Electronic supplementary information

Lateral resolution of desorption nanoelectrospray: nanospray tip without nebulizing gas as a source of primary charged droplets

L. Hartmanová,[a] I. Lorencová,[a] M. Volný,[b] P. Fryčák,[a] V. Havlíček,[a,c] H. Chmelíčková,[d] T. Ingr,[e] and K. Lemr*[a]

[a] Regional Centre of Advanced Technologies and Materials, Department of Analytical Chemistry, Faculty of Science, Palacký University in Olomouc, 17. listopadu 12, 771 46 Olomouc, Czech Republic. E-mail: Karel.Lemr@upol.cz; Tel: +420-585634415; Fax: +420-585634433

[b] Applied Physics Laboratory, University of Washington, 1013 NE 40th St, Seattle, WA, 98105, USA

[c] Institute of Microbiology AS CR, v.v.i., Videnska 1083, 142 20 Prague 4, Czech Republic

[d] Institute of Physics of the Academy of Sciences of the Czech Republic, Joint Laboratory of Optics of Palacký University and Institute of Physics AS CR, 17. listopadu 50a, 772 07 Olomouc, Czech Republic.

[e] Department of Experimental Physics, Faculty of Science, Palacký University in Olomouc, 17. listopadu 12, 771 46 Olomouc, Czech Republic.

Experimental

Desorption nanoelectrospray

A home-made ion source consisted of a metal-coated fused silica nanoelectrospray tip (PicoTip emitter, I.D. = 2±1 µm; New Objective, Woburn, MA, USA) in a holder allowing us for positioning of the tip in the x-y-z axes. The typical geometry was as follows: vertical distance between the nanoelectrospray tip and a sample plate: 2 mm; horizontal distance between the tip and the centre of a sample spot: 2 mm; impact angle: 45°; vertical distance between the sample plate and the heated capillary: 1 mm; horizontal distance between the centre of the sample spot and the heated capillary: 3 mm; collection angle: 18°. A motorized stage allowed automatic sample positioning in x-y plane, manual sample movement was possible in x-y-z directions. Two stepper motors were driven by a commercially available control card SMC 800 supplied with software (EMIS GmbH, Weiden, Germany). Two leadscrews (M6, 1 mm thread pitch) translated the rotation into a linear motion. One rotation of the shaft of the motor was carried out in 400 steps, i.e. one step corresponded to 2.5 µm of linear displacement. Full range of sample motion was 20 x 20 mm.

In imaging experiments, scans were performed with the fixed position of the nanoelectrospray tip and continuous or step sample movement in the x-axis or the y-axis, respectively. The nanoelectrospray tip was loaded with a spray liquid: water : methanol : formic acid = 48 : 50 : 2, v/v/v, unless stated otherwise. Positive voltage was applied to generate the spray.

Preparation of Rhodamine B patterns

Etched microscope slide (Thermo Scientific laboratory slides, Gerhard Menzel, Braunschweig, Germany) was coated homogenously with Rhodamine B (Figure 1S) using Spin coater SPIN150-v3 (APT GmbH, Bienenbüttel, Germany). Slides were washed in acetone (ultrasonic bath, 46 kHz, 1 min), rinsed by water and finally washed in ethanol (ultrasonic bath, 46 kHz, 2 min). To eliminate ethanol, slides were dried using a stream of nitrogen, heated on a heating plate to 80 °C, and then put into the spin coater and fixed by vacuum. After 1 min of cooling, 1 ml of saturated solution of Rhodamine B in ethanol was applied. Deposition was performed for 30 s at 3 000 rpm (acceleration 1 500 rpm/s). Residues of ethanol were removed by heating to 80 °C. Underneath contamination of slides by the dye was carefully removed using cotton wetted by ethanol.

Fig. 1S Homogenous layer of Rhodamine B prepared by spincoating.

To create defined patterns of Rhodamine B, the dye was removed from the glass surface by pulsed Nd:YAG laser 1064 nm (Lasag, Thun, Switzerland) with theoretical average diameter of a laser beam 200 μm. Examples of prepared patterns are shown in Figure 2S.

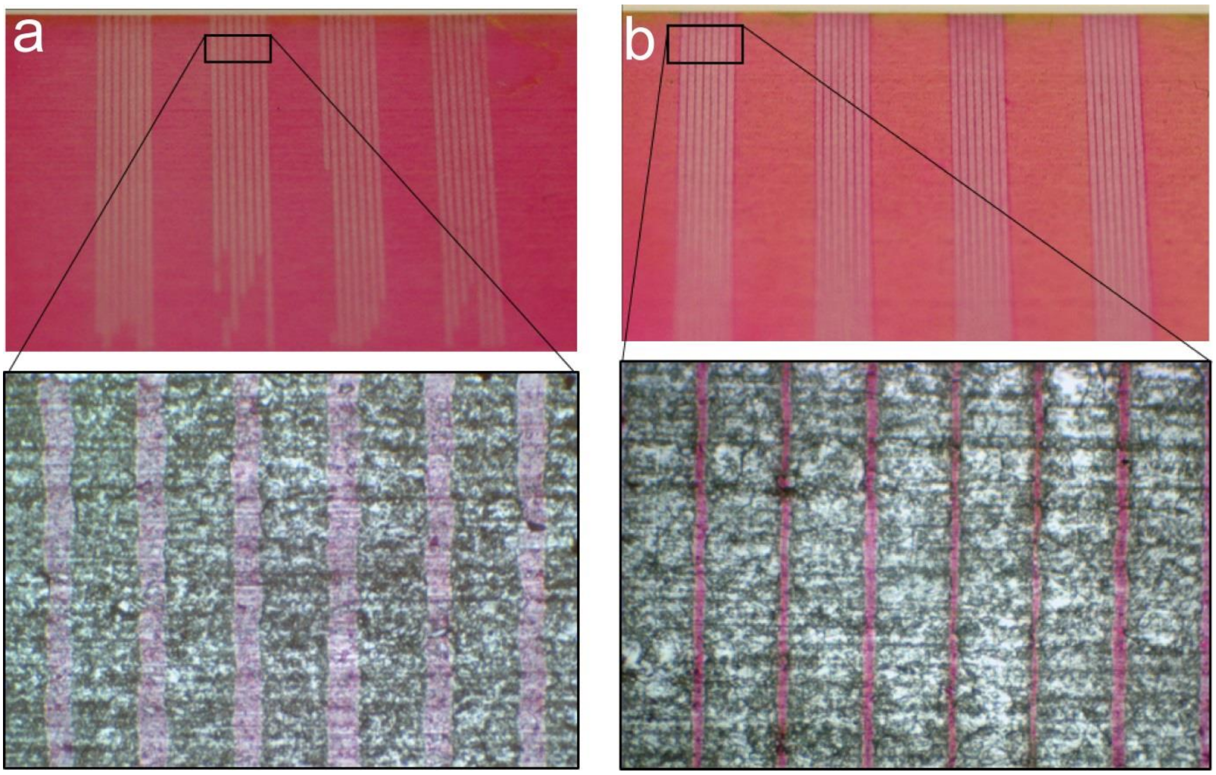

Fig. 2S Patterns of Rhodamine B. Lines of the dye, a) 60 μm; b) 23 μm, alternate with spaces 190 μm wide.

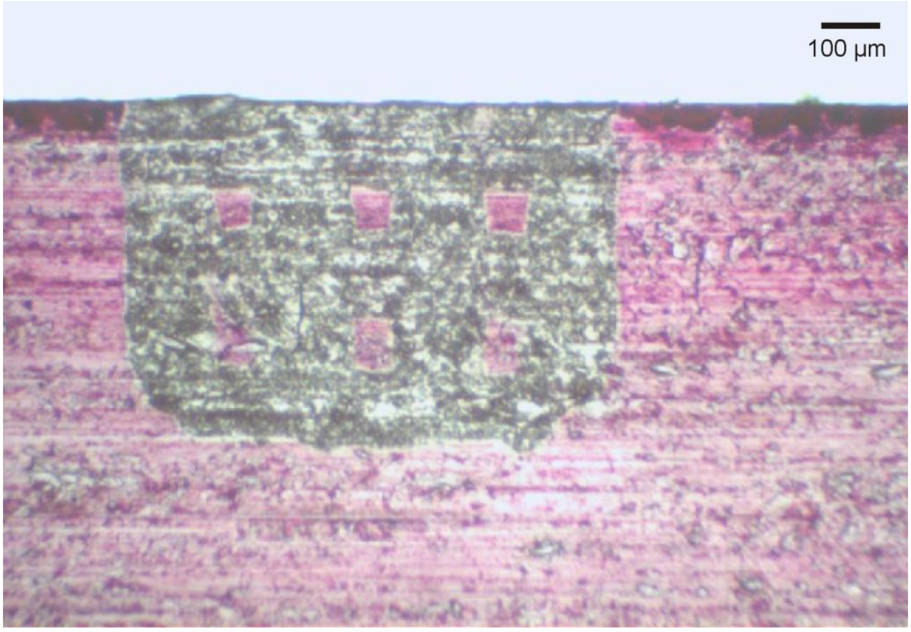

Fig. 3S Squares of Rhodamine B (nominally 60 μm x 60 μm). Colour intensity and shape irregularities were caused by more extensive laser heating during the pattern preparation.

Mass spectrometers

A heated capillary of an LCQ Deca inlet provided sufficient ion transmission. The commercially available Q-TOF Premier was stripped of the standard Z-spray ion source and the Waters stainless steel ion block was replaced by a compatible custom-made aluminium block that mounts axially on the instrument using the original flanging. Similar modification for axial inlet was previously described for efficient droplet sampling on Waters ESI-TOF instrument.[1] Based on the Waters ion block, the new aluminium block was machined as a short cylinder (diameter = 78 mm; height = 26 mm) and mounted using the two original bolts and a viton o-ring on the insulating spacer (part of the preceding assembly). A stainless steel capillary (0.5 mm i.d., length 55 mm) passed through the centre of the aluminium block and was fitted using Swagelok connectors and ferrules. The inlet capillary was heated resistively by a 100 W high density heater cartridge (Omega Engineering) that was inserted into a heater block mounted on the first 10 mm of the inlet capillary. External heating power supply and thermocouple feedback was used to control the temperature (Regbox heater driver, Jakar electronics, Karviná, Czech Republic).

Both used mass spectrometers were tuned to get suitable signal of Rhodamin B. The following settings were used. LCQ Deca ion trap (Thermo Scientific, San Jose, USA): spray voltage 3 kV; heated capillary temperature 200 °C; heated capilary voltage 15 V; tube lens 10 V. Q-TOF Premier (Waters, Manchester, UK): spray voltage 3 kV; heater block temperature 120 °C, heated capillary voltage 0 V (grounded); ion guide 2.5 V.

Results

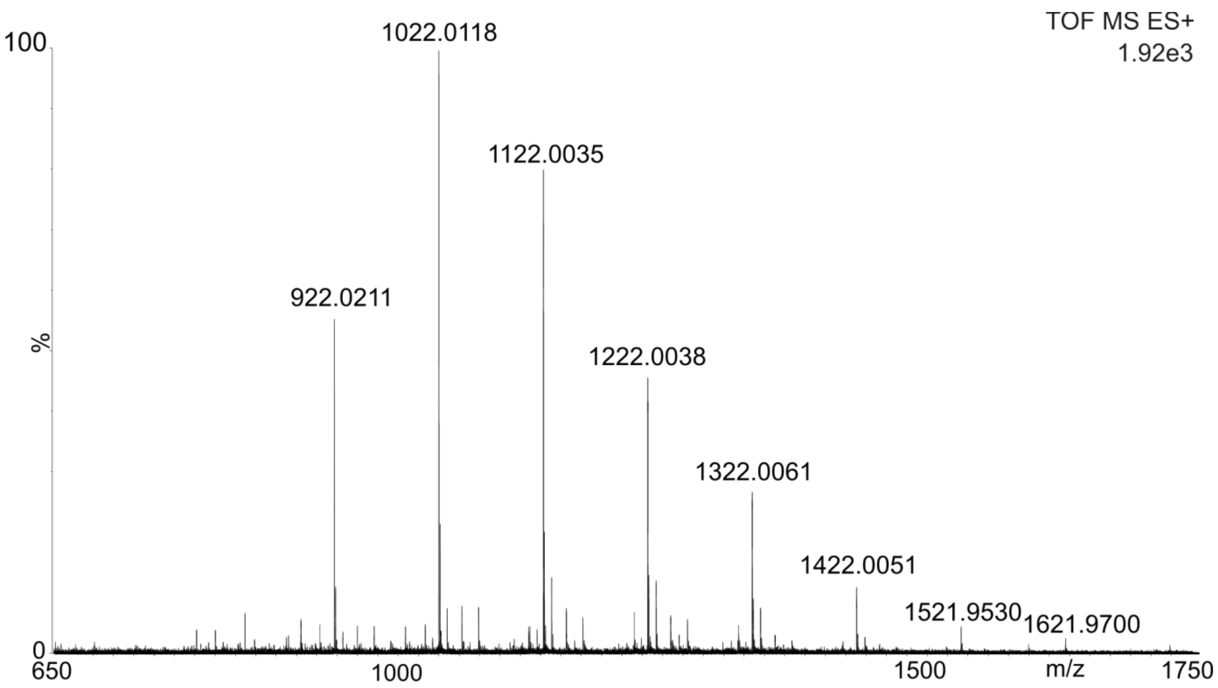

Fig. 4S NanoDESI-Q-TOF mass spectrum of Ultramark 1621 demonstrating ion transmission (spray liquid: water : acetonitrile = 1 : 1, 1% formic acid).

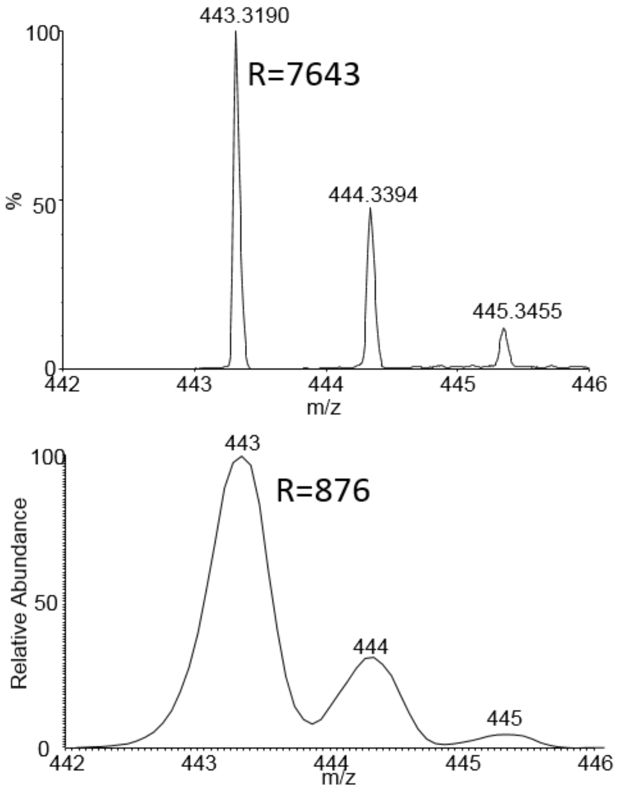

Fig. 5S Mass spectra of Rhodamine B: a) Q-TOF Premier with a custom-made inlet; b) LCQ Deca with commercial heated capillary inlet. R – resolving power.

Table 1S Determined widths for the pattern: line/space 60/190 μm

Imaging scan rate (μm/s)	Number of lines/spaces (nominal width in μm)	Mean (μm)	Standard Deviation (μm)	Confidence interval (μm) (95%)
10	6 (60)	66	4	63-70
5	6 (60)	60	4	56-64
2.5	6 (60)	62.7	1.7	60.9-64.4
10	6[a] (190)	182	4	178-185
5	7 (190)	190	4	186-194
2.5	7 (190)	188.1	2.6	185.8-190.5

[a] One significant outlier was excluded (Dixon´s Q-test, α = 0.05).

Table 2S Determined widths for the pattern: line/space 30/190 μm

Number of lines/spaces (nominal width in μm)	Determined values (μm)	Mean (μm)	Standard deviation (μm)	Confidence interval (μm) (95%)
6 (30)	43.8; 31.9; 34.2; 34.2; 36.7; 30.9	35.3	4.6	30.4-40.2
6 (190)	182.3; 189.3; 185.7; 186.2; 185.7; 184.7	185.7	2.3	183.3-188.0

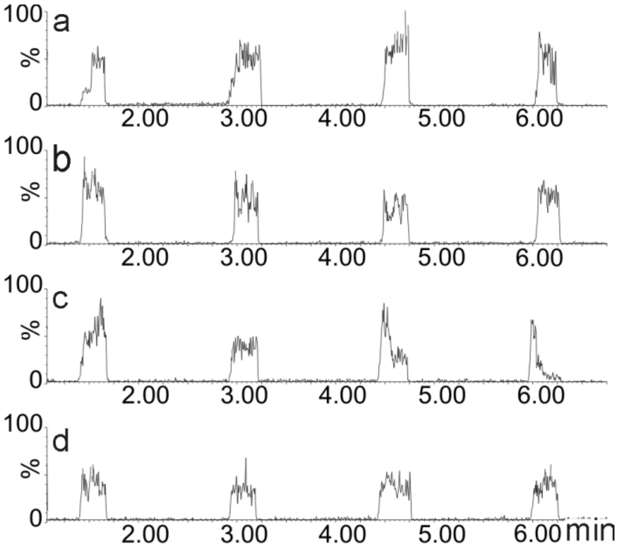

Fig. 6S Image of Rhodamine B lines. Profiles of ion signal at m/z 443.3 for the same dye lines at different positions of a microscope slide edge along the y-axis: a) 0 μm (the slide touching the heater block); b) 40 μm; c) 80 μm and d) 160 μm. The pattern: line/space 40/190 μm, imaging scan rate: 2.5 μm/s, Q-TOF scan rate: 4 Hz.

Reference

1. M. Volný, J. Rolfs, B. Hakimi, P. Fryčák, T. Schneider, D. Liu, G. Yen, D. T. Chiu and F. Tureček, *Anal. Chem.*, 2014, **86**, 3647-3652.