Airbrush deposition for improving homogeneity of laser desorption/ionization targets

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Objectives

- Laser desorption ionization in mass spectrometry requires deposition of the analyte onto a target plate
- Homogeneous distribution is optimal
- Smaller spot diameters are prefered

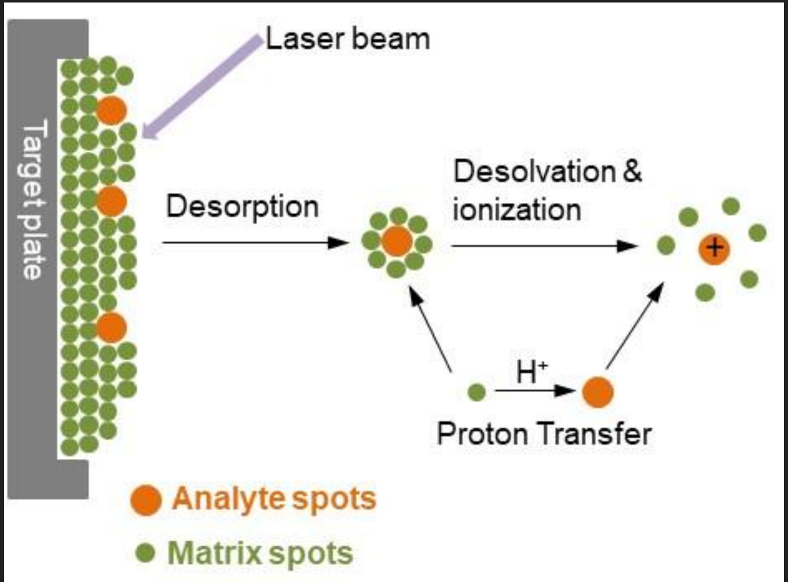

Figure 1: Graphic showing matrix crystals (usually CHCA or DHB) along with analyte molecules to be studied with MALDI[1]

[1]Editors at Creative Proteomics, “MALDI-TOF Mass Spectrometry,” Creative Proteomics. 2020. creative-proteomics.com/technology/maldi-tof-mass-spectrometry.htm

Dried droplet method limitations

- Dropper or micropipette is used to create a droplet on a sample plate, which then dries and deposits the solute.
- Usually leads to “coffee stain” effect, spatially inhomogeneous distribution
- Also difficult to get small spot diameters.

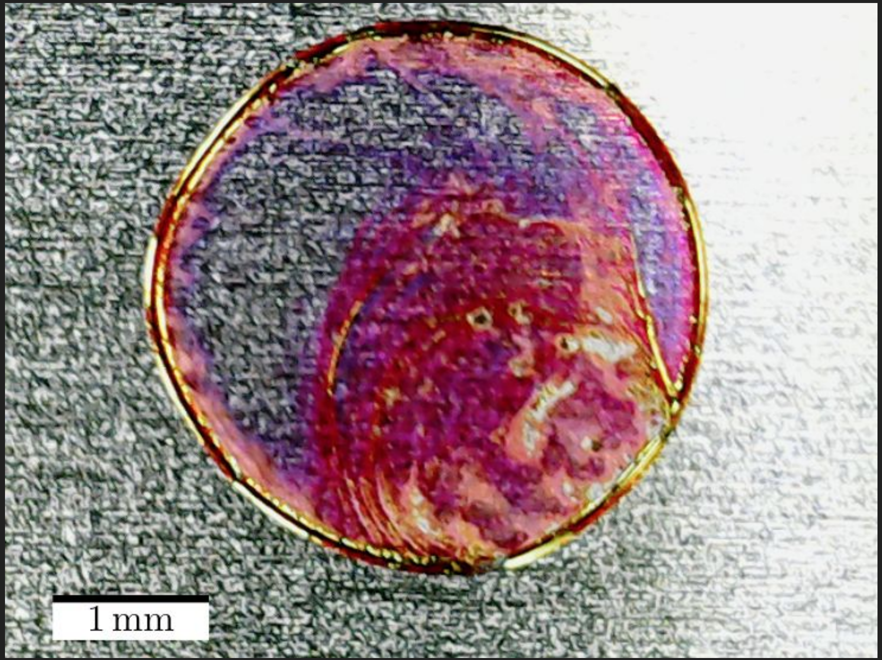

Figure 2: Deposition from a 0.5 microliter droplet with a rhodamine concentration of 0.49 mg/mL

Methodology & Testing

- Used rhodamine as a substitute for MALDI matrices
- Altered solute concentration, droplet volume, number of applications, target plate temperature and solvent type
- Repeated with an airbrush, used a stencil to control spot size.

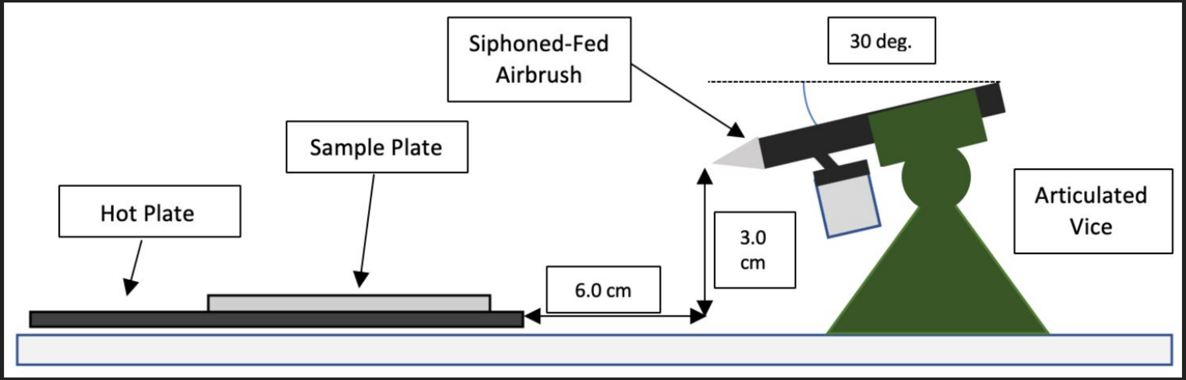

Figure 3: Example apparatus setup diagram for an airbrush test

Dried droplet data

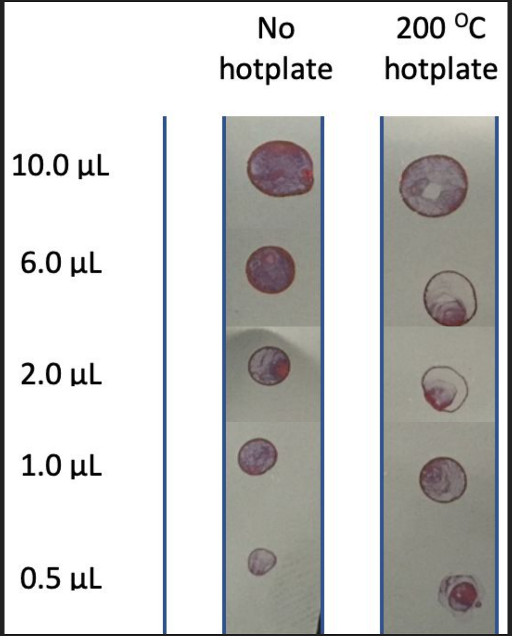

Figure 4: Volume test with water as a solvent, with and without a hot plate. Smaller droplets ‘coffee-stained’ more than larger ones.

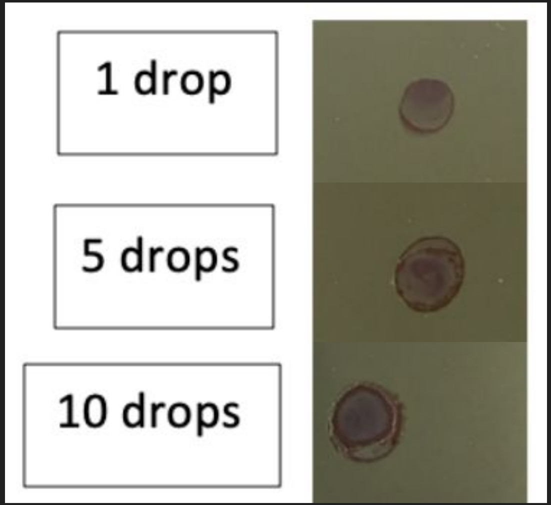

Figure 5: Reapplication test, where droplets were applied, allowed to dry, and then reapplied on top of the last. The coffee stain effect was still noticed.

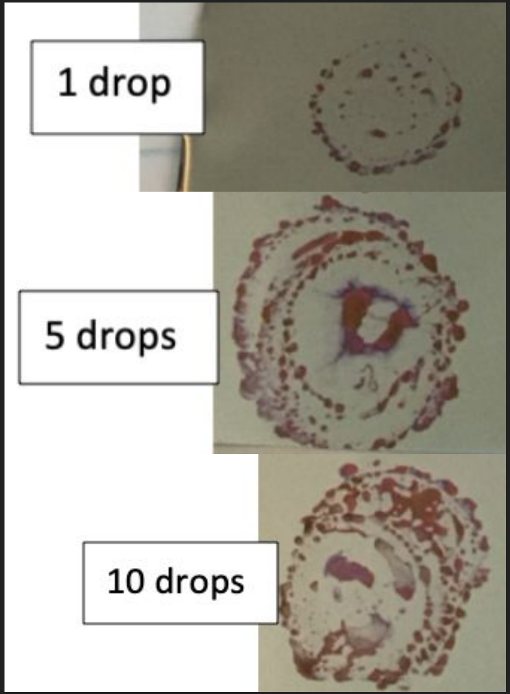

Figure 6: Reapplication test, with identical methodology as Figure 4, only with 70% isopropanol as solvent. Reapplication did not improve results.

Airbrushing helps prevent larger droplets from forming

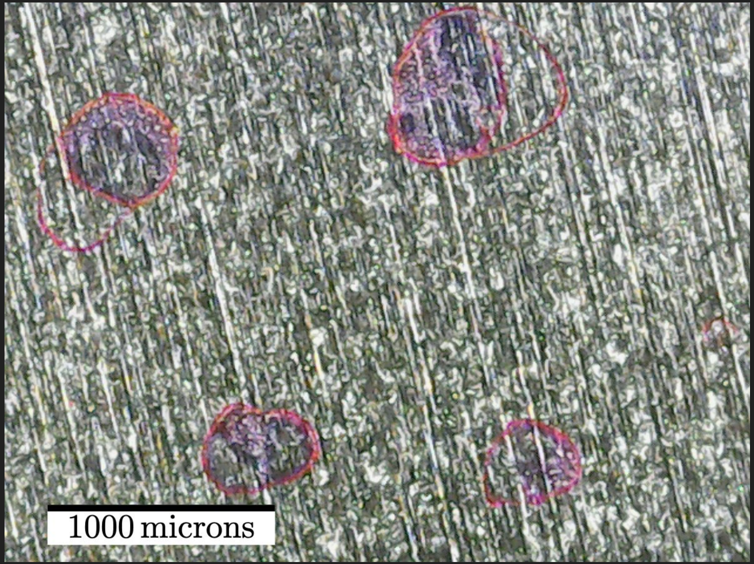

Figure 7: Example results from an airbrushing test with water as a solvent. The droplets were smaller than in dried droplet tests, and the coffee stain effect was present in them.

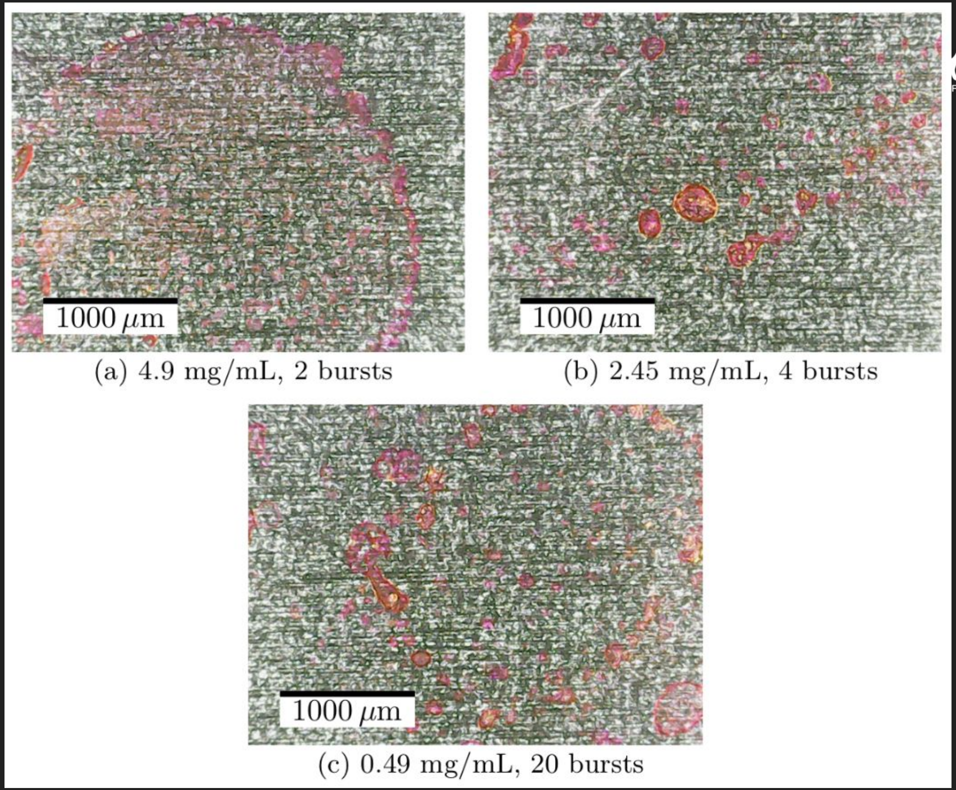

Figure 8: Example stencil test with 70% isopropanol that altered concentration while keeping the mass of applied rhodamine constant by increasing number of bursts at lower concentrations. There was a clearly defined spot, but within that spot the solvent coalesced into droplets before drying.

Higher target plate temperatures, with volatile solvent, improve homogeneity

- Heating the target plate made significant improvements in both spot size and homogeneity.
- At high temperature (~200℃), the definition drops. With smaller holes, no spot is visible.

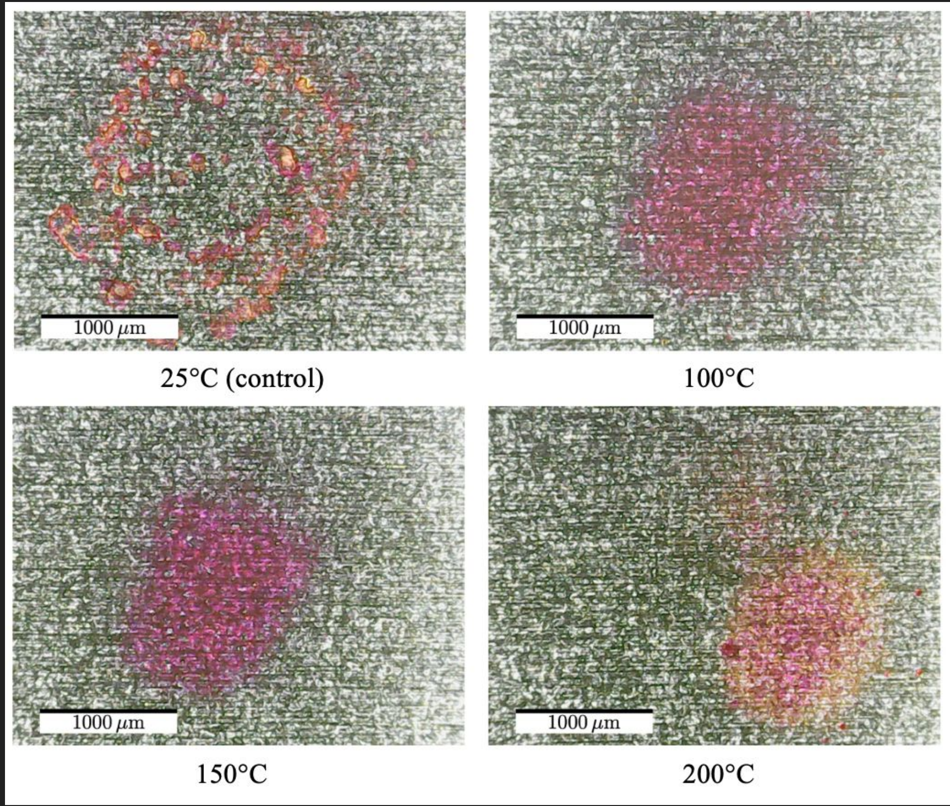

Figure 9: Spots of rhodamine using a 1.5 mm wide stencil hole. These spots are significantly smaller than in dried droplet tests (3 mm at minimum) and homogeneity is greatly improved.

Airbrushing produces a more homogenous distribution than the dried droplet method

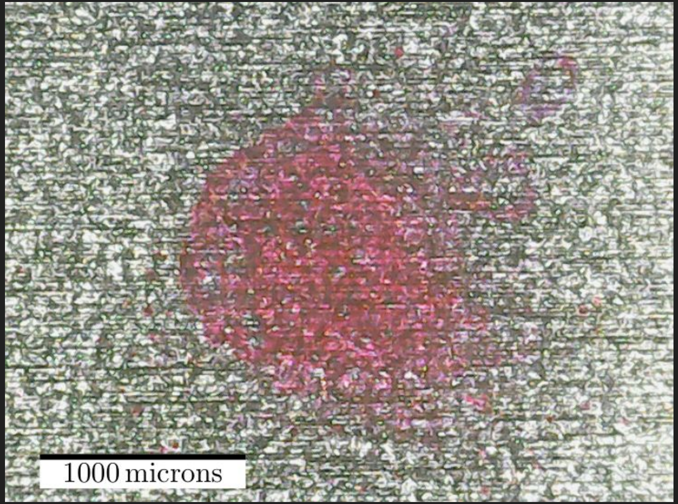

Figure 12: Direct comparison between dried droplet and airbrushing. On the left has 0.5 microliter volume and 0.049 mg/mL concentration. On the right is an airbrushing trial that applied 3 bursts of solvent with a concentration of 4.9 mg/mL from 4 cm above a 1.0 mm stencil onto a 100℃ hot plate. Both methods applied approximately 250 ng of rhodamine, yet the airbrushing method drastically improves both homogeneity and spot size.

Conclusions & benefits from airbrushing

- Airbrushing with a hot plate and stencil improved homogeneity and reduced spot size
- Harder to calculate the mass of analyte that reaches the target plate when using an airbrush
- Hot plates could also break down fragile analytes

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