

## Modeling of AP-MALDI processes

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The Boundary Element Method (BEM) was applied to a situation where the same geometry was defining a scene for two potential theory problems: potential flow of fluid and electric field distribution around a system of electrodes. Cylindrical symmetry of the flow made the problem pseudo-two-dimensional. Boundaries of domains (electrodes and free space between them) are pseudo-one-dimensional in this case. Each boundary element (or panel) not only represents geometry but also carries a solution for boundary values of potential theory problems. In our particular case values of potentials (electric potential and flow potential) and their gradients normal to the boundary were assumed to be constant within each (out of  $N$ ) panel and were obtained through standard procedure of solving this problem within BEM<sup>1,2</sup>.

$$\phi(\vec{r}) = \int_{\Gamma} \left( G(\vec{r}, \vec{r}') \vec{\nabla} \phi(\vec{r}') - \phi(\vec{r}') \vec{\nabla} G(\vec{r}, \vec{r}') \right) d\vec{\Gamma} + \int_V G(\vec{r}, \vec{r}') \rho(\vec{r}') dV$$

$$G(\vec{r}, \vec{r}') = 1/(4\pi |\vec{r} - \vec{r}'|)$$

where  $V$  and  $\Gamma$  are domain and its boundary,  $\rho$  is fixed charge (source) density and  $\phi$  is potential.

With the known values of potential and its normal derivative on the boundary of domains in question the values of potentials and their gradients (representing electric field and fluid velocity in our case) for internal points of the domain can be easily obtained by direct quadratures with the use of the above relation<sup>1-3</sup>.

In classical AP-MALDI ions created by laser irradiation are extracted into an atmospheric pressure inlet of a mass spectrometer with the aid of a static electric field and the mass spectrometer's intake airflow<sup>4</sup>. In this AP-MALDI configuration, positioning of the laser beam directly on-axis with the aperture provides the best sensitivity.

Another approach would be a new dynamic focusing technique we call pulsed dynamic focusing or PDF. Pulsed dynamic focusing operates on the basis of switching an extraction field to zero, when ions are just outside of the MS entrance, to allow the intake gas flow of the MS to entrain and focus the ions into the MS. Results of modeling of this technique is shown in Fig.1:

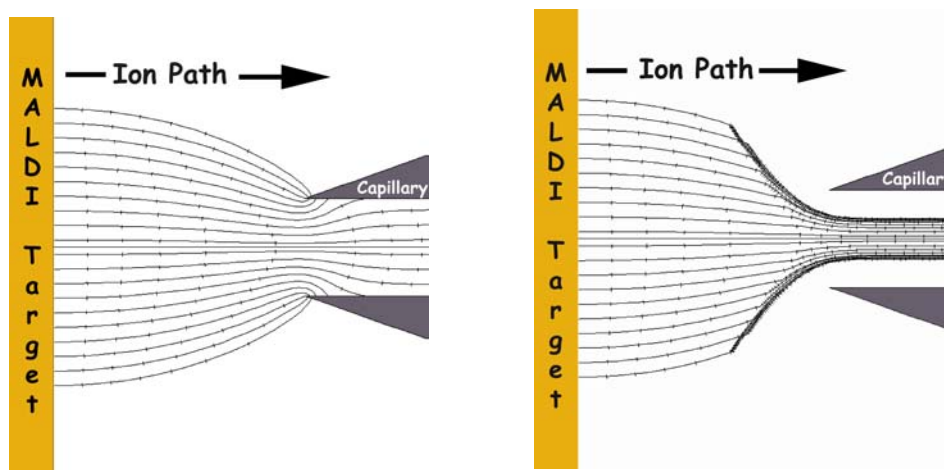


Figure 1: Modeling of a PDF technique (lines represent ion trajectories).

To explain the experimentally observed dependence of ion signal on voltage applied to MALDI target<sup>4</sup> we propose the following model of AP-MALDI process:

- The cloud of positive and negative ions is created near the surface after the laser pulse
- Positive and negative ions move in the opposite direction in the electrical field between target and capillary
- Recombination of positive and negative ions is taking place where these clouds overlap

The calculation results using this model of AP-MALDI process are shown in Fig.2:

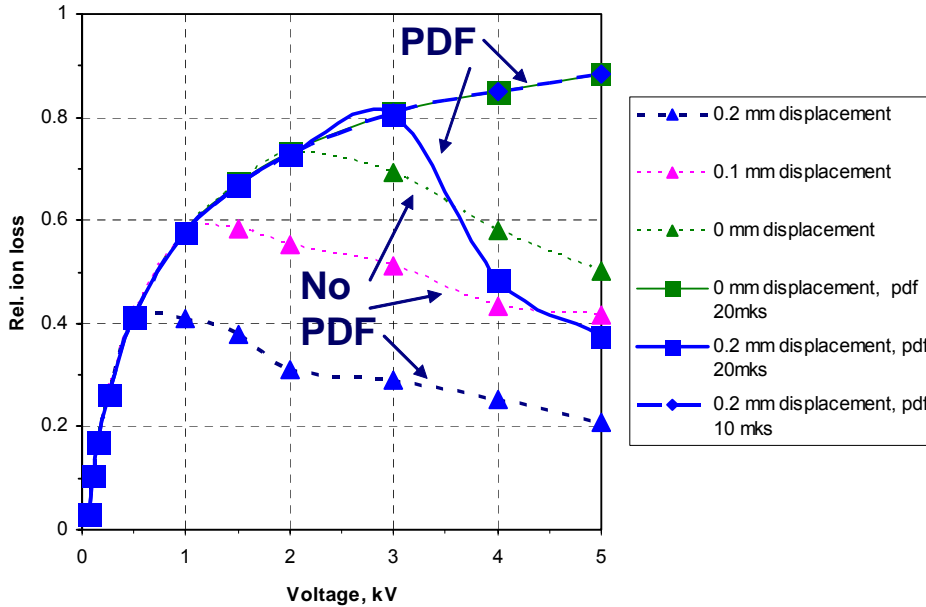


Fig.2 Ion transmission efficiency.

The thickness of original cloud of positive and negative ions was assumed to be 100  $\mu\text{m}$ . The initial concentration of ions was estimated on the base of the fact, that, if we apply the electric field with 3-4  $\mu\text{s}$  delay, the ion signal drops 3 times. Together with a value of recombination constant  $\sim 10\text{-}6 \text{ cm}^3/\text{c}$ , this gives an estimate of initial ion concentration  $3 \cdot 10^{11} \text{ cm}^{-3}$ . The capillary i.d. was 0.8 mm and the distance between capillary and MALDI target was 2.0 mm. The intake flow rate was measured to be  $\sim 0.5 \text{ L}/\text{mn}$ . Laser spot radius was 0.2 mm and ion mobility was assumed to be  $1 \text{ cm}^2/\text{V} \cdot \text{s}$ .

The results for laser spot positioned exactly on the capillary axis coincide well with experimental dependence<sup>4</sup>. The increase of the ion signal at lower voltages is due to a quicker pulling of ions, which reduces the probability of their recombination. The reduction of the signal at higher voltages is explained by increased heterogeneous loss on the capillary tip. When the laser spot is displaced from the central axis, this effect is more pronounced.

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3. Stakgold, I., Green's Functions and Boundary Value Problems; John Wiley & Sons, N. Y., 638 pp., 1979.
4. Laiko, V.V., Taranenko, N.I., Berkout, V.D., Lee, H.S., Doroshenko, V.M., *Int. J. Mass Spectrom.*, **221** (2002) 39-58.