

## Radionuclide analysis by laser spectroscopy

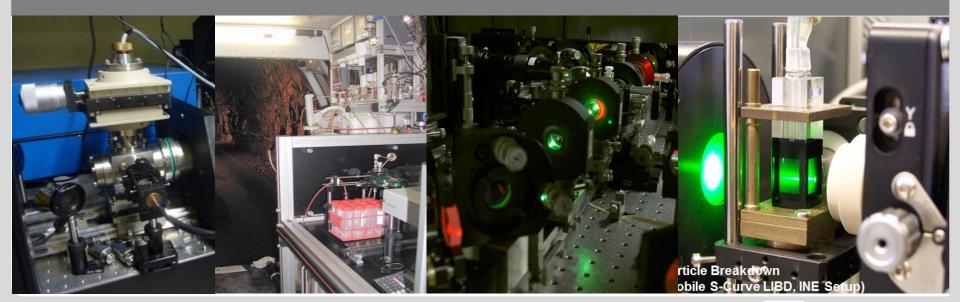
Dr. Carmen C. Garcia Perez

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**European Summer School 2017** 

"Radiochemistry and nuclear instrumentation (low level radioactivity)"

#### Institute for Nuclear Waste Disposal (INE)



## Laser Spectroscopy (LS) methods



✓ Methods where the interaction of laser light with matter is used as excitation or sampling tool in its characterization.

## Speciation analysis

Dr. Carmen C. Garcia Perez

Analytical activities of identifying and/or measuring the quantities of one or more individual chemical species - specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure- in a system

PAC, 2004, 76, 1033 (IUPAC Recommendations 2003)

Colloids determination or elemental composition...speciation analysis?

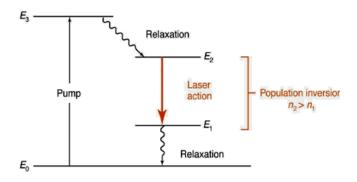
## Laser as excitation / sampling tool

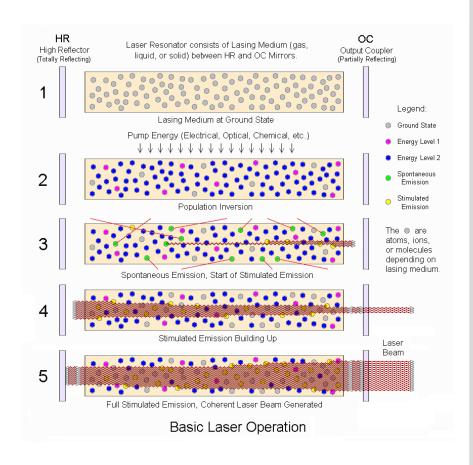




## <u>LASER-Light Amplification by Stimulated Emission of Radiation</u>

Laser radiation is any electromagnetic radiation with wavelengths in the range between 100 nm and 1 mm, which arises as a result of controlled stimulated emission.

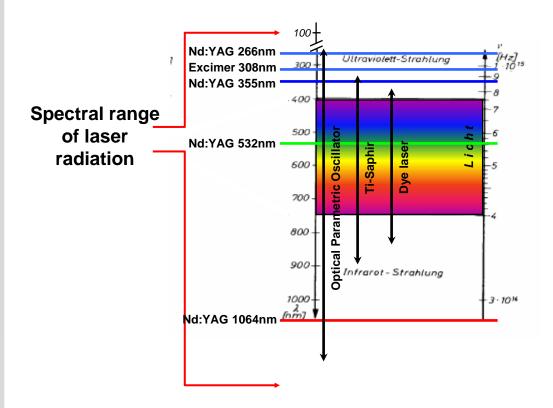




Advantages of lasers in spectroscopy: temporal and spatial <u>coherence</u>, narrow <u>linewidth</u> and <u>wavelength tunability</u>, <u>optical power</u> (particularly peak power), <u>ultrashort pulse</u> generation etc.

## Typical lasers used in LS





- ✓ Nd:YAG (ns,ps,fs)
- √ Tuneable lasers: dye laser, OPO, Ti:Saphire laser
- √ Fiber laser
- ✓ Diode pumped solid state (DPSSL)

#### **Pulse duration**

- cw Laser (continuous wave laser)
- Q-Switch Laser (ns, ps)
- Mode-locked Laser (ps, fs)

## Two regimes of power

- Low fluence: no plasma formation
- High fluence: threshold for plasma formation exceeded

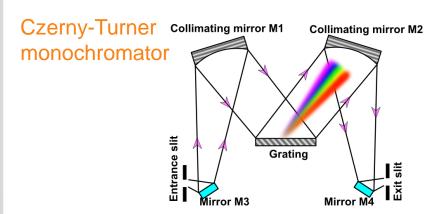
## **Optical Spectrometers (spectrophotometer)**

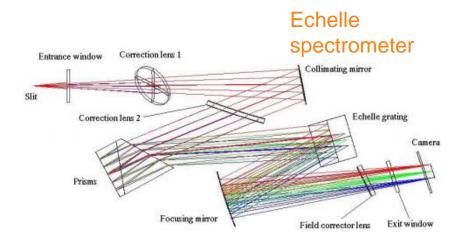


Measure properties of light over a specific portion of the electromagnetic spectrum

#### Wavelength selectors: Narrow bandwidth required

Monochromator-Polichromator (Separation of multi- $\lambda$  light into individual  $\lambda$ 's)





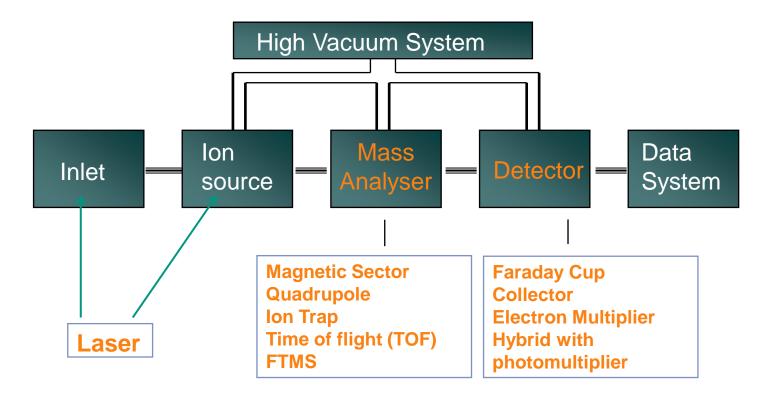
## **Detectors:** High quantum efficiency and dynamic range, low level noise and dark current

- CCD (charge coupled device) camera- intensified
- •sCMOS (scientific complementary metal—oxide—semiconductor) camera
- ■PMT (Photomultiplier tube)
- Photondetector- Photoacustic detectors

## **Mass spectrometer**

# Karlsruhe Institute of Technology

### Getting isotopic information

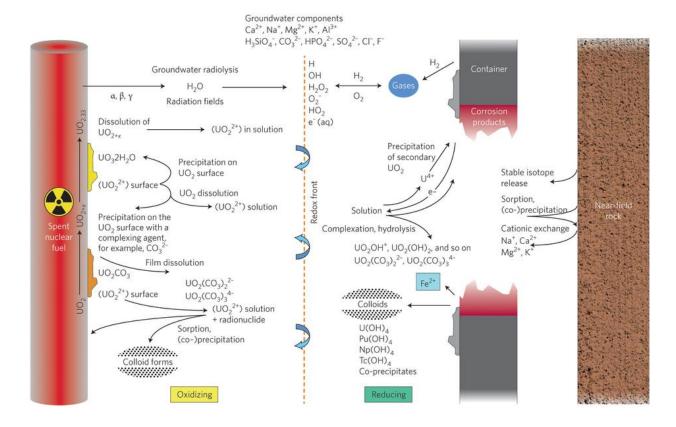


MS is generally considered a spectroscopic method; although instead of sorting a beam of light containing different frequencies, you sort a beam of atoms or small molecules.

## Nuclear waste disposal: important processes to be studied



- spent fuel characterization and alteration mechanisms
- > mechanisms controlling radionuclide concentration in solution in the near-field environment of the fuel (groundwater, corroded waste package, or backfill if present) and in surrounding rocks/soils



## Laser Spectroscopy techniques



(Development of Laser Spectroscopic Methods for RNs analysis at INE)

- TRLFS (at room, high and low temperature)
- S-Curve LIBD and Optical LIBD
- LPAS/LIPAS
- LIBS
- LA-ICP-MS
- RAMAN

Main applications of laser spectroscopy at INE:

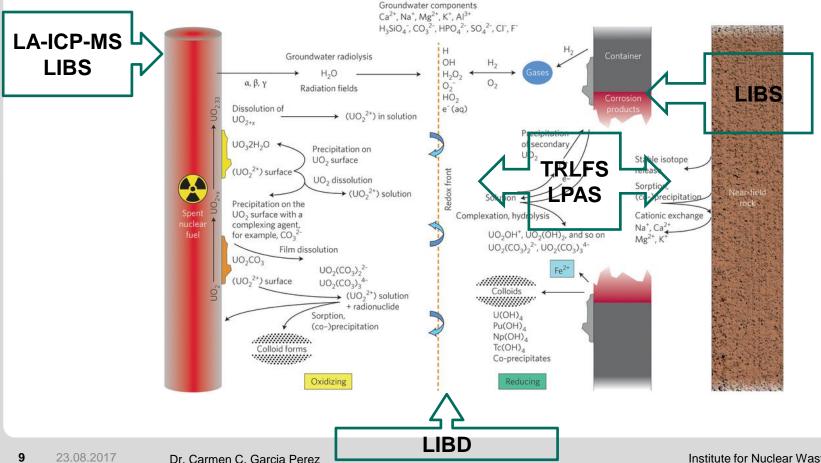
- ☐ Speciation; coordination chemistry of complexes, sorption and
  - incorporation studies (TRLFS, LPAS, RAMAN)
- ☐ Colloids formation, detection and quantification (LIBD)
- □ Surface analysis with spatial resolution (LIBS/LA-ICPMS)

## Nuclear waste disposal: important processes to be studied

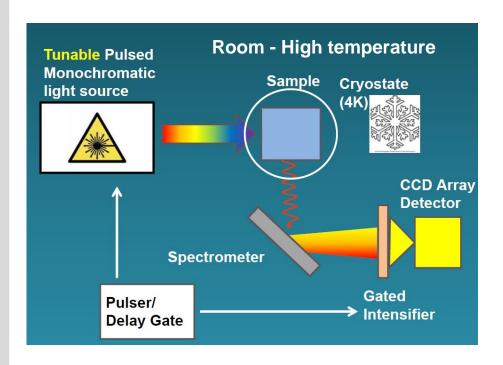


- > spent fuel characterization and alteration mechanisms
- ➤ mechanisms controlling radionuclide concentration in solution in the near-field environment of the fuel (groundwater, corroded waste package, or backfill if present) and in surrounding rocks/soils

#### Applications of Laser Spectroscopy Techniques







- **TRLFS** main facts
  - No disturbance of the chemical equilibrium
  - High sensitivity
  - Speciation in the nanomolar range
  - Applicable to solutions suspensions and solids
  - Possibility of studies at low, room and high temperature
  - Characterization of metal ion complexes
    - Coordination sphere
    - Hydration sphere

#### Limit of Detection

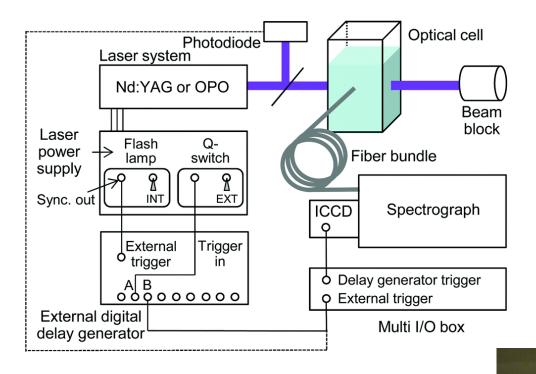
lon	<b>TRLFS</b>
U-(VI)	1E-10 Mol/I
U-(IV)	<1E <sup>-6</sup> Mol/l
Pa-(IV)	<1E <sup>-8</sup> Mol/l
Am-(III)	1E <sup>-9</sup> Mol/l
Cm-(III)	2E <sup>-11</sup> Mol/l
Nd-(III)	3E <sup>-7</sup> Mol/l

Speciation typ. at 100x higher concentrations

- ✓ Actinides: Cm(III),Am(III),U(VI),Pa(IV),Bk(III),Cf(III)
- ✓ Lanthanides: Eu(III),Gd(III),Tb(III) (Ce(III),Sm(III),Dy(III))

## **TRLFS typical SET-UP**





TRLFS at high temperature / high pressure cell





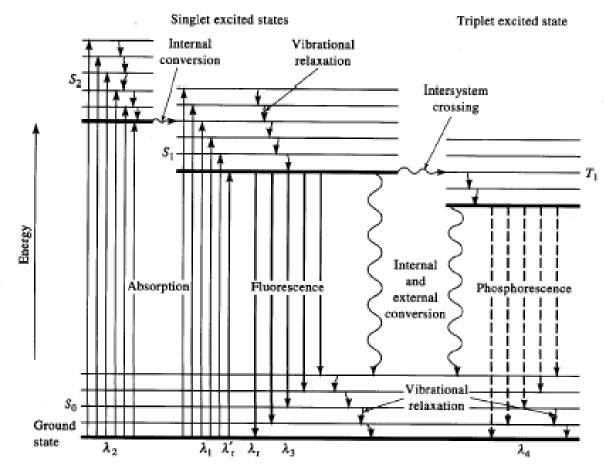
**TRLFS** at liquid He temp. (4K)

## **Energy Level- Jablonski Diagram**



Molecules: Numerous vibrational energy levels for each electronic state

Absorption 10<sup>-15</sup> s Vibrat. Relaxation 10<sup>-12</sup> s Fluorescence 10<sup>-8</sup> s Phosphorescence >10<sup>-4</sup> s

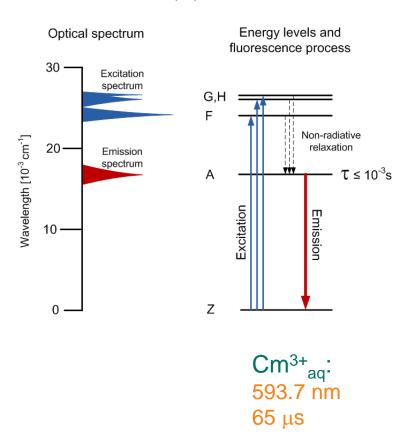


Non-radiative deactivation in absorption spectroscopy: electronic energy is converted into vibrational energy via an internal conversion (IC)

23.08.2017



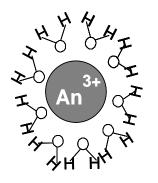
#### Term scheme of Cm(III)

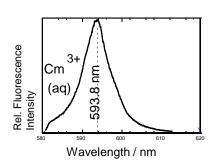


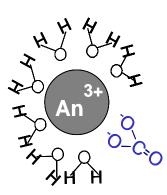
- Fluorescence effects result from f-f- transitions of electrons after excitation by laser light of a certain wavelength (e.g. 396.6 nm Cm(III)).
- <u>Fluorescence lifetime</u>: average time the molecule stays in its excited state before emitting a photon.
- No disturbance of chemical equilibrium (compare extraction)
- Transition highly sensitive to minor changes in the environment.
- High sensitivity → ultratrace analysis, An / Ln speciation in nanomolar range (e.g. 10<sup>-9</sup> mol/L Cm(III))
- Due to low f-f- transition probability (Laporte forbidden) long fluorescence lifetimes (τ = μs-ms)

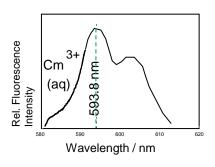


#### Fluorescence spectrum

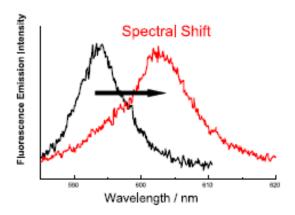








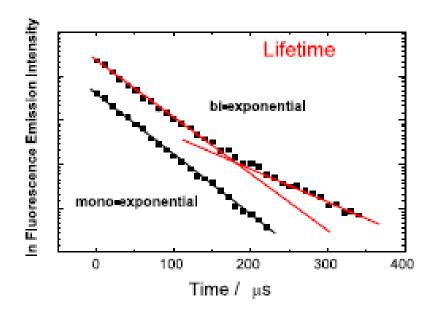
- "Inner-Sphere" complexation
- Identification und quantification of different species

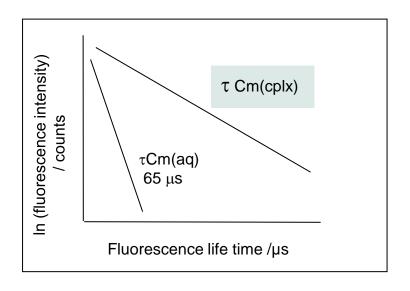


Bathochromic shift ('redshift') of the fluorescence emission caused by a change of the ligand field



#### Fluorescence life time





- The number of coordinated quenching ligands determines the fluorescence lifetime.
- Information on the number of water molecules in the inner coordination sphere
- Identification of different species
- A biexponential decay indicates the simultaneous presence of two species with different numbers of quenching ligands

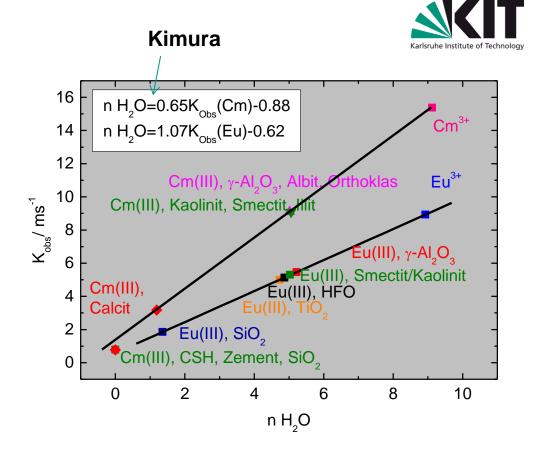
23.08.2017

## TRLFS of Eu(III) and Cm(III)

- Coordination symmetry (emission spectrum) and...
- Hydration state (fluorescence lifetime)

#### Fluorescence Lifetime τ:

OH-oscillations = quencher! The more OH (H<sub>2</sub>O), the shorter the fluorescence lifetime n(H<sub>2</sub>O) in first coordination sphere:



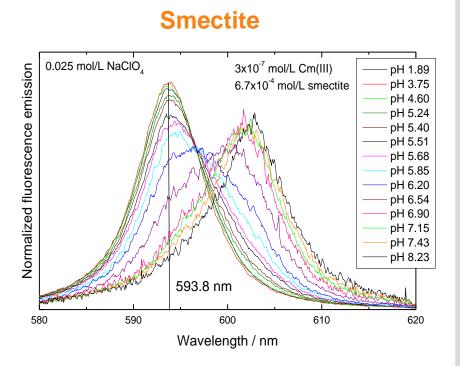
Lifetime	Aquoion	0 H <sub>2</sub> O	Longest τ
Eu <sup>3+</sup>	0,110 ms	1,726 ms	4,368 ms (CaCO <sub>3</sub> )
Cm <sup>3+</sup>	0,065 ms	0,739 ms	5,067 ms (CaCO <sub>3</sub> )

Kimura et al. Radiochimica Acta 72 (1996) 61-64



### **Emission spectra of Cm(III) in aqueous** Mineral suspensions (kaolinite and smectite) at various pH

#### **Kaolinite** 0.025 mol/L NaClO 3x10<sup>-7</sup> mol/L Cm(III) Normalized fluorescence emission pH 1.89 9.7x10<sup>-4</sup> mol/L kaolinite pH 3.68 pH 5.00 pH 5.40 pH 5.37 pH 5.54 pH 5.79 pH 6.18 pH 6.65 pH 7.22 pH 7.68 pH 8.22 593.8 nm 590 600 610 580 620



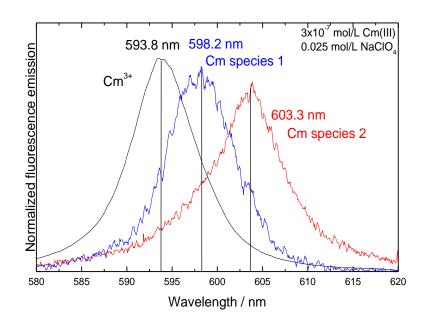
Stumpf et al., Environ. Sci. Technol. 35 (2001) 3691-3694

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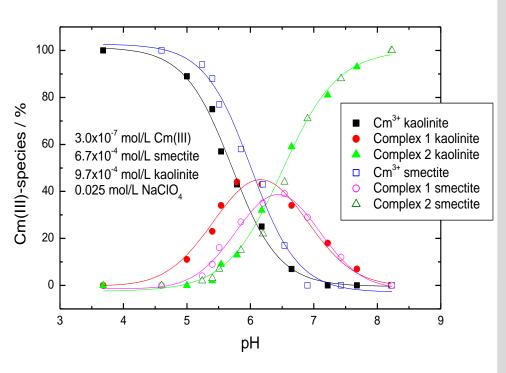
Wavelength / nm



#### Spectra of Cm<sup>3+</sup>, Cm/clay sorption species 1 and 2 derived by peak deconvolution



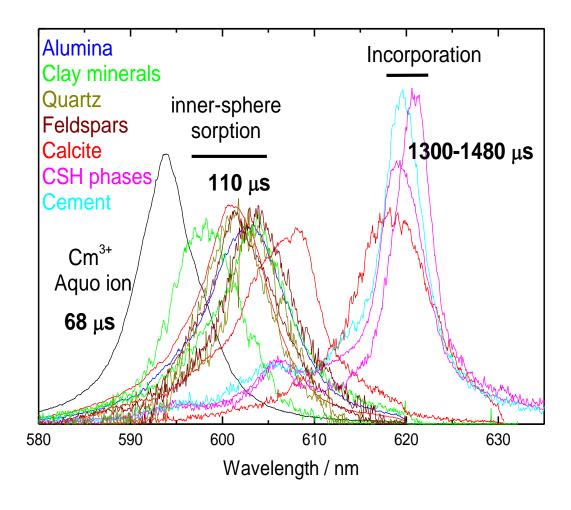
### Species distribution of Cm(III) as a function of pH in presence of kaolinite and smectite



Stumpf et al., Environ. Sci. Technol. 35 (2001) 3691-3694

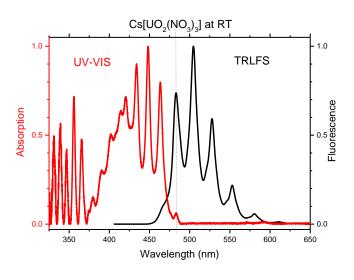


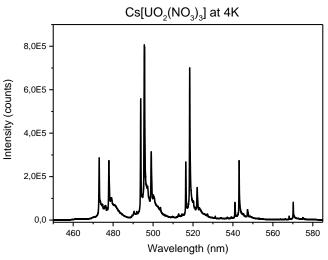
#### Spectra from aqueous Cm<sup>3+</sup>, sorbed and incorported species



**Uran (VI)- Speciation** 

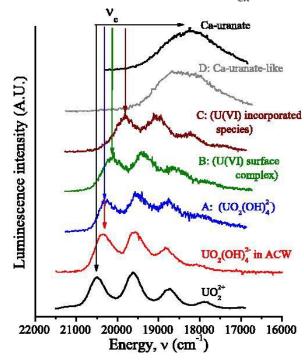






# Comparison of spectra from sorbed and aqueous uranyl species





Increasing red shift (lower energy):
Indication of weakening of the axial U=O
bond, (lower stretch frequency)

J. Tits et al, J. Colloid Interf. Sci.359 (2011) 248-256

#### LIBD - Laser Induced Breakdown Detection

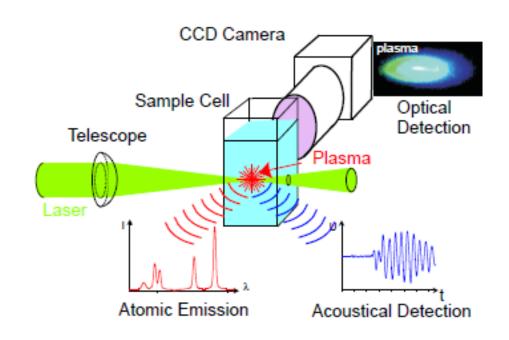


#### **Information:**

Size and number density of particles / aquatic colloids < 1000 nm determined down to the ppt-concentration range (10<sup>5</sup> particles/ml)

#### Two configurations:

- Optical detection of the BD events with a CCD camera
- Acoustic detection of th generated shockwave with a piezo detector
- Possibility of coupling with LIBS



Irradiance for BD generation:













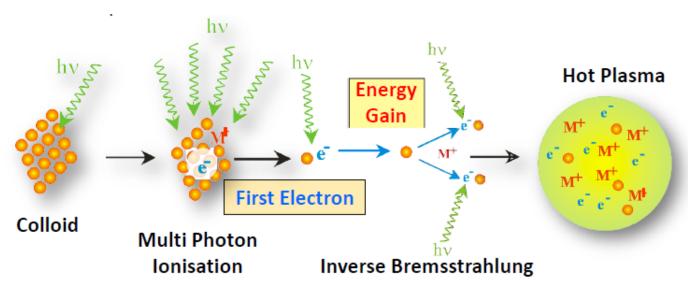






#### **Fundamentals: Plasma Generation**





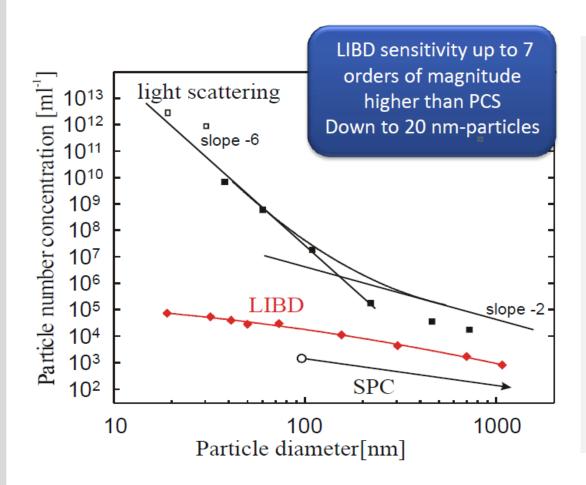
When a laser shot is focused tightly into a medium and a certain pulse energy threshold is exceeded, a so called breakdown (BD) occurs.

- In the beginning at least one atom is ionized by multi-photon ionization (MPI), resulting in a seed 1. electron which is accelerated by inverse Bremsstrahlung in the high electric field of the laser pulse.
- After gaining sufficient energy additional atoms are ionized by collisions, multiplying the number of electrons.
- As a result, the density of the free charge carriers increases in avalanche after a few consecutive interactions inducing the plasma formation.

#### LIBD - Laser Induced Breakdown Detection



#### Detection limit compared to different nanoparticle detection methods



#### Advantages:

- Direct method
- Detection limit in the sub-ppt-range (<10<sup>5</sup> particles/ml)
- Highest sensitivity for particles <100nm
- Suited for in-situ & online detection
- Simultaneous detection of particle diameter and concentration
- Compact, mobile instrumentation
- BUT: not suited for high concentration

#### LIBD - Laser Induced Breakdown Detection



#### Since 1996 in KIT-INE...

Appl. Phys. B 63, 299-306 (1996)



## Counting of particles in aqueous solutions by laser-induced photoacoustic breakdown detection

F. J. Scherbaum<sup>1,2</sup>, R. Knopp<sup>1</sup>, J. I. Kim<sup>1,2</sup>

Received: 13 November 1995/Accepted: 1 April 1996

Abstract. Laser-induced photoacoustic breakdown detection is applied for the determination of particles in aqueous dispersion. Polystyrene (latex), alumina and thoriscal

presence of particles, plasma is formed even at a power density much lower than the breakdown threshold of pure liquids. This is attributed to the plasma generation on

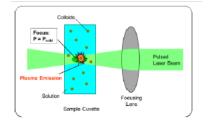
### ....at present in KIT-INE...

- Applications: nucleation and solubility measurements and, colloid mobility in natural formations
- Improving the analytical performance of the technique
- Working in further development (automatization: measuring process and data processing)

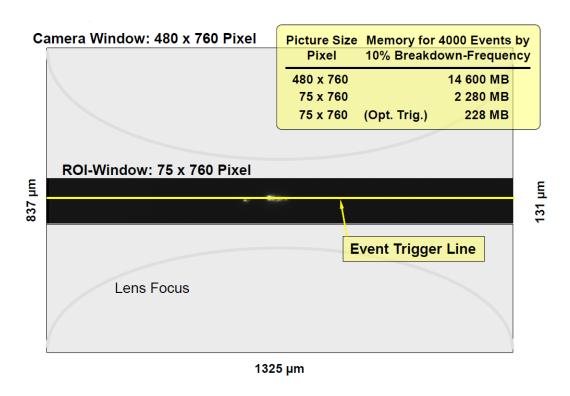
<sup>&</sup>lt;sup>1</sup> Institut für Radiochemie, Technische Universität München, D-85747 Garching, Germany (Fax: +49-89/3261115)

<sup>&</sup>lt;sup>2</sup> Forschungszentrum Karlsruhe, Institut f
ür Nukleare Entsorgungstechnik, D-76021 Karlsruhe, Germany

# LIBD – Optical Detection with a CCD (Definition of an optical trigger event)

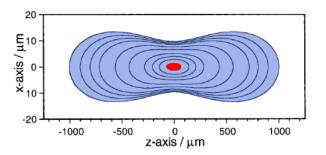




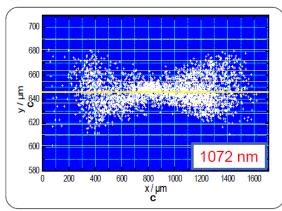


- ✓ Typical ionization energies of solids: 6 eV < E₁ < 10 eV (lower energy for larger colloids needed)
- ✓ Typical ionization energies of water: 18.11 eV < E₁ < 18.72 eV
  </p>

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



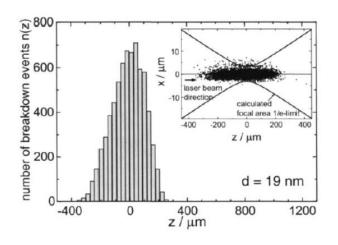


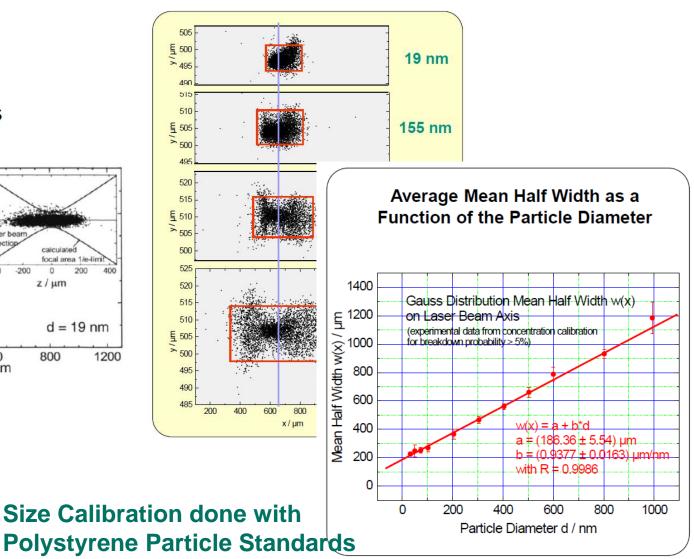


## LIBD – Optical Detection with a CCD camera



Particle Size
Dependence of
Breakdown
Emission Centers



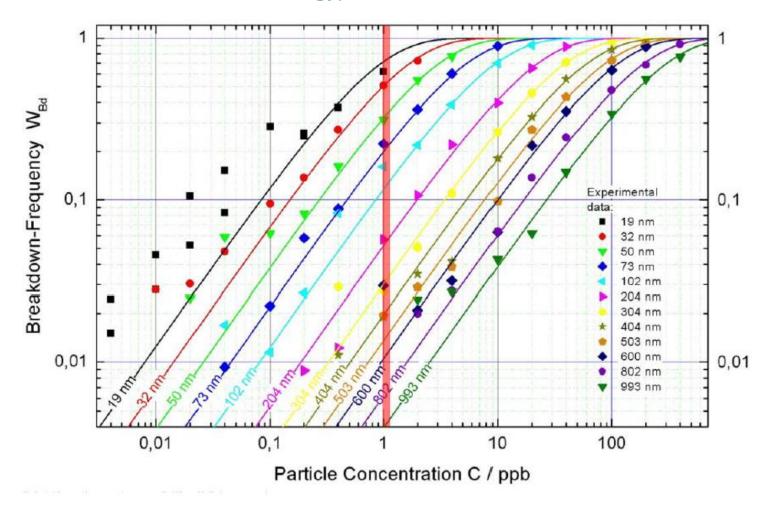


## **2D Optical LIBD**



## Concentration Calibration done with Polystyrene Particle Standards Karlsruhe Institute or

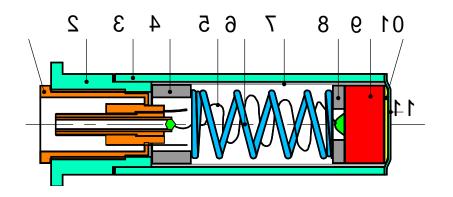
(Measurement at constant laser energy)



## LIBD – Acoustic detection (Building S-Curves)



### **INE Photoacoustic Sensor** (\*)

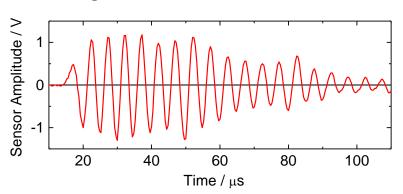


Ø 13 mm, length 44 mm

- (1) coaxial socket
- (2) steel casing back end
- (3) steel casing
- (4) Teflon ring
- (5) isolated Cu wire
- (6) spring

- (7) polyethylene foil
- (8) Teflon disc
- (9) piezoceramic detector
- (10) indium disc
- (11) steel diaphragm (25 µm, Al coated)

#### **Sensor-Signal**



#### **Sensor Characteristics**

- Sensor optimizes the acoustic contact between PZT and the sample cuvette itself
- No agents for the acoustic contact (reduction of scattered light)
- Sensor oscillates longitudinal without transversal components
- High reproducibility (A series of sensors with identical response signals)

(\*) Patent KIT (Forschungszentrum Karlsruhe GmbH),
Piezoelektrischer Druckwellensensor, Deutsches Patent DE 196 02 048 C2 (1999), European Patent EP 874978 (1998)

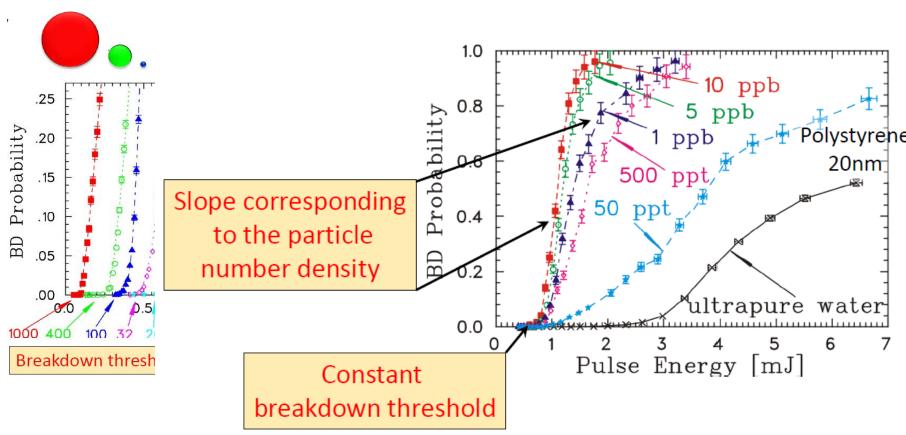
## LIBD – Acoustic detection (Building S-Curves)



## Size-dependency of BDP

## Concentration-dependency of BDP

(20 nm polystyrene particles)

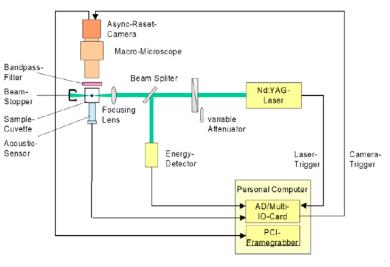


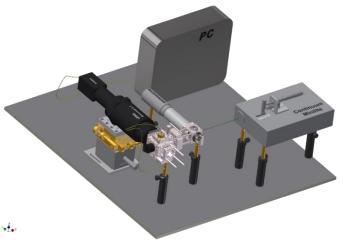
## LIBD – Developments at INE



#### **2D Optical LIBD Instrumentation**

**Offline Picture Processing** 





#### **S-curve LIBD Instrumentation**

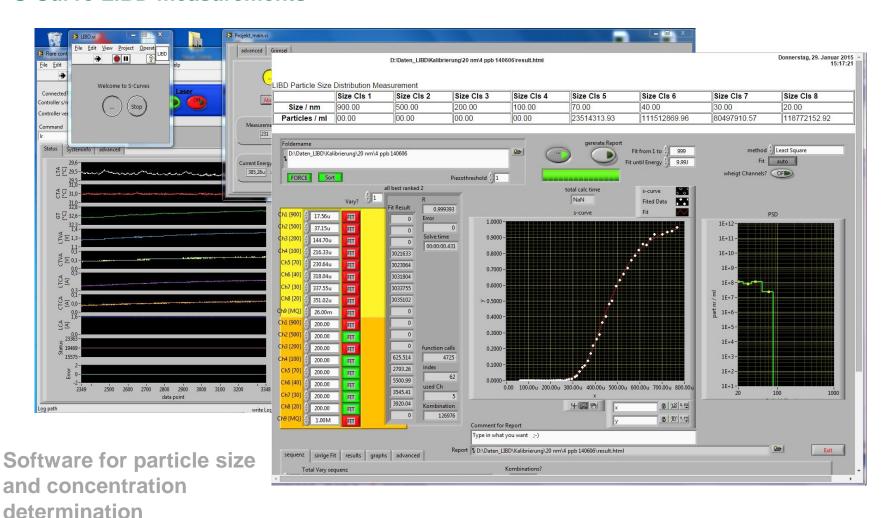
Acoustic detection with piezo detector



## LIBD - Acoustic detection (Building S-Curves)



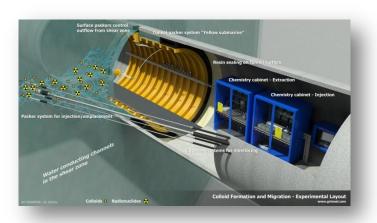
#### INE Development\* of a LabVIEW® program for automatization of the S-Curve LIBD measurements

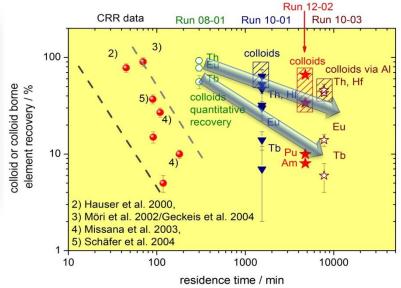


\*by S. Büchner, W. Hauser, R. Götz, F. Rinderknecht, M. Trumm

## **LIBD Field Experiment- Grimsel Test Site**







Colloid filtration observed RN-colloid desorption kinetics

Colloids enhance transport of tri- and tetravalent actinides in ground water. Large colloids travel faster through a column than small ones (size dispersion). By measuring PSD with LIBD this effect is observed for colloids <200 nm at sub-ppb concentration

Dr. Carmen C. Garcia Perez

#### **LIBD - SUMMARY**



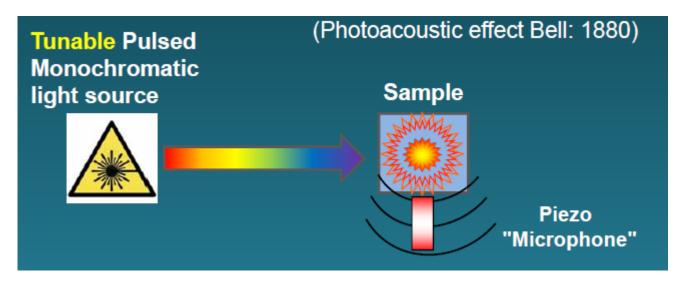
#### **Characteristics of the INE LIBD Instruments**

	2D-Optical Detection LIBD (*) 3 Systems	S-Curve Detection LIBD 3 Systems
	680 640 620 600 600 600 600 600 600 60	993nm 200pb  993nm 200pb  993nm 200pb  19nm 18ppt  90 0.0  15 1.0 1.5 2.0 2.5 3.0 Laser Pulse Energy / mJ
Application	mobile, robust system for field experiments, long time online detection	precise instrument for laboratory-, and field-experiments, commercial, and INE instrument, mini OEM-Laser
Breakdown Detection Method	optical detection, constant laser pulse energy (~1.3 mJ)	photoacoustic detection, varying laser pulse energy (0 - 5 mJ), < 500 µJ
Special Features	pressurized (60 bar, 200°C) flow-through detect. cells, geo-monitoring	flow-through detection cell, pressurized (60 bar, 200°C) cells
Detection Form	online (offline evaluation)	offline
Typical Measurement Duration	1 - 10 min., > 50 h detection mode	0.5 - 1.5 h
Colloid Size Detection	average particle diameter	8 particle size fractions
Colloid Size Range	20 - 1000 nm	15 - 1000 nm
Colloid Concentration Range	ppt - ppm	ppt - ppm

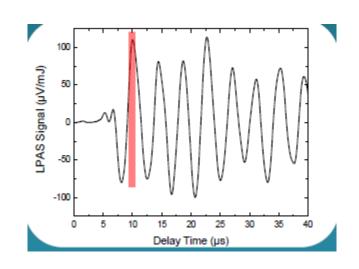
<sup>(\*)</sup> Patent KIT (Forschungszentrum Karlsruhe GmbH), Verfahren zur Bestimmung der Größe von Partikeln, Deutsches Patent DE 198 33 339.0-52 (2000)

## Laser Photoacoustic Spectroscopy (LPAS)





- Ion specific absorption
- **Volume expansion**
- **Generation and propagation** of acoustic wave
- **Detection of acoustic wave** by piezoelectric transducer

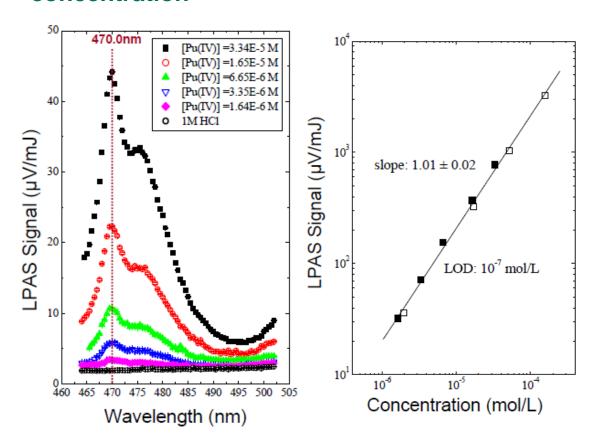


LPAS Prinziple: R. Stumpe, et al., Appl. Phys. B 34 (1984) 203

## Laser Photoacoustic Spectroscopy (LPAS)



## LPAS Signal linear with absorptivity and concentration

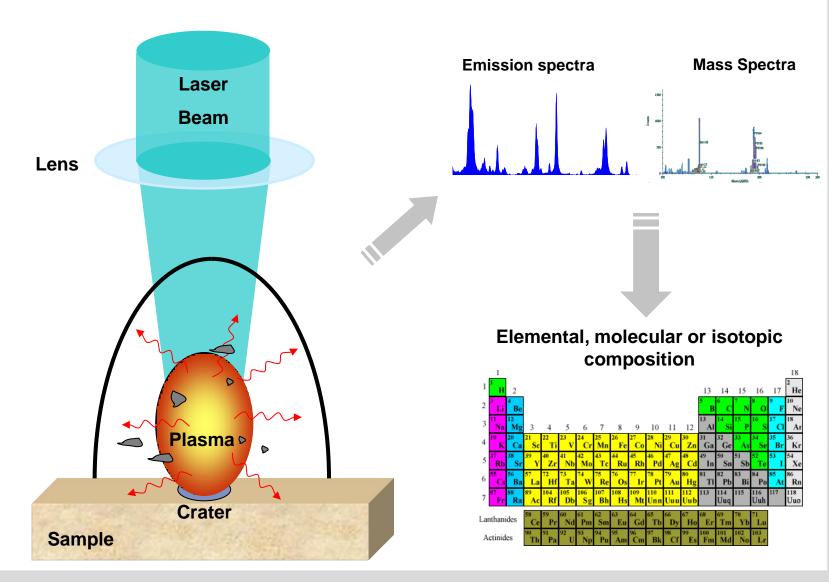


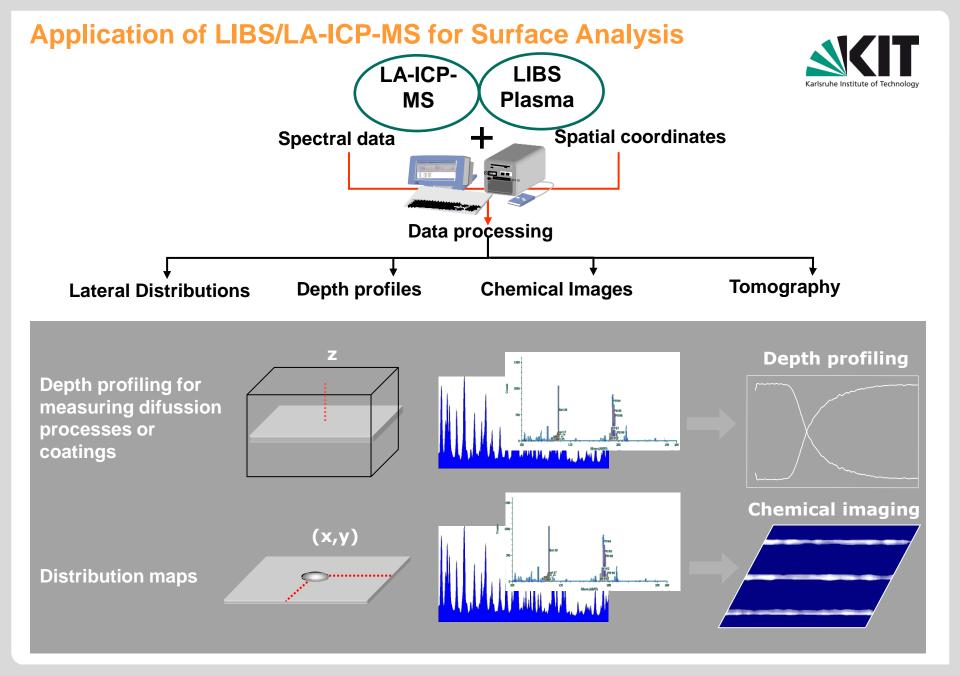
### **Limit of Detection**

lon	TRLFS	LPAS
U-(VI)	1E-10 Mol/l	1E-6 Mol/l
U-(IV)	<1E-6 Mol/l	1E-7 Mol/l
Np-(V)		1E-7 Mol/l
Pa-(IV)	<1E-8 Mol/l	
Pu-(IV)		1E-7 Mol/l
Am-(III)	1E-9 Mol/l	1E-8 Mol/l
Cm-(III)	2E-13 Mol/l	
Nd-(III)	3E-7 Mol/l	1E-5 Mol/l

# Laser Induced Breakdown Spectroscopy (LIBS) Laser Ablation ICP - Mass Spectrometry (LA-ICP-MS)

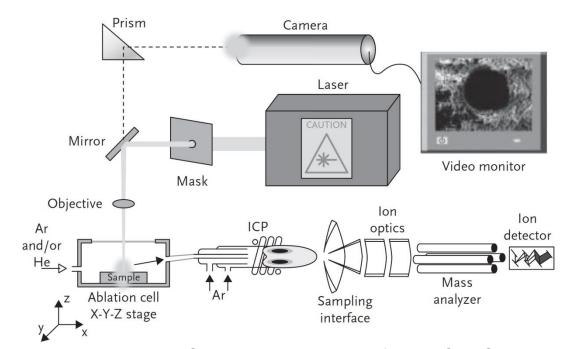






# Laser Ablation ICP-Mass Spectrometry (LA-ICP-MS)



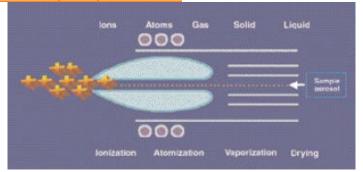


Schematic representation of an LA-ICP-MS set-up

Powerful analytical technology that enables highly sensitive elemental and isotopic analysis to be performed directly on solid samples without sample preparation.

**Semi-quantitative Analysis** 

#### **Inductively Coupled Plasma**

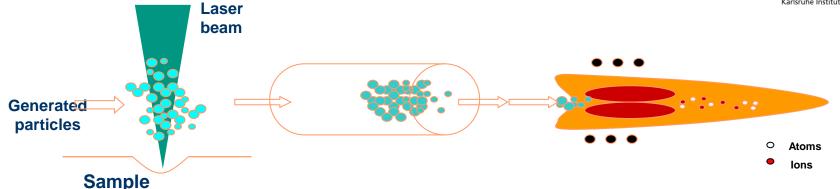


Atmospheric pressure discharge

- Relatively high argon flow rate (Liters per minute)
- After ignition, coupling of ionic charge with RF magnetic field "forces" ions to move
- Heating results, plasma is sustained

### Ideal scenario in LA-ICP-MS/OES ...





Laser ablation without fractionation

No mass losses from the ablation cell to the ICP

Laser generated particles which are completely atomized in the ICP

**Particle size distribution** 

good for transport good to avoid losses good for atomization

**Non-matrix calibration** with LA-ICP-OES/MS

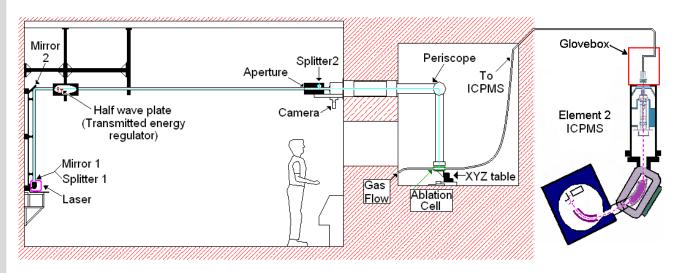
Best conditions for getting semi quantitative information: use of short UV wavelength, He for particle transport, short pulse duration (fs) and fast transport cells

# LA-ICP-MS application for spent fuel characterization

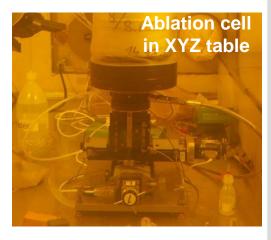
(collaboration with ITU)

#### **Experimental LA-ICP-MS set-up ITU Hot Cells**

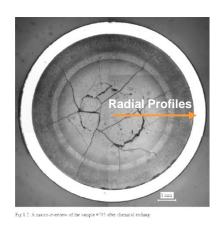


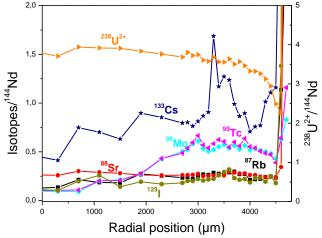


## Spatial analysis of highradioactive samples



#### Characterization of SNF\*





Radial profiles of actinides and fission products including gasses

# Coupling of a Micro ablation system to ICP-MS systems



#### LA-ICP-MS system with micrometric spatial resolution

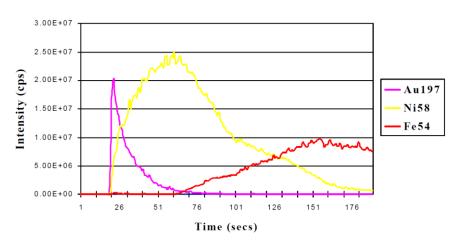
- ✓ Spatial distribution in the microscopic scale of radioisotopes and elements of interest in potential host rocks
- ✓ Diffusion studies
- √ Low or non-radioactive samples

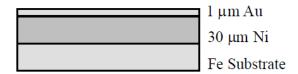
#### Teledyne µablation system Coupled to HR- ICP-MS or TOF-ICP-MS



High spatial depth resolution 0.5-1 μm High precision XY stages (0.16 μm/step)

NIST 1387 Coating Standard





## Laser Induced Breakdown Spectroscopy (LIBS)

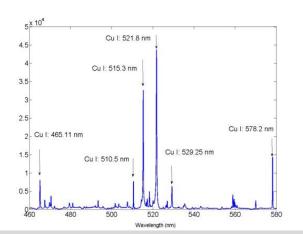


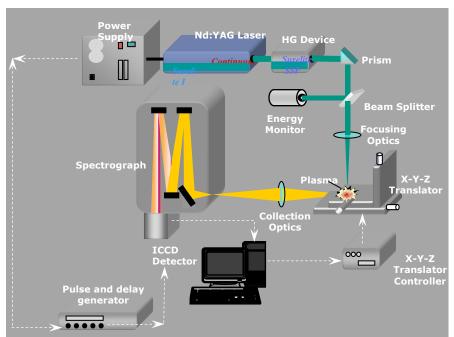
#### **Analytical Capabilities of LIBS:**

- Solid, liquid or gas analysis
- Fast multi-elemental analysis, even isotopic

#### information

- No sample preparation needed
- Minimal sample destruction
- Possibilities of remote analysis
- Qualitative and /or semi-quantitative Information
- Depth profiling, chemical mapping possibilities





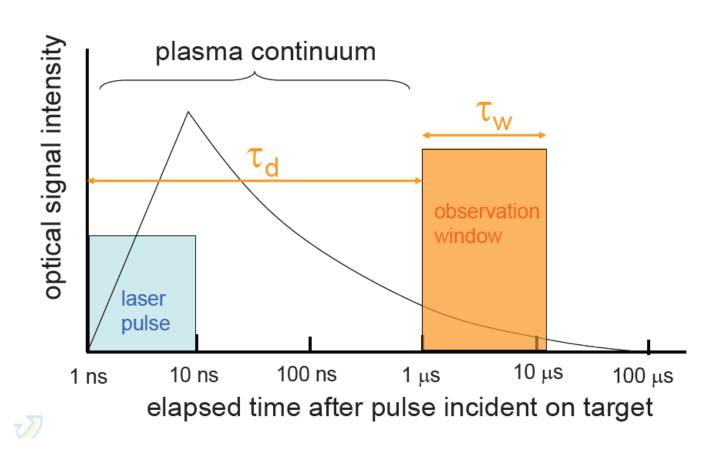
**Typical LIBS Set-up** 

Typical Cu LIBS spectrum with characteristic emission lines: "Spectral Fingerprint"

## Laser Induced Breakdown Spectroscopy (LIBS)



## **Temporal History of a LIBS plasma**



D.A. Cremers and L.J. Radziemski, in "Handbook of Laser-Induced Breakdown Spectroscopy," (2006)

### LIBS configurations for remote LIBS

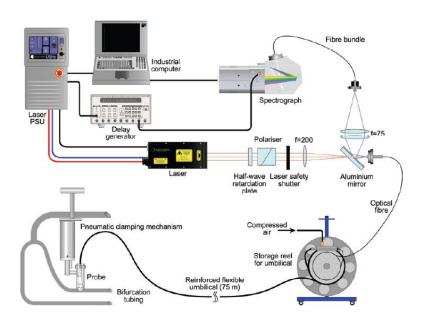


## Open-Path LIBS (Telescope)



- For samples no physically accessible
- Possible optical access
- Instrument contamination reduced or minimal

### Fiber-optic LIBS



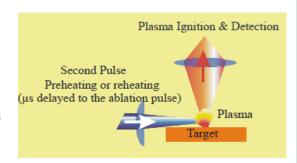
- More simple optical configuration
- For cases where not direct line of sight to the target is possible
- Non high laser energy needed
- Possible Fiber-optic contamination

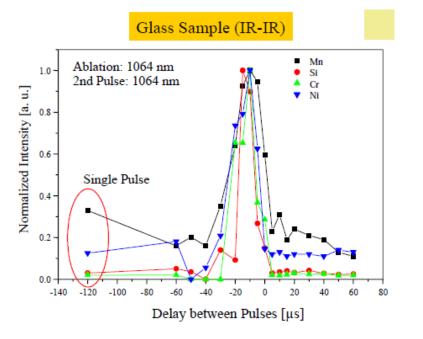
23.08.2017

### **LIBS Developments**

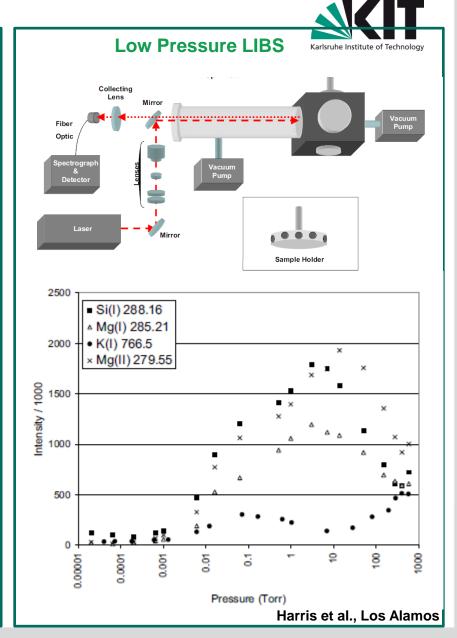
#### **Double pulse LIBS**

Use two laser pulses separated by a small time interval to modulate the plasma and improve LODs





- Signal enhancement for 2<sup>nd</sup> pulse
- Improved LODs



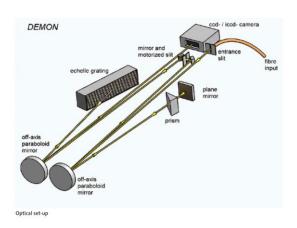
## <u>Determining isotope ratios in uranium samples in air at atmospheric pressure</u> using a high-resolution spectrometer for LIBS analysis

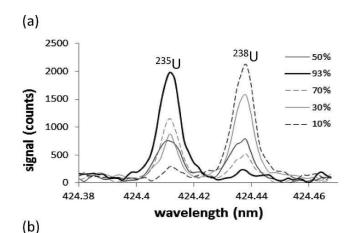


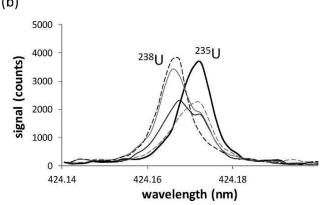
 Demon - Echelle spectrometer with pre-monochromator and active wavelength stabilization (LTB Berlin)



Spectral resolving power  $\lambda$  /min. measurable FWHM: 75,000 (150,000 possible)





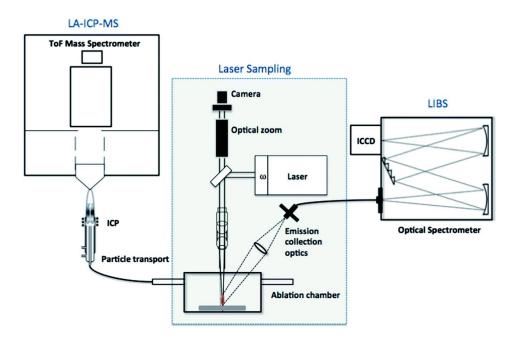


Isotope shift using the (a) 424.437 nm and (b) 424.167 nm U(II) emission lines for Y-12 glass samples of different <sup>235</sup>U enrichments.

<sup>\*</sup>Cremers et al. Applied Spectroscopy 66 (2012)250

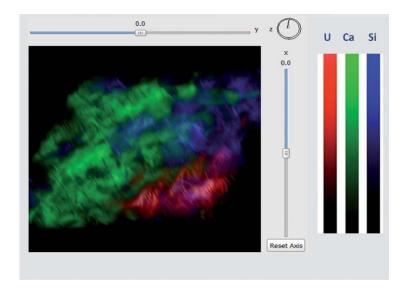
# Possibilities of coupling analytical methods (LIBS and LA-ICP-MS)





Combination of LIBS and LA-ICP-MS has the potential of providing expanded elemental coverage from a single sampling event

# Simultaneous 3-dimensional elemental imaging with LIBS and LA-ICP-MS

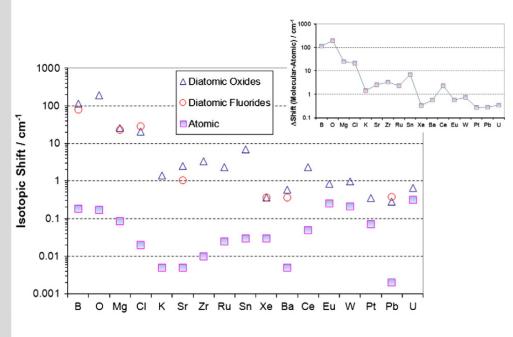


Russo et al., J. Anal. At. Spectrom., 2014,29, 1292-1298

### Other Option\_ Laser Ablation Molecular Isotopic Spectrometry (LAMIS)



# New approach for fast optical isotopic analysis of solid samples at ambient pressure



SRM-987

88 SrO

87 SrO

88 SrO

0.6

0.7 SrO

88 SrO

87 SrO

88 SrO

Wavelength (nm)

Molecular vs. atomic isotopic shifts for various elements\*

Spectrally resolved measurements of the three individual Sr-86, Sr-87, and Sr-88 isotopes\*\*

<sup>\*</sup>Russo et al., Spectrochim.Acta B 66(2011) 99

<sup>\*\*</sup>Mao et al., Spectrochim. Acta B 66(2011) 767



# Thank you for your attention

Heat-Ray used by the Martians in H. G. Wells' War of the Worlds

"in some way they are able to generate an intense heat in a chamber of practically absolute nonconductivity. This intense heat they project in a parallel beam against any object they choose, by means of a polished parabolic mirror of unknown composition, much as the parabolic mirror of a lighthouse projects a beam of light... it is certain that a beam of heat is the essence of the matter. Heat, and invisible, instead of visible, light. Whatever is combustible flashes into flame at its touch, lead runs like water, it softens iron, cracks and melts glass, and when it falls upon water, incontinently that explodes into steam.

"The War of the Worlds" H. G. Wells in 1898