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Colloquium Spectroscopicum Internationale XL
9th Euro-Mediterranean Symposium on LIBS
Congress Center, 11-16 June 2017, Pisa, Italy



NANO SAMPLING OF METALS WITH ULTRA SHORT LASER PULSES

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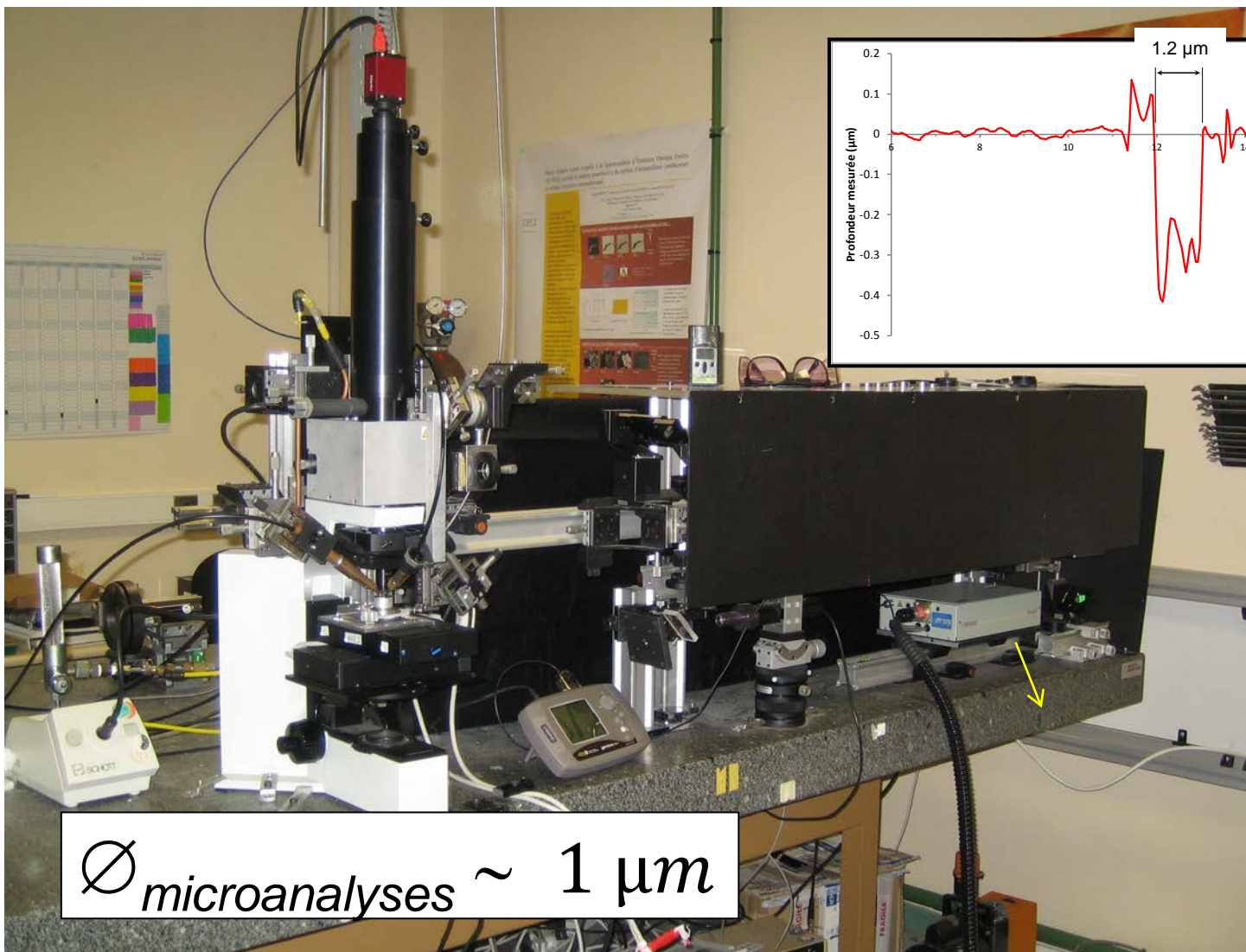
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Colloquium Spectroscopicum Internationale XL | IX Euro-Mediterranean Symposium on LIBS

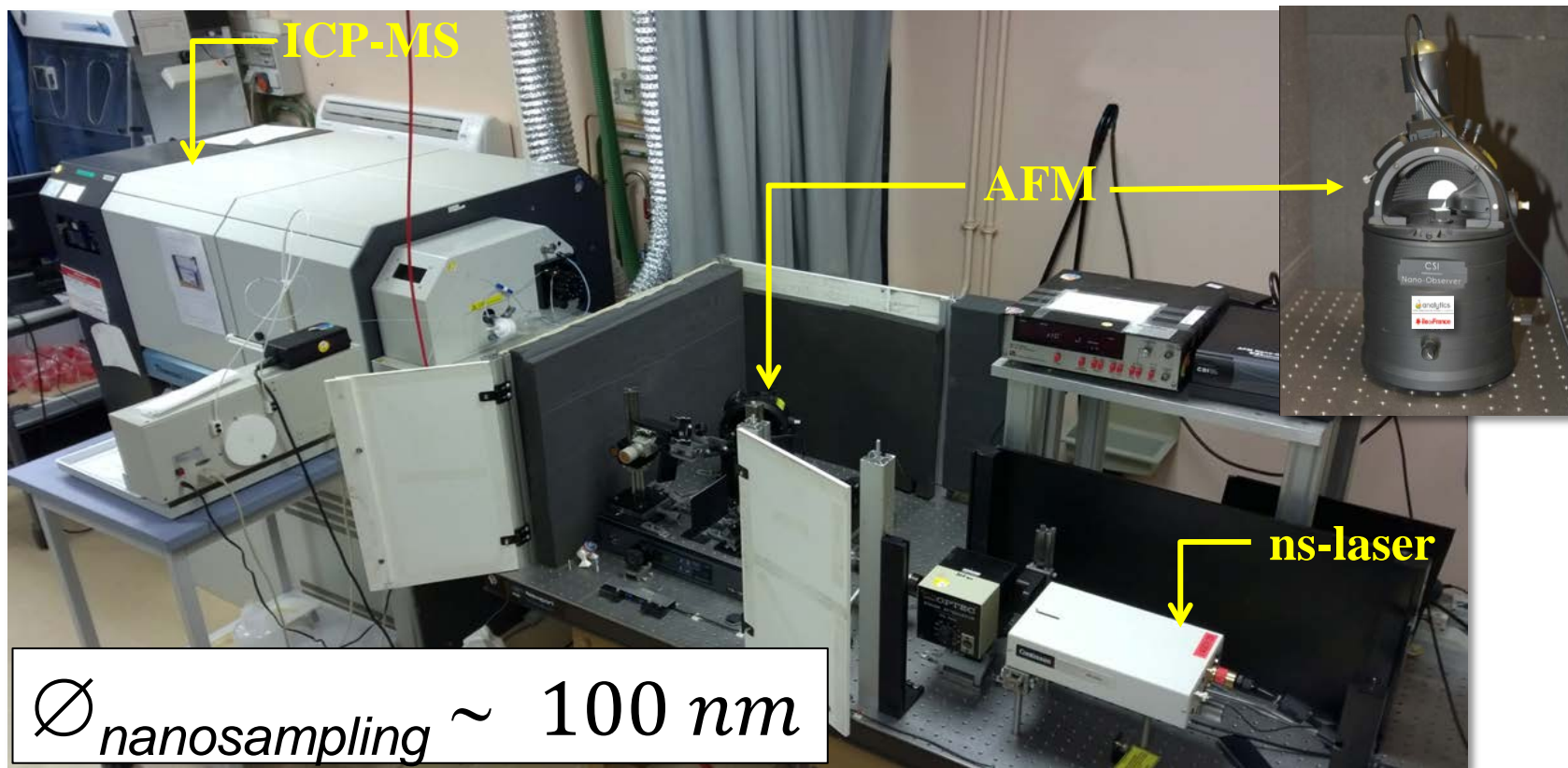


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CEA Saclay micro-LIBS instrument for surface micro-imaging / elemental cartography



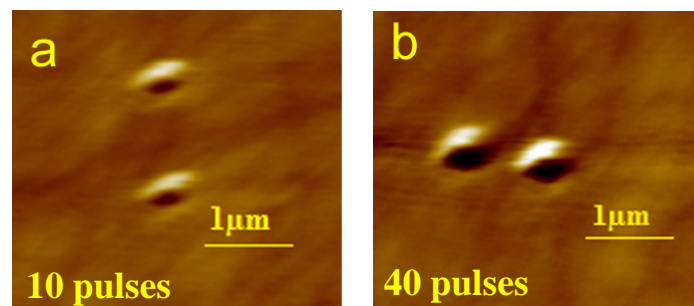
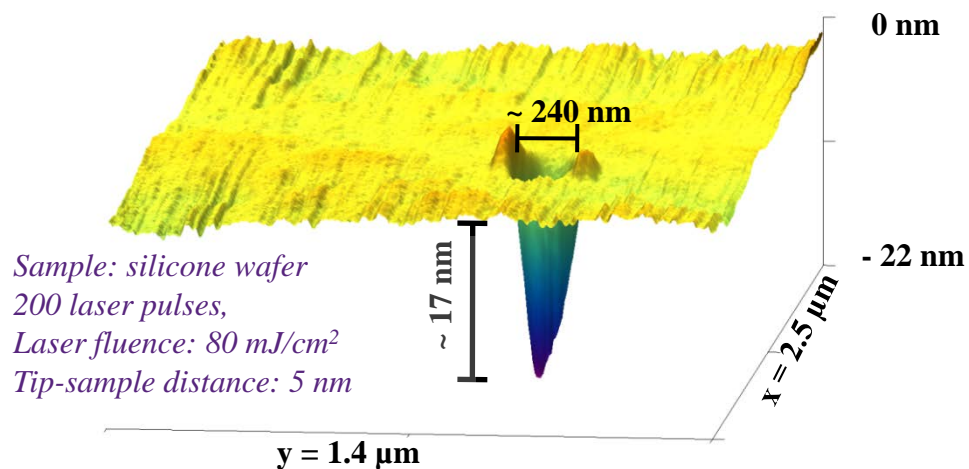
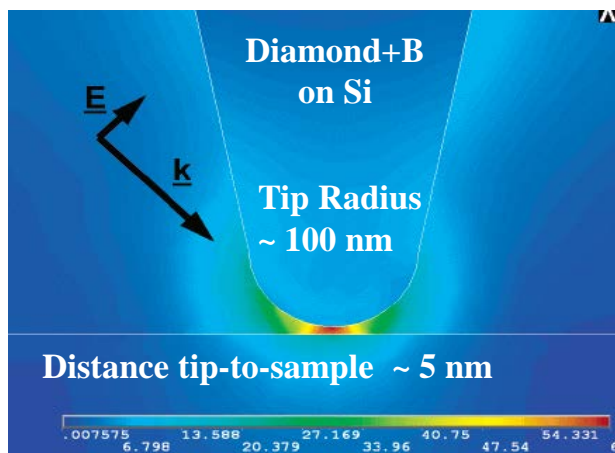
CEA Saclay near-field LA-ICP-MS installation



Nd-YAG laser (266 nm) , pulse duration 4 ns.

AFM: Atomic Force Microscope.

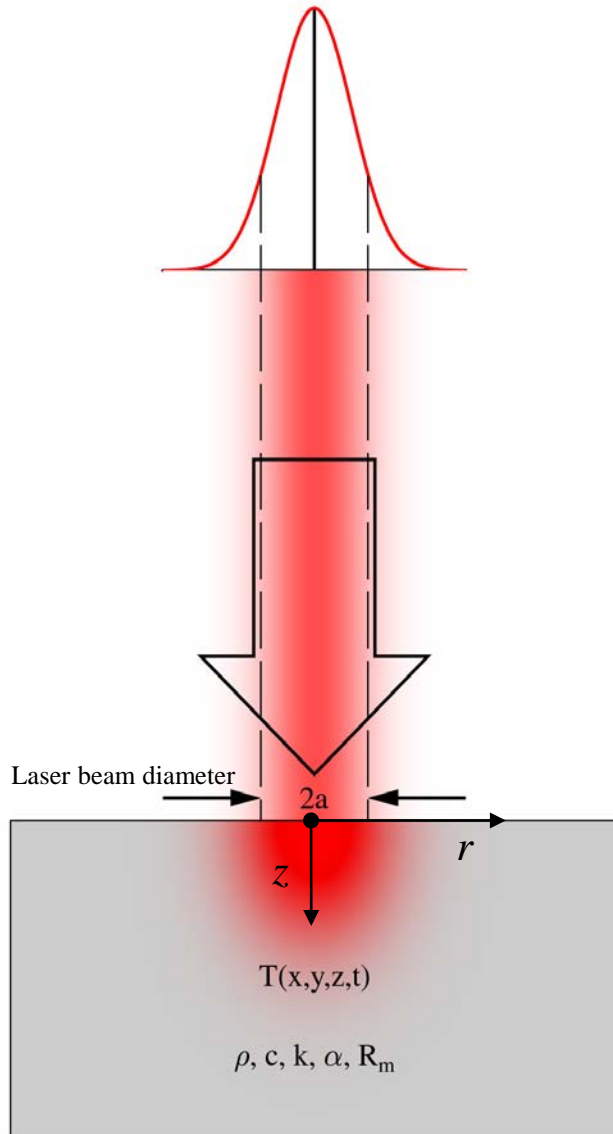
ICP-MS: Inductively Coupled Plasma - Mass Spectrometry : double focusing sector field



[**] C. Jabbour, J.-L. Lacour, M. Tabarant, A. Semerok and F. Chartier, Development of a tip enhanced near-field laser ablation system for sub-micrometric analysis of solid samples, *J. Anal. At. Spectrom.*, 2016, **31**, 1534–1541

Aim of our theoretical studies

$$I(r) = I_0 \exp(-r^2/a^2)$$



for $a \in [100 \mu\text{m} \rightarrow 10 \text{ nm}]$

for $\tau \in [4 \text{ ns} \rightarrow 100 \text{ fs}]$

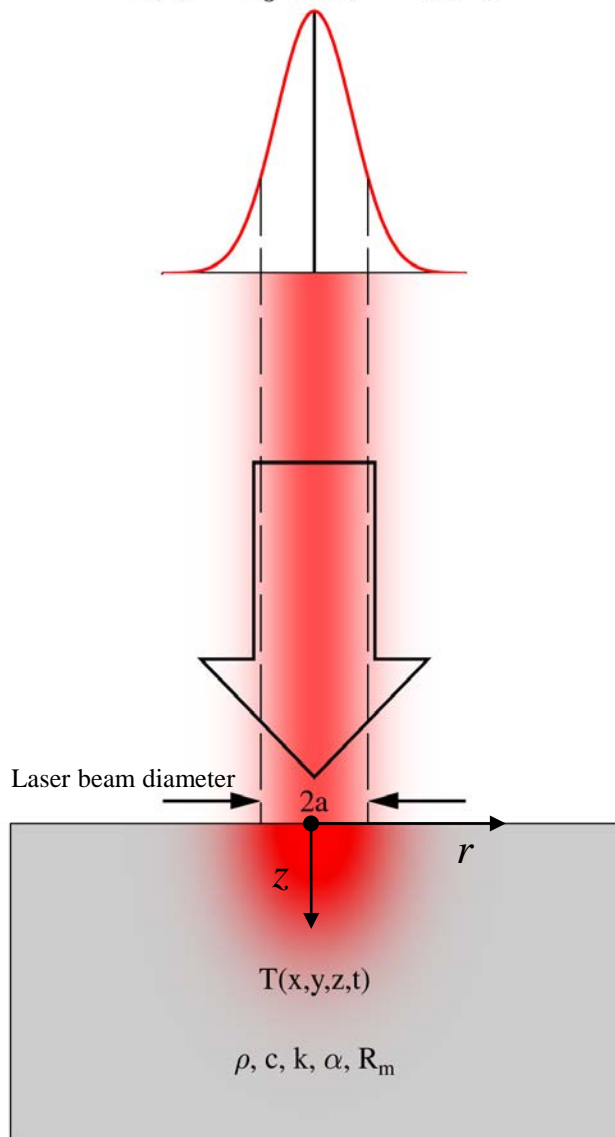
$$Q(t, x, y, z) \Rightarrow T(t, x, y, z)$$

$$T_{max} = f(\text{interaction parameters}) \Leftrightarrow T_{ablation}$$

Laser pulses: 266 nm, 4 ns or 100 fs;

Samples: Si or Au

$$I(r) = I_0 \exp(-r^2/a^2)$$



$$c(T) \frac{\partial T}{\partial t} = \text{div}(k(T) \nabla T) + Q(t, r, z)$$

$$Q(t, r, z) = I(t, r) A \alpha \exp(-\alpha z)$$

or

$$Q(t, x, y, z) = \alpha n \frac{c |\vec{E}|^2}{8\pi} \text{ from near-field calculations}$$

$$T(t = 0, r, z) = T_0 \quad \text{and} \quad \left. \frac{\partial T(t, r, z)}{\partial z} \right|_{z=0} = 0$$

c ($\text{J m}^{-3} \text{K}^{-1}$) – thermal capacity;

k ($\text{W m}^{-1} \text{K}^{-1}$) – thermal conductivity;

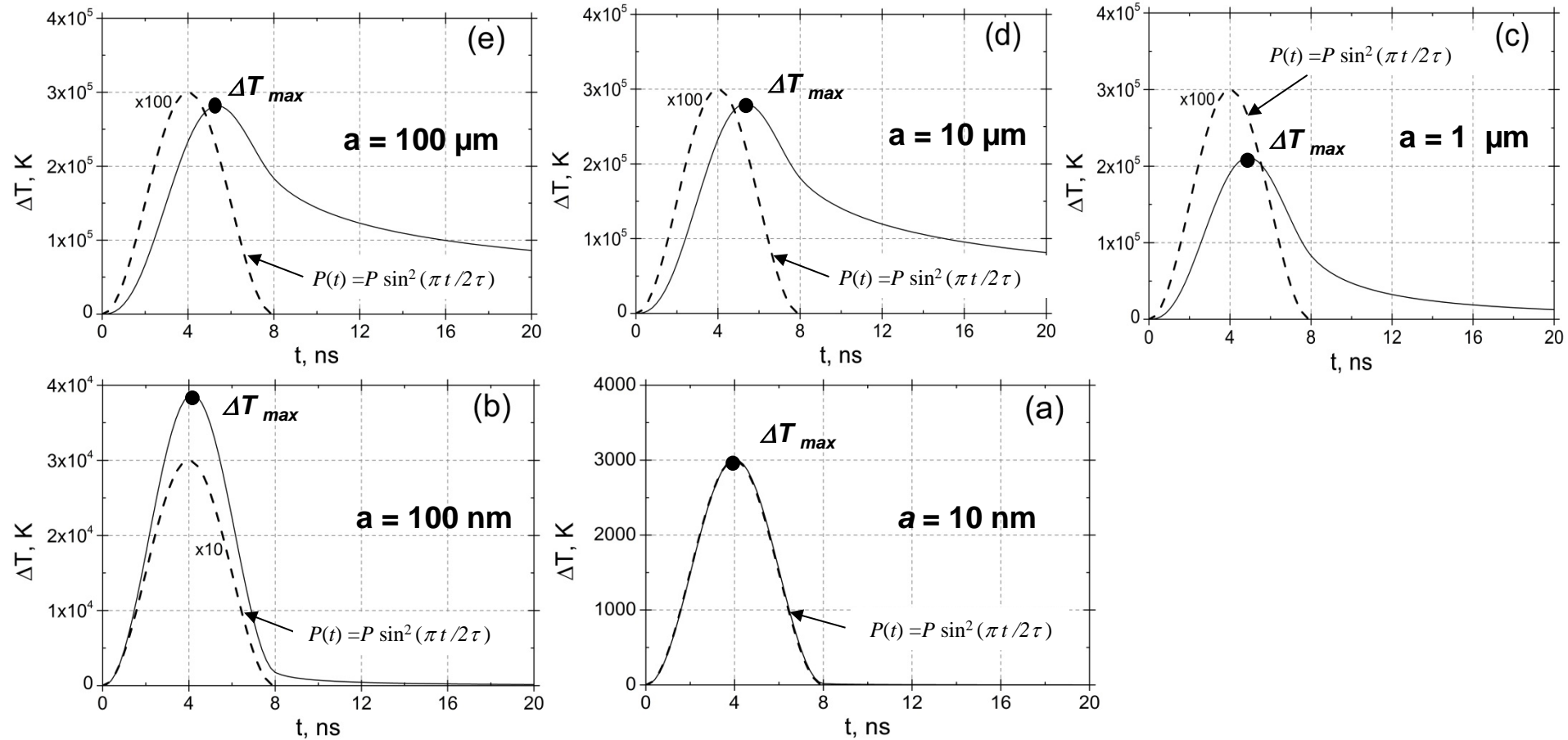
α (m^{-1}) – absorption coefficient of media;

A – surface absorptivity at laser wavelength;

[***] A. Semerok, S. V. Fomichev, J.-M. Weulersse, F. Brygo, and P.-Y. Thro, Heating and ablation of tokamak graphite by pulsed nanosecond Nd-YAG lasers, JOURNAL OF APPLIED PHYSICS **101**, 084916, 2007.

Si-bulk: $c = 700 \text{ J/kg K}$, $k = 149 \text{ W/m K}$, $\rho = 2330 \text{ kg/m}^3$, $\alpha = 200 \text{ }\mu\text{m}^{-1}$, $A = 0.3$.

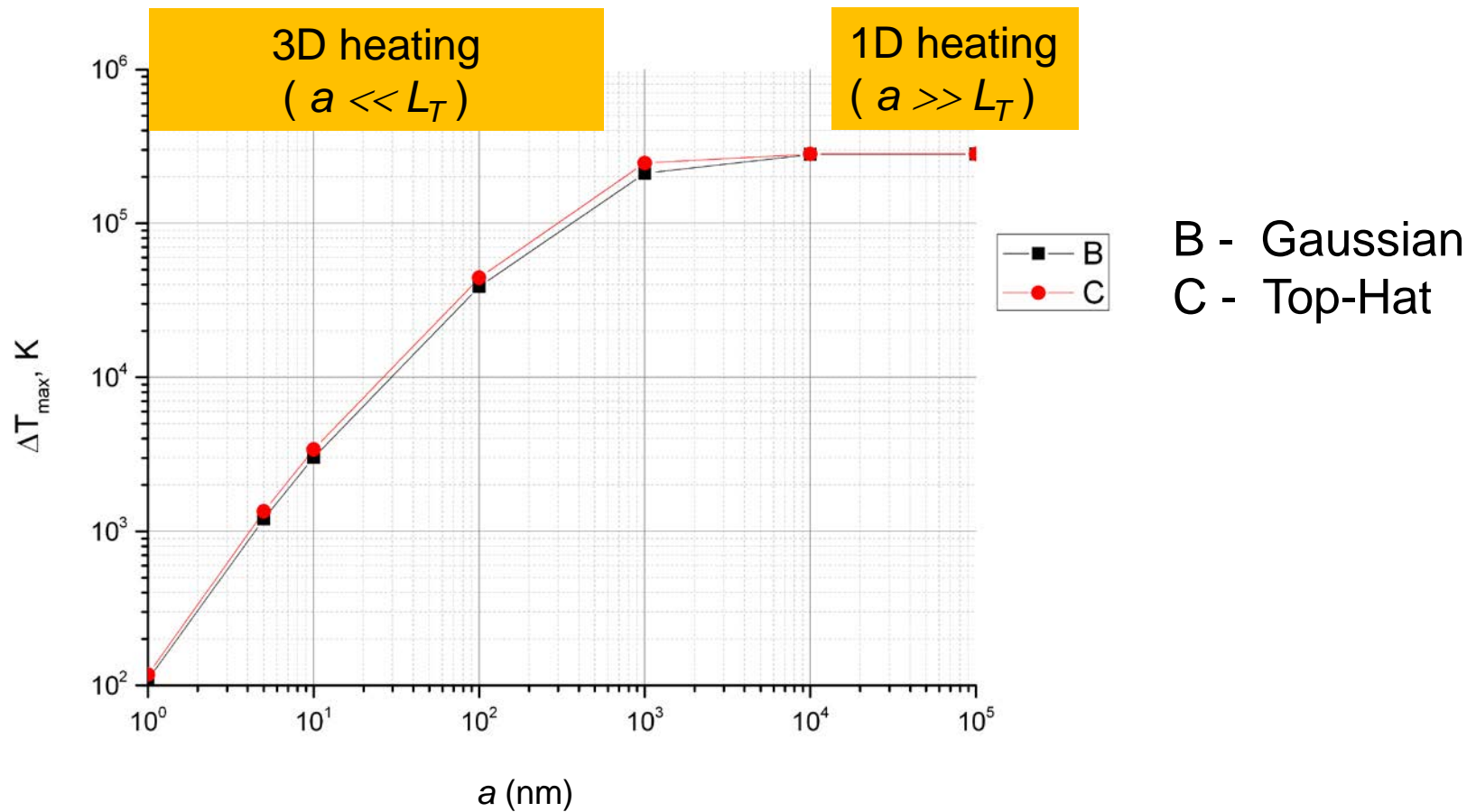
Laser: Gaussian $F(r)=F_o \exp -(r^2/a^2)$, $P(t) = P \sin^2 (\pi t/2 \tau)$ - pulse of $\tau = 4 \text{ ns}$, $\lambda = 266 \text{ nm}$, $F = 100 \text{ J/cm}^2$;



Heating temperature $\Delta T_{max} = f(a)$ for given $F = 100 \text{ J/cm}^2$, Si -bulk

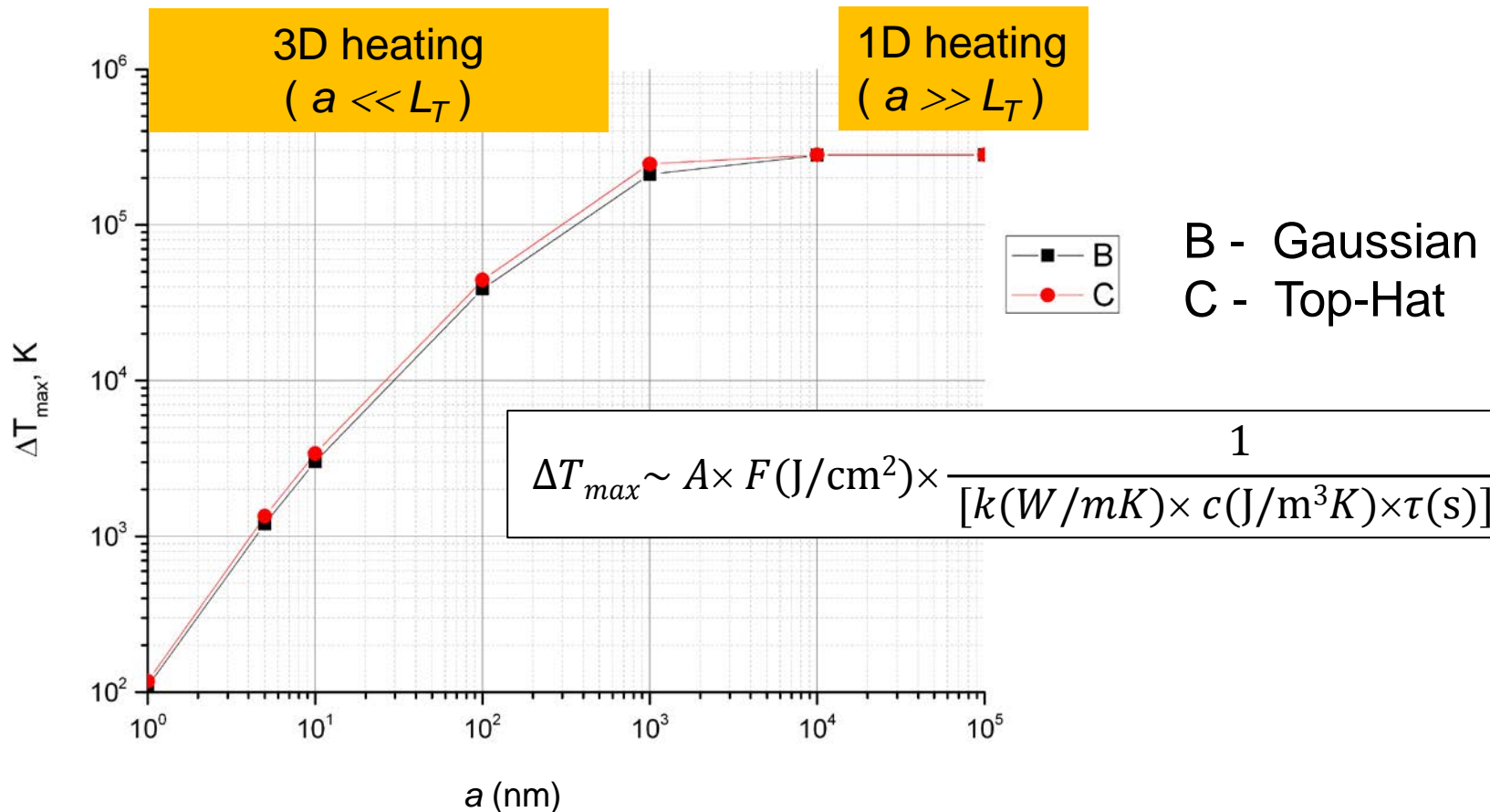
$$\text{Heating length: } L_T = [4 \times D(\text{m}^2/\text{s}) \times \tau(\text{s})]^{0.5}$$

Typical heating lengths: $L_T \sim 1 \mu\text{m}$



Analytical solutions in linear approximation

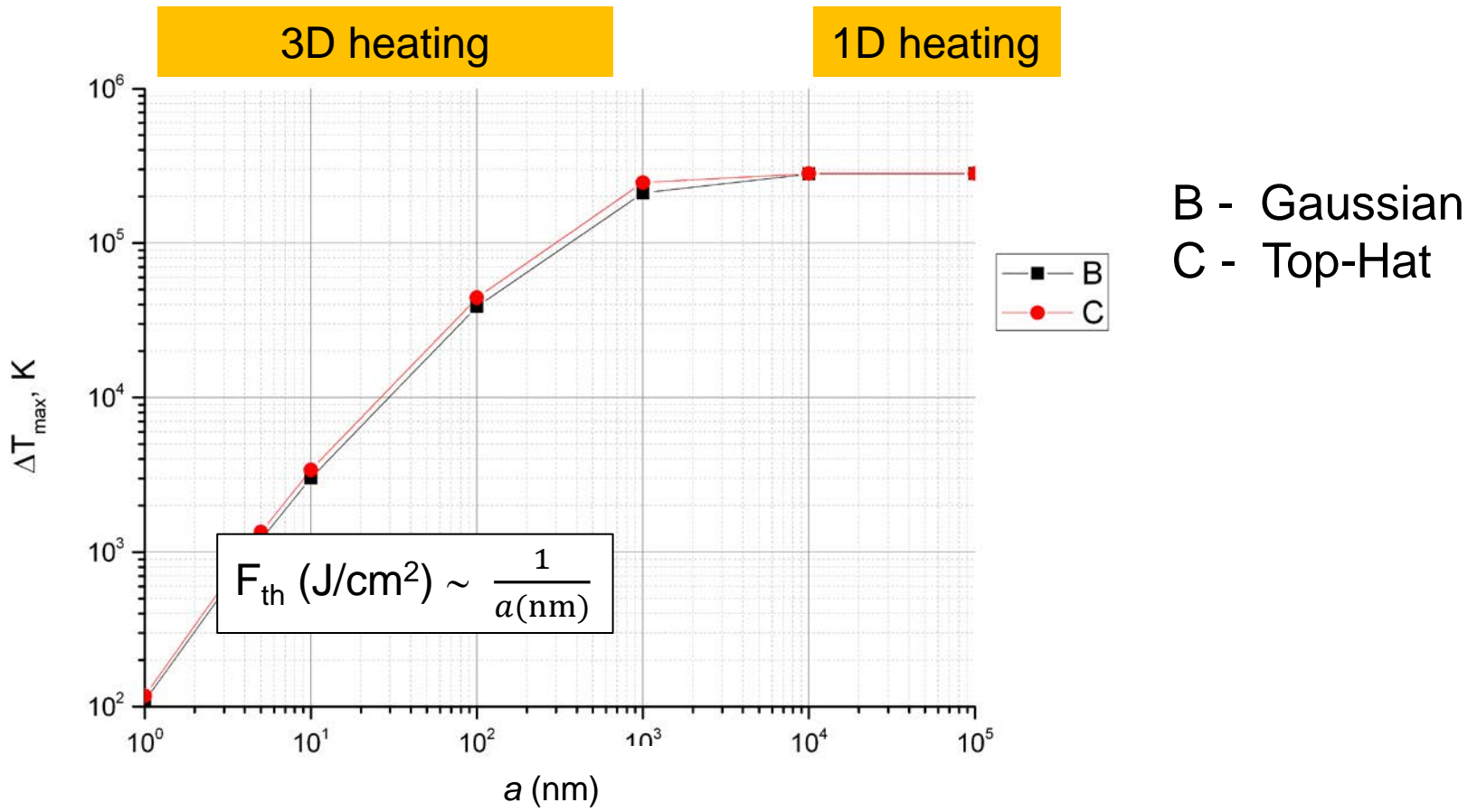
$$\Delta T_{max} \sim A \times F (\text{J/cm}^2) \times \frac{a (\text{nm})}{k (\text{W/mK}) \times \tau (\text{s})}$$



$$\Delta T_{max} \sim A \times F (\text{J/cm}^2) \times \frac{1}{[k (\text{W/mK}) \times c (\text{J/m}^3\text{K}) \times \tau (\text{s})]^{0.5}}$$

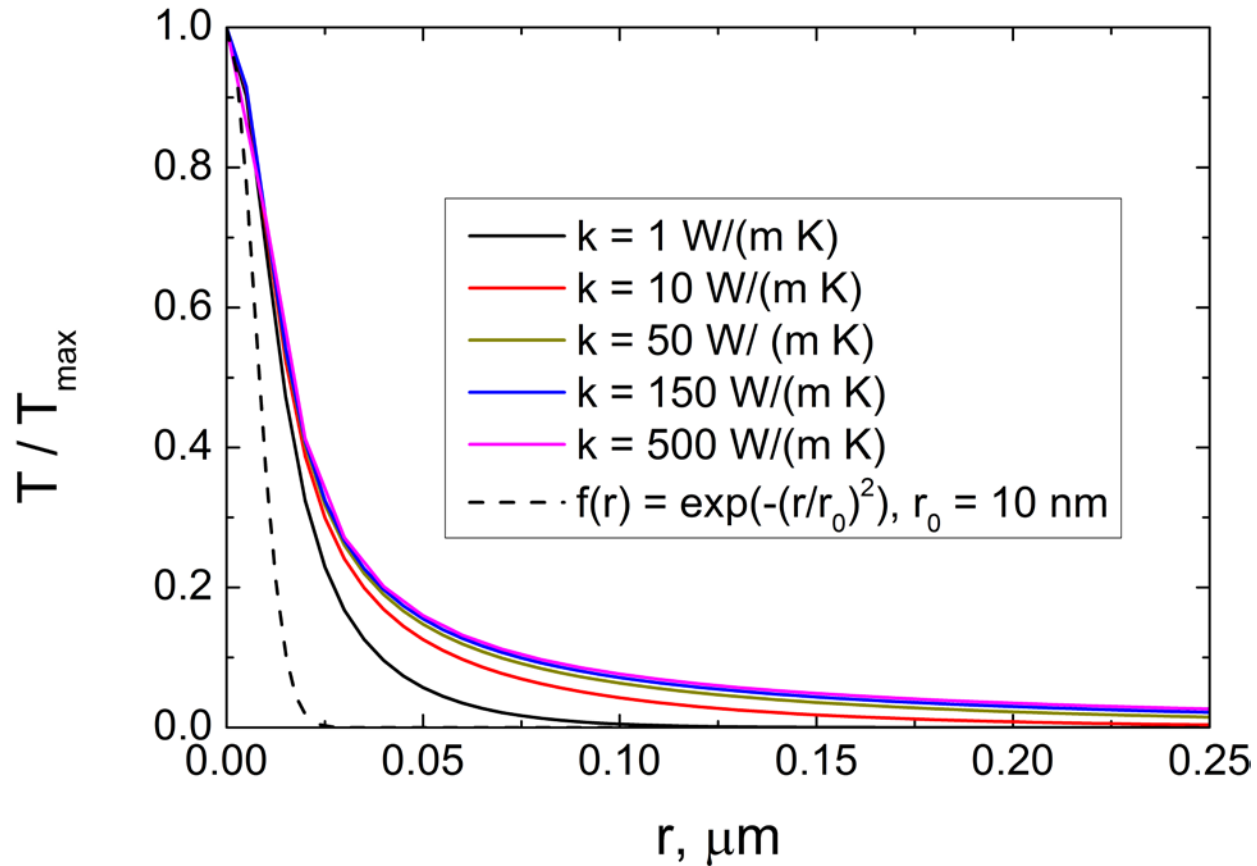
«Ablation» threshold F_{th} (J/cm²)

$$F_{th} \text{ (J/cm}^2\text{)} \neq f(a)$$



Normalized curves $T(r)$ for different k (W/m K) (thermo conductivity coefficient)

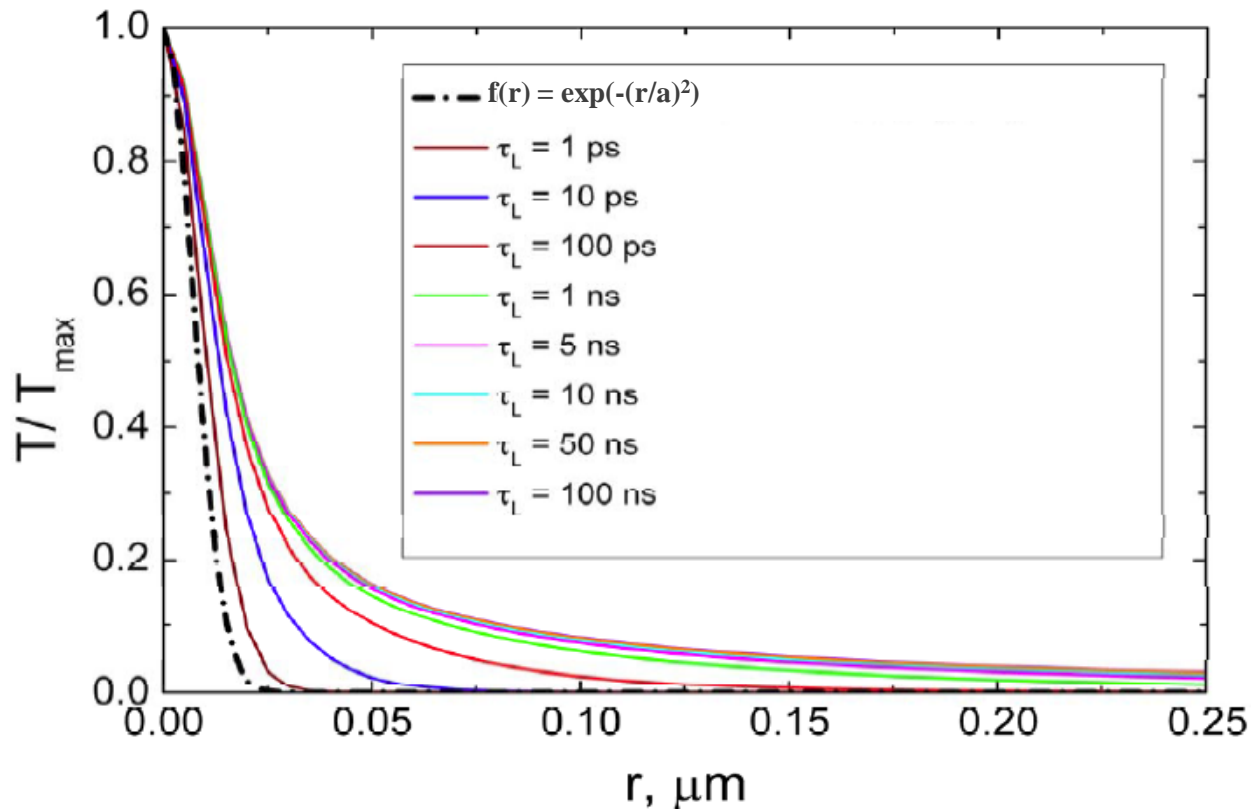
Si, $\lambda=266$ nm, $\alpha^{-1} = 5$ nm, $L_T = 100$ nm \div 2.0 μ m, $a = 10$ nm



$T = f(r)$ for $z = 0$ and $t = \tau_{\text{laser}} = 4$ ns

Normalized curves $T(r)$ for different laser pulse duration τ

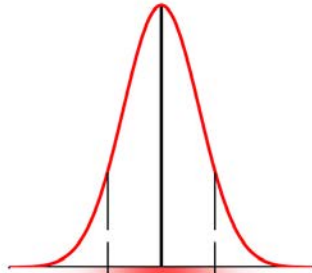
Si, $\lambda=266$ nm, $\alpha^{-1} = 5$ nm, $D_T = 0.8$ cm²/s, $L_T = 20$ nm \div 6.0 μ m, $a = 10$ nm



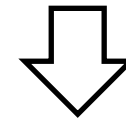
$T = f(r)$ for $z = 0$ and $t = \tau_{laser}$

Two-temperature equations for fs laser heating of metals

$$I(r) = I_0 \exp(-r^2/a^2)$$



$$c(T) \frac{\partial T}{\partial t} = \text{div}(k(T) \nabla T) + Q(t, r, z)$$



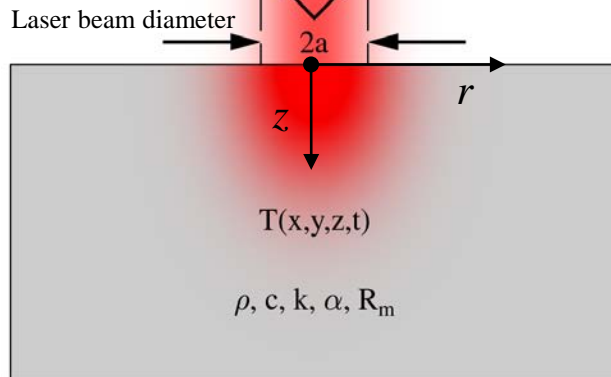
$$c_e \frac{\partial T_e}{\partial t} = \text{div}(k_e \nabla T_e) - \beta(T_e - T_i) + Q$$

$$c_i \frac{\partial T_i}{\partial t} = \text{div}(k_i \nabla T_i) + \beta(T_e - T_i)$$

$$Q(t, r, z) = I(t, r) A \alpha \exp(-\alpha z)$$

or

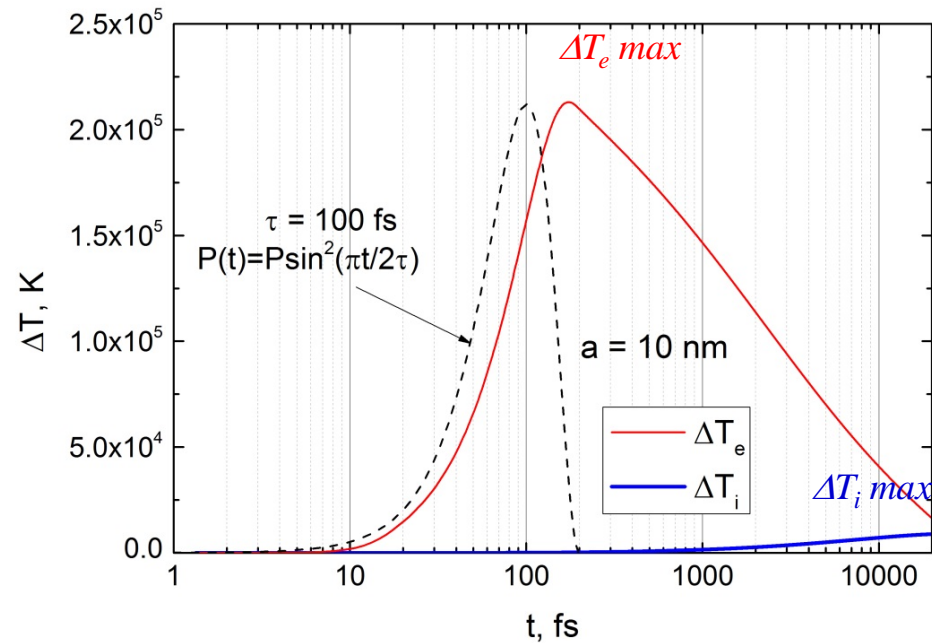
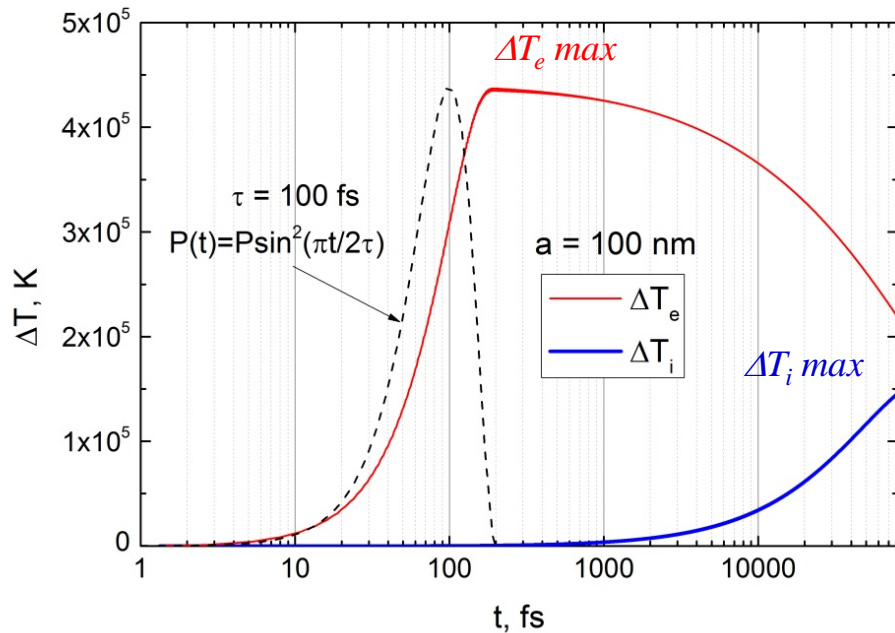
Q – from near-field calculation



Two-temperature “3D+t” heating model, Au

$$\Delta T_e(t, r = 0, z = 0) = f(t) \quad \text{and} \quad \Delta T_i(t, r = 0, z = 0) = f(t)$$

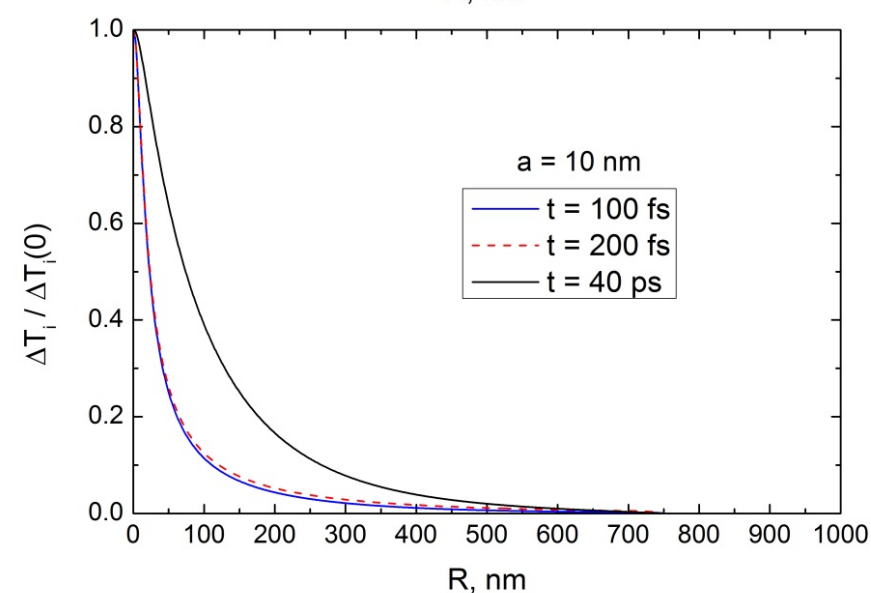
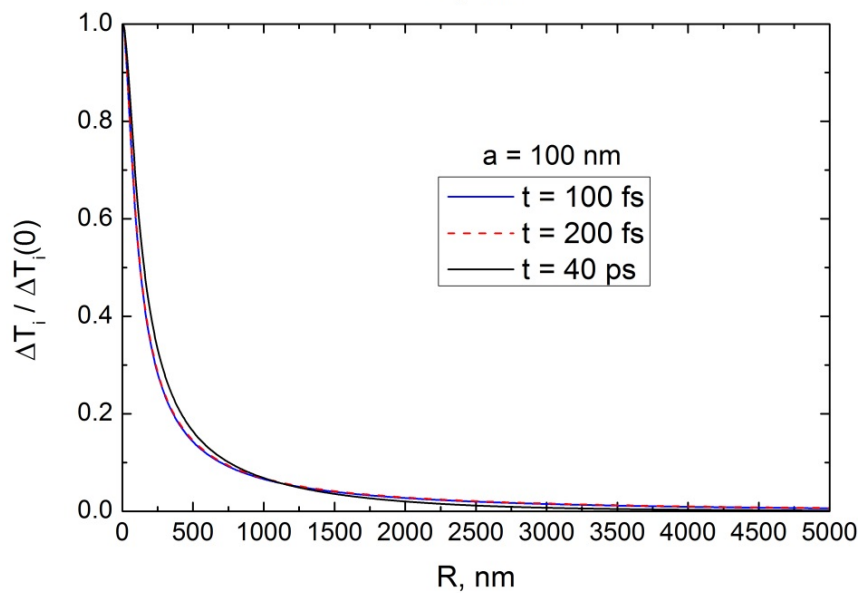
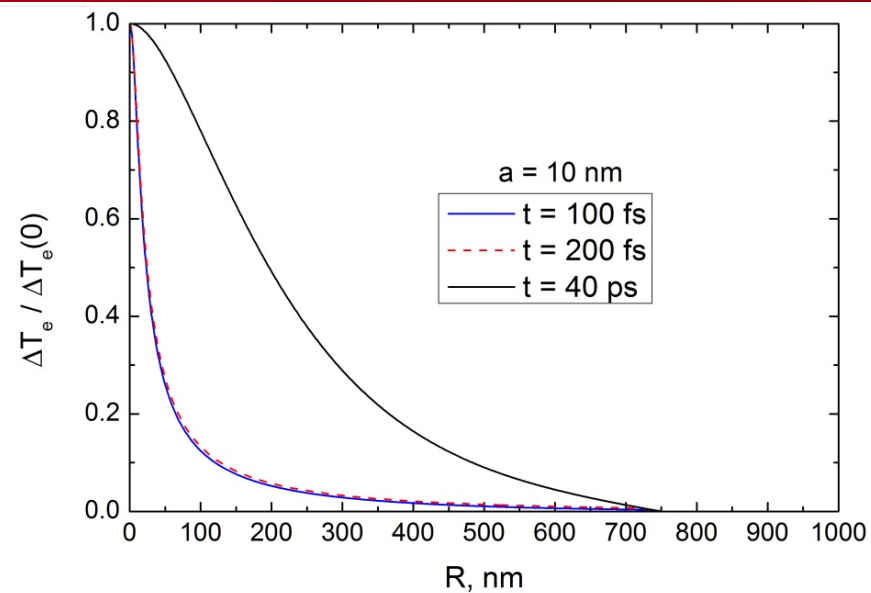
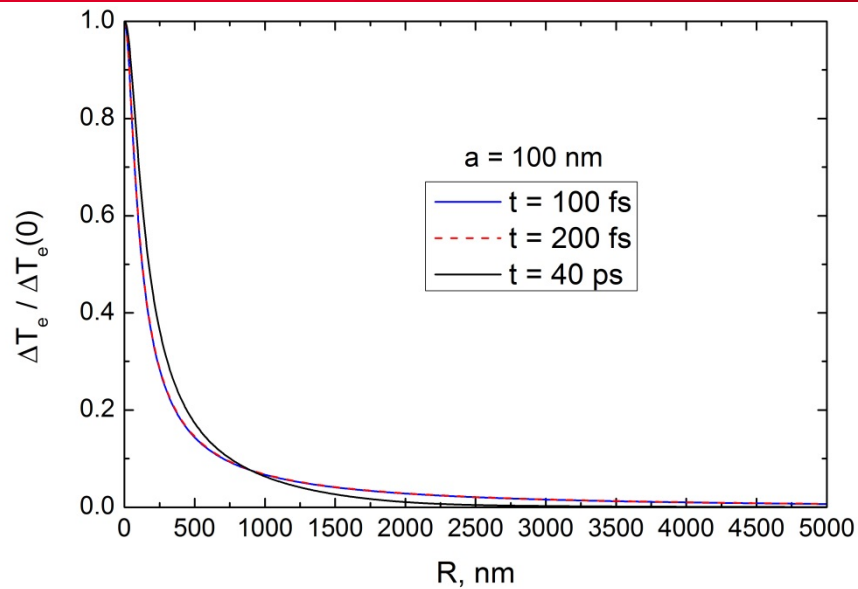
$$F = 100 \text{ mJ/cm}^2$$



$$\Delta T_i \text{ max } (t = \tau_{ei} \approx 100 \text{ ps}) \sim a \text{ (nm)}$$

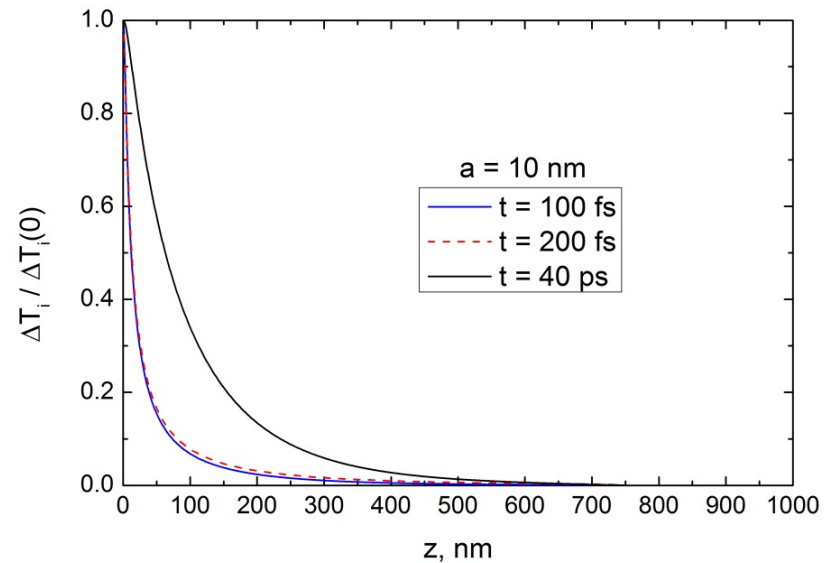
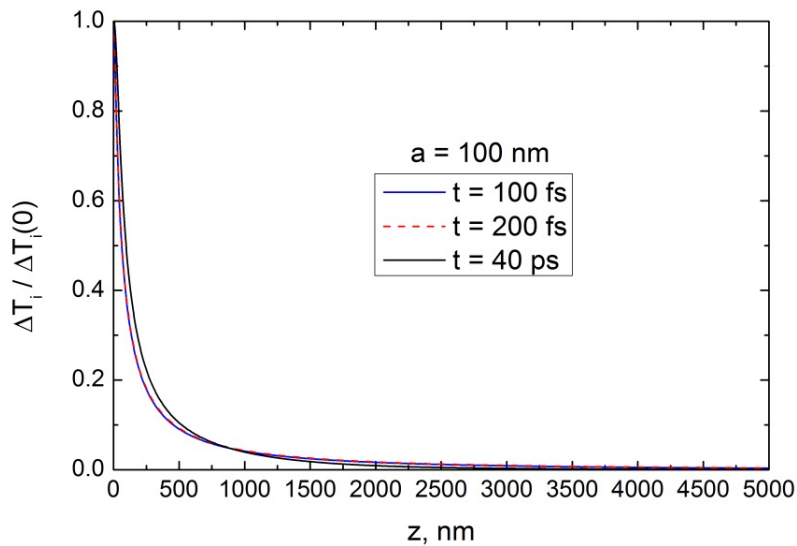
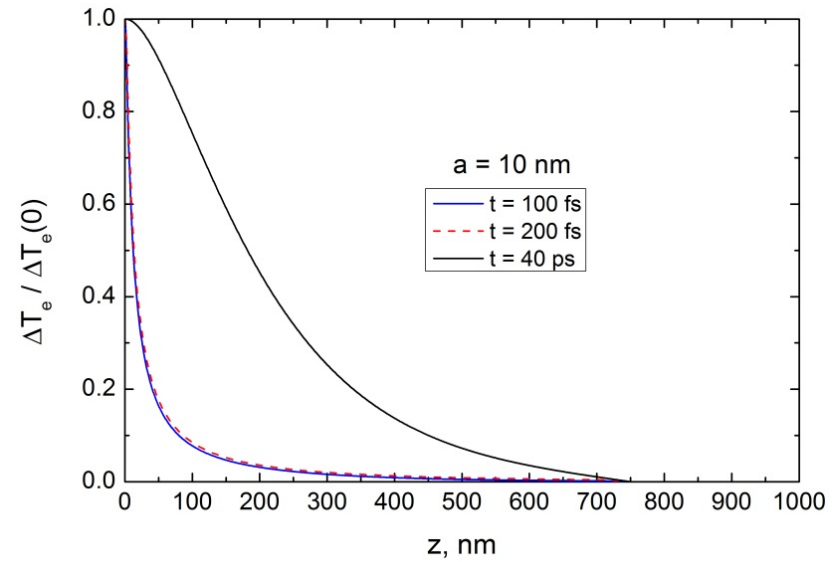
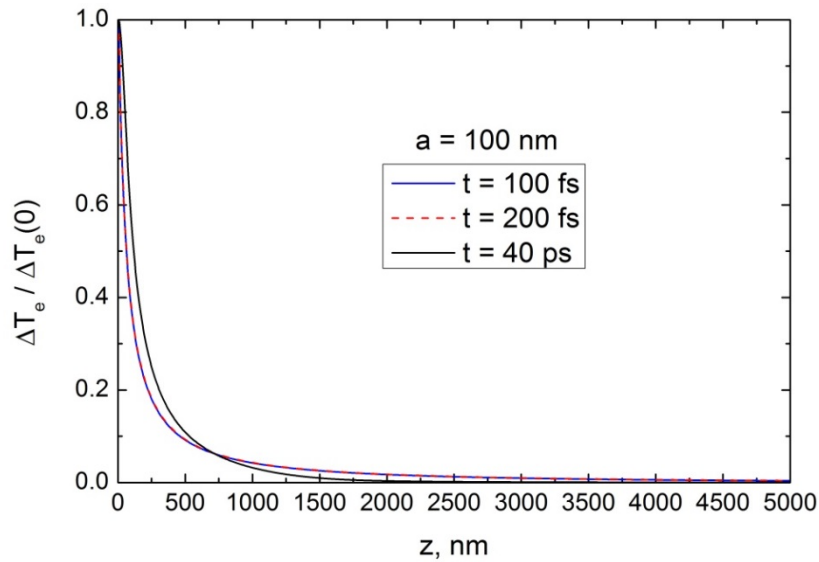
Two-temperature "3D+t" heating model, Au

$$\Delta T_{e \text{ or } i}(t = t_n, r, z = 0) = f(r)$$



Two-temperature "3D+t" heating model, Au

$$\Delta T_{e\text{ or }i}(t = t_n, r = 0, z) = f(z)$$



- 1) **Nanometric** laser ablation is possible with ns laser pulses when $L_T \gg a$;
- 2) “**Ablation threshold**” F_{th} depends on laser spot diameter a for $a < 1 \mu m$:
 $F_{th} \sim 1/a$;
- 3) **Low dependence** of $T(r, z)/T_{max}$ on k (W/m K) for 3D heating regime;
- 4) **Low dependence** of $T(r, z)/T_{max}$ on τ (s) for 3D heating regime;
- 5) T_{max} is for $t \approx \tau$ ei for fs heating of metals:

[****] A. Semerok, S.V. Fomichev, C. Jabbour, J.-L. Lacour, M. Tabarant, F. Chartier, **Multi-parametric modeling of solid sample heating by nanosecond laser pulses in application for nano-ablation**, Oral presentation on LIBS'2016 conference, Chamonix; France; was sent in Spectrochimica Acta Part B.

**Thank you
for your
attention**

ABSTRACT

In sample microanalysis by laser ablation (LA), spatial resolution is determined by laser beam diffraction limits (of the order of a laser wavelength) and thermal diffusion of a deposited heating energy during laser pulse (proportional to the square root of pulse duration and matter diffusivity). Being limited by these laser beam features and those of heating energy, spatial resolution (a crater diameter) of $\approx 1 \mu\text{m}$ was obtained with 4 ns laser pulses on 266 nm wavelength. To improve spatial resolution of microanalysis, the application of lasers with the pulses of shorter durations (ps and fs) may be advised. As another way to improve spatial resolution of microanalysis up to $\approx 100 \text{ nm}$, one may advise LA with a highly localized laser field created by a tip near-field enhancement. The experiments with ns laser pulses were made along with multi-parametric theoretical studies based on one-temperature heating model.

In this work, the theoretical studies were extended on ultra-short laser pulses (ps or fs) to analyze the effect of pulse duration and matter properties (absorption coefficient, thermal conductivity and capacity) on the resulting temperature field spatial distribution $T(t, x, y, z)$. A two-temperature model was applied for $T(t, x, y, z)$ calculations. The results of these simulations are compared to temperature distributions for ns laser pulses. Discussion on advantages of ultra-short pulses application for LA with a tip near-field enhancement for consecutive chemical analysis with nanometric resolution will be presented.