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Effect Of Chemical Matrices On The Charged Ion Peaks Produced By NSI And SAWN MS

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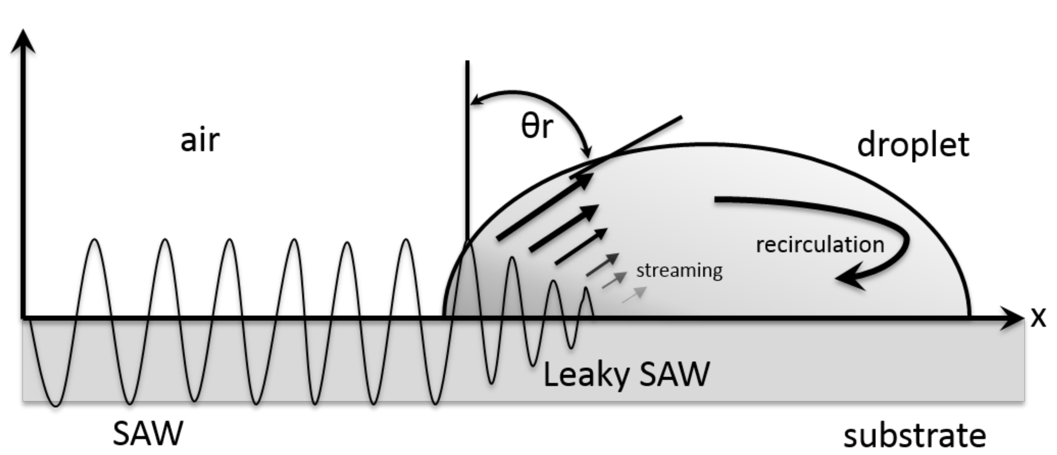
Introduction

Surface Acoustic Wave Nebulization (SAWN) is a new ionization technique that facilitates analysis of nonvolatile materials by MS (Heron Anal. Chem. 2010). Although shown to produce ions of lower energy than ESI (Huang JASMS 2012), mass spectral signal intensity is typically lower than ESI. In order to improve the sensitivity of SAWN-MS, we are exploring addition of chemical matrices such as m-nitrobenzonitrile (3-NBN). This matrix has been used to improve multiple charging in protein complexes in ESI. (Lomeli JASMS 2010). Here, we characterize the effect of 3-NBN on SAWN mass spectra compared to those of ESI MS.

We have also tried to characterize an alternative SAWN substrate, a novel black lithium niobate (LN) standing wave chip for charge state reduction. The black LN crystal is grown in a chemically reducing atmosphere and has been shown to have a high DC conductivity and a significantly reduced pyroelectric effect over white LN. The black LN will offer a reduced surface charge on heating and therefore will prevent surface warping and shattering.

Surface Acoustic Wave Nebulization



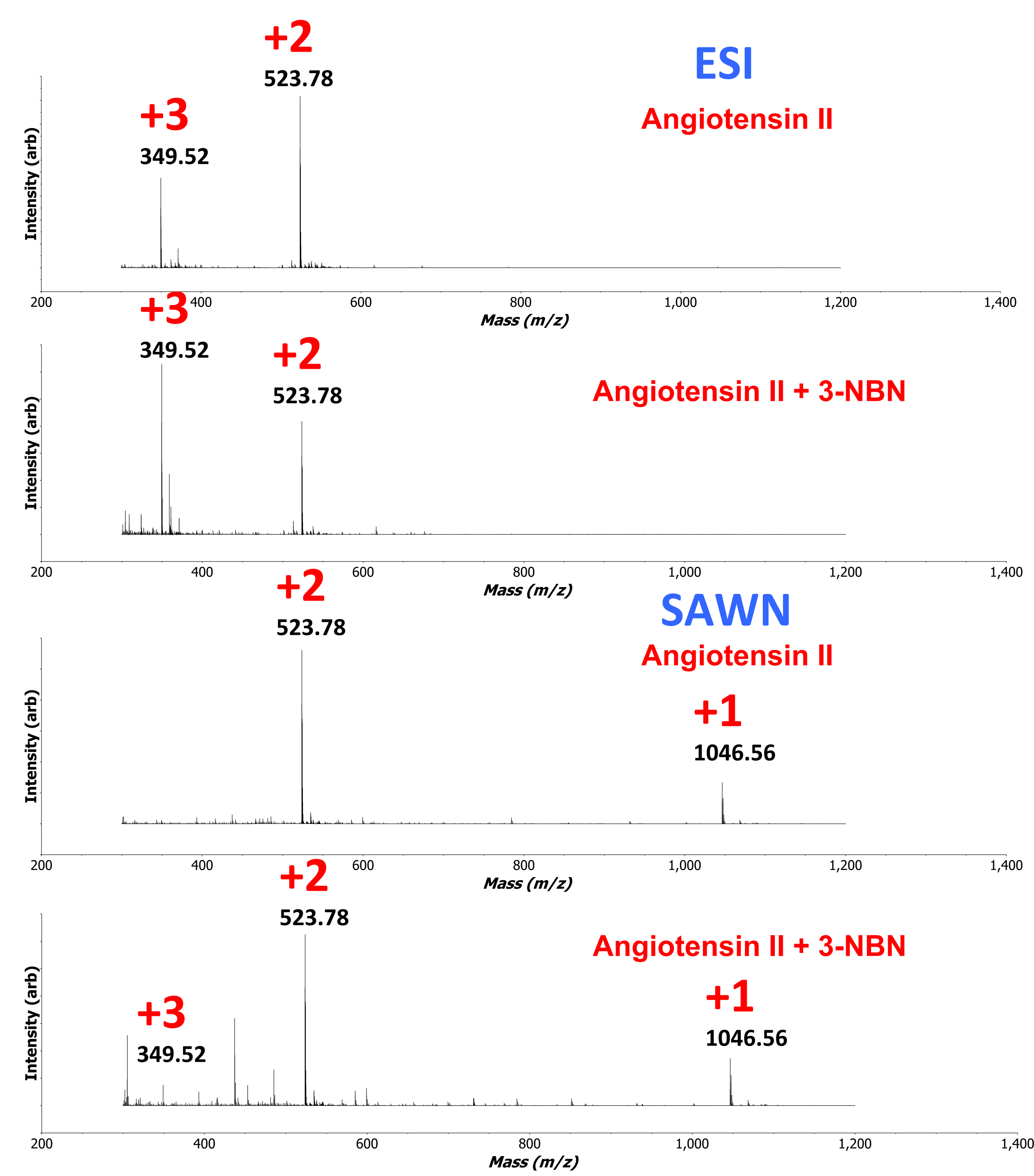
Application of a SAW leads to disruption of the surface tension of a liquid droplet placed on the SAWN piezoelectric chip, which leads in turn to the production of aerosols. Subsequently, the nebulized liquid containing analytes enter the atmospheric pressure ionization (API) orifice where desolvation occurs and ions are generated. Compared to ESI, SAWN produces on average larger aerosolized droplets. For SAWN, heating occurs during wafer processing by photolithography and when the chip is being operated. Excess surface charge can interfere with wave propagation. Since Black LN chips show less surface charging and differences in the mechanical properties to white chips, we proposed that the black LN chips will offer more efficient operation due to uniform wave propagation and charge state reduction.

	Black LN	White LN
Bulk Resistivity (Ω.cm)	2.40 E+11	3.80E+14
Bulk Conductivity (S/cm)	4.17E-11	2.63E-15
Surface Electric Potential (kV)	<0.05	3.05
Electrical Charge neutralization (sec)	1.5	∞
Optical Transmission%	<60	73
Color	Dark Grey	Colorless

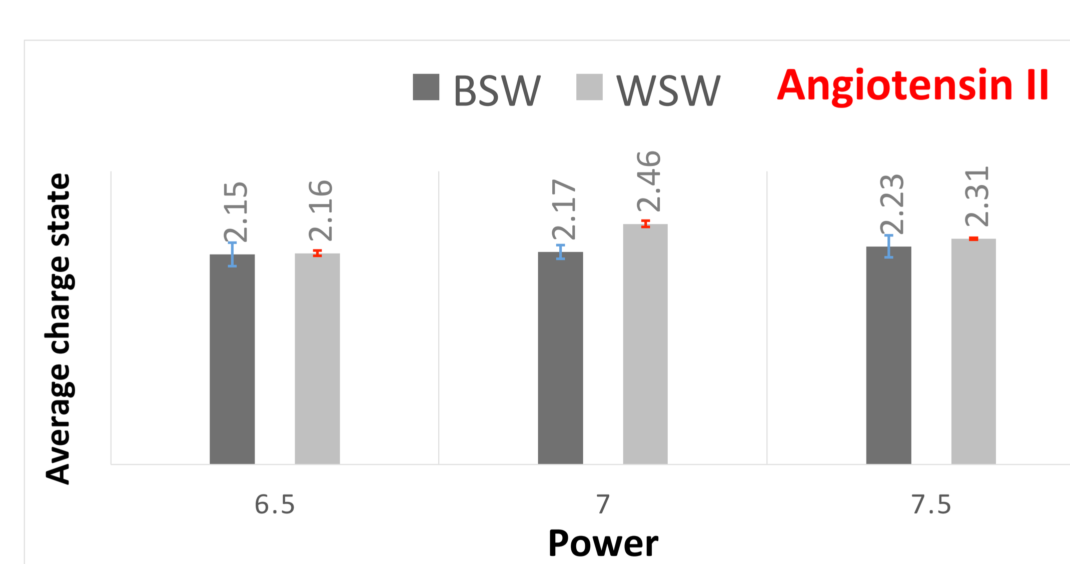
Methods

Angiotensin II was prepared at a concentration of 1 pmol/μL in 50:50 methanol-water with 0.1% formic acid. 3-NBN was added to each sample to make a final concentration of 0.05M. Both NSI and SAWN sources were mounted on a Thermo Exactive instrument with exactly same settings except for transfer capillary temperature, which was 150°C for NSI and 350°C for SAWN. For comparison between the black and white chips, average charge state calculations were done at three different SAWN powers(6.5,7,7.5).

MS of Angiotensin II



Comparison between Black and White Standing Wave Chips



Conclusions

- Our first hypothesis was that addition of 3-NBN to samples for SAWN MS analysis would shift observed charge states. However, the effect was greater for ESI than for SAWN.
- The ESI spectra of Angiotensin II (M.W. 1046.18) showed a significant increase in the peak area for higher charge state ions with the matrix. The $[M+3H]^{3+}$ (m/z=349.52) was increased compared to the $[M+2H]^{2+}$ (m/z=523.78). The ratios of the peak area for m/z=349 vs. m/z=523 with matrix were observed to be 0.895 compared to 0.513 for the blank.
- For SAWN-MS experiments, the percentage of the peak area of different charged state ions were calculated. A consistent increase of the percentage of triply charged ions was observed (13% at 200°C, 17% at 300°C, 9% at 350°C).
- Given that black and white lithium niobate wafers have different pyroelectric potentials when compressed, our second hypothesis was that there might be a change in observed charge state between the two. However, this hypothesis was not confirmed. Thorough examination of the spectra obtained from black and white LN chips show no significant differences between the two.

References

1. Heron et al., *Anal. Chem.*, **82**, 3985-3989 (2010)
2. Huang et al., *J. Am. Soc . Mass Spectrom.*, **23**, 1062-1070 (2012)
3. Lomeli et al., *J. Am. Soc . Mass Spectrom.*, **21**, 127-131 (2010)

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