SLIMS 2024

8th Venice International School on Lasers in Materials Science

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Laser-induced breakdown spectroscopy (LIBS)

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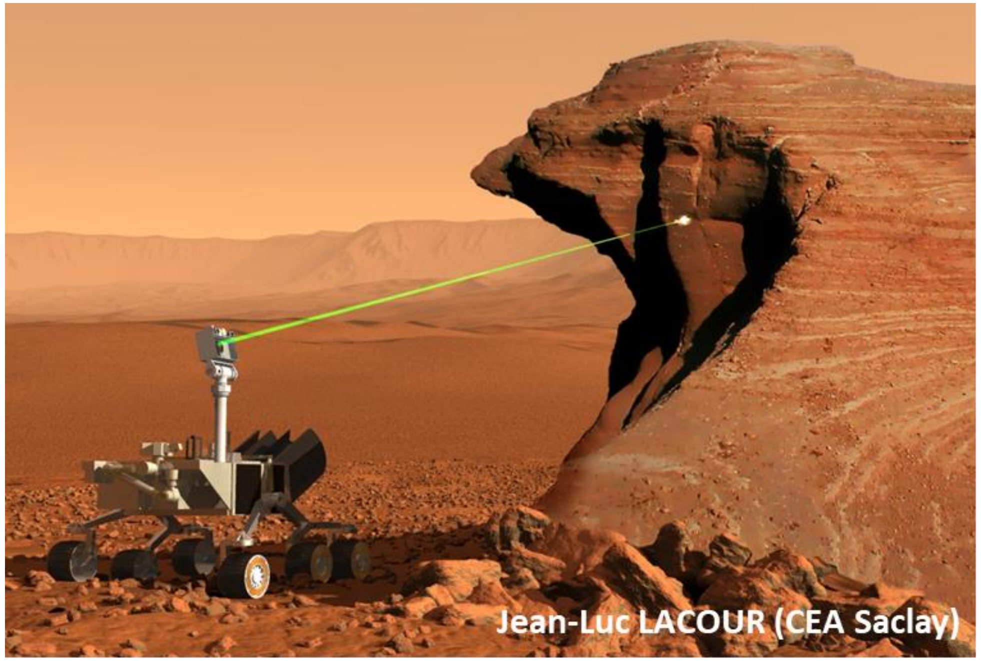


Jean-Luc LACOUR (CEA Saclay)

LP3 in Marseille

LP3 – Lasers, Plasmas, and Photonic Processing

www.lp3.fr

CNRS / Aix-Marseille University

staff ≅ 35

pétanque

Calanques national park

Elemental analyses of materials today

collect sample

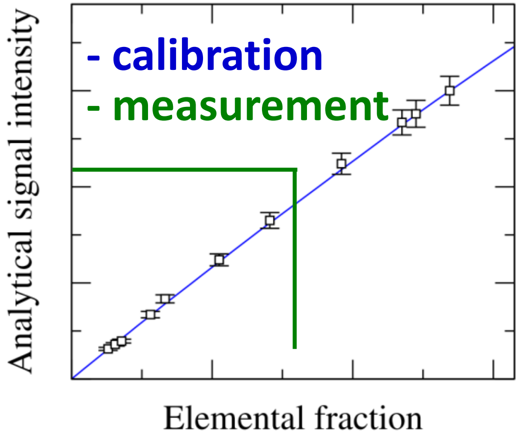
prepare sample

proceed analyses

get result

standard technique = ICP-AES/MS

Inductively **C**oupled **P**lasma



sample preparation ☞ dissolution in acid

- ☞ time expensive
- ☞ high cost
- ☞ chemical waste

☞ **incompatible with upcoming needs**

Modern world requires fast analyses

example : milk production and trading

farmer

buying agent

evaluation of quality

price setting

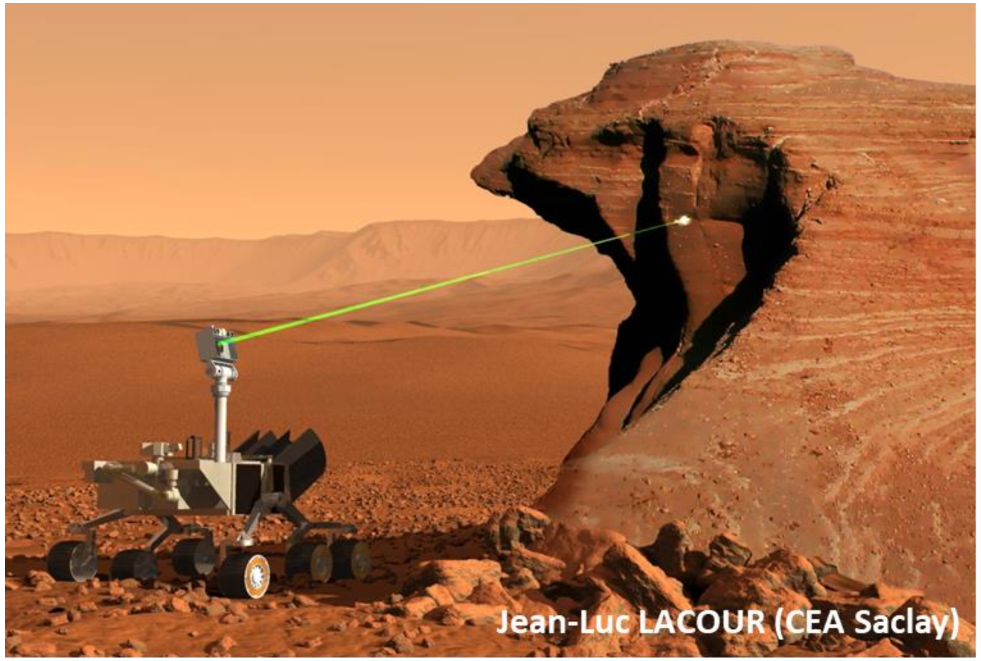
need of fast (in situ, stand off) **analyses**

☞ quality control in industry
☞ materials recycling
☞ environmental survey
☞ food security
☞ biomedical applications
☞ …

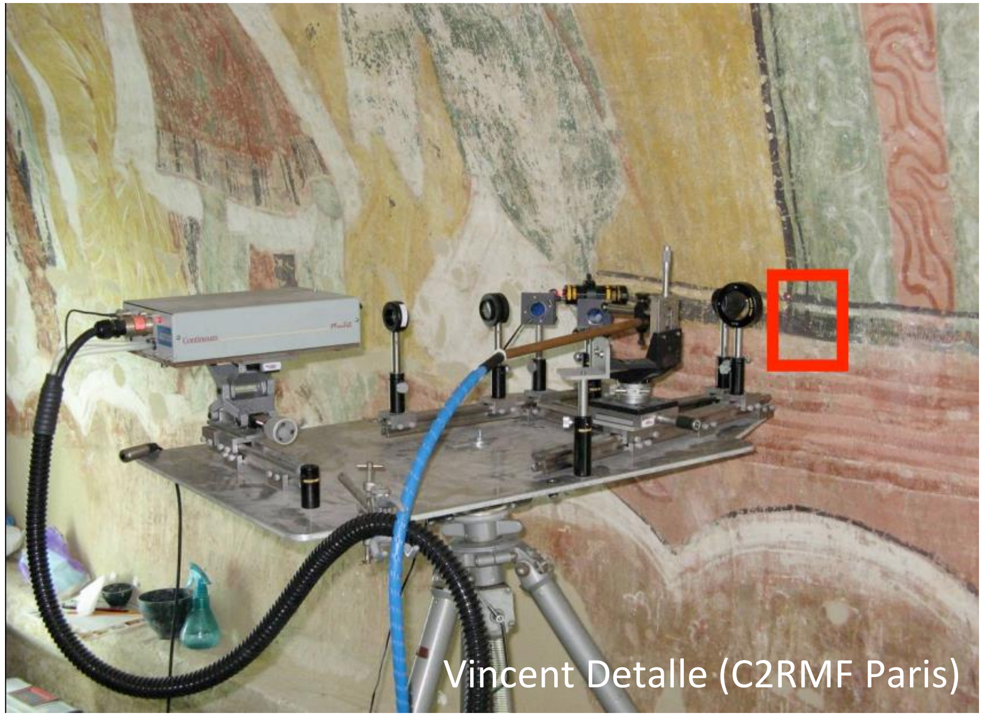
LIBS features

LIBS = Laser-induced breakdown spectroscopy

- **no sample preparation**
- **standoff measurements**
- **real-time analysis**
- **minimum damage**



Jean-Luc LACOUR (CEA Saclay)



Vincent Detalle (C2RMF Paris)

☞ **meets needs of modern applications**

History of LIBS

1963 ☞ 1st publication, ruby laser

1967 ☞ 1st instruments by Zeiss (Germany) et Jarrel-Ash (USA)

no success ↔ low precision

1980 ☞ reliable pulsed lasers

→ **development of *LIBS***

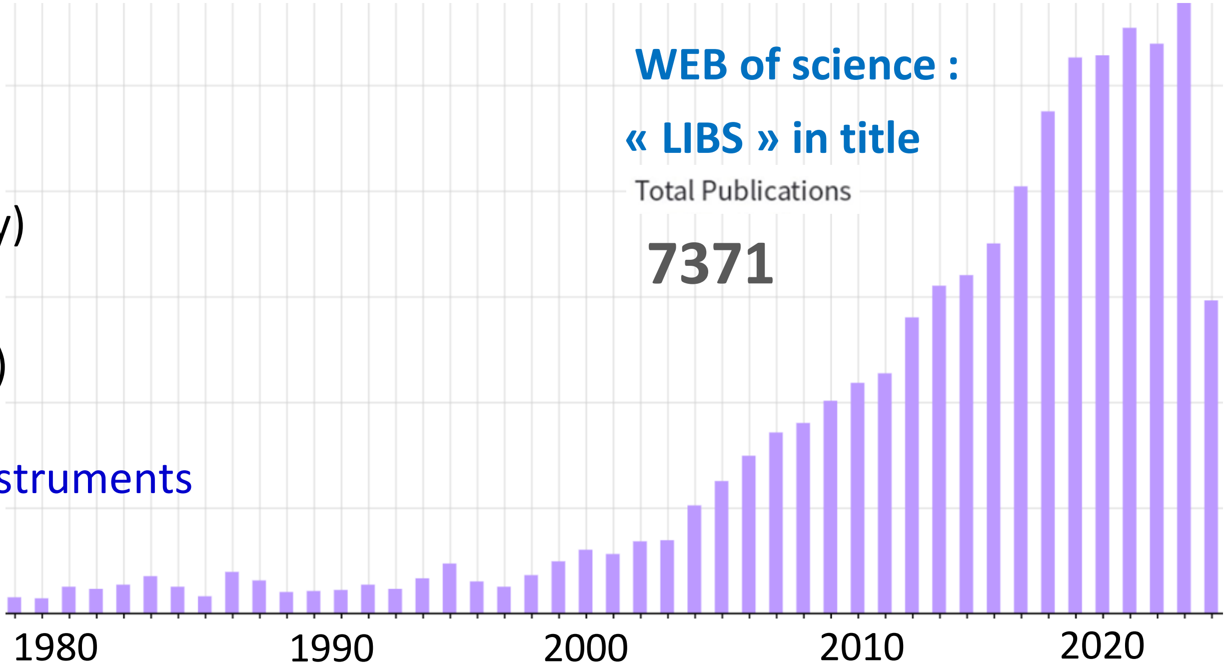
1990 ☞ acceleration du development

2000 ☞ 1st international conference (Pisa, Italy)

2006 ☞ 1ères Journées LIBS France (CEA Saclay)

today ☞ many companies commercialize LIBS instruments

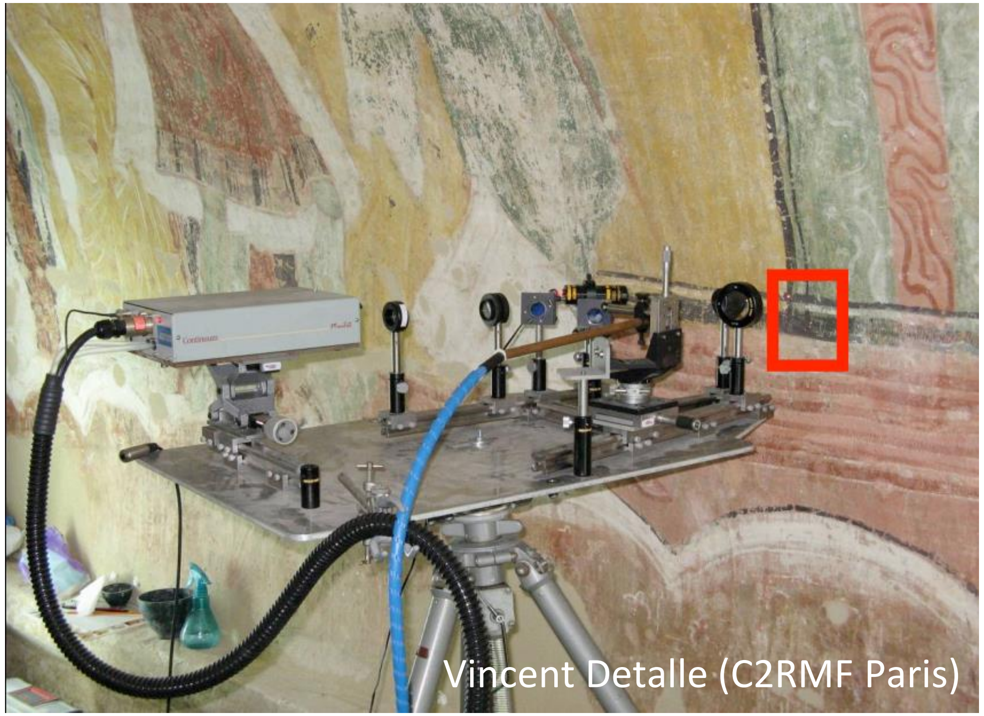
(USA, Germany, Japan, Italy, France, …)



WEB of science :

« LIBS » in title

LIBS analysis today

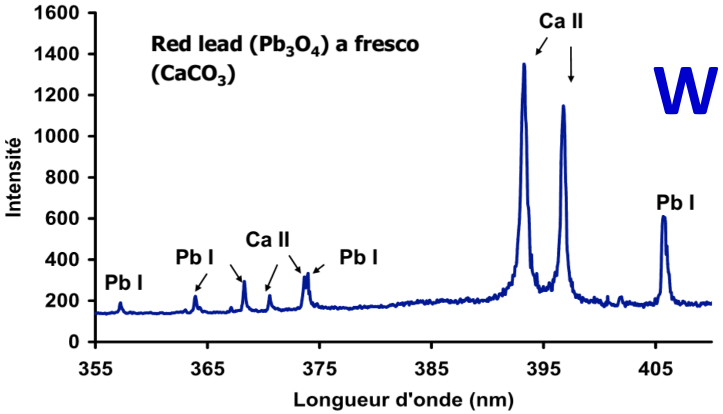

Vincent Detalle (C2RMF Paris)

+ promising for many applications

- not fully recognized as analytical technique

☞ easy to make qualitative analyses

☞ accurate quantitative analyses are difficult



What causes the large measurement uncertainty ?

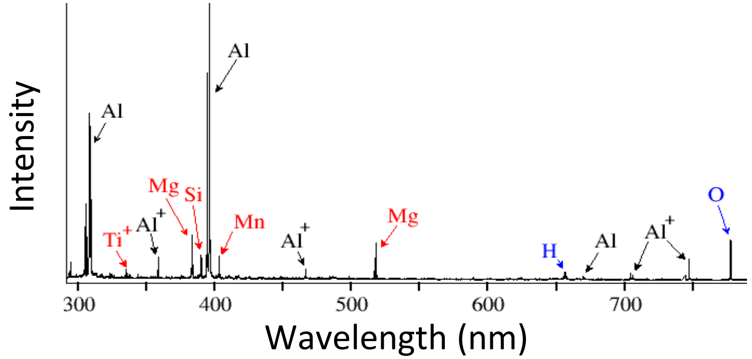
Procedure of elemental analysis

any method (ICP-MS, ICP-AES, AAS, XRF, EDS, …)

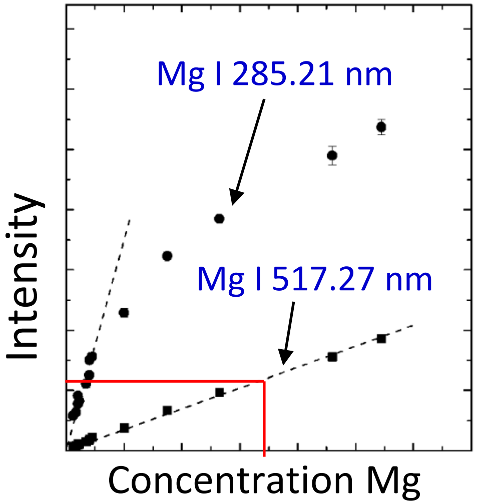
1. Calibration

with *"matrix-matched"* standards

⇨ calibration curve for each element



2. Measurement

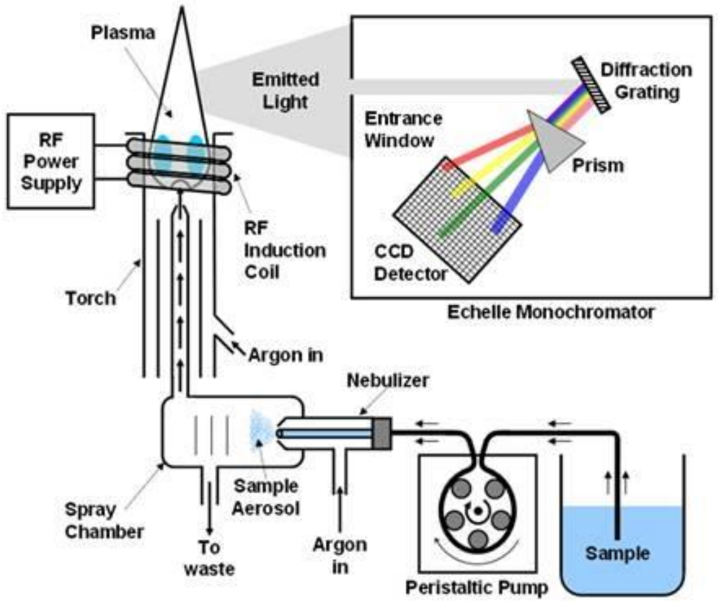


☞ **signal does not only depend on element fraction**
but also on material (matrix)

☞ **matrix effect**

Matrix effects : ICP vs LIBS

ICP-AES



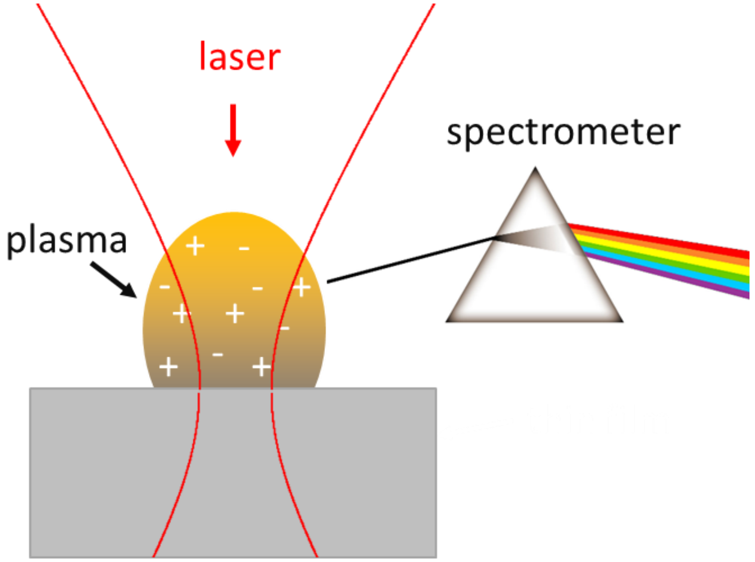
☞ sampling and plasma excitation independent

☞ argon dominates plasma

⇨ plasma properties independent of sample material

☞ weak matrix effects

LIBS



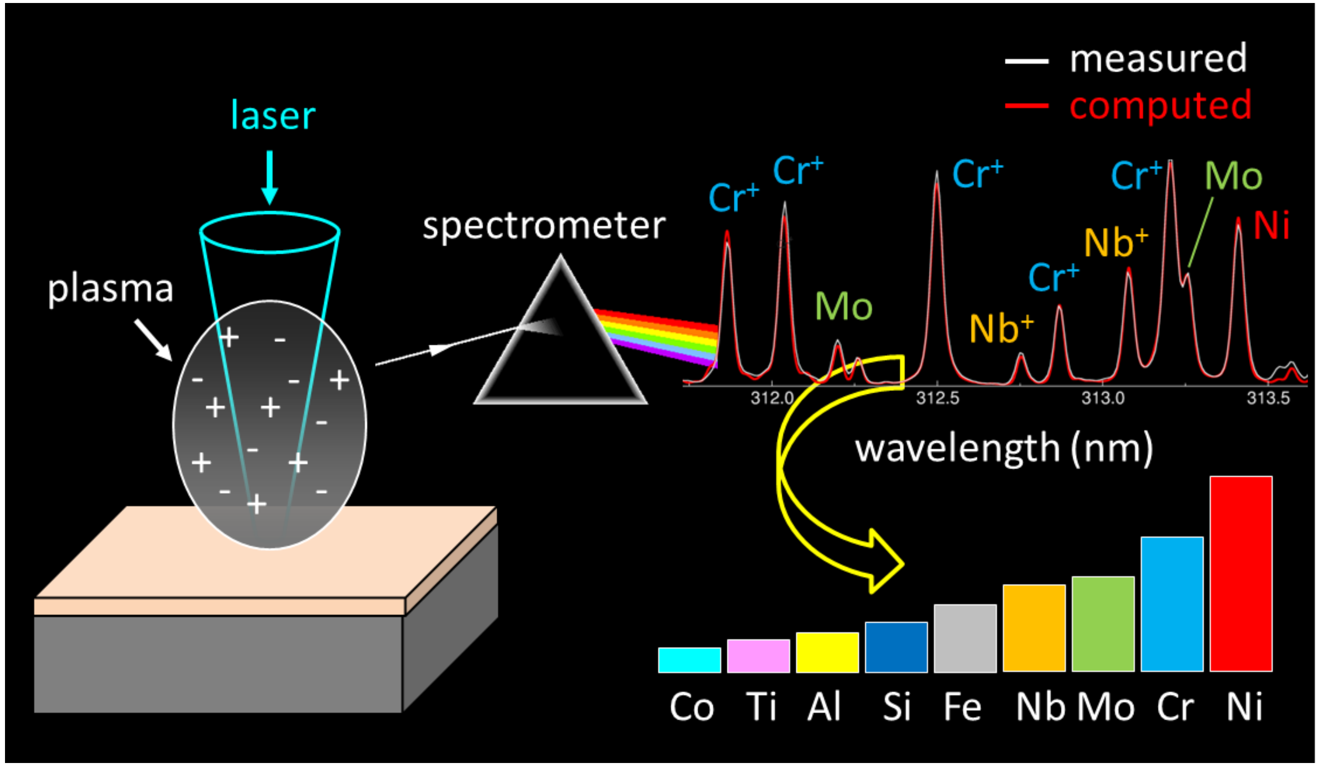
☞ sampling and plasma excitation in single step

☞ plasma = vaporized material

⇨ plasma properties depend on - sample material
- surface state
- laser focusing

☞ strong matrix effects

Solution = calibration-free LIBS



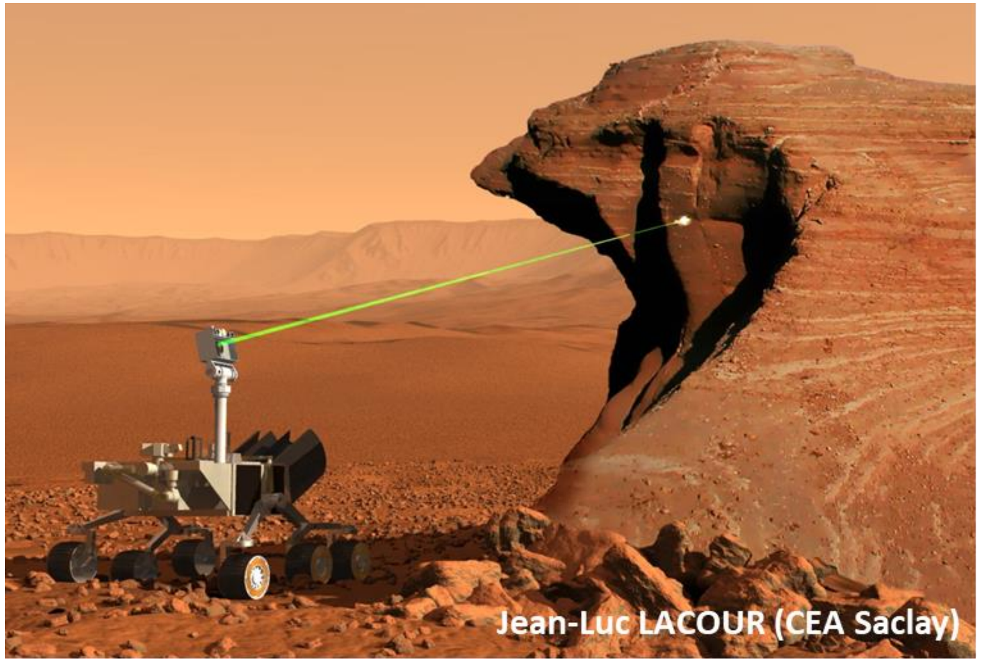
- modeling of plasma emission

- comparison to measured spectrum

☞ **Revolution in materials analysis**

Outline

- **Singular properties of “LIBS” plasma**
- **Development of calibration-free LIBS**
- **Analytical performance**
- **Upcoming improvements**
- **Conclusion**



Outline

- **Singular properties of “LIBS” plasma**
- **Development of calibration-free LIBS**
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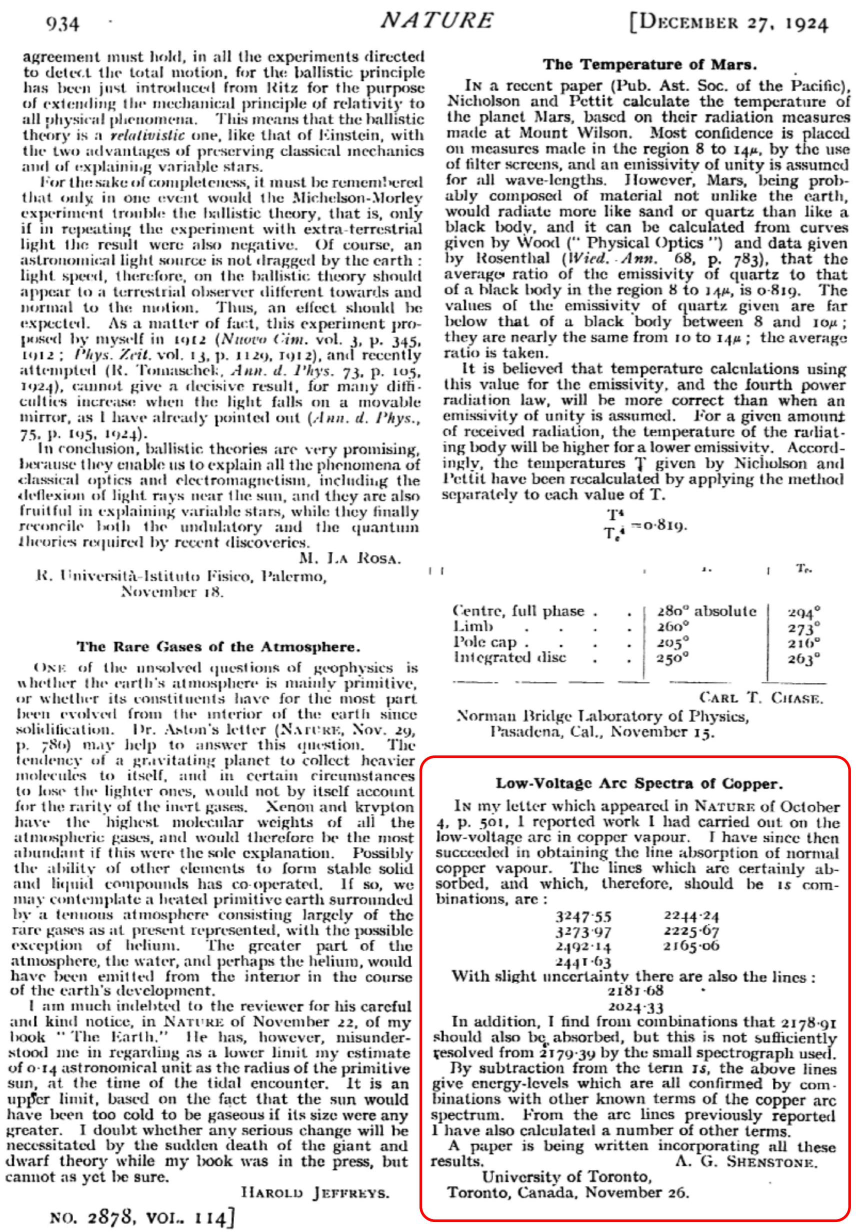
Singular properties of “LIBS” plasma



agreement must hold, in all the experiments directed to detect the total motion, for the ballistic principle has been just introduced from Ritz for the purpose of extending the mechanical principle of relativity to all physical phenomena. This means that the ballistic theory is a *relativistic* one, like that of Einstein, with the two advantages of preserving classical mechanics and of explaining variable stars.

For the sake of completeness, it must be remembered that only in one event would the Michelson-Morley experiment trouble the ballistic theory, that is, only if in repeating the experiment with extra-terrestrial light the result were also negative. Of course, an astronomical light source is not dragged by the earth: light speed, therefore, on the ballistic theory should appear to a terrestrial observer different towards and normal to the motion. Thus, an effect should be expected. As a matter of fact, this experiment proposed by myself in 1912 (*Nuovo Cim.* vol. 3, p. 345, 1912; *Phys. Zeit.* vol. 13, p. 1129, 1912), and recently attempted (R. Tomaschek, *Ann. d. Phys.* 73, p. 105, 1924), cannot give a decisive result, for many difficulties increase when the light falls on a movable mirror, as I have already pointed out (*Ann. d. Phys.*, 75, p. 195, 1924).

In conclusion, ballistic theories are very promising, because they enable us to explain all the phenomena of classical optics and electromagnetism, including the deflexion of light rays near the sun, and they are also fruitful in explaining variable stars, while they finally reconcile both the undulatory and the quantum theories required by recent discoveries.

M. La Rosa.

R. Università-Istituto Fisico, Palermo,
November 18.

The Rare Gases of the Atmosphere.

One of the unsolved questions of geophysics is whether the earth's atmosphere is mainly primitive, or whether its constituents have for the most part been evolved from the interior of the earth since solidification. Dr. Aston's letter (Nature, Nov. 29, p. 786) may help to answer this question. The tendency of a gravitating planet to collect heavier molecules to itself, and in certain circumstances to lose the lighter ones, would not by itself account for the rarity of the inert gases. Xenon and krypton have the highest molecular weights of all the atmospheric gases, and would therefore be the most abundant if this were the sole explanation. Possibly the ability of other elements to form stable solid and liquid compounds has co-operated. If so, we may contemplate a heated primitive earth surrounded by a tenuous atmosphere consisting largely of the rare gases as at present represented, with the possible exception of helium. The greater part of the atmosphere, the water, and perhaps the helium, would have been emitted from the interior in the course of the earth's development.

I am much indebted to the reviewer for his careful and kind notice, in Nature of November 22, of my book "The Earth." He has, however, misunderstood me in regarding as a lower limit my estimate of 0·14 astronomical unit as the radius of the primitive sun, at the time of the tidal encounter. It is an upper limit, based on the fact that the sun would have been too cold to be gaseous if its size were any greater. I doubt whether any serious change will be necessitated by the sudden death of the giant and dwarf theory while my book was in the press, but cannot as yet be sure.

Harold Jeffreys.

The Temperature of Mars.

In a recent paper (Pub. Ast. Soc. of the Pacific), Nicholson and Pettit calculate the temperature of the planet Mars, based on their radiation measures made at Mount Wilson. Most confidence is placed on measures made in the region 8 to 14μ, by the use of filter screens, and an emissivity of unity is assumed for all wave-lengths. However, Mars, being probably composed of material not unlike the earth, would radiate more like sand or quartz than like a black body, and it can be calculated from curves given by Wood ("Physical Optics") and data given by Rosenthal (*Wied. Ann.* 68, p. 783), that the average ratio of the emissivity of quartz to that of a black body in the region 8 to 14μ, is 0·819. The values of the emissivity of quartz given are far below that of a black body between 8 and 10μ; they are nearly the same from 10 to 14μ; the average ratio is taken.

It is believed that temperature calculations using this value for the emissivity, and the fourth power radiation law, will be more correct than when an emissivity of unity is assumed. For a given amount of received radiation, the temperature of the radiating body will be higher for a lower emissivity. Accordingly, the temperatures T given by Nicholson and Pettit have been recalculated by applying the method separately to each value of T.

$$\frac{T^4}{T_e^4} = 0{\cdot}819.$$

	T.	T_e.
Centre, full phase . .	280° absolute	294°
Limb	260°	273°
Pole cap	205°	216°
Integrated disc . .	250°	263°

Carl T. Chase.

Norman Bridge Laboratory of Physics,
Pasadena, Cal., November 15.

Low-Voltage Arc Spectra of Copper.

In my letter which appeared in Nature of October 4, p. 501, I reported work I had carried out on the low-voltage arc in copper vapour. I have since then succeeded in obtaining the line absorption of normal copper vapour. The lines which are certainly absorbed, and which, therefore, should be 1*s* combinations, are:

3247·55	2244·24
3273·97	2225·67
2492·14	2165·06
2441·63	

With slight uncertainty there are also the lines:

2181·68
2024·33

In addition, I find from combinations that 2178·91 should also be absorbed, but this is not sufficiently resolved from 2179·39 by the small spectrograph used.

By subtraction from the term 1*s*, the above lines give energy-levels which are all confirmed by combinations with other known terms of the copper arc spectrum. From the arc lines previously reported I have also calculated a number of other terms.

A paper is being written incorporating all these results.

A. G. Shenstone.

University of Toronto,
Toronto, Canada, November 26.

beginning of last century

development of plasma technologies

- ☞ **understanding of astrophysical plasmas**
- ☞ **study of atomic structure and plasma fundamentals**

later

concept of local thermodynamic equilibrium (LTE)

- ☞ **simplified description of elementary processes**

Singular properties of “LIBS” plasma

SLIMS

elementary processes

collisional processes

collisional excitation / desexcitation

$$A^{l} + e^{-}(E) \Leftrightarrow A^{u} + e^{-}(E')$$

electron impact ionization / 3 body recombination

$$A + e^{-}(E) \Leftrightarrow A^{+} + e^{-}(E') + e^{-}(E'')$$

radiative processes

spontaneous emission / absorption

$$A^{u} \Leftrightarrow A^{l} + h\nu$$

photoionization / radiative recombination

$$A + h\nu \Leftrightarrow A^{+} + e^{-}(E)$$

bremsstrahlung emission / inverse bremsstrahlung absorption

$$A + e^{-}(E) \Leftrightarrow A + e^{-}(E')$$

out of equilibrium ☞ collisional-radiative modeling

⇨ **requires rates of all processes**

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- ☞ **simplified description of elementary processes**

LP3 Aix*Marseille université cnrs

Singular properties of “LIBS” plasma

Thermodynamic Equilibrium

☞ **principle of microscopic reversibility**

⇨ each process is counterbalanced by its reverse process

☞ **simplified description via statistical laws**

velocities:	$f(\upsilon) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\upsilon^2\ e^{-m\upsilon^2/2kT}$	*Maxwell*
population densities:	$n_i = n\frac{g_i}{Q}e^{-E_i/kT}$	*Boltzmann*
chemical composition:	$\frac{n_A n_B}{n_{AB}} = \frac{(2\pi\,\mu\,kT)^{3/2}}{h^3}\frac{Q_A\,Q_B}{Q_{AB}}e^{-E_{AB}/kT}$	*Saha*

radiation: $\cancel{U_\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}}$ *Planck*

characteristic length of absorption

laboratory plasmas ☞ size $L < \delta_{abs} = \frac{1}{\alpha}$

⇨ **no microreversibility for radiative processes**

☞ **equilibrium still exists, if collisional processes dominate**

beginning of last century

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later

concept of local thermodynamic equilibrium (LTE)

- ☞ **simplified description of elementary processes**

development of appropriate plasma sources

- ☞ **large N_e , slow enough time-evolution**

Singular properties of "LIBS" plasma

SLIMS

Local Thermodynamic Equilibrium

atmospheric pressure plasmas

arcs, shock tubes, spark discharges

☞ **time of thermalization ≈ time of diffusion**

⇨ **LTE plasmas are spatially non-uniform**

accurate spectroscopic measurements

⇨ space-resolved observations

⇨ complex data analysis

beginning of last century

development of plasma technologies

☞ **understanding of astrophysical plasmas**

☞ **study of atomic structure and plasma fundamentals**

later

concept of local thermodynamic equilibrium (LTE)

☞ ***simplified description of elementary processes***

development of appropriate plasma sources

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space-resolved spectroscopic measurements (Abel-Inversion, …)

laser-produced plasmas

☞ study of laser-matter interaction

☞ analytical measurements and other applications

☞ **limited interest as source for plasma spectroscopy**

Singular properties of “LIBS” plasma

Plasma produced by laser ablation

- small size
- fast expansion dynamics
- low reproducibility (early experiments)

Technological advances changed the situation

☞ **reliable laser sources**

☞ **fast and sensitive detectors**

Increasing interest for LIBS

☞ **interest for LIP as a plasma source**

☞ **measurements of spectroscopic data**

☞ **study of plasma fundamentals**

small size = advantage ⇨ limits self-absorption

beginning of last century

development of plasma technologies

☞ **understanding of astrophysical plasmas**

☞ **study of atomic structure and plasma fundamentals**

later

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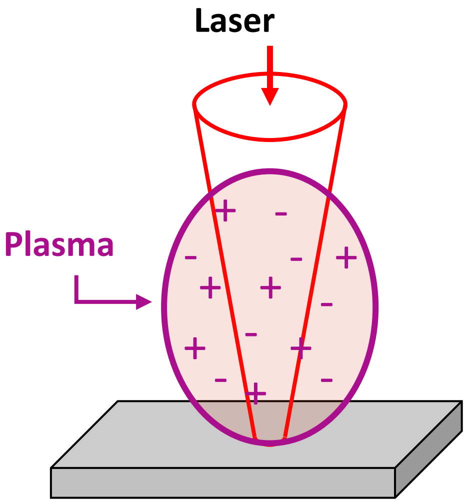
Singular properties of "LIBS" plasma

atmospheric plasmas ☞ **time of thermalization ≈ time of diffusion**

plasma produced by laser ablation = singular plasma source



☞ fast expansion
from near-solid density until pressure equilibrium

high initial density ⇒ fast thermalization
⇒ slow diffusion

⇨ **time of thermalization << time of diffusion**

LIP may combine two properties usually not observed together

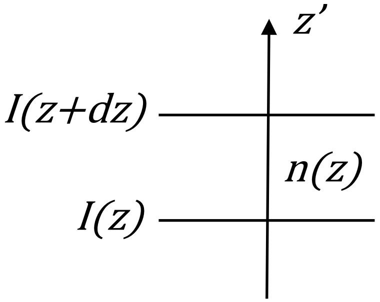
Laser-Induced Plasma

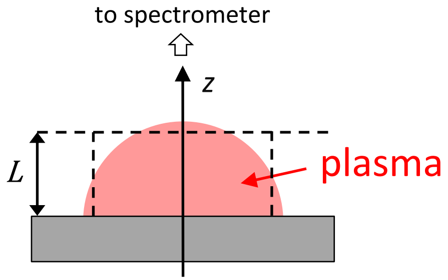
☞ **LTE + spatially uniform**

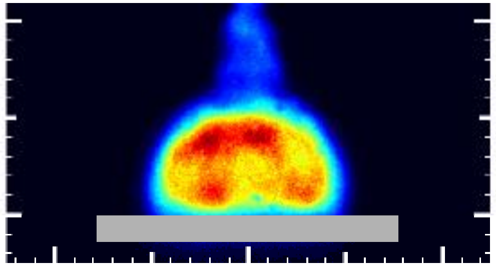
Local-Thermodynamic Equilibrium

Singular properties of “LIBS” plasma

spatially uniform LTE plasma : demonstration via signatures in emission spectrum







UV laser ablation in argon

radiation transfer equation

emission coefficient

$$n(z)\frac{d}{dz}\left(\frac{I(z)}{n^2(z)}\right) = \varepsilon(z) - \alpha(z)I(z)$$

absorption coefficient

plasma: $n \cong 1$

assuming uniform plasma $I(z) = \frac{\varepsilon}{\alpha}\left(1 - e^{-\alpha z}\right)$

blackbody spectral radiance

Kirchhoff $B^o_\lambda = \frac{\varepsilon}{\alpha}$

spectral radiance of plasma $B_\lambda = B^o_\lambda\left(1 - e^{-\tau(\lambda)}\right)$

$$\tau(\lambda) = \int \alpha(\lambda, z)dz = \alpha(\lambda)\, L$$

optical thickness

☞ **optically thick** (τ >> 1) ⇒ $B_\lambda = B^o_\lambda$

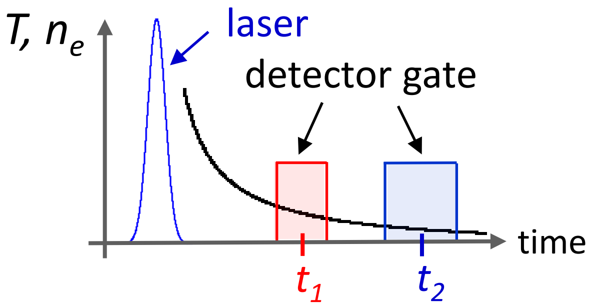
⇨ **strong lines saturate at blackbody radiance**

Singular properties of “LIBS” plasma

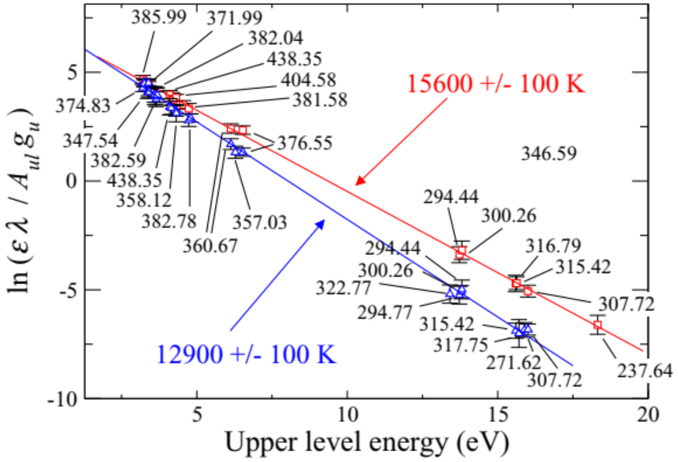
spatially uniform LTE plasma : demonstration via signatures in emission spectrum

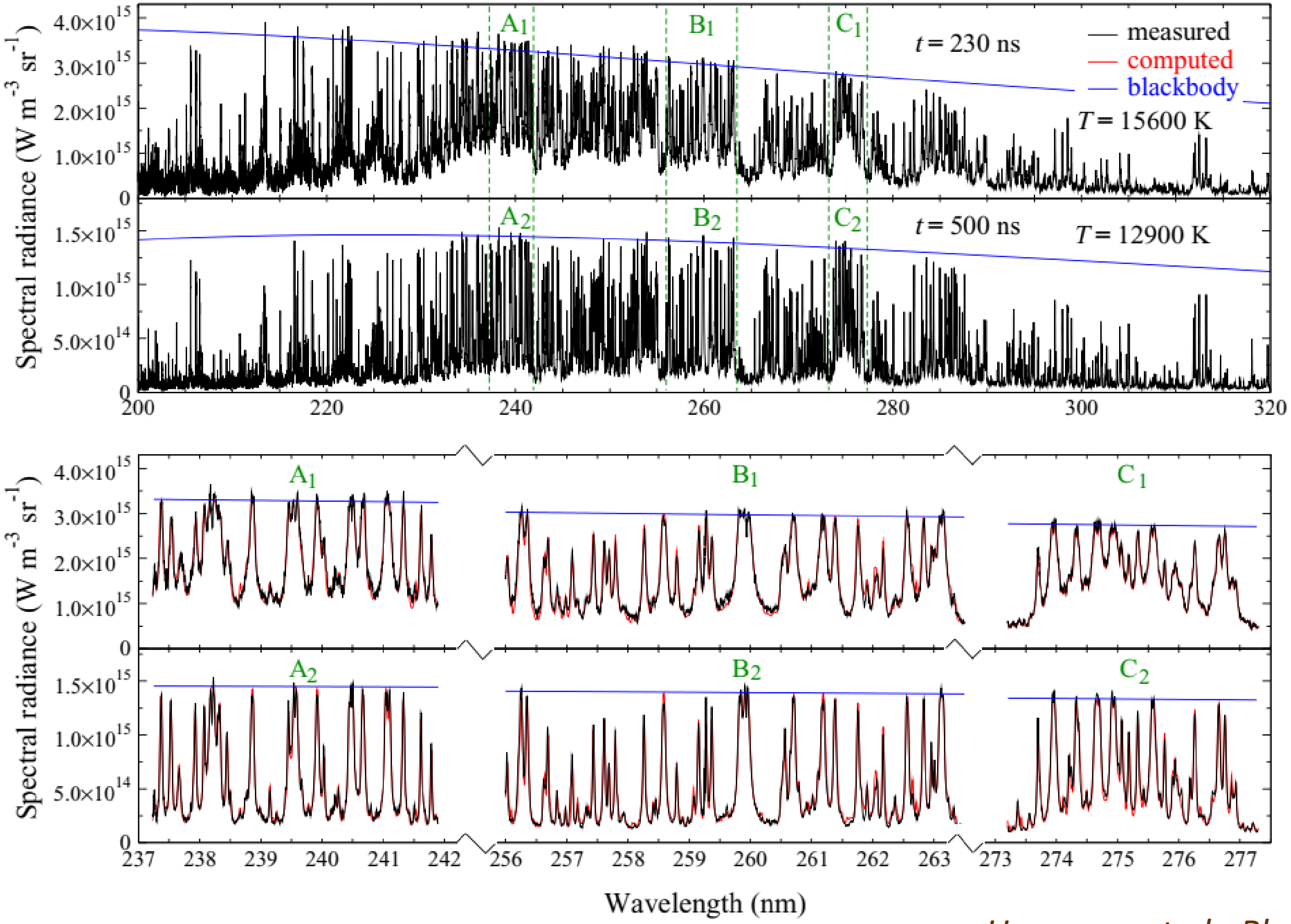
1.

$$B_\lambda = B^o_\lambda\left(1 - e^{-\tau(\lambda)}\right)$$



T-measurement





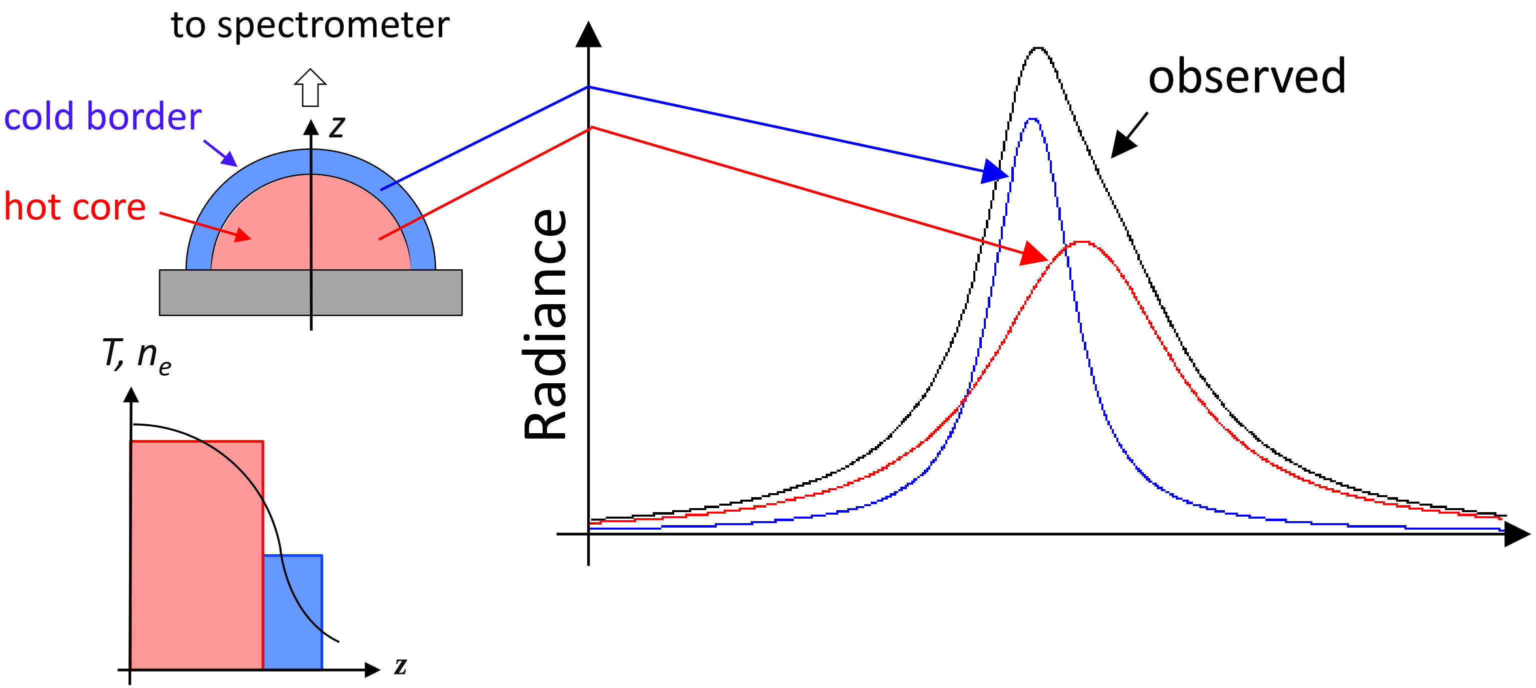
UV laser ablation of steel in argon

Hermann et al., Phys. Rev. E 2017

Singular properties of “LIBS” plasma

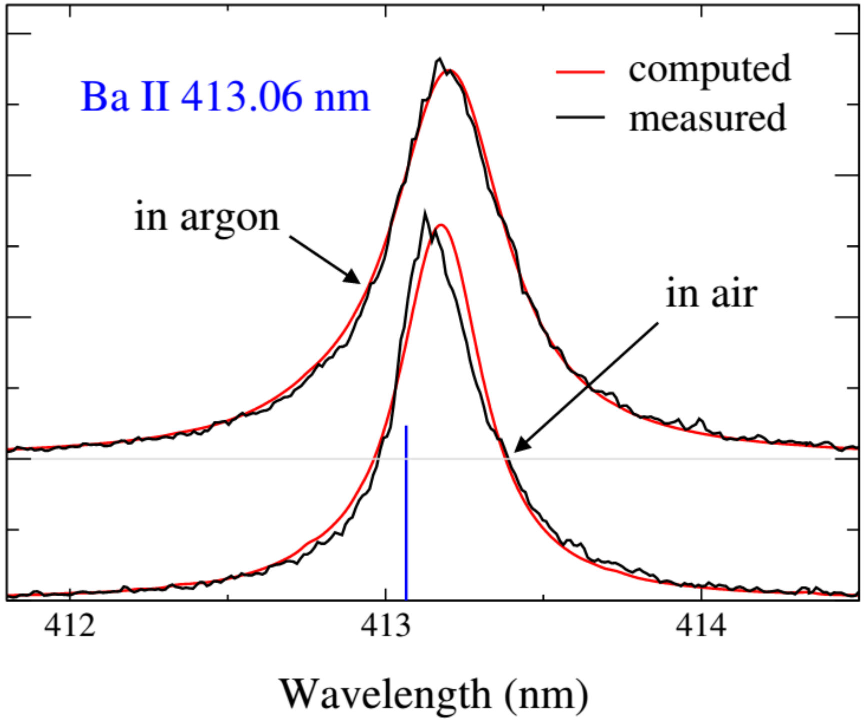
spatially uniform LTE plasma : demonstration via signatures in emission spectrum

2. Spectral shape of strongly Stark-shifted transition



N-BaK4 glass

E_{las} = 6 mJ, λ = 266 nm, τ = 5 ns



nonuniform plasma ⇨ asymmetric profile

in argon ☞ uniform plasma

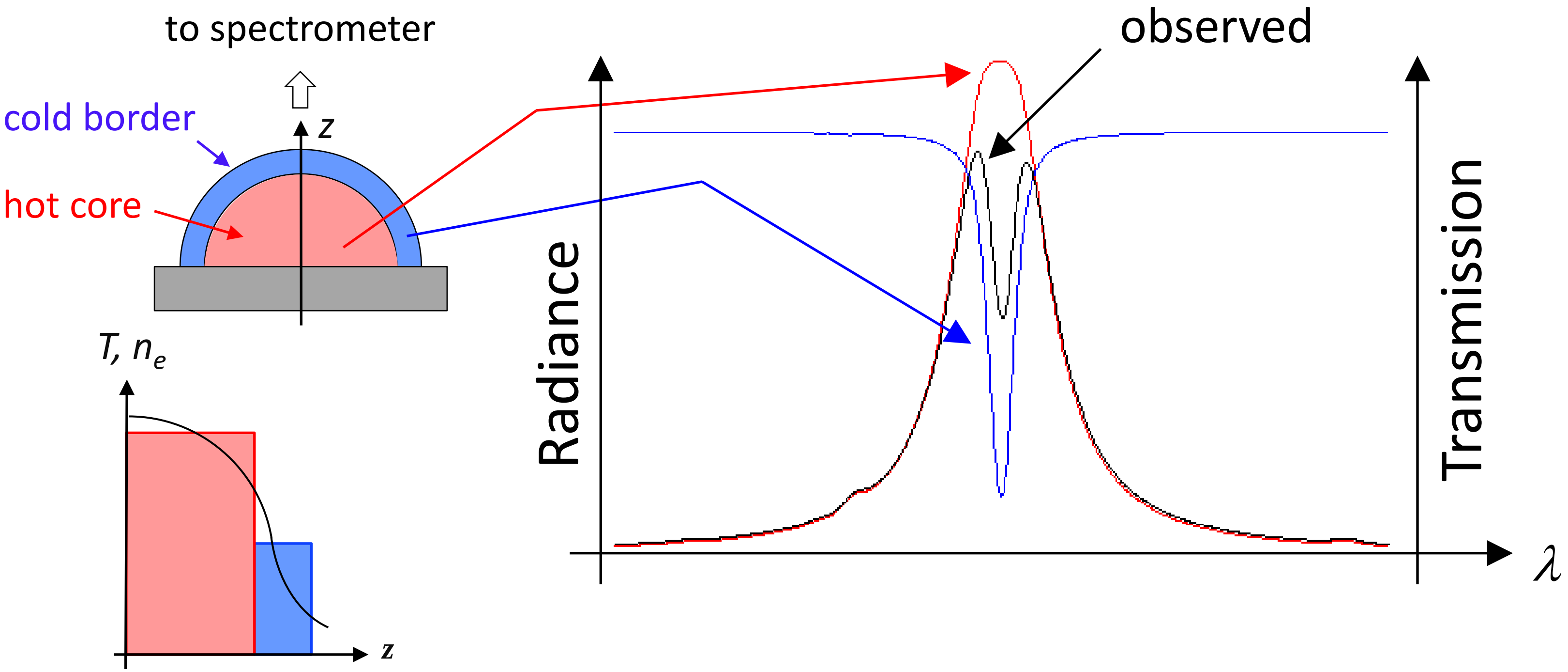
Hermann et al., Phys. Rev. E 2017

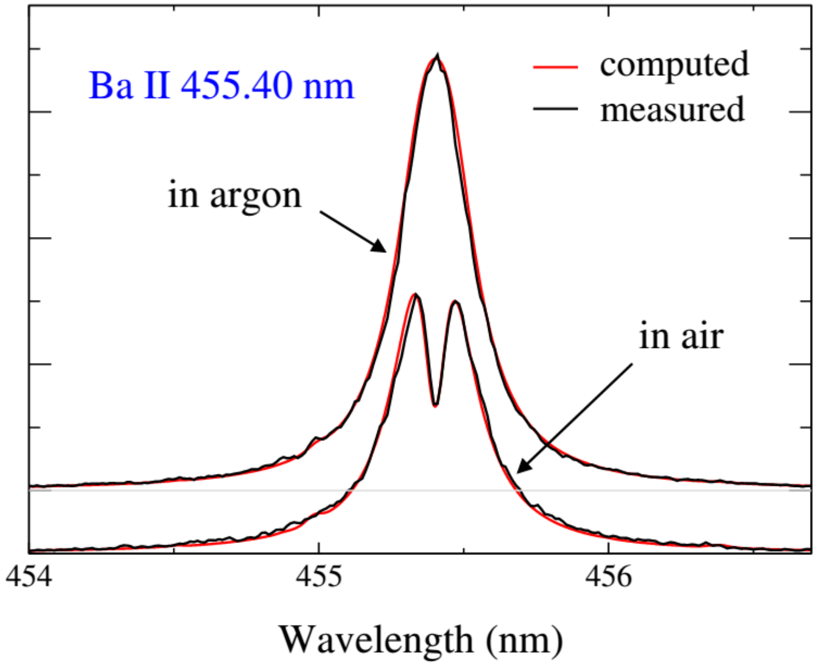
Singular properties of “LIBS” plasma

spatially uniform LTE plasma : demonstration via signatures in emission spectrum

3. Spectral shape of strongly self-absorbed resonance line

N-BaK4 glass
E_{las} = 6 mJ, λ = 266 nm, τ = 5 ns



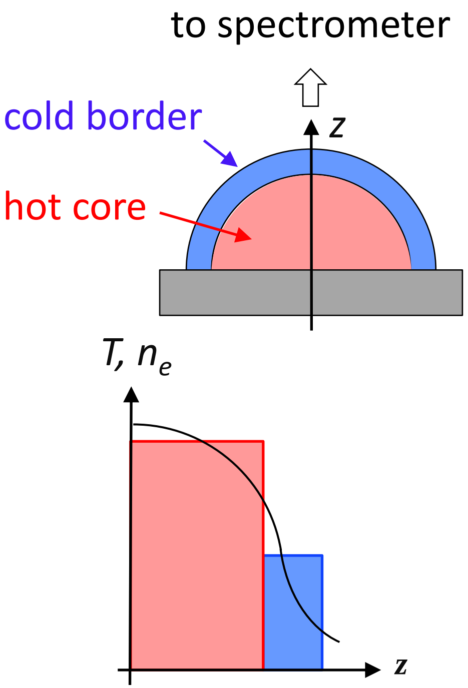


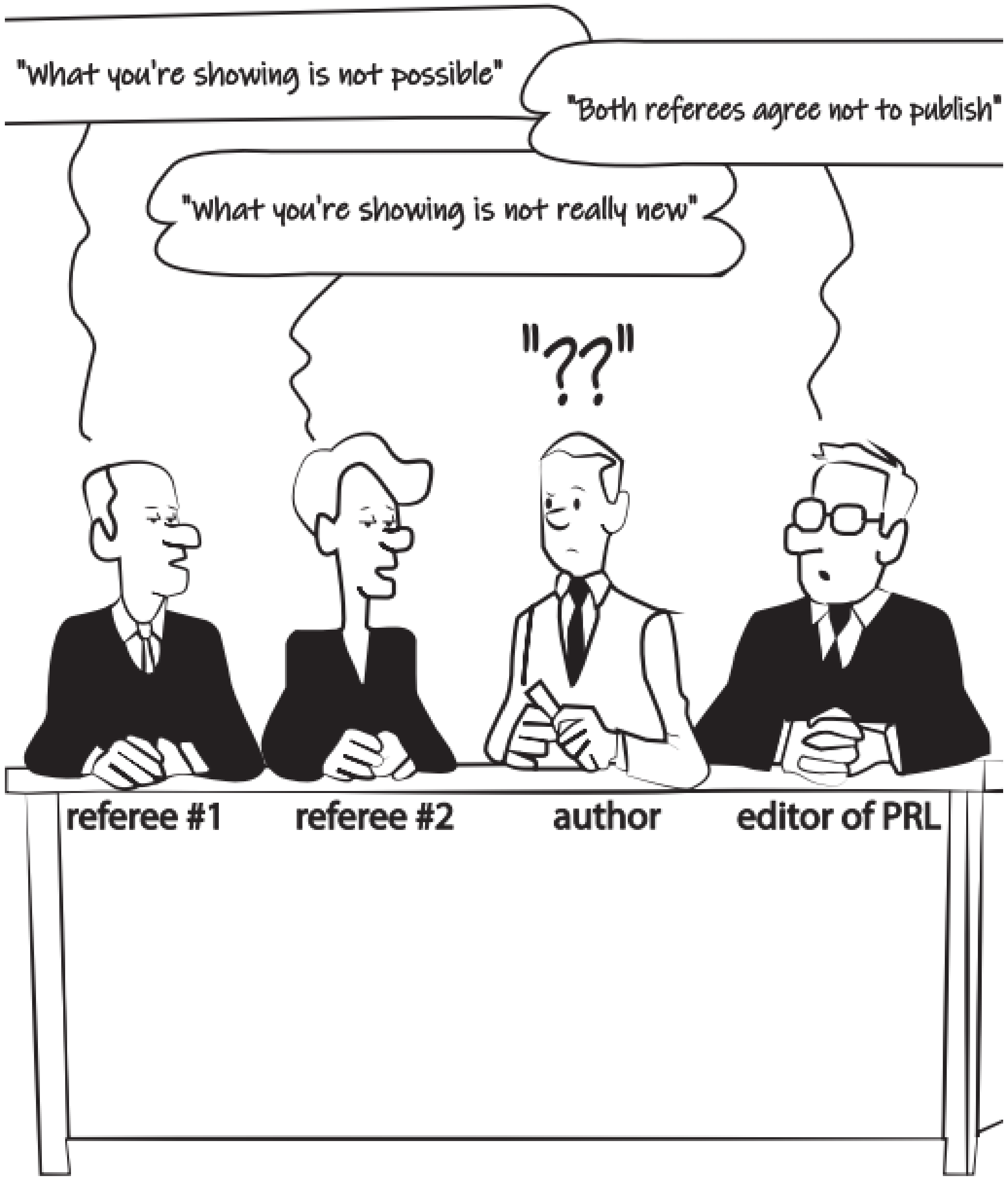
cold border ⇨ absorption dip

in argon ☞ uniform plasma

Hermann et al., Phys. Rev. E 2017

Singular properties of “LIBS” plasma





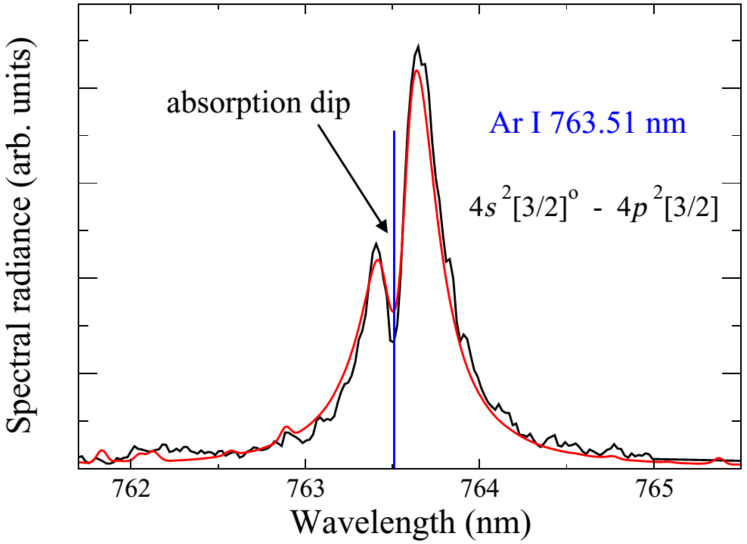
referee #1 :

a plasma cannot be spatially uniform

we do **not** claim that **the entire plasma is uniform**

⇨ **ablated vapor plume is uniform**

⇔ **gradients are in the gas**



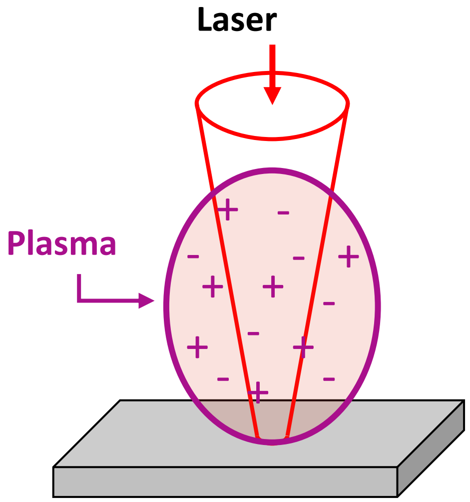
Hermann et al., Phys. Rev. E 2017

Outline

- Singular properties of “LIBS” plasma
- **Development of calibration-free LIBS**
- Analytical performance
- Upcoming improvements
- Conclusion

Development of calibration-free LIBS

First approach by *Ciucci et al., Appl. Spectrosc. 1999*



hypotheses :

- **stoichiometric ablation** ✓
- **local thermodynamic equilibrium** ✓
- **plasma uniform** (✓)
- ~~**plasma optically thin**~~

optically thin ☞ $I \propto \varepsilon_{ul} = A_{ul}\frac{h\nu}{4\pi} n_u$

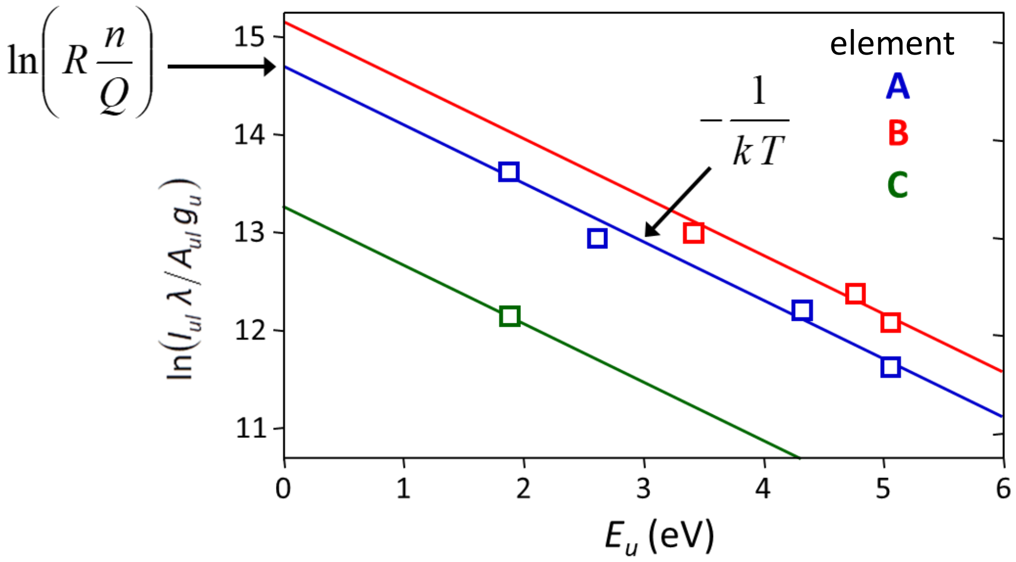
upper level number density

ion density

neutral density

moderate ionization ☞ $n_i << n_n$ ⇨ $n_n \cong n$

Boltzmann $n_u = n\frac{g_u}{Q(T)}e^{-E_u/kT}$ ⇨ $\ln\left(\frac{I\,\lambda}{A_{ul}g_u}\right) = -\frac{E_u}{kT} + \ln\left(R\frac{n}{Q}\right)$



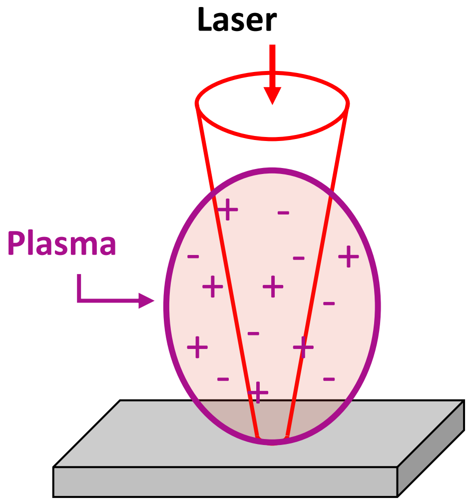
☞ **easy handling ⇨ large success**

⇨ evaluation by many groups on all kind of materials

☞ **limited analytical performance**

Development of calibration-free LIBS

First approach by *Ciucci et al., Appl. Spectrosc. 1999*



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- **stoichiometric ablation** ✓
- **local thermodynamic equilibrium** ✓
- **plasma uniform** (✓)
- **~~plasma optically thin~~**

☞ **mostly dedicated to correction for self-absorption**

- *Lazic et al., Spectrochim. Acta Part B 2001*
- *Bulajic et al., Spectrochim. Acta Part B 2002*
- *El Sherbini et al., Spectrochim. Acta Part B 2005*
- …

☞ **easy handling ⇨ large success**

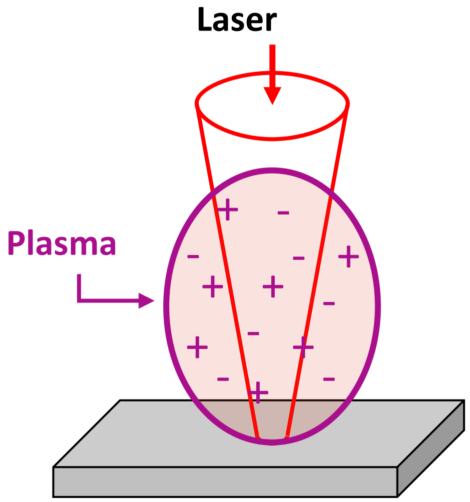
⇨ evaluation by many groups on all kind of materials

☞ **limited analytical performance**

☞ **amended approaches**

Development of calibration-free LIBS

First approach by *Ciucci et al., Appl. Spectrosc. 1999*



hypotheses :

- **stoichiometric ablation** ✓
- **local thermodynamic equilibrium** ✓
- **plasma uniform** (✓)
- **~~plasma optically thin~~**

☞ **mostly dedicated to correction for self-absorption**

- *Lazic 2001, Bulajic 2002, El Sherbini 2005, …*

☞ **approaches based on spectra simulation**

- *D'Angelo et al., Spectrochim. Acta Part B 2008*
- *Hermann, Patent US8942927B2, deposit 2008*
- *Wester and Noll, J. Appl. Phys. 2009*
- …

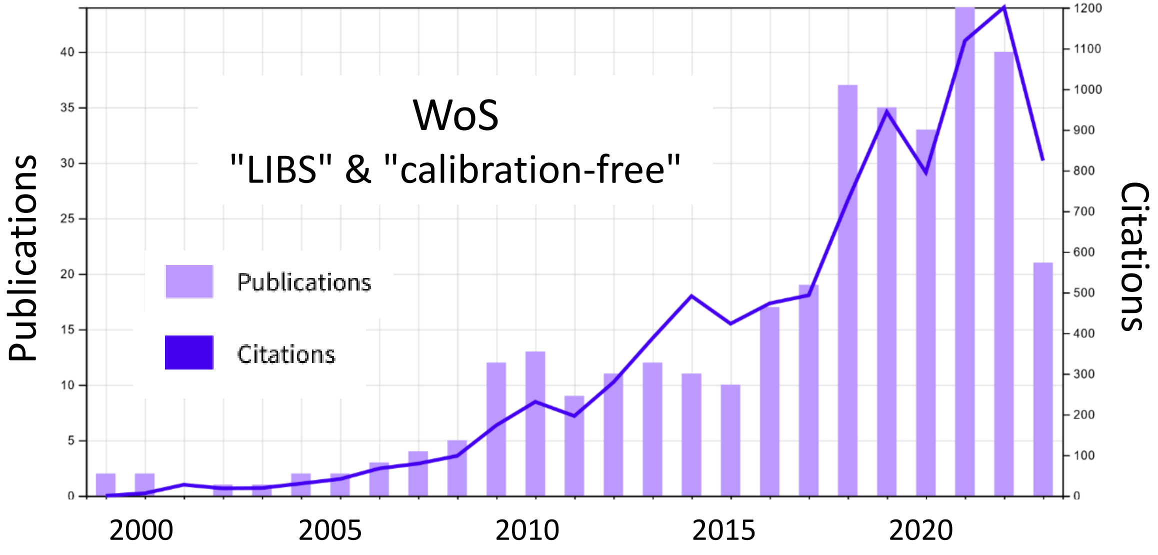
⇨ **intrinsically account for self-absorption**

☞ **easy handling ⇨ large success**

⇨ evaluation by many groups on all kind of materials

☞ **limited analytical performance**

☞ **amended approaches**



Outline

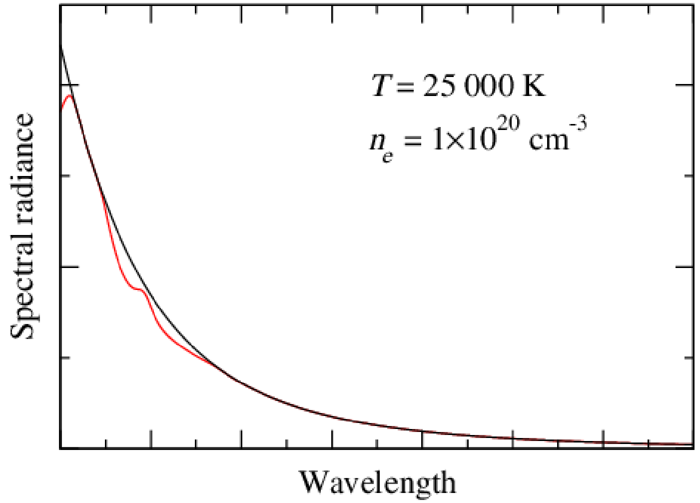
- Singular properties of “LIBS” plasma
- Development of calibration-free LIBS
- **Analytical performance**
- Upcoming improvements
- Conclusion

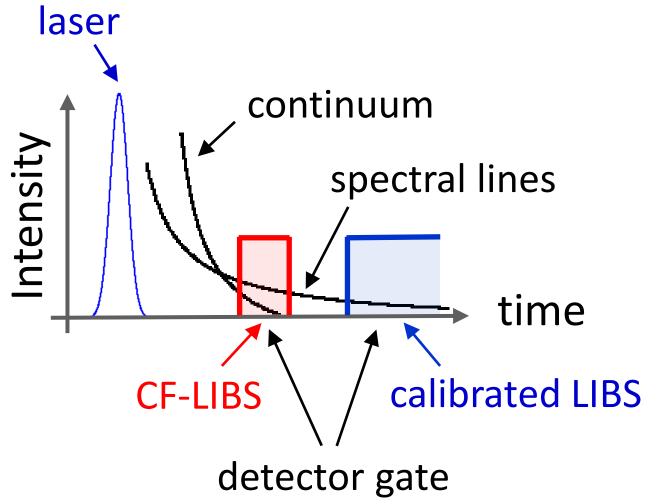
Analytical performance

Calibration-free LIBS : low accuracy in minor and trace element quantification ?

+ requirement of LTE ⇨ lowering of signal-to-noise ratio

- ⇨ large electron density required
- ⇨ intense continuum (collisions between charged particles)




laser
continuum
spectral lines
Intensity
time
CF-LIBS
calibrated LIBS
detector gate

Analytical performance

Calibration-free LIBS : low accuracy in minor and trace element quantification ?

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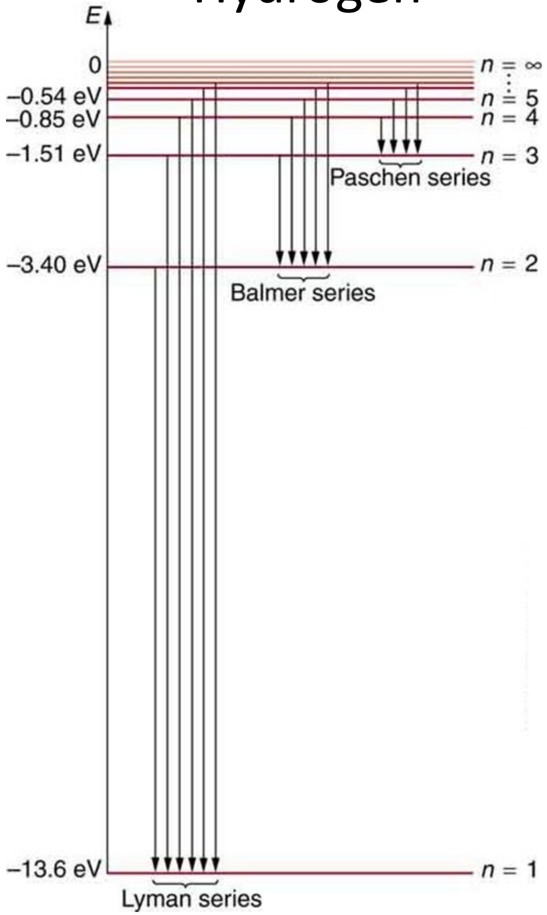
☞ materials with atoms of large energy gaps (C, H, N, O, …)

⇨ S/N lowering amplified

Hydrogen



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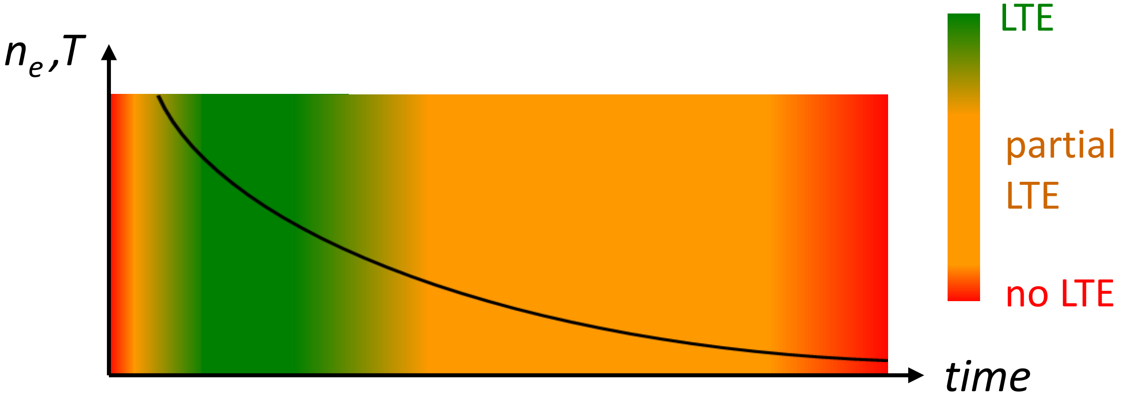
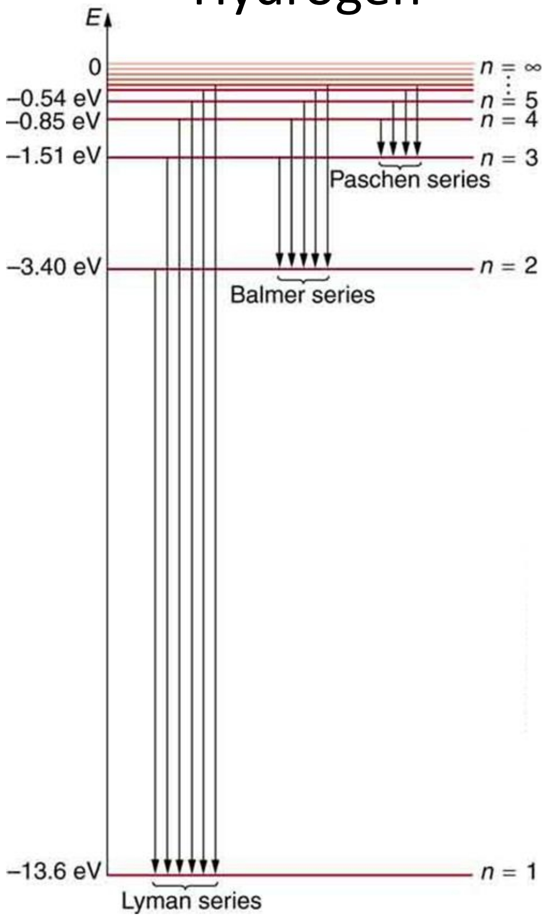
☞ solution = two-step procedure



Hydrogen



Analytical performance

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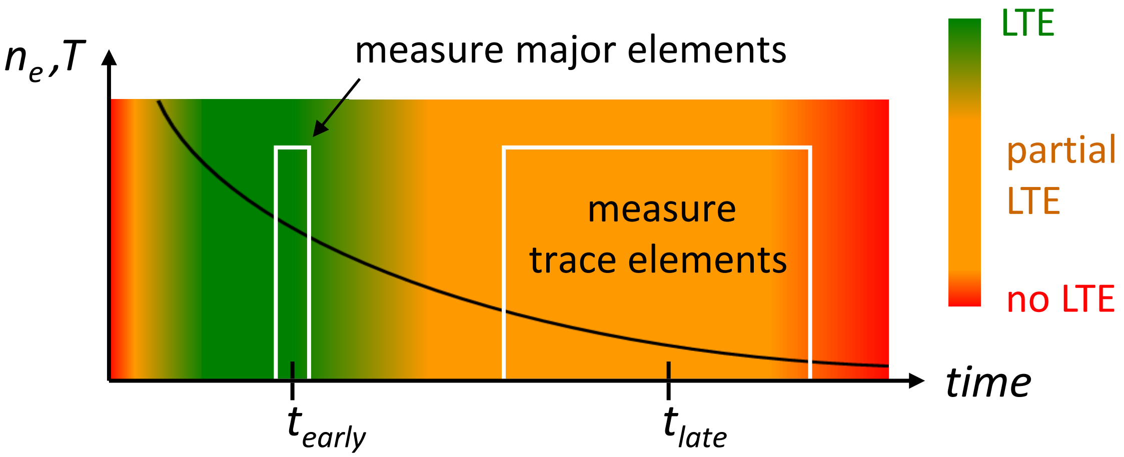


1. early measurement

☞ large N_e
⇨ full LTE
⇨ low signal-to-noise
☞ measure major elements

2. late measurement

☞ reduced N_e
⇨ partial LTE
⇨ high signal-to-noise
☞ measure minor and trace elements

trace element quantification in
- seafood, *Chen et al., SAB 2018*
- optical glass, *Gerhard et al., Appl. Surf. Sci. 2021*

Analytical performance

Calibration-free LIBS : low accuracy in minor and trace element quantification ?

+ requirement of LTE ⇨ lowering of signal-to-noise ratio

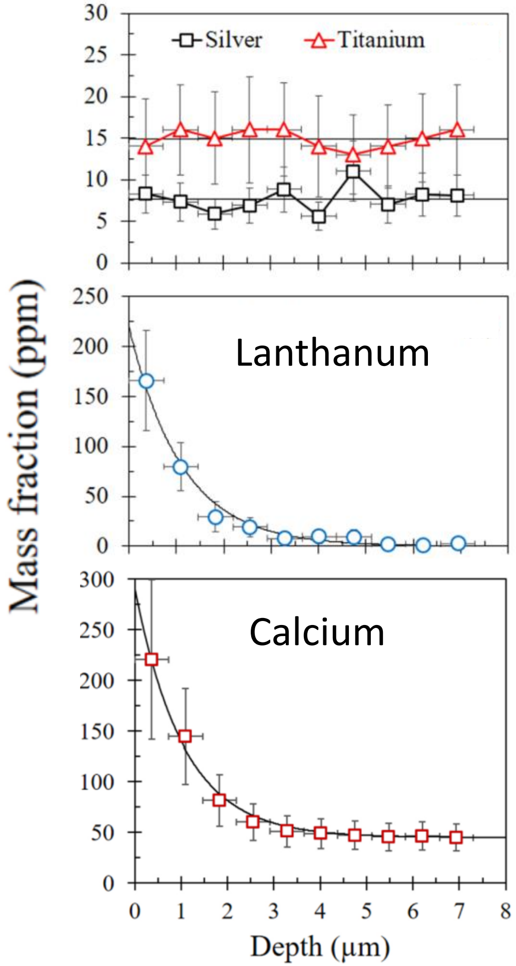
+ probe volume (differs for LIBS and reference method)

trace elements : fraction on surface may differ from those in the bulk

☞ **solution = in-depth measurement**

(combination with CF-LIBS is of particular interest)

example :
heavy flint glass
(SF5)



Gerhard et al., Appl. Surf. Sci. 2021

Analytical performance

Calibration-free LIBS : ~~low~~ accuracy in minor and trace element quantification

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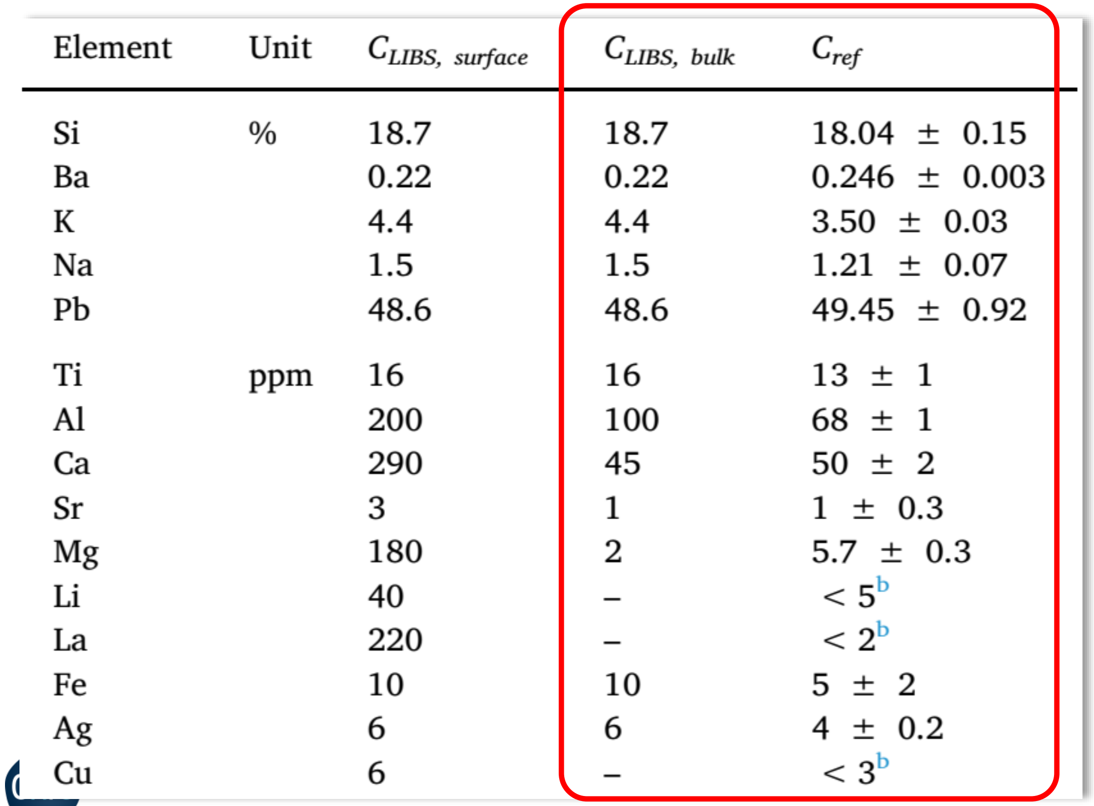
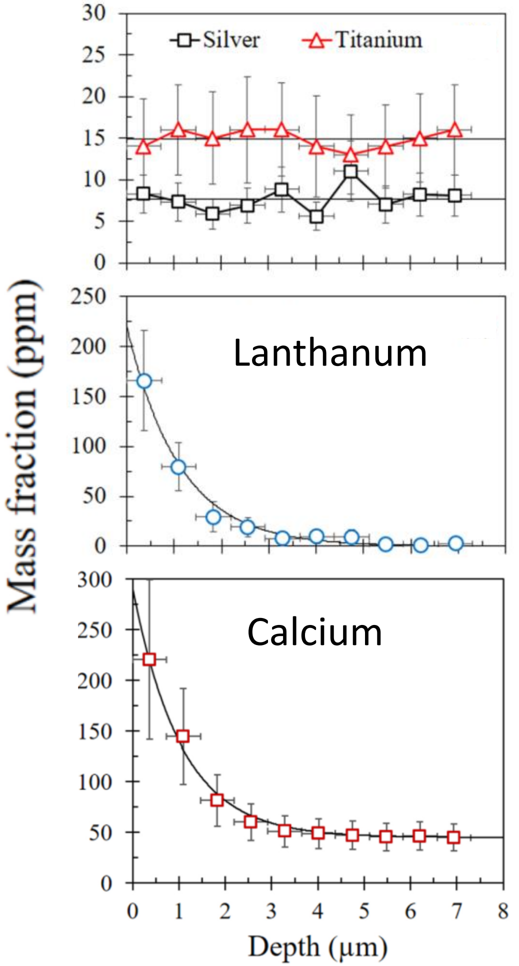


Element	Unit	$C_{LIBS,\ surface}$	$C_{LIBS,\ bulk}$	C_{ref}
Si	%	18.7	18.7	18.04 ± 0.15
Ba		0.22	0.22	0.246 ± 0.003
K		4.4	4.4	3.50 ± 0.03
Na		1.5	1.5	1.21 ± 0.07
Pb		48.6	48.6	49.45 ± 0.92
Ti	ppm	16	16	13 ± 1
Al		200	100	68 ± 1
Ca		290	45	50 ± 2
Sr		3	1	1 ± 0.3
Mg		180	2	5.7 ± 0.3
Li		40	–	< 5[b]
La		220	–	< 2[b]
Fe		10	10	5 ± 2
Ag		6	6	4 ± 0.2
Cu		6	–	< 3[b]

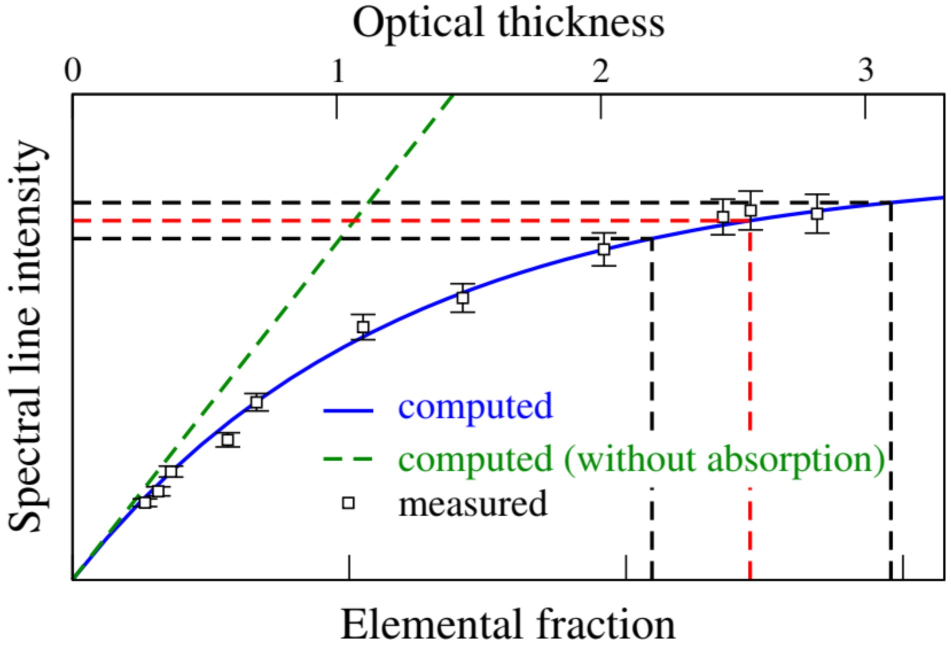
example :
heavy flint glass
(SF5)



Gerhard et al., Appl. Surf. Sci. 2021

Analytical performance

How does self-absorption influence the analytical performance ?



- ⇨ **selection of spectral lines**
- ⇨ **optimization of measurement accuracy**
- ⇨ **automation of calibration-free LIBS analysis**

atomic number density

atomic mass

mass fraction of element A : $C_A = \frac{n_A m_A}{\rho_{tot}}$ $\rho_{tot} = \sum_A n_A m_A$

$$\frac{\Delta C_A}{C_A} = \sqrt{(1 - C_A)^2 \left(\frac{\Delta n_A}{n_A}\right)^2 + \sum_{j \neq A}^{N} C_j^2 \left(\frac{\Delta n_j}{n_j}\right)^2}$$

$$\frac{\Delta n_A}{n_A} = \ ?$$

SLIMS

Analytical performance

$$\frac{\Delta n_A}{n_A} = ?$$

Taleb et al., Anal. Chim. Acta 2021

---

optically thin case :

measured line intensity

using Boltzmann and Saha equations : $$n_A = \Theta_1(T, n_e)\,\frac{I}{A_{ul}\,L}$$

plasma size along the line of sight

neglecting T and n_e errors : $$\boxed{\frac{\Delta n_A}{n_A} = \sqrt{\left(\frac{\Delta I}{I}\right)^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2}}$$

ΔI includes errors due to S/N ratio, apparatus response, line interference

---

general case :

line center optical thickness

line width due to Stark and Doppler broadening

integrating $\alpha(\lambda)$ over the line profile
+ using Boltzmann and Saha equations : $$n_A = \Theta_2(T, n_e)\,\frac{\tau_0\, w_{sd}}{A_{ul}\, L}$$

factor empirically inserted to retrieve optically thin case

neglecting T and n_e errors : $$\boxed{\frac{\Delta n_A}{n_A} = \sqrt{\left(\frac{\Delta \tau_0}{\tau_0}\right)^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2 + (1 - e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2 + \left(\frac{\Delta L}{L}\right)^2\right)}}$$

additional error sources

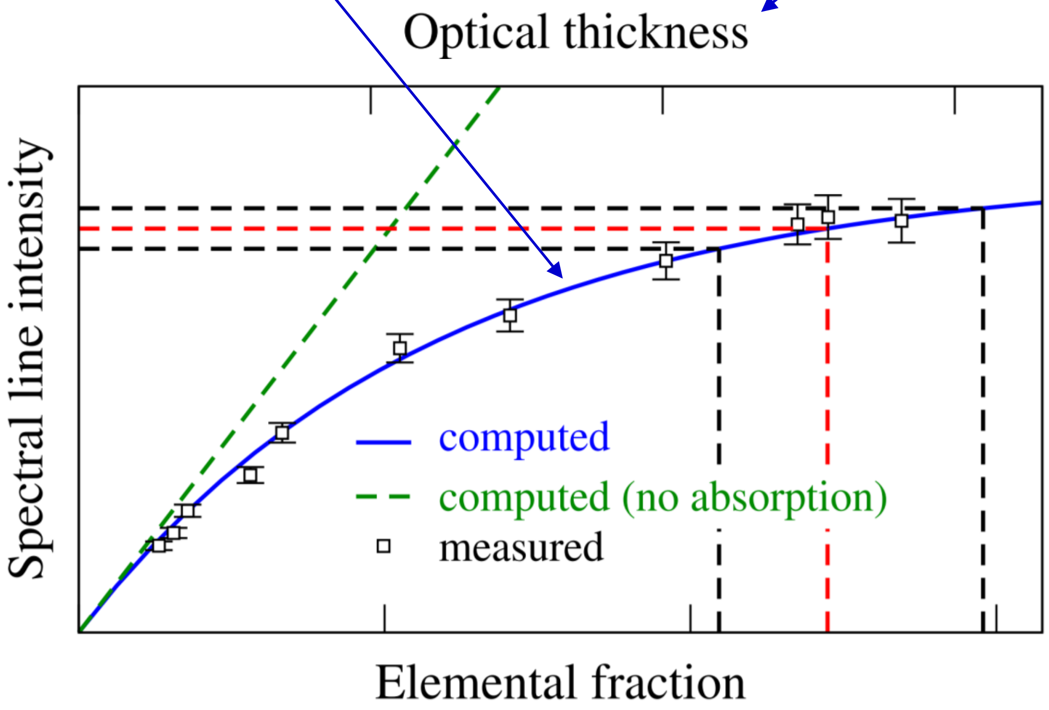
Analytical performance

$$\frac{\Delta n_A}{n_A} = \sqrt{\boxed{\left(\frac{\Delta\tau_0}{\tau_0}\right)}^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2 + (1-e^{-\tau_0})\left(\boxed{\left(\frac{\Delta w_{sd}}{w_{sd}}\right)}^2 + \boxed{\left(\frac{\Delta L}{L}\right)}^2\right)}$$

Taleb et al., Anal. Chim. Acta 2021

error growth (of $\frac{\Delta I}{I}$) due to change of slope

uncertainty of τ_0-axis



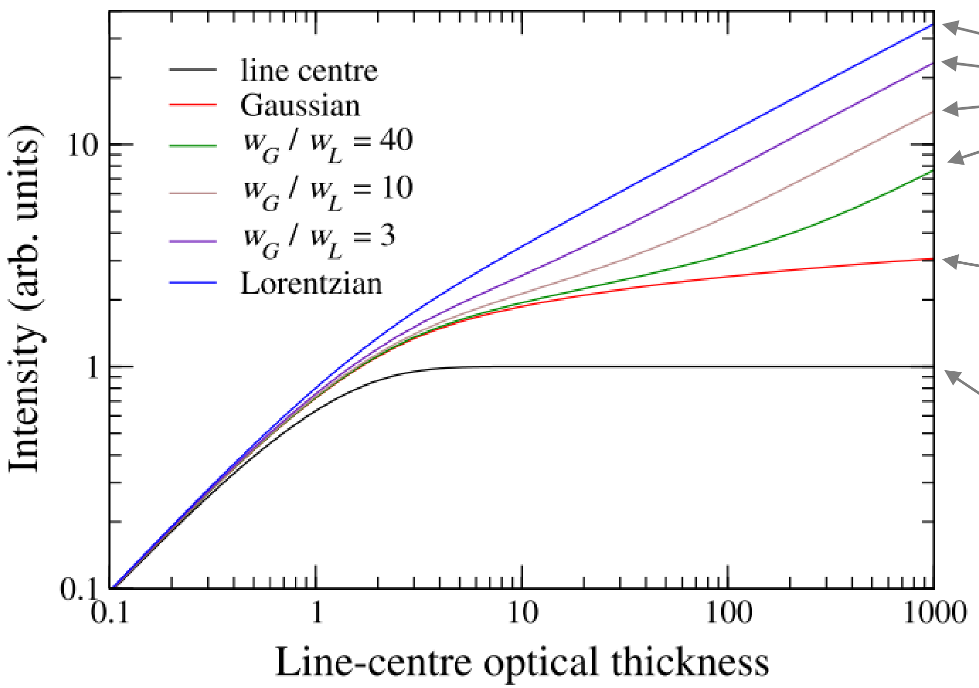
Analytical performance

$$\frac{\Delta n_A}{n_A} = \sqrt{\boxed{\left(\frac{\Delta \tau_0}{\tau_0}\right)}^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2 + (1 - e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2 + \left(\frac{\Delta L}{L}\right)^2\right)}$$

Taleb et al., Anal. Chim. Acta 2021

error growth factor

$$B_\lambda = B_\lambda^o\left(1 - e^{-\tau(\lambda)}\right) \Rightarrow I = f(\tau_0) \Rightarrow \frac{\Delta\tau_0}{\tau} = \frac{1}{\tau_0}\frac{f(\tau_0)}{f'(\tau_0)}\frac{\Delta I}{I} \equiv g(\tau_0)\frac{\Delta I}{I}$$



Gornushkin et al. SAB 1999

$I \propto \sqrt{\tau_0}$

contribution of large Lorentzian wings

quasi saturation due to small Gaussian wings

saturation at B_λ^o

Analytical performance

SLIMS

$$\frac{\Delta n_A}{n_A}=\sqrt{\boxed{\left(\frac{\Delta\tau_0}{\tau_0}\right)}^2+\left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2+(1-e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2+\left(\frac{\Delta L}{L}\right)^2\right)}$$

Taleb et al., Anal. Chim. Acta 2021

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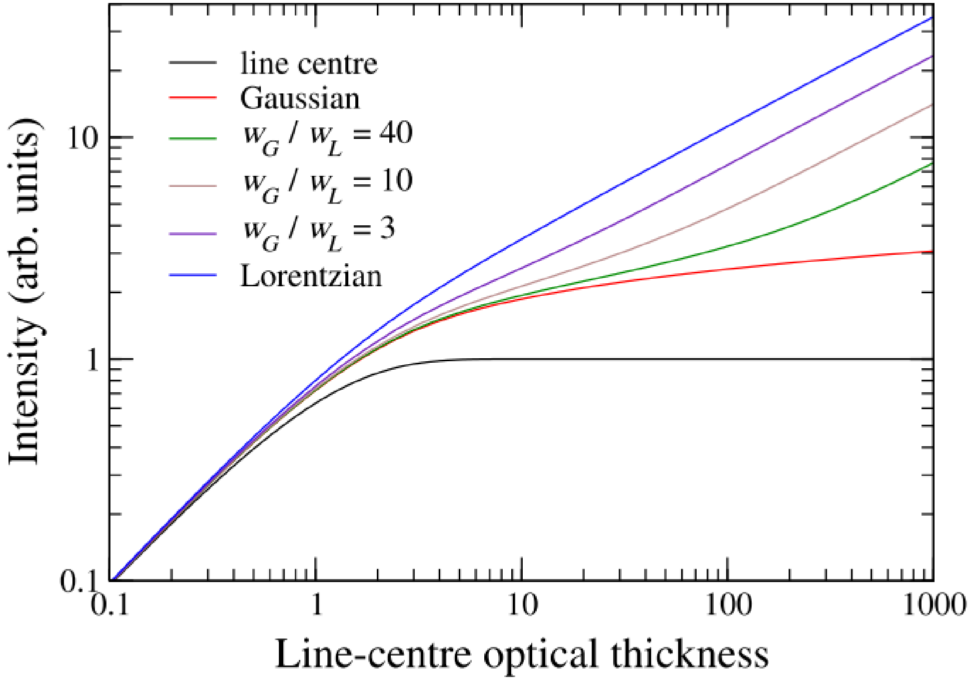

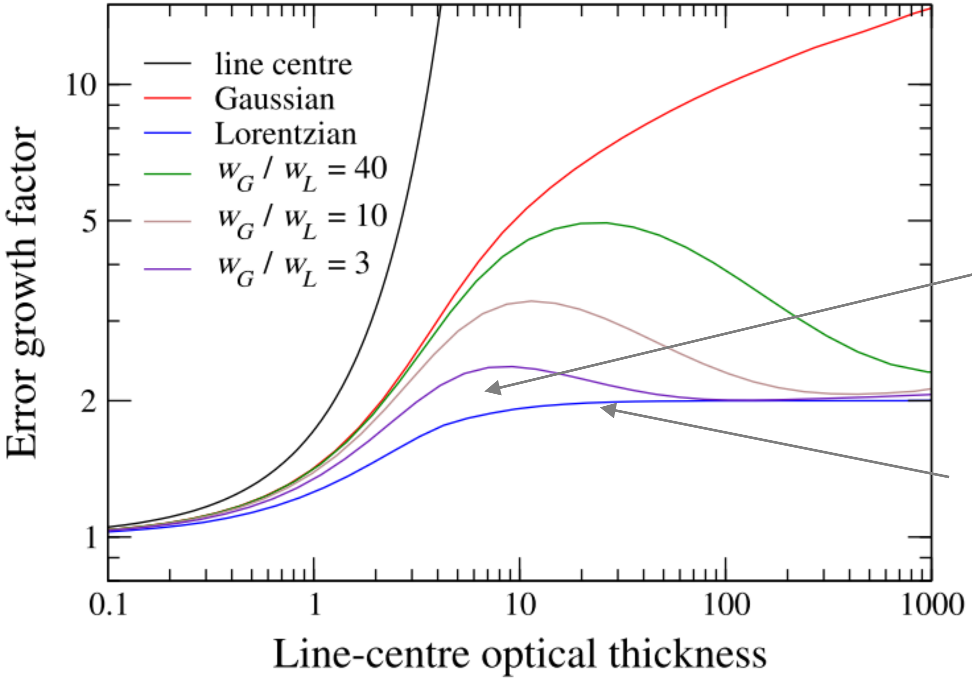

exponential error growth

(if $w_{ap} \ll w_{sd}$)

apparatus width

most lines

moderate error growth

$g \leq 2$

Analytical performance

$$\frac{\Delta n_A}{n_A} = \sqrt{\boxed{\left(\frac{\Delta \tau_0}{\tau_0}\right)}^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2 + (1 - e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2 + \left(\frac{\Delta L}{L}\right)^2\right)}$$

Taleb et al., Anal. Chim. Acta 2021

LIBS plasma ☞ Stark effect dominates line broadening ⇨ $\frac{\Delta \tau_0}{\tau_0} \leq 2\frac{\Delta I}{I}$

Analytical performance

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Taleb et al., Anal. Chim. Acta 2021

LIBS plasma ☞ Stark effect dominates line broadening ⇨ $\frac{\Delta\tau_0}{\tau_0} \leq 2\frac{\Delta I}{I}$

apparatus width

If line width can be precisely measured $(w_{ap} < w_{sd})$ ☞ $\frac{\Delta w_{sd}}{w_{sd}} \cong 5\%$

large uncertainties

opposite case $(w_{ap} > w_{sd})$ ☞ w_{sd} computed $\frac{\Delta w_{sd}^c}{w_{sd}^c} \simeq \frac{\Delta w_s}{w_s} = \sqrt{\left(\frac{\Delta\omega_s}{\omega_s}\right)^2 + \left(\frac{\Delta n_e}{n_e}\right)^2}$ ⇨ **large error** $\frac{\Delta w_{sd}}{w_{sd}}$

Stark broadening parameter

Analytical performance

$$\frac{\Delta n_A}{n_A} = \sqrt{\left(\frac{\Delta\tau_0}{\tau_0}\right)^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2 + (1-e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2 + \boxed{\left(\frac{\Delta L}{L}\right)}^2\right)}$$

Taleb et al., Anal. Chim. Acta 2021

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Stark broadening parameter

Plasma size L can be deduced - from intensity ratio of lines with different τ_0
- from fast plume imaging

$\Big\}$ **large error** , in the best case $\frac{\Delta L}{L} \cong 10\%$

Analytical performance

$$\frac{\Delta n_A}{n_A} = \sqrt{\left(\frac{\Delta \tau_0}{\tau_0}\right)^2 + \left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2 + (1 - e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2 + \left(\frac{\Delta L}{L}\right)^2\right)}$$

Taleb et al., Anal. Chim. Acta 2021

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Stark broadening parameter

Plasma size L can be deduced - from intensity ratio of lines with different τ_0
- from fast plume imaging

large error , in the best case $\frac{\Delta L}{L} \cong 10\%$

- ☞ **self-absorption lowers the accuracy of the analytical measurement**
- ☞ **error growth moderate if w_{sd} and L are precisely known**
  - ☞ **for resonance lines Δw_{sd} is often large**

Analytical performance

example :

analytical chemistry

Article

Cite This: *Anal. Chem.* 2019, 91, 2544−2550

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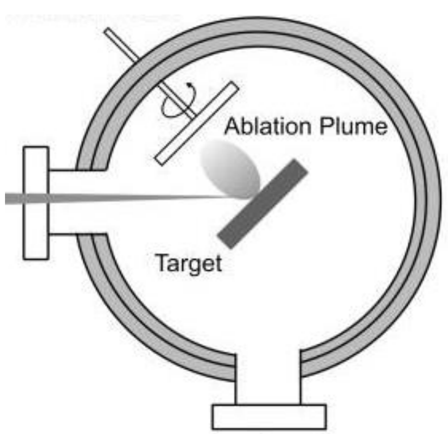
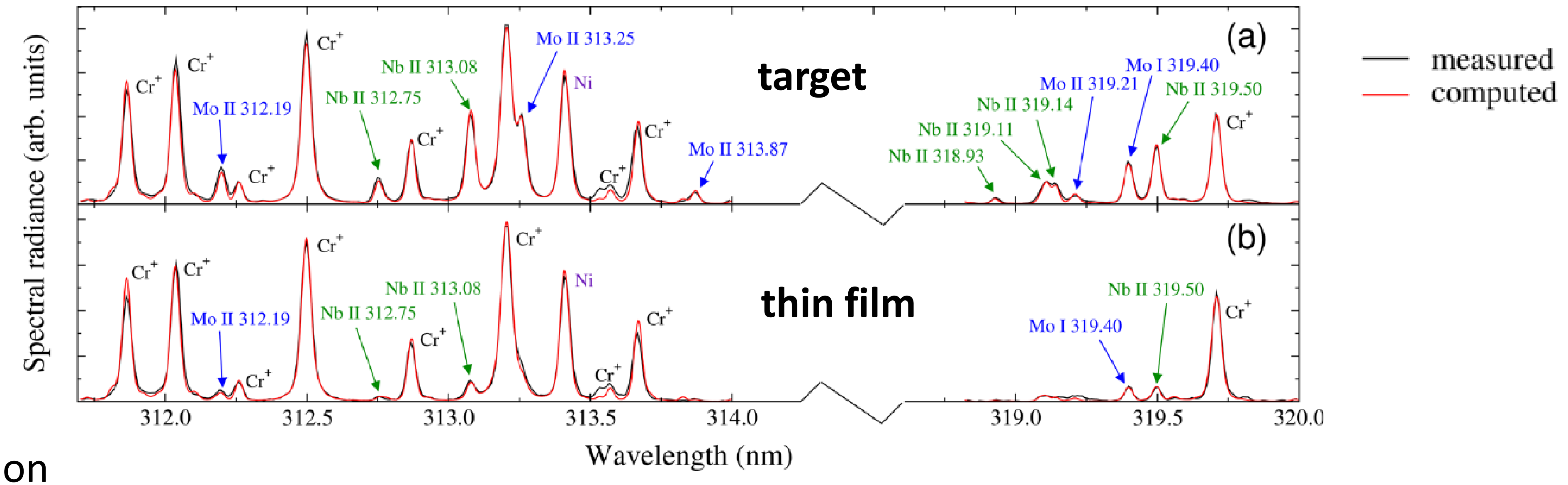
Analysis of Multi-elemental Thin Films via Calibration-Free Laser-Induced Breakdown Spectroscopy

Jörg Hermann,*[,†] Emanuel Axente,[‡] Frédéric Pelascini,[§] and Valentin Craciun[‡]





Pulsed **L**aser **D**eposition

of **Inconel superalloy**

Analytical performance

example :

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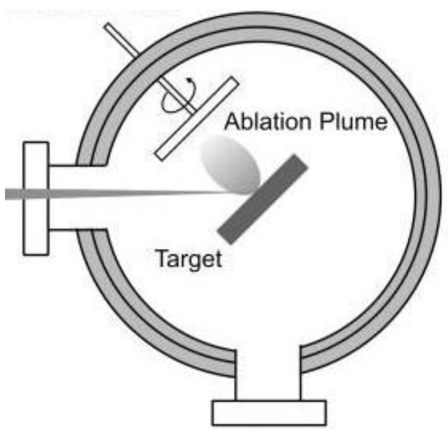
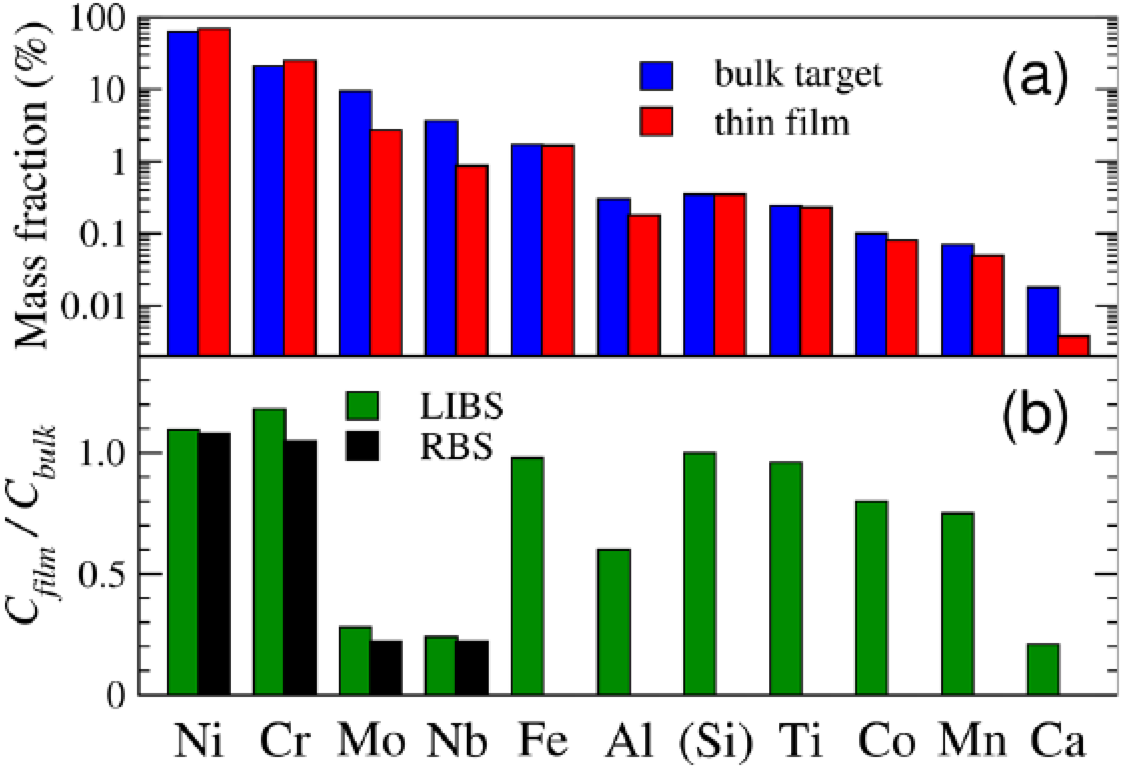


Pulsed **L**aser **D**eposition



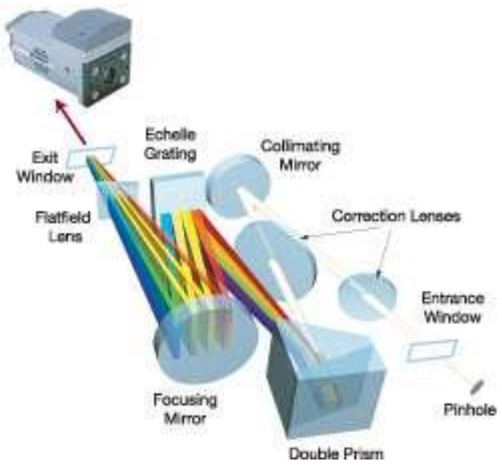
Outline

- Singular properties of “LIBS” plasma
- Development of calibration-free LIBS
- Analytical performance
- **Upcoming improvements**
- Conclusion

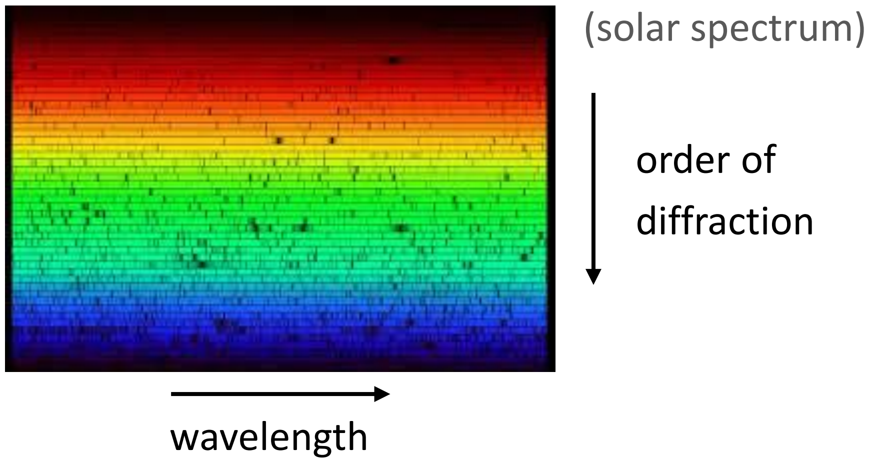
Upcoming improvements

calibration-free LIBS ☞ observation of **lines from all sample composing elements**

⇨ **use of echelle spectrometer** (combines broadband spectrum with high resolving power)



Intensity distribution on ICCD detector



problem ☞ high sensitivity to temperature variation

alteration of ⇨ **spectral calibration**

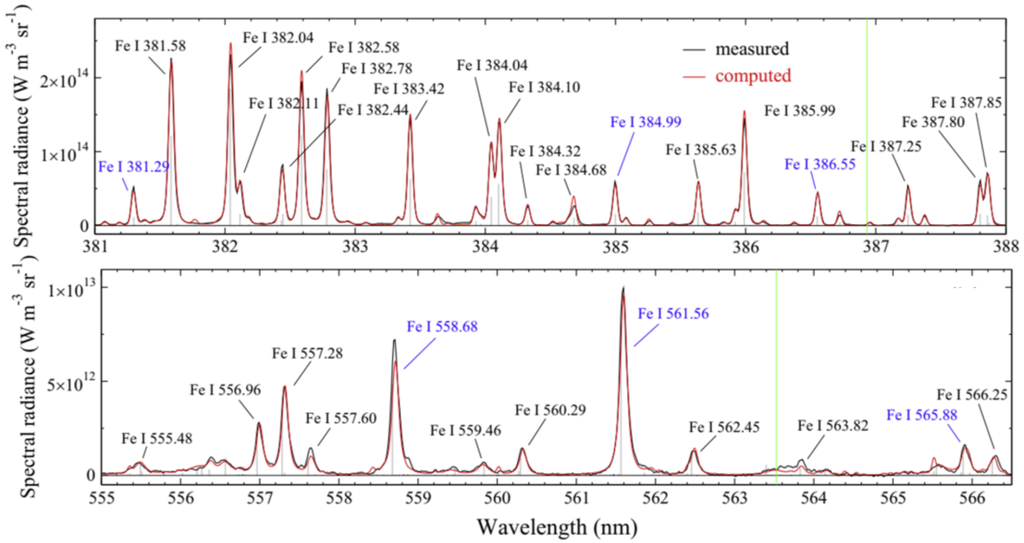
⇨ **apparatus response $R(\lambda)$**

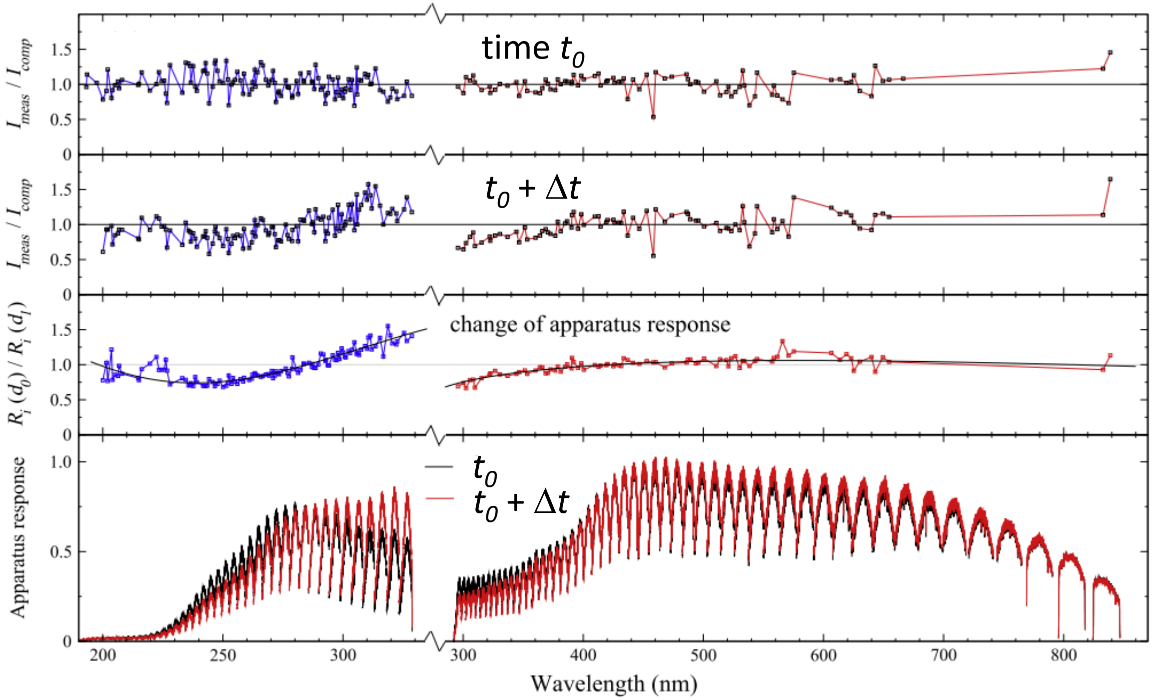
Upcoming improvements

Method for checking and correcting apparatus response $R(\lambda)$

- simulation of LIBS spectrum of steel (exp. conditions for uniform LTE plasma, UV laser, argon)
- NIST : accurate spectroscopic data available for iron

Taleb et al., SAB 2021





⇨ alteration of $R(\lambda)$ even in T-stabilized laboratory ☞ **attributed to thermal load of ICCD detector**

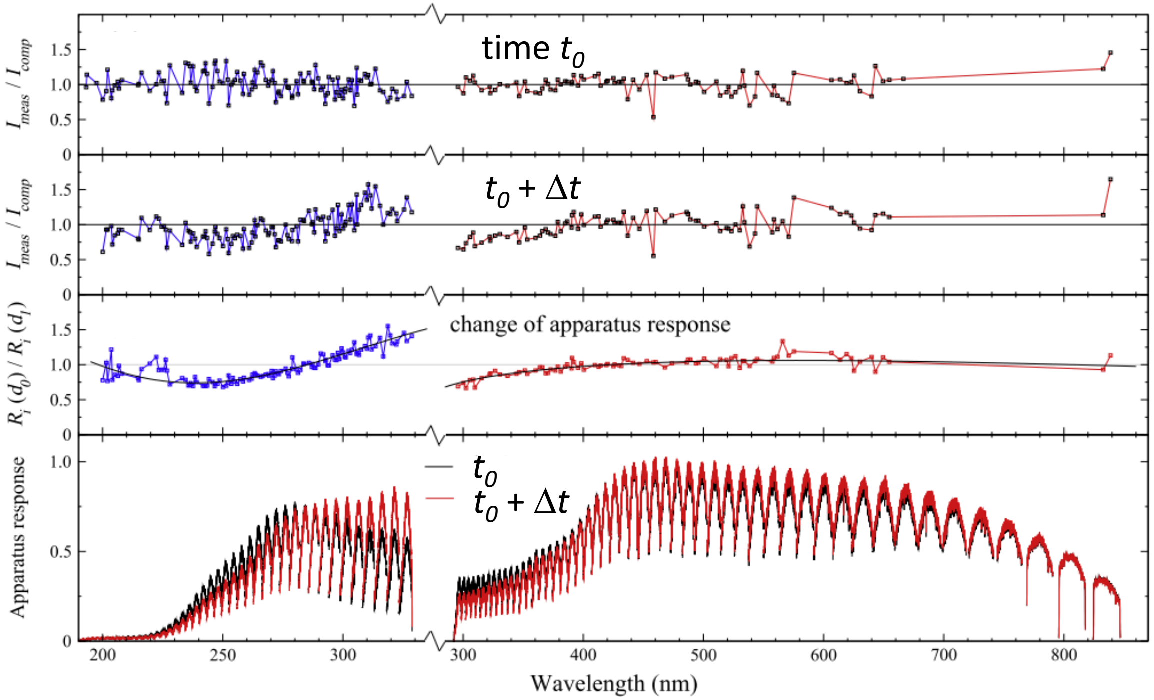
⇨ $R(\lambda) = $ const only for T-stabilized spectrometer (LTB, industrial prototype with 4 Peltier cooling stages)

Upcoming improvements

uncertainty of apparatus response = major issue in calibration-free LIBS

correction method (LIBS spectrum of steel) ☞ **partial solution**

Taleb et al., SAB 2021



Upcoming improvements

uncertainty of apparatus response = major issue in calibration-free LIBS

correction method (LIBS spectrum of steel) ☞ **partial solution**

☞ **requires preliminary calibration with radiation standards**

(deuterium arc and tungsten filament lamp)

drawbacks of calibration with radiation standards (deuterium and tungsten lamps) :

- **use same optical path** (as LIBS spectra recording) ☞ **difficult, often impossible** (industrial LIBS systems)
- radiation standards have limited lifetime (typically 2 years or 50 hours of use)
- radiation standards are expensive

solution :

☞ **use LIBS plasma as radiation standard** (exploit continuum emission)

Upcoming improvements

another major issue in calibration-free LIBS ☞ spectroscopic data

$$\frac{\Delta n_A}{n_A}=\sqrt{\left(\frac{\Delta\tau_0}{\tau_0}\right)^2+\left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2+(1-e^{-\tau_0})\left(\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2+\left(\frac{\Delta L}{L}\right)^2\right)}$$

⇧ ⇧

Transition probabilities given by NIST

NIST = National Institute of Standards and Technology

https://www.nist.gov/pml/atomic-spectra-database

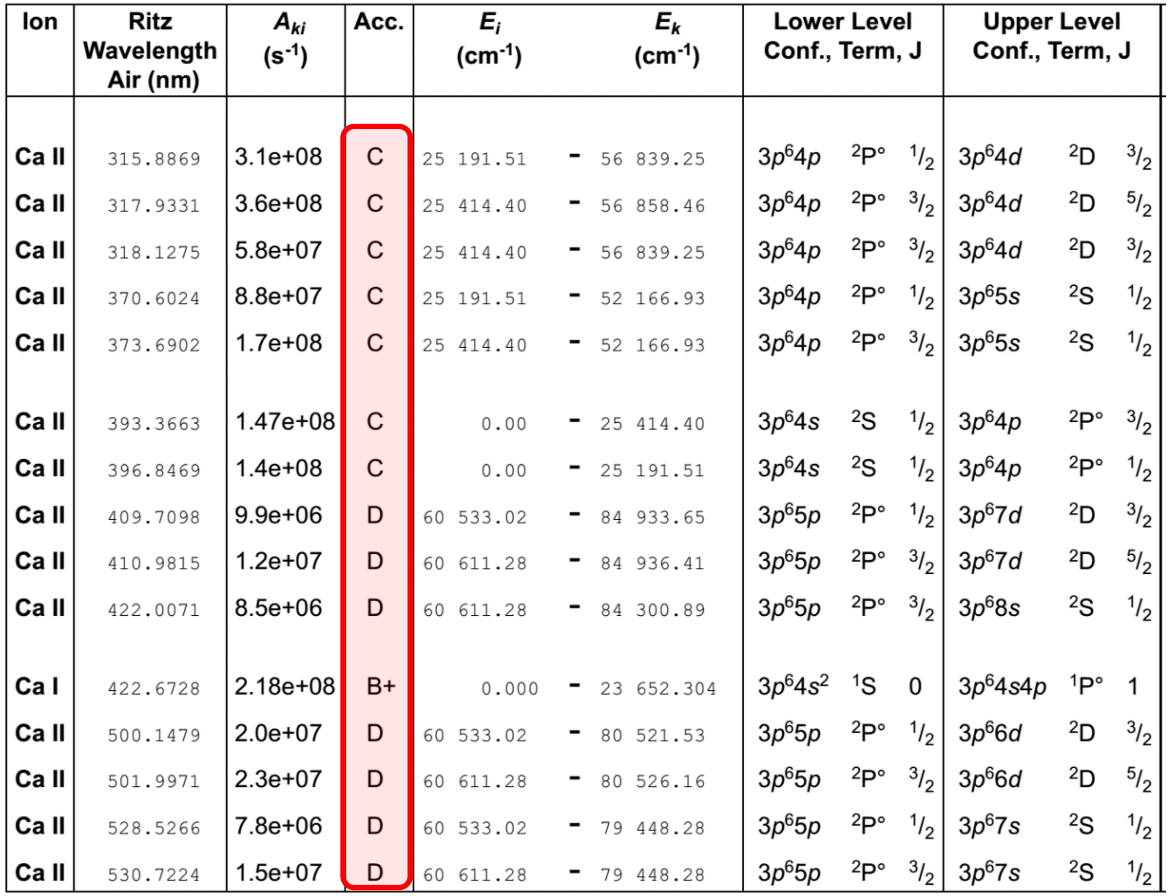
calcium

most intense lines

accuracy

C = 25%

D = 50%



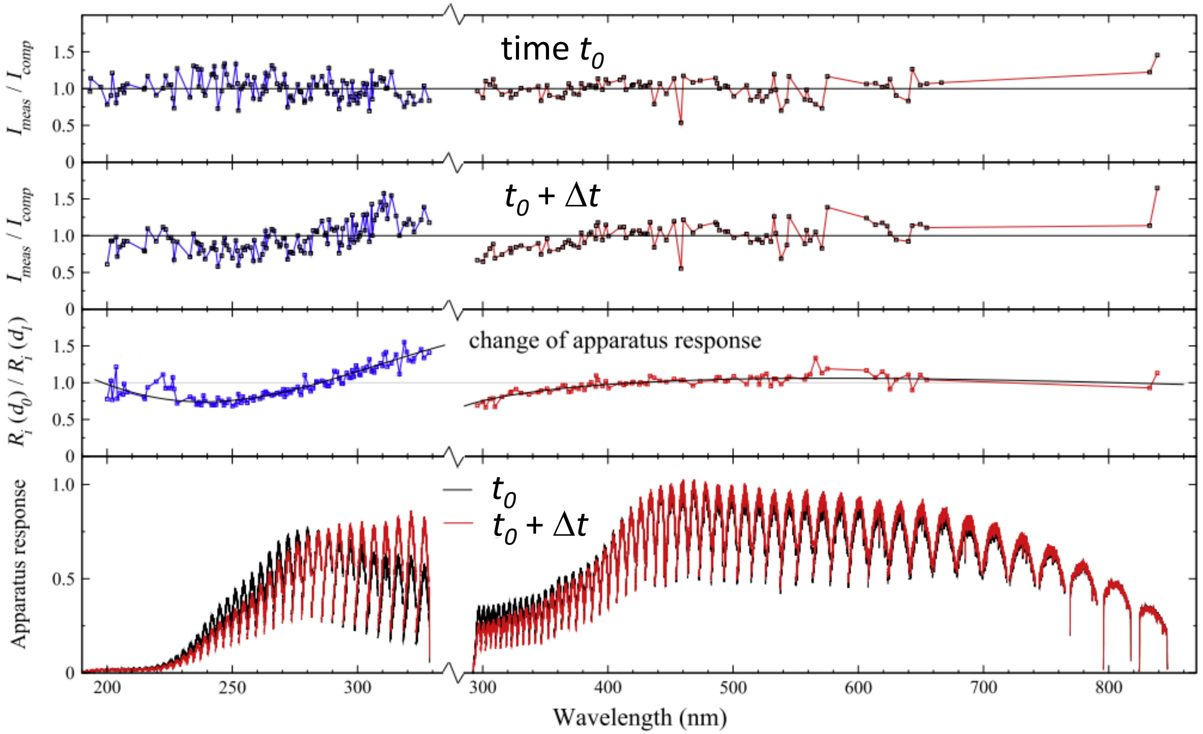
Ion	Ritz Wavelength Air (nm)	A_{ki} (s^{-1})	Acc.	E_i (cm^{-1})		E_k (cm^{-1})	Lower Level Conf., Term, J			Upper Level Conf., Term, J		
Ca II	315.8869	3.1e+08	C	25 191.51	-	56 839.25	$3p^64p$	$^2P°$	$^1/_2$	$3p^64d$	^2D	$^3/_2$
Ca II	317.9331	3.6e+08	C	25 414.40	-	56 858.46	$3p^64p$	$^2P°$	$^3/_2$	$3p^64d$	^2D	$^5/_2$
Ca II	318.1275	5.8e+07	C	25 414.40	-	56 839.25	$3p^64p$	$^2P°$	$^3/_2$	$3p^64d$	^2D	$^3/_2$
Ca II	370.6024	8.8e+07	C	25 191.51	-	52 166.93	$3p^64p$	$^2P°$	$^1/_2$	$3p^65s$	^2S	$^1/_2$
Ca II	373.6902	1.7e+08	C	25 414.40	-	52 166.93	$3p^64p$	$^2P°$	$^3/_2$	$3p^65s$	^2S	$^1/_2$
Ca II	393.3663	1.47e+08	C	0.00	-	25 414.40	$3p^64s$	^2S	$^1/_2$	$3p^64p$	$^2P°$	$^3/_2$
Ca II	396.8469	1.4e+08	C	0.00	-	25 191.51	$3p^64s$	^2S	$^1/_2$	$3p^64p$	$^2P°$	$^1/_2$
Ca II	409.7098	9.9e+06	D	60 533.02	-	84 933.65	$3p^65p$	$^2P°$	$^1/_2$	$3p^67d$	^2D	$^3/_2$
Ca II	410.9815	1.2e+07	D	60 611.28	-	84 936.41	$3p^65p$	$^2P°$	$^3/_2$	$3p^67d$	^2D	$^5/_2$
Ca II	422.0071	8.5e+06	D	60 611.28	-	84 300.89	$3p^65p$	$^2P°$	$^3/_2$	$3p^68s$	^2S	$^1/_2$
Ca I	422.6728	2.18e+08	B+	0.000	-	23 652.304	$3p^64s^2$	^1S	0	$3p^64s4p$	$^1P°$	1
Ca II	500.1479	2.0e+07	D	60 533.02	-	80 521.53	$3p^65p$	$^2P°$	$^1/_2$	$3p^66d$	^2D	$^3/_2$
Ca II	501.9971	2.3e+07	D	60 611.28	-	80 526.16	$3p^65p$	$^2P°$	$^3/_2$	$3p^66d$	^2D	$^5/_2$
Ca II	528.5266	7.8e+06	D	60 533.02	-	79 448.28	$3p^65p$	$^2P°$	$^1/_2$	$3p^67s$	^2S	$^1/_2$
Ca II	530.7224	1.5e+07	D	60 611.28	-	79 448.28	$3p^65p$	$^2P°$	$^3/_2$	$3p^67s$	^2S	$^1/_2$

Upcoming improvements

another major issue in calibration-free LIBS ☞ spectroscopic data

$$\frac{\Delta n_A}{n_A} = \sqrt{\left(\frac{\Delta\tau_0}{\tau_0}\right)^2 + \underset{\Uparrow}{\left(\frac{\Delta A_{ul}}{A_{ul}}\right)^2} + (1-e^{-\tau_0})\left(\underset{\Uparrow}{\left(\frac{\Delta w_{sd}}{w_{sd}}\right)^2} + \left(\frac{\Delta L}{L}\right)^2\right)}$$

Taleb et al., SAB 2021



intensity ratio $R_I = \frac{I_{meas}}{I_{comp}}$

average uncertainty by NIST

$$\frac{\Delta R_I}{R_I} \cong \frac{\Delta A_{ul}}{A_{ul}}$$

⇨ LIBS plasma appropriate to measure spectroscopic data

uniform LTE plasma

⇨ simple and accurate measurements

(no need of space-resolved measurements)

Outline

- Singular properties of “LIBS” plasma
- Development of calibration-free LIBS
- Analytical performance
- Upcoming improvements
- **Conclusion**

Conclusion

in appropriate experimental conditions

- ☞ **Plasma produced by laser ablation = ideal radiation source**
  - ☞ **simple and accurate modeling of emission spectrum**
- ☞ **Calibration-free LIBS is a powerful analytical tool**

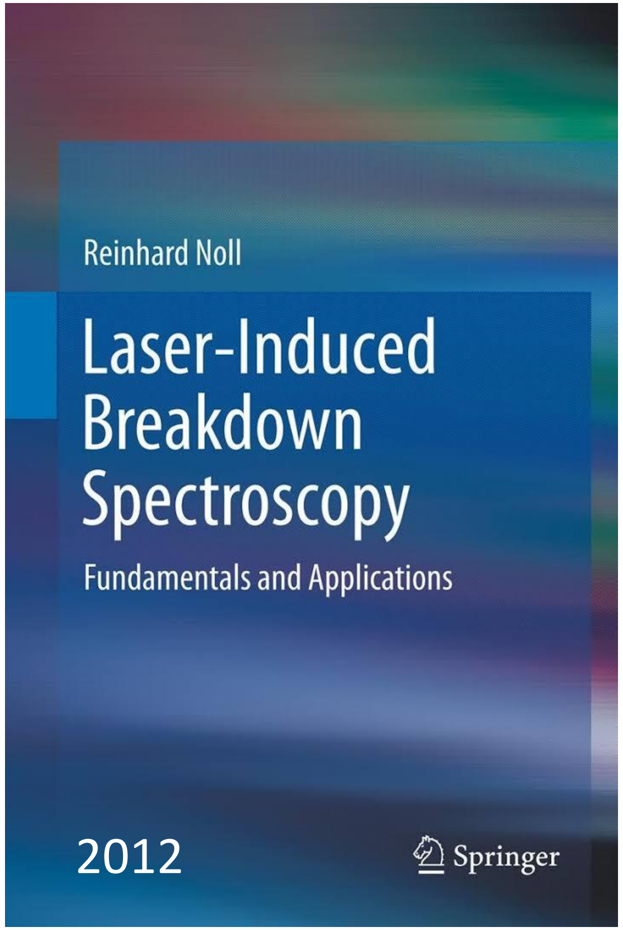
- Principal limitations of analytical performance

- ☞ **spectroscopic data** (A_{ul}-values, Stark broadening parameters)
  - ⇨ **accurate measurements using ideal radiation source**
- ☞ **apparatus response** (measurement difficult, *T*-sensitivity of echelle spectrometer)
  - ⇨ **LIP as radiation standard**
    (exploit continuum emission during initial plume expansion)

☞ **Revolution in materials analysis**

Literature

LIBS



Reinhard Noll

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Fundamentals and Applications

2012

Springer

Calibration-free LIBS

book chapter

"Calibration-free laser-induced breakdown spectroscopy"

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