Determination of Molecular and Topographical Organization on Cicada Wings: Mass Spectrometry's Impact on Material Characterization and Design

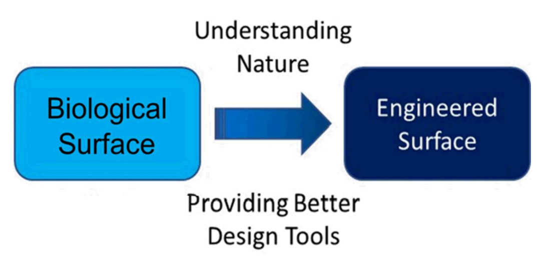
[1,3] Jessica K. Román, [2] Junho Oh, [1] Kyoo D. Jo, [2] Catherine E. Dana, [2] Marianne Alleyne, [2] Nenad Miljkovic, [1] Donald M. Cropek

[1]U.S. Army Engineering Research and Development Center; [2]University of Illinois at Urbana-Champaign, [3]Sandia National Laboratories Albuquerque NM . Unlimited, Unclassified Release.

Connecting Nature and Engineering

Purpose:

- Demonstrate how changes in chemical and structural profiles of cicada wing surfaces influence their functionality.
- Untargeted search for correlation of these profiles to the investigated functionalities.



Methods:

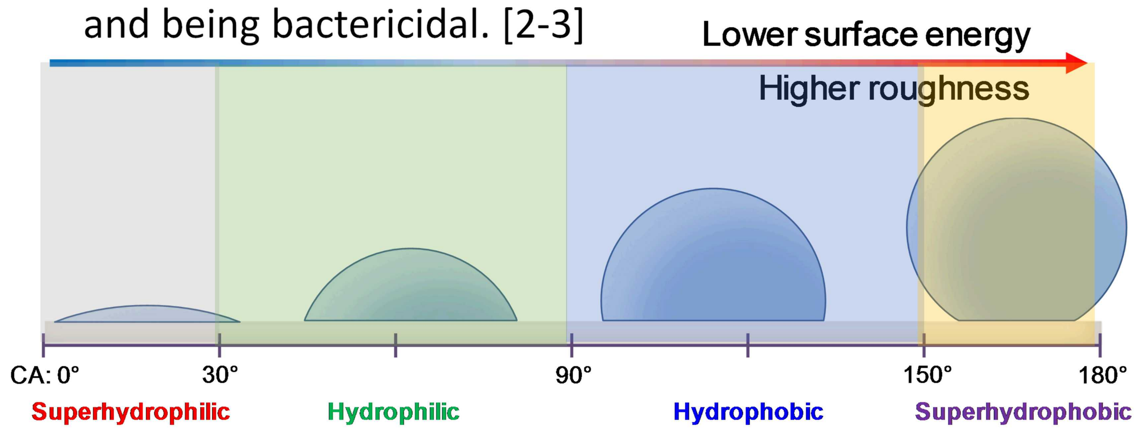
- Investigate wing functionalities (hydrophobicity, biofouling, antimicrobial).
- Utilize GC-MS to detect compounds extracted from wing surfaces.
- Develop in-situ method for spatially-resolved analysis of cicada wings.

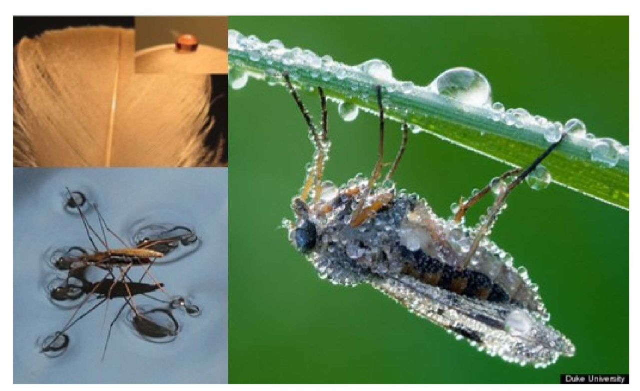
Results:

- Hydrophobic components were observed in chemical extract of cicada wing surfaces.
- Functionality directly correlates to structural and chemical changes on the wing surface.
- Designed a novel method for the analysis of desiccated materials with LAESI. [1]

Introduction

- Understanding what physical and chemical elements give biological materials favorable characteristics will help in the design of engineered materials with similar characteristics which can be used in various applications.
- Insect wings have been shown to possess nanostructures that affect wettability which in turn results in functionalities such as droplet jumping, self-cleaning, anti-fogging, anti-reflectivity and being bactericidal. [2-3]

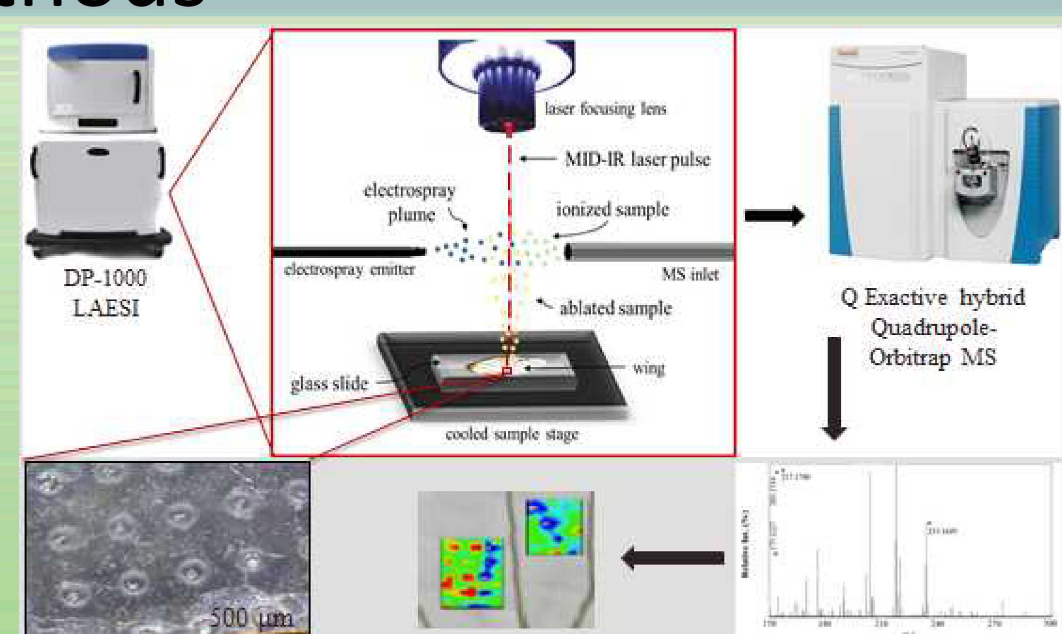




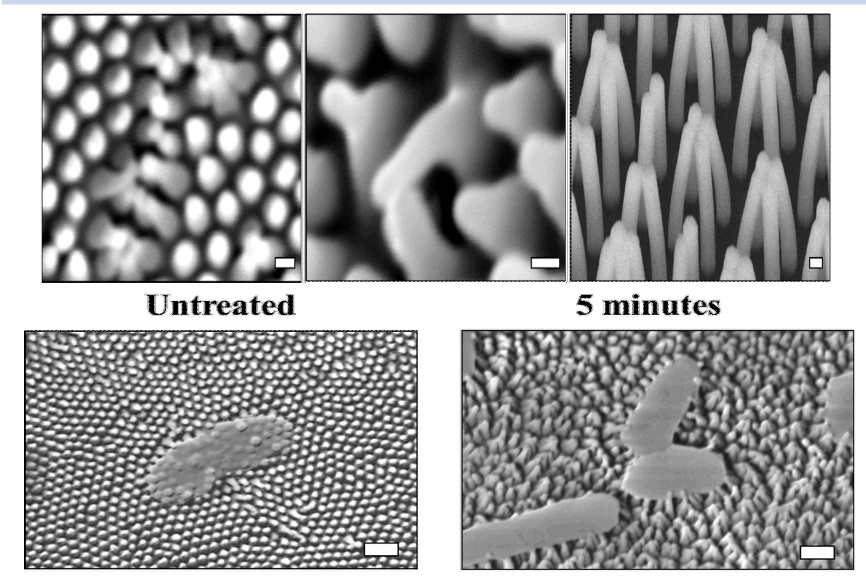
(a) Different regime of wetting and characterization of wetting phenomena, from superhydrophilic (CA<30º) to superhydrophobic (CA<150º), **(b)** various wetting phenomena observed in nature.

Methods

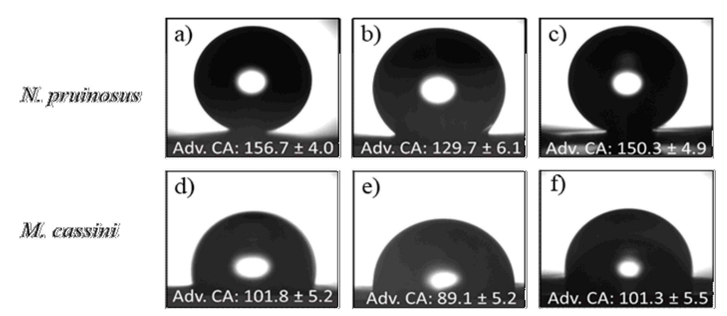
1. Microwave-assisted extraction of wing (*N. pruinosus* and *M. cassini*) surface components.
2. Identify the composition of the extracted material via GC-MS and GCxGC-MS.
3. Track wing functionality over various extraction degrees.
4. Determine optimal analysis conditions for wing analysis on laser-ablation electrospray ionization (LAESI), for which there was no previous method for the analysis of desiccated materials. [1]
5. Correlate chemical and physical analysis to the functionality of wing surfaces.

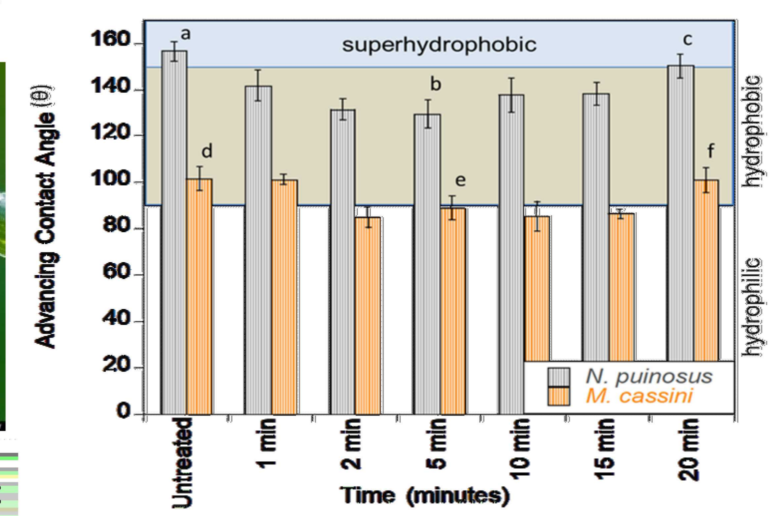


Results



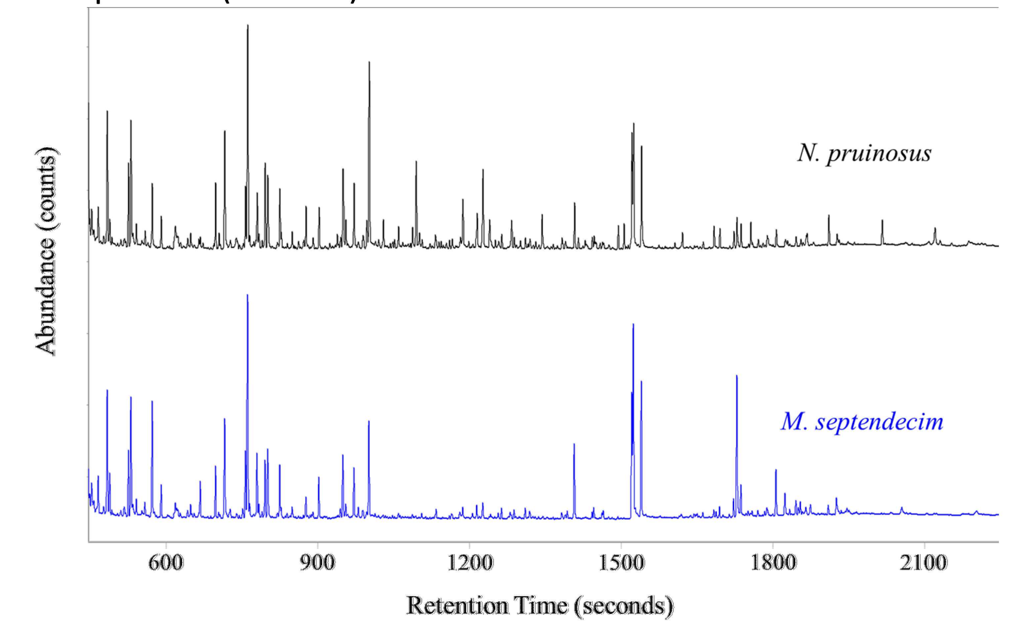
SEM: Post microwave-assisted extraction cicada wing (top- left/middle), artificial structures (top- right), attached bacteria to cicada wing surface (bottom).

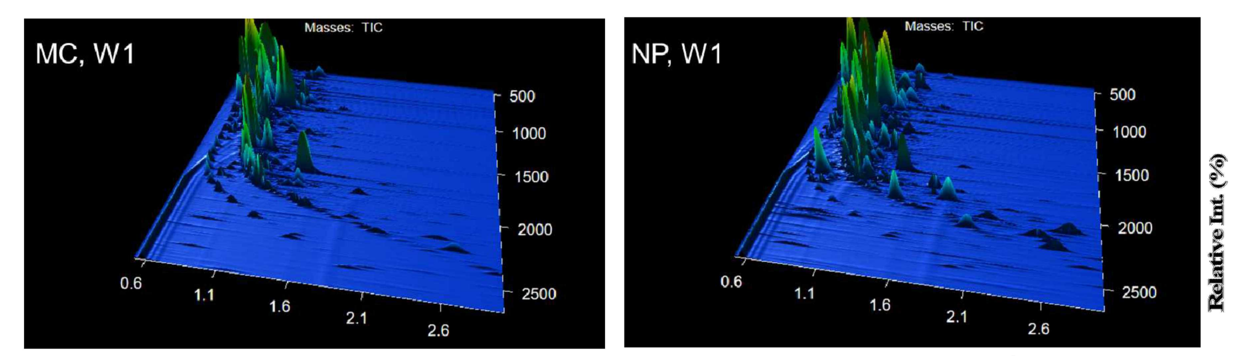




(Above): Advancing contact angles for *Neotibicen pruinosus* and *M. cassini* cicada wings, pre- and post-extraction.

Chemical composition (below): GC-MS of surface extract (top), GCxGC of surface extract (middle), relative proportions of select compounds (bottom).





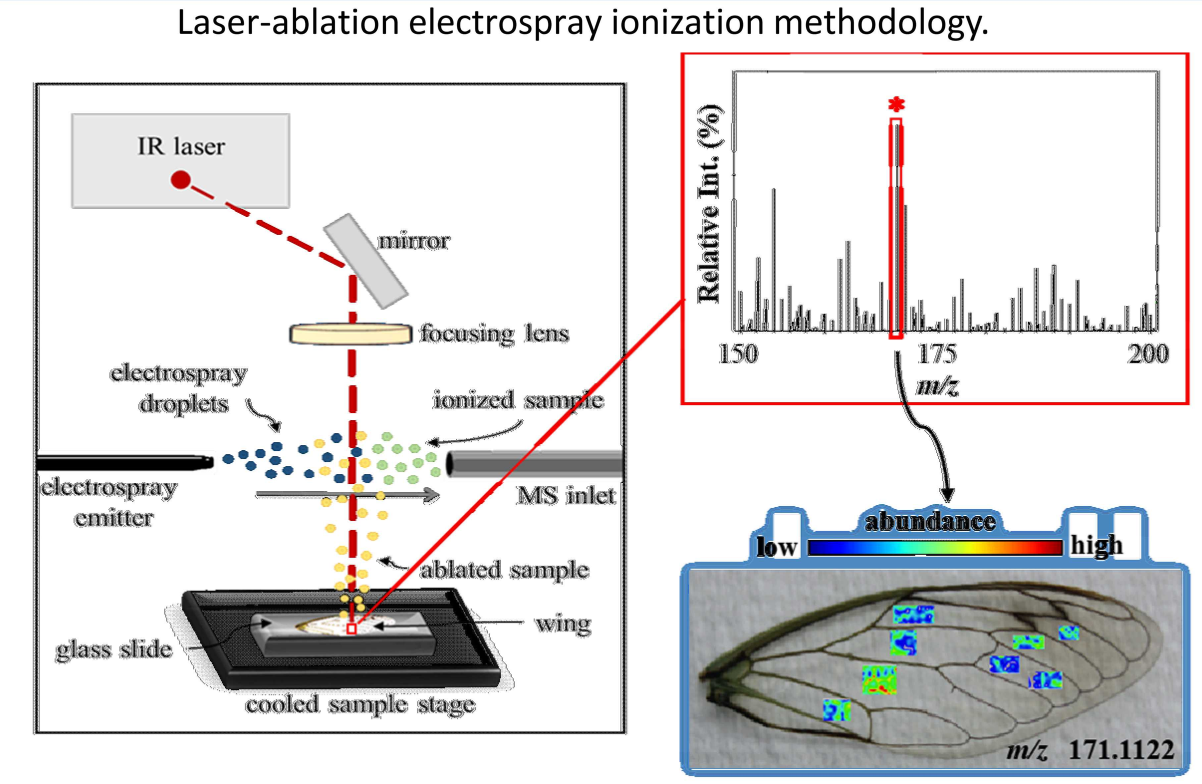
Increases

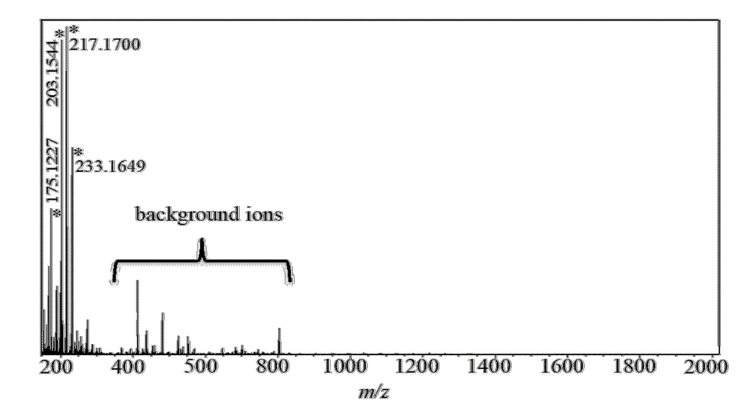
Decreases (C20-C29)

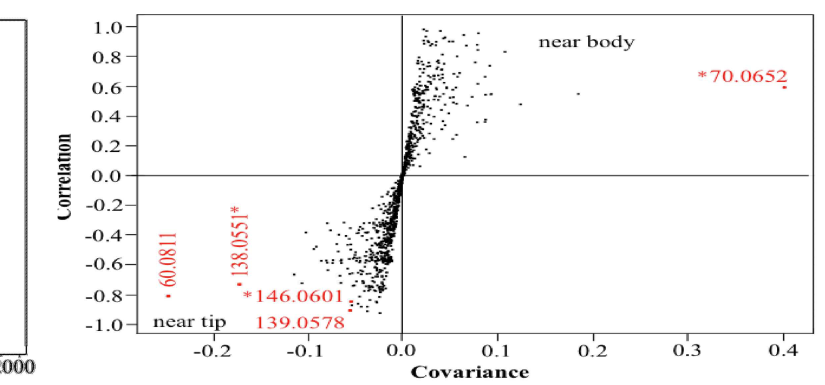
Decreases (C10-C19)

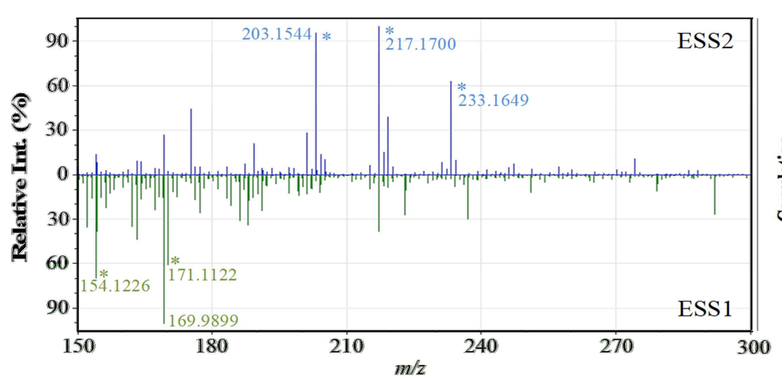
	N. pruinosus 1 min	*N. pruinosus* 5 min	*N. pruinosus* 20 min	*M. cassini* 1 min	*M. cassini* 5 min	*M. cassini* 20 min
Saturated hydrocarbons						
C20-C29	8.8 ± 3.4	5.6 ± 0.1	2.8 ± 0.2	12.9 ± 7.6	12.8 ± 2.9	22.8 ± 1.7
C30-C39	2.2 ± 2.6	3.3 ± 2.1	0.0 ± N/A	4.7 ± 1.7	8.9 ± 1.8	10.0 ± 0.6
C40-C49	1.5 ± 0.5	1.3 ± 0.3	0.0 ± N/A	2.1 ± 1.5	3.4 ± 2.1	0.3 ± 0.5
Lipids						
C10-C19	40.1 ± 1.5	25.9 ± 5.3	30.3 ± 4.2	40.9 ± 2.6	28.1 ± 4.8	17.1 ± 0.4
C20-up	0.0 ± N/A	1.7 ± 0.1	3.3 ± 0.5	0.7 ± 0.5	0.3 ± 0.2	1.1 ± 0.4
Individual compounds						
n-hexadecenoic acid*	11.5 ± 1.8	7.6 ± 0.6	6.1 ± 1.1	11.0 ± 2.4	7.1 ± 0.1	6.3 ± 0.5
oleic acid*	3.8 ± 2.7	3.4 ± 0.1	1.8 ± 1.2	0.8 ± 0.1	0.2 ± 0.3	1.9 ± 1.7
octadecanoic acid*	21.8 ± 7.0	16.0 ± 3.8	23.3 ± 4.0	27.5 ± 2.9	23.4 ± 1.0	13.5 ± 1.7

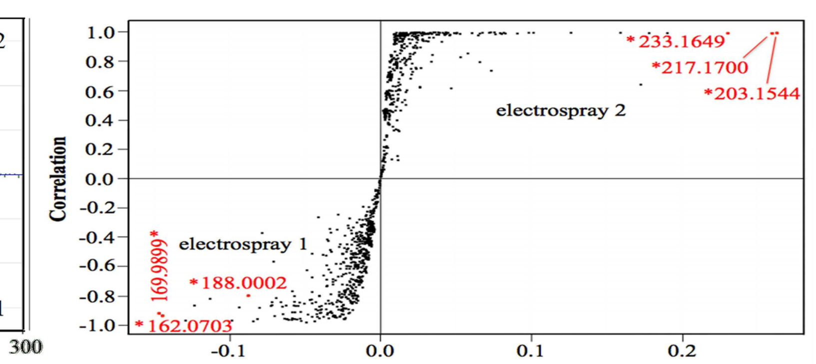
Laser-ablation electrospray ionization methodology.











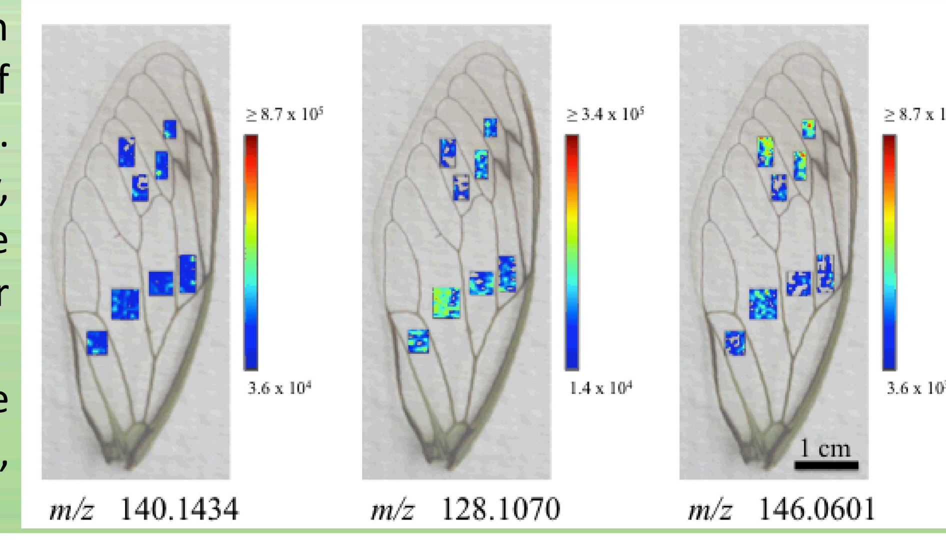
ESS1: methanol-water-formic acid (50:50:0.1)

ESS2: methanol-acetonitrile-toluene-formic acid (50:35:15:0.1)

Conclusions

This study investigated the influence of surface chemistry, in combination with wing topography, on the functionalities of the wing, including wettability and antimicrobial properties. By being able to predict and study wing topology, wettability, the development of rational design tools for the manufacture of artificial surfaces for energy and water applications can be expedited.

Developing a method for the LAESI analysis of fragile samples expands the range of testable sample materials, whether biological or man-made.



References

1. Román JK, Walsh CM, Oh J, Dana CE, Hong S, Jo KD, et al. Spatially Resolved Chemical Analysis of Cicada Wings Using Laser-Ablation Electrospray Ionization (LAESI) Imaging Mass Spectrometry (IMS). Anal Bioanal Chem.; 2018 March 410(7):1911-21.
2. Oh J, Dana CE, Hong S, Román JK, Jo KD, Hong JW, et al. Exploring the Role of Habitat on the Wettability of Cicada Wings. ACS Appl Mater Interfaces. American Chemical Society; 2017 Aug 1;9(32):27173–84.
3. Hasan J, Webb HK, Truong VK, Watson GS, Watson JA, Tobin MJ, et al. Spatial variations and temporal metastability of the self-cleaning and superhydrophobic properties of damselfly wings. Langmuir. 2012 Dec 4;28(50):17404–9.
4. Watson GS, Myhra S, Cribb BW, Watson JA. Putative functions and functional efficiency of ordered cuticular nanoarrays on insect wings. Biophys J. 2008 Jan 11;94(8):3352–60.

Acknowledgements This work was supported by the Army Basic Research Program through collaboration with the U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory under grant number ARMY CESU W9132T-16-2-0011.