**Field Desorption Mass Spectrometry**

**Background**

Insects and arachnids secrete fluids that covers their cuticle and adhesive pads. These fluids are mixtures dominated by hydrophobic, involatile compounds and are, therefore, stable when exposed to water.1 It is hypothesized that these secreted fluids are biphasic, namely containing hydrophobic and hydrophilic phases2, with the hydrophobic phase made of involatile molecules of long aliphatic chains and hydrophilic phase which is volatile.3 The cuticular and tarsal fluids are similar in their chemical composition,4 and are mostly identified as a mixture of hydrocarbons, triglycerides, fatty acids and cholesterols.5 The fluid composition and length of the carbon chains governs the dynamic viscosity of the secreted fluid and consequently the frictional and adhesion forces the beetles rely on for locomotion on different surfaces.6 It remains unclear why the adhesion strength of insects relying on wet adhesion depends on humidity.2 A previous study reported that such a secreted lipid mixture does not dissolve in water.1 To confirm this statement in the case of the ladybird, investigated in this study, we performed Field Desorption Mass Spectrometry (FDMS) measurements before and after the immersion of legs in water. Table 1 shows the molecular masses of secreted fluid mixtures extracted from an Asian ladybird (*Harmonia axyridis)* without (left) and with (right) immersion in water. Except from two molecular weights (406.8 g/mol and 331.6 g/mol), the chemical fingerprint remained unchanged, indicating stability of the lipid mixture underwater. Possible molecules, corresponding to the resulting molecular weights, include:

|  |  |
| --- | --- |
| Peak position (Mw)  Without rinsing in water (g/mol) | Peak position (Mw)  After immersion in water (g/mol) |
| 324.5 | 324.5 |
| 350.5 | 350.5 |
| 352.5 | 352.5 |
| 378.5 | 378.5 |
| 404.6 | 404.5 |
| 406.8 |  |
| 432.8 | 432.7 |
|  | 331.6 |
| 432.8 | 432.7 |

Table 1: Asian ladybird (*Harmonia axyridis*)

**Experimental methods**

Field Desorption Mass Spectrometer (name of device, company, resolution of the device). The middle leg of an Asian ladybird was immersed in 50 µL THF for 20 m and then transferred to the measurement chamber of the FDMS. As a reference, pure THF was used. The second middle leg of the same ladybird was immersed in 100 µL milli-Q water for 15 m, then in THF for 20 m and then transferred to the measurement chamber of the FDMS.

**References**

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