

A study on matrix preparation towards MALDI-Imaging of synthetic polymer samples



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Introduction

MALDI-Imaging is an analytical method used to visualize the spatial distribution of various molecular species using MS as detector. While well established and frequently used in the life science field, there are few studies using MALDI-imaging in the synthetic chemical industry. The lack of basic know-how for MALDI matrix preparation remains a significant barrier to such applications. Here we test the use of manual airbrush and automated device to generate matrix deposition via spraying a matrix solution. Since the default methods provided by the manufacturer are intended for life science samples, preparation conditions optimized for synthetic polymer samples were explored and evaluated.

Methods

Thin films of polyethyleneglycol (PEG, selected as typical example of hydrophilic polymer, mixture of Mn 1000, 2000, and 3000) and polystyrene (PS, an example of hydrophobic polymer, mixture of Mn 3000 and 5000) were formed on ITO coated glass slides as model samples. DCTB as matrix was prepared on the sample glass slides using TM-Sprayer (HTX Imaging) and a commercial airbrush with varying spray conditions. Typical spray condition of TM-Sprayer is following unless there are other descriptions specific for each experiment, matrix: DCTB 5mg/ml, salt: TFANa

or TFAAg 0.5 mg/ml, solvent: 90 % acetone and 10 % water, Nozzle Temperature: 40 degrees Celsius, #passes: 8, flow rate: 0.13 ml/min, nozzle velocity: 1000 mm/min, track spacing: 2.5 mm, and nozzle height: 40 mm. MALDI-TOF MS (ultrafleXtreme with fleximaging 4.1, Bruker) under reflector positive mode was used for imaging measurements in which approximately 1000 spectra per spray condition were acquired. After the measurements, signal intensity information from all spectra were collected to calculate average intensity and standard deviation using SCLIS Lab 2019a/b.

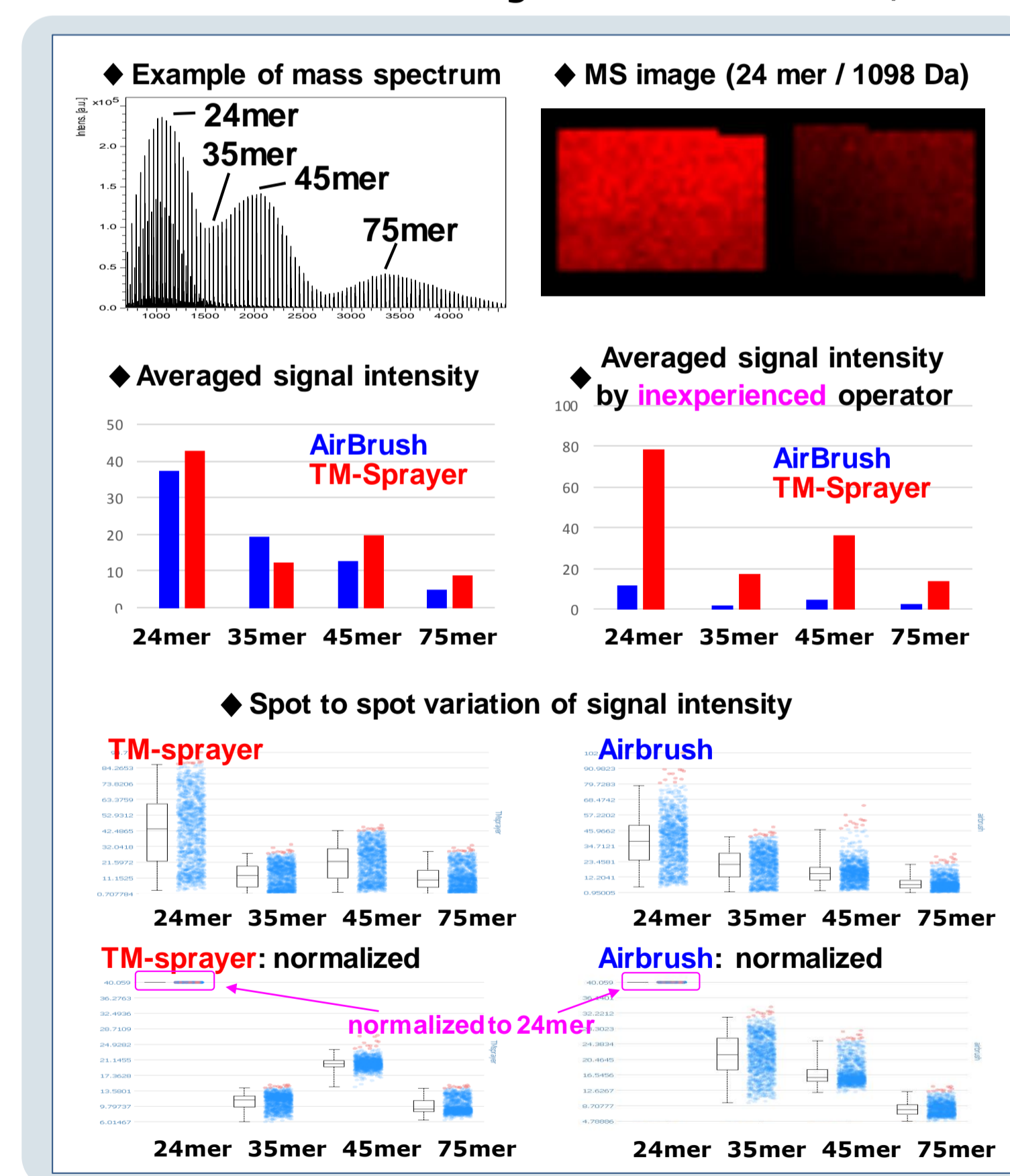


Fig. 1 Comparison between TM-Sprayer and airbrush (sample: PEG). Airbrush needs skilled operation. TM-Sprayer is better for matrix preparation with less variation.

Results

<TM-Sprayer vs. airbrush, Sample: PEG>

The result is shown in Fig.1. TM-Sprayer shows slightly higher average signal intensity, and apparently higher (about factor of 5) average signal intensity in case of inexperienced operator. This indicates that the quality of matrix spray using airbrush largely depends on the skill of its operator. And concerning to the spot to spot variation of signal intensity, TM-Sprayer shows its advantage with lower

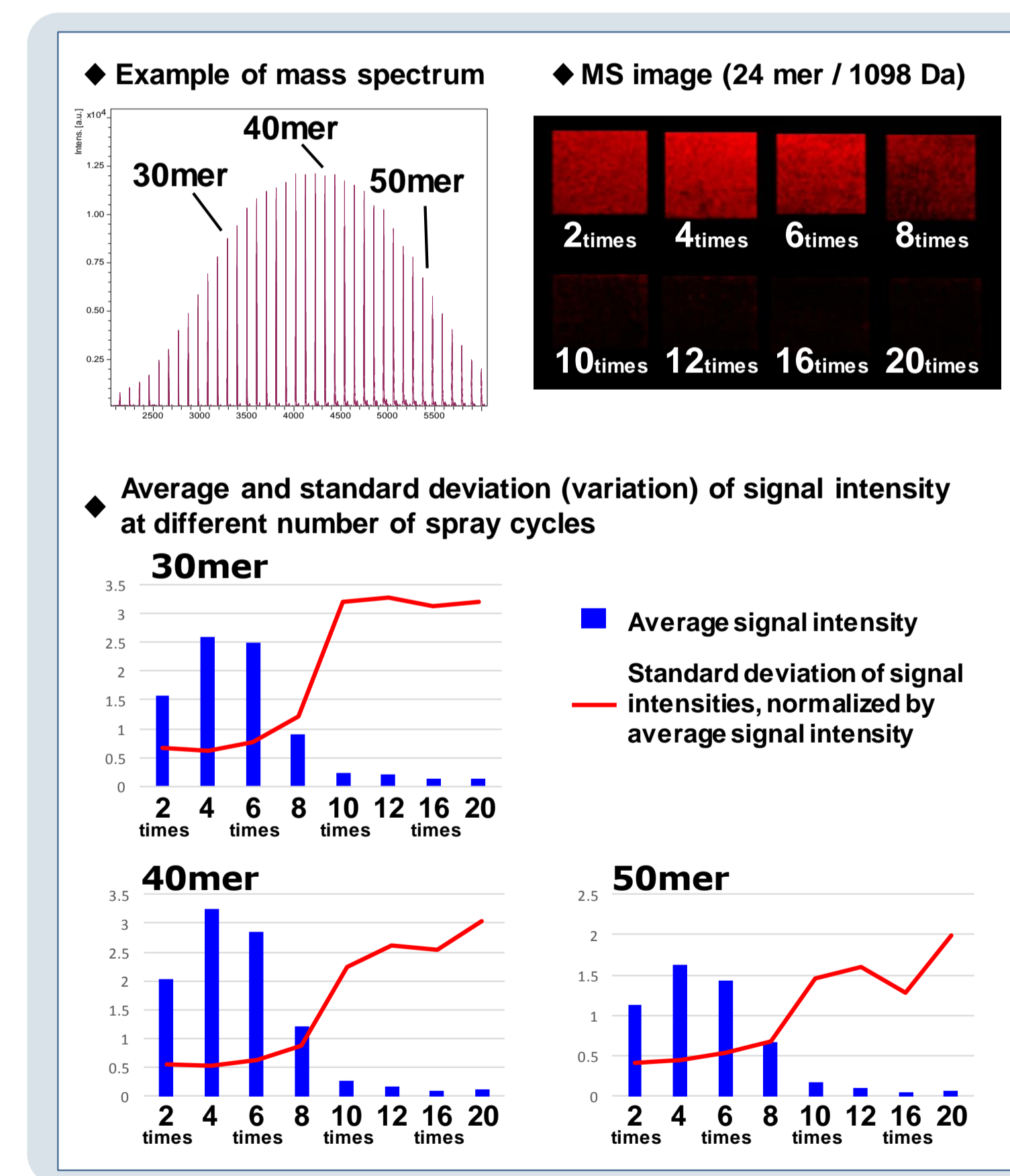


Fig. 2 Comparison on the amount of matrix sprayed by TM-Sprayer (sample: PS). Matrix amount with 4 times spray-overlapping was best for higher intensity and lower variation.

variation especially after normalization using the signal intensity of 24 mer.

<Optimization of the amount of matrix, PS>

Fig.2 shows the result from an experiment in which the amount of matrix sprayed was varied by changing the number of spray cycles overlaid. Average signal intensity was best at 4 spray cycles. Standard deviation (spot to spot variation) of signal intensity was also best at 4 spray cycles and got worse with iterating the matrix spray cycles.

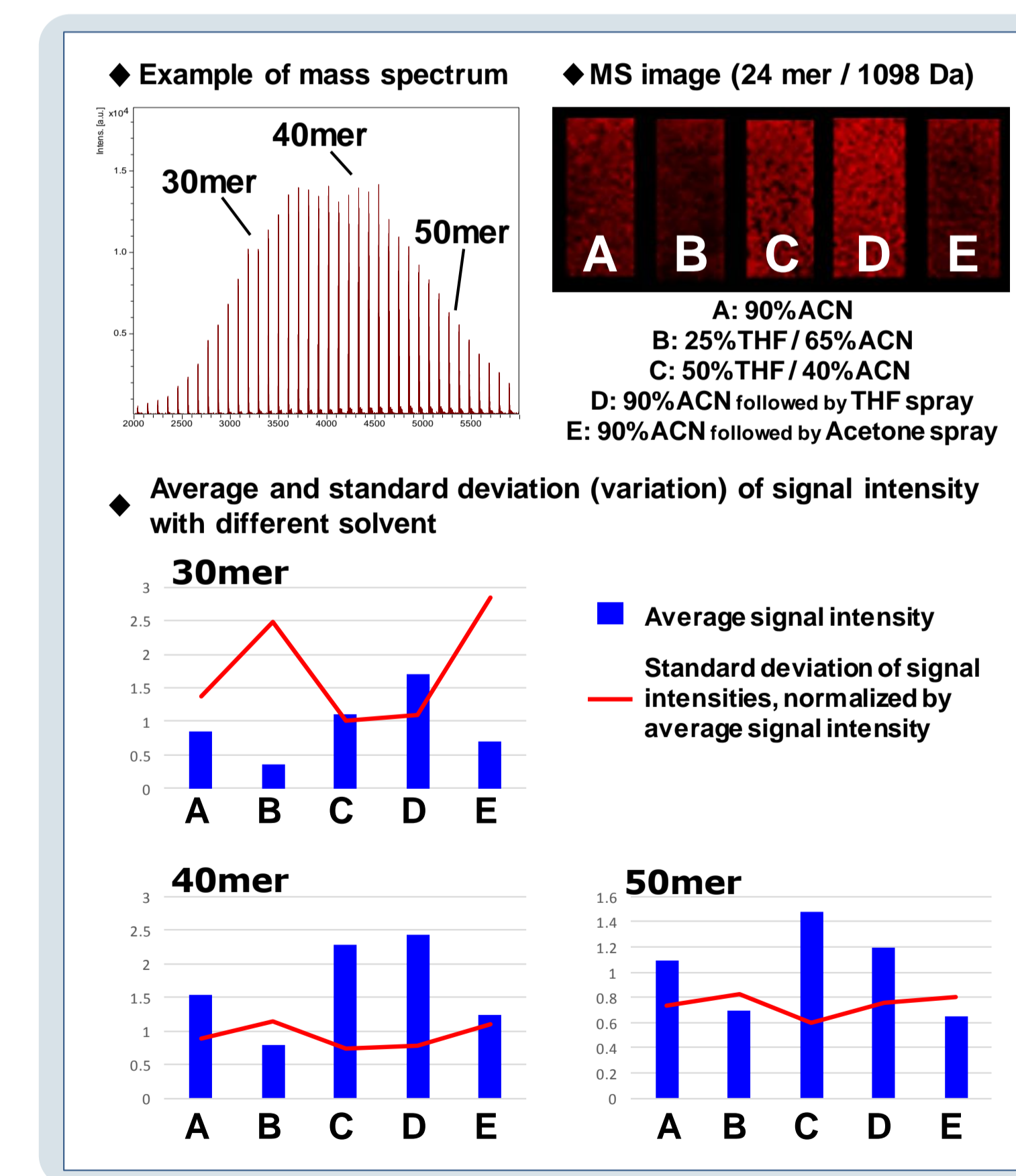


Fig. 3 comparison on the solvents of matrix solution sprayed with TM-Sprayer (sample: PS). Additional THF spray without matrix (D in the figure) is effective and nearly best.

<Optimization of spray solvent, PS>

Fig.3 shows the result from an experiment in which the solvent of matrix solution sprayed was varied. Five types of solvents tried are listed in the figure. The result shows that higher signal intensity was acquired with higher mixing ratio of tetrahydrofuran (THF). THF is a solvent which can easily dissolve the sample polymer (PS, in this experiment). Also, in addition to varying mixing ratio of solvent, additional spray of THF without matrix after matrix solution spray (D in Fig.3) was tried and found to be effective showing nearly best results both on average signal intensity and standard deviation of signal intensity. This additional solvent spray without matrix after matrix spray should be useful to utilize a variety of solvents, even in case that desirable solvents for samples and matrices are different each other.

Conclusions

- Airbrush needs skilled operator.
- TM-Sprayer has advantage for better matrix preparation with higher signal intensity and lower spot to spot variation of signal intensity.
- TM-Sprayer is compatible with synthetic polymer samples.
- There is an optimum amount of matrix.
- The solvent of matrix solution sprayed should be optimized according to the type of samples. And additional solvent spray after matrix spray is effective.

MALDI Imaging