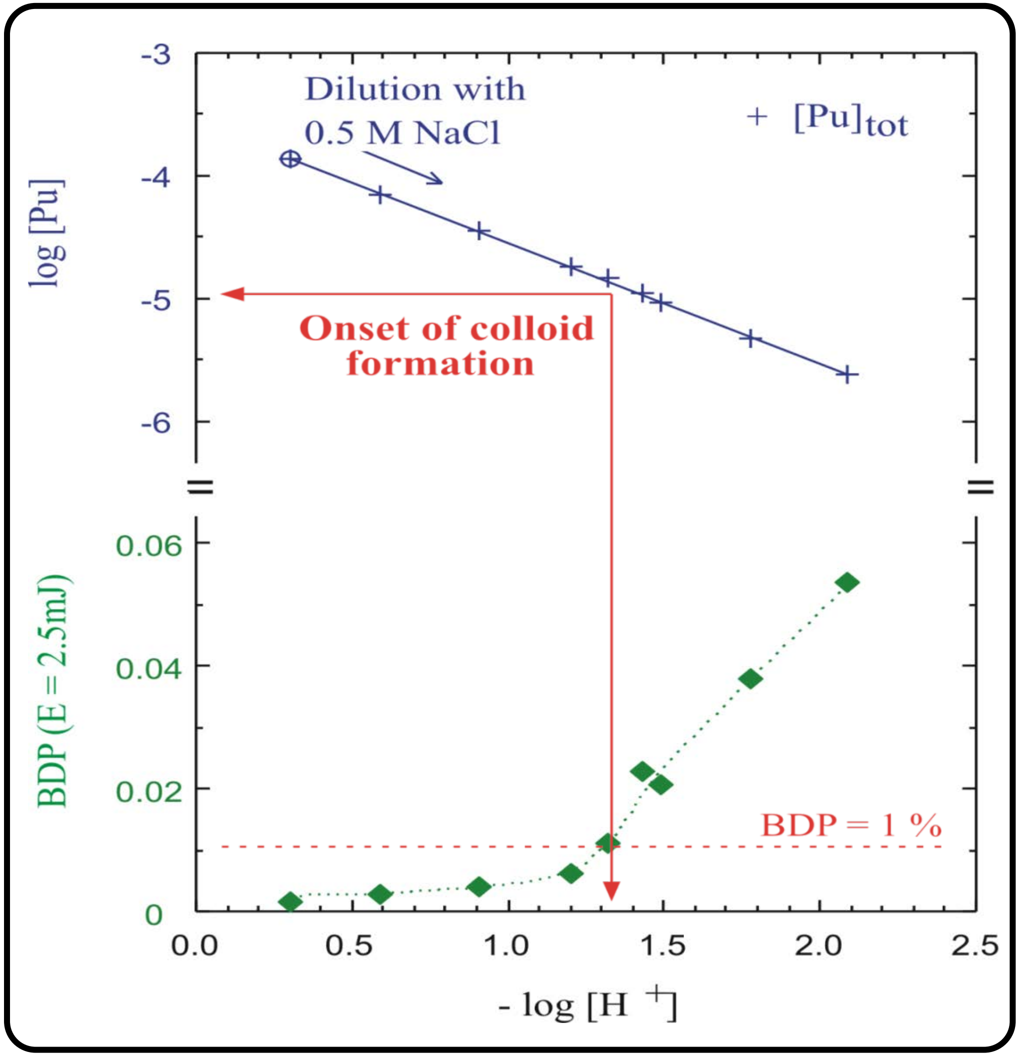
Precipitation Kinetic of Celestite, Saturation Index 0.8 (Example Long Time Online-Detection Mode)

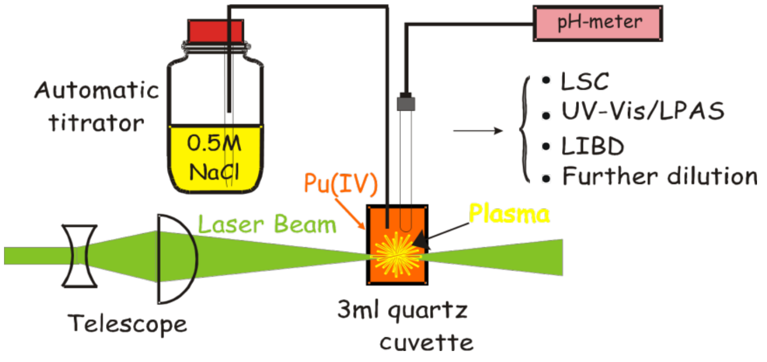
LIBD Parameter:
- Online storage of breakdown images on data server
- Image detection 5 Hz
- 150 000 laser shots → 500 min. detection time (max. 900 000 → 3 000 min. , 100% BDP)

LIBD Result:
- 35 767 breakdown images → Integral BDP: 24%



Solubility determination:
Example Colloid formation in Pu(IV) solutions

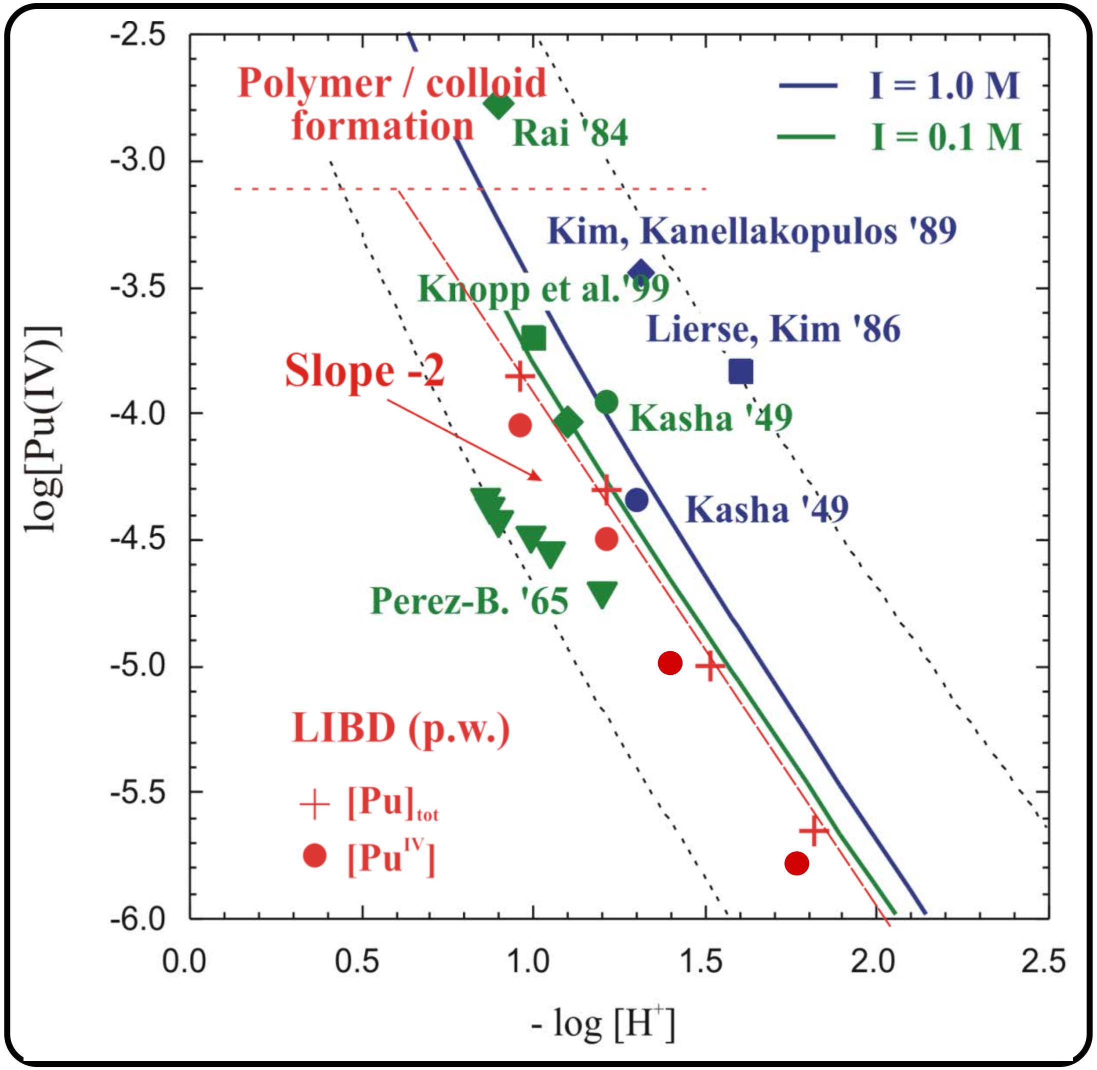




[3] Walther, Cho, Fanghänel, Appl. Phys. Lett. **85**, 6329-6331 (2004).
[4] Neck, Müller, Bouby, Altmaier, Rothe, Denecke, Kim, Radiochim. Acta, **90** 485-494 (2002).

Solubility determination:

Example Colloid formation in Pu(IV) solutions



$Pu^{4+} + 2H_2O \leftrightarrows Pu(OH)_2^{2+} + 2H^+$

$Pu(OH)_2^{2+} \leftrightarrows$ Colloids

$\log K^{O}_{SP} = -59.0$

A $^{242}Pu(IV)$ solution (pH=0.3) is very slowly diluted with 0.5M NaCl (pH increase, [Pu] decrease) which leads to the formation of Pu(IV) colloids, as observed by LIBD. From the crossing-points of colloid formation (log of [Pu(IV)] ↔ pH), we obtain the solubility curve (slope = -2) indicating that $Pu(OH)_2^{2+}$ represents the dominant species.[4,5]

[3] Walther, Cho, Fanghänel, *Appl. Phys. Lett.* **85**, 6329-6331 (2004).
[4] Neck, Müller, Bouby, Altmaier, Rothe, Denecke, Kim, *Radiochim. Acta*, **90** 485-494 (2002)

Sampling sites (in situ & off site analysis)

KIT
Karlsruher Institut für Technologie

Forsmark/ Laxemar (sampling cylinder)

INE (laboratory)

SKB
Svensk Kärnbränslehantering AB

Äspö Underground Laboratory (in-situ)

nagra

Grimsel Test Site (in-situ)

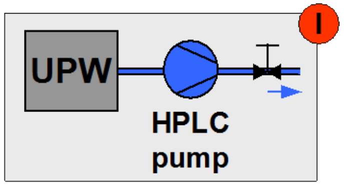
SÚRAO

ÚJV

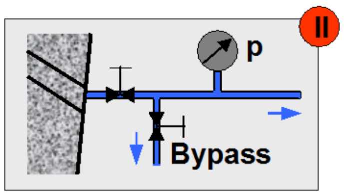
GRS
Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH

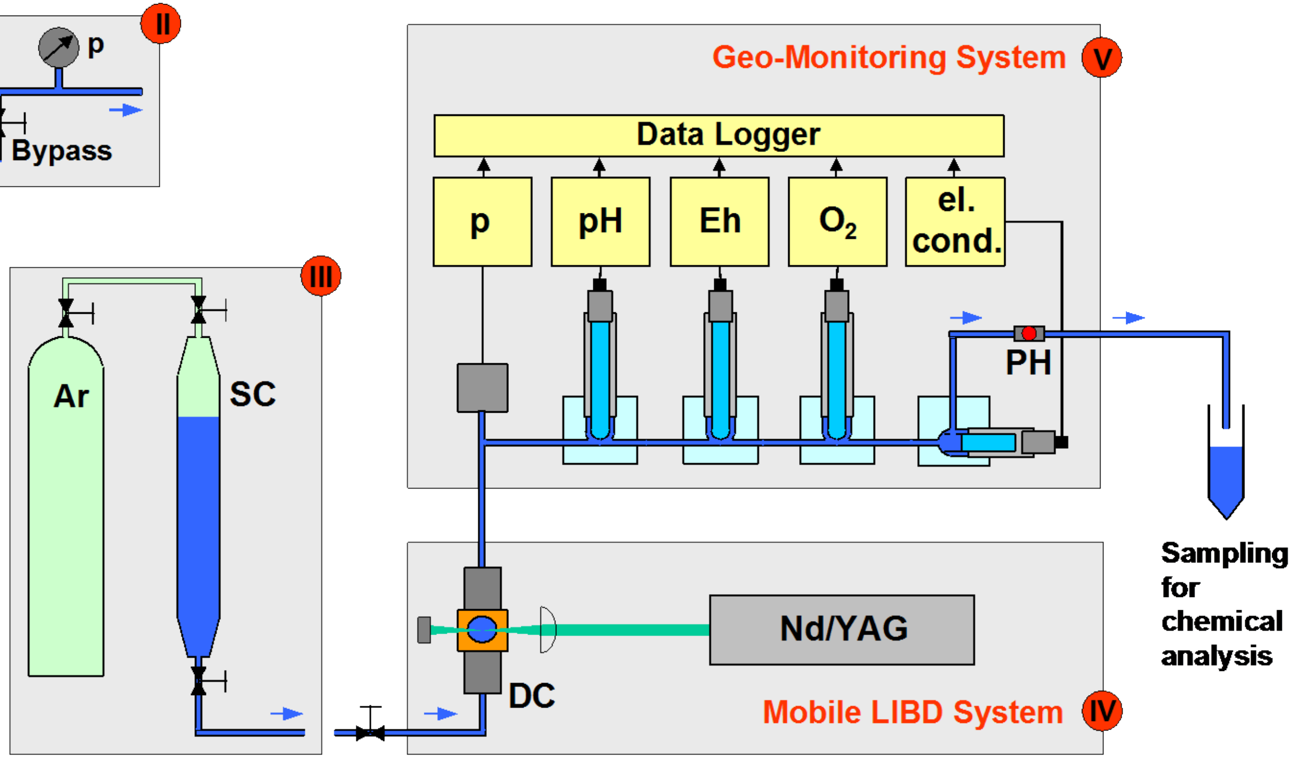
Ruprechtov (remote operated sampling cylinder)

The sampling and detection system



Variable configuration for
- system rinsing with ultra-pure water I
- in-situ detection (inline borehole sampling) II
- detection with sampling cylinder III





UPW: ultra-pure water processing unit
SC: sampling cylinder
DC: LIBD detection cell
PH: pressure holder

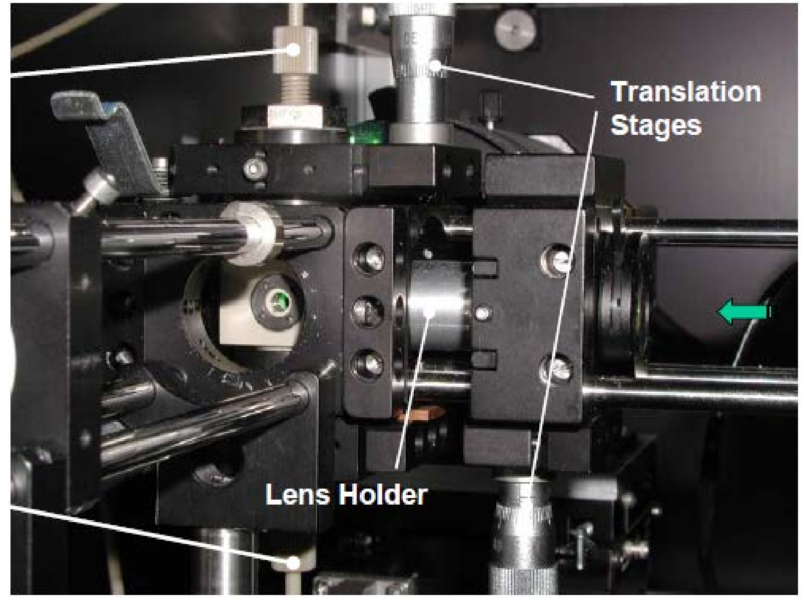
Flow through cell design

Normal Pressure Flow-Through Detection Cell

Hellma Cuvette (Silica)

High Pressure Flow-Through Detection Cell

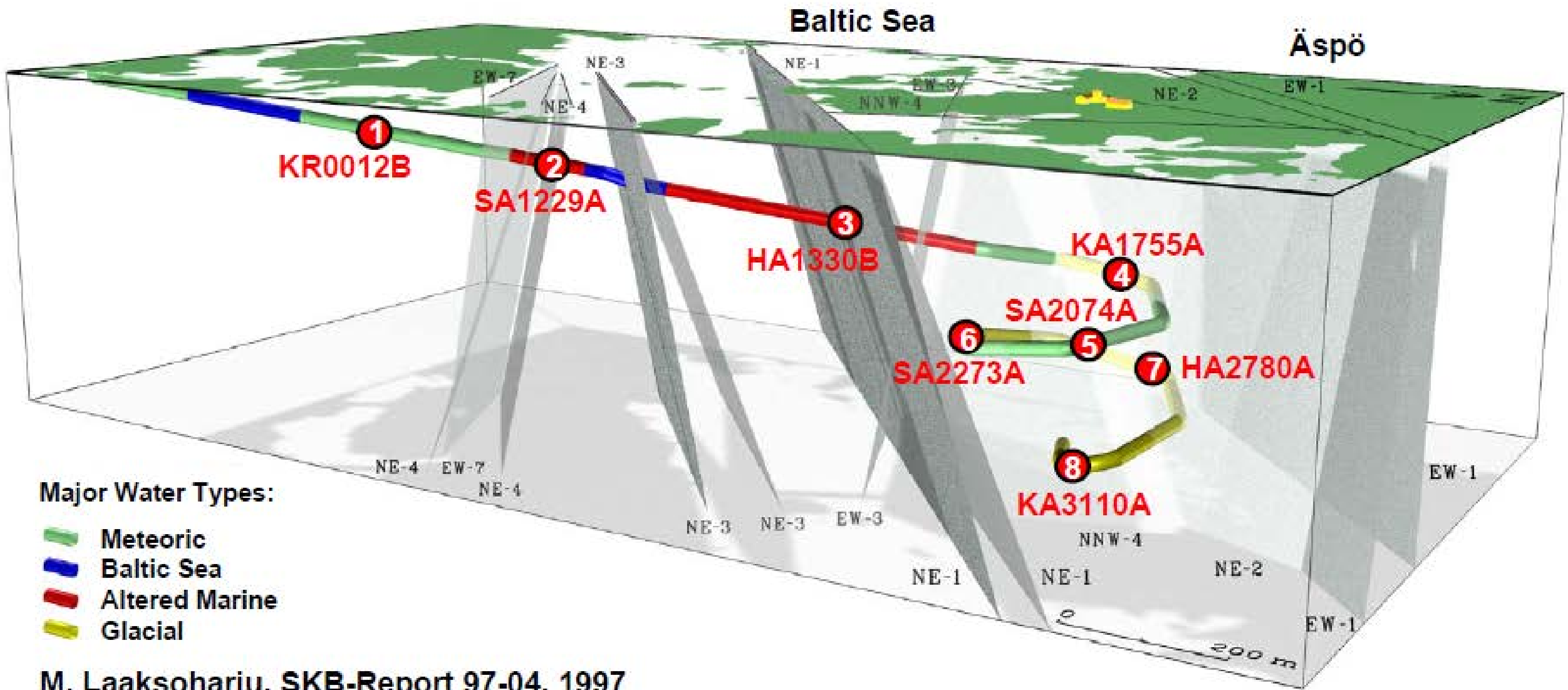
INE-Developed (PEEK with Stainless Steel Housing)



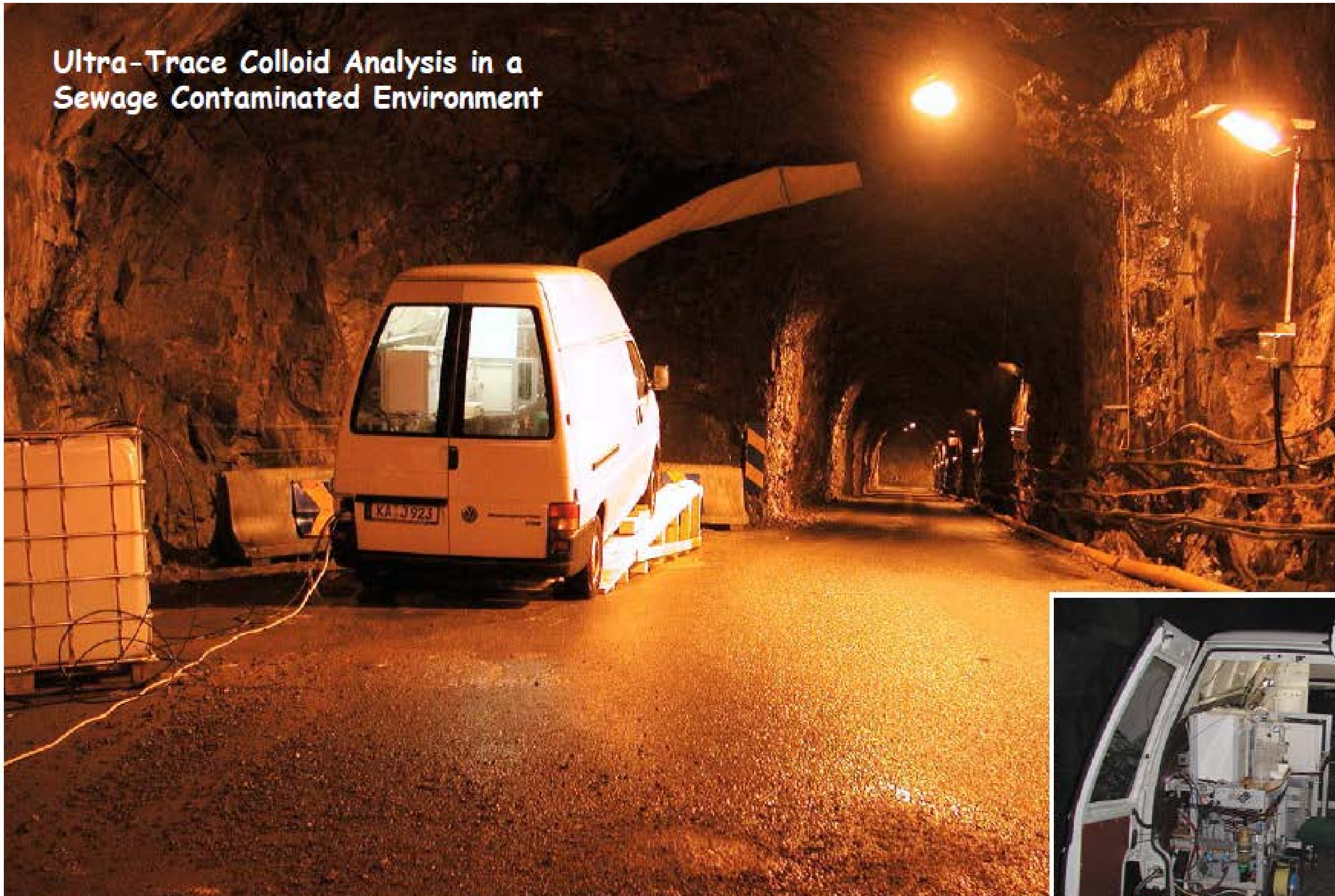
Mounted High Pressure Flow-Through Detection Cell

Max. pressure:	60 bar
Sample volume:	0.83 ml
Absorption length:	12 mm
Window diameter:	4 mm

Sampling locations along the Äspö HRL-tunnel

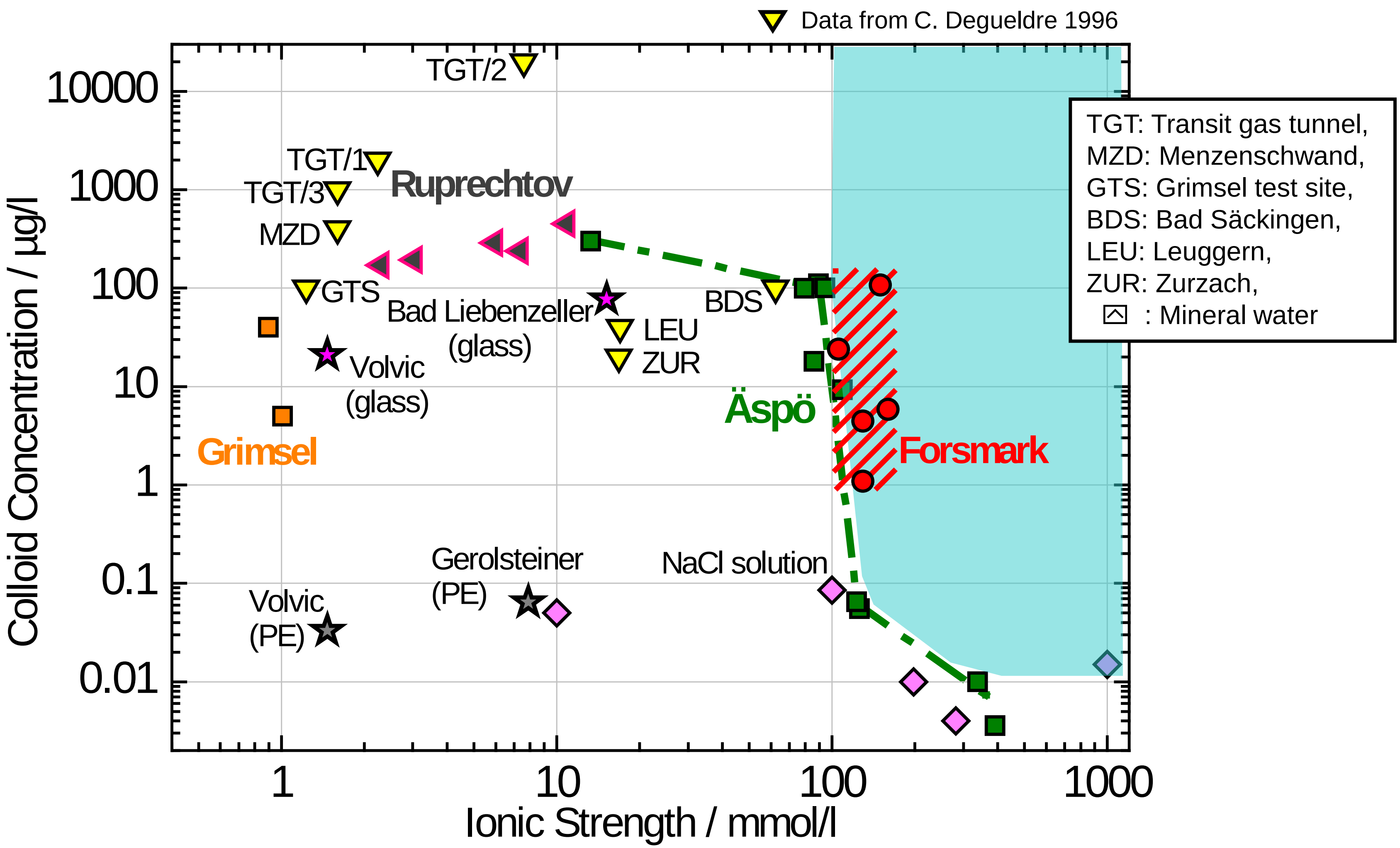


M. Laaksoharju, SKB-Report 97-04, 1997



LIBD Van in the Äspö HRL-Tunnel

Natural groundwater colloid concentration as a function of the ionic strength



Acknowledgement

INE Personnel involved in the LIBD development and application since the 90ties:

- **Franz Scherbaum**
- **Roger Knopp**
- **Tobias Bundschuh**
- **Il Yun**
- **Wolfgang Hauser**
- **Robert Götz**
- **Muriel Bouby**
- **Sebastian Büchner**
- **Clemens Walther**
- **Tobias Hippel**
- **Carmen Garcia**
- **Franz Rinderknecht**
- **Louis Temgoua**

With a lot of contributions & ideas from INE colleagues……