Pesticide Detection using SERS Techniques

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Application Note

Keywords

- Honeybee die-offs
- Imidacloprid
- Pollination

Techniques

- Surface enhanced Raman spectroscopy (SERS)

Applications

- Pesticide detection
- Trace level analysis

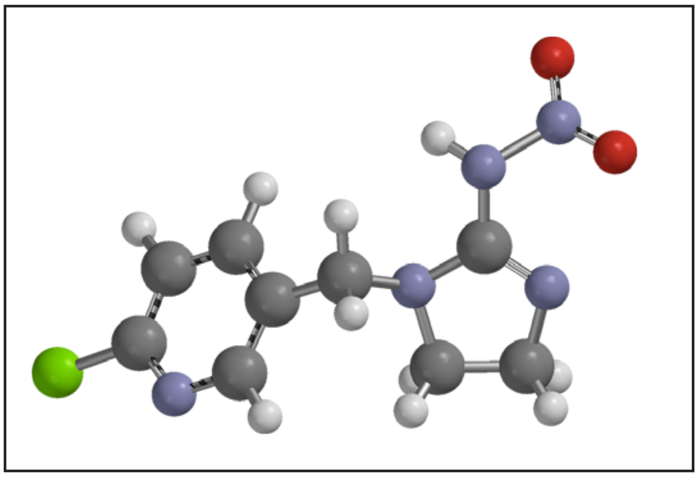
SERS Detects Insecticide Associated with Loss of Honeybee Colonies

Bees play a vital role in pollinating crops that help drive agricultural economies worldwide. With honeybee die-offs increasing in recent years, researchers are investigating the use of spectroscopy techniques to monitor concentration levels of potentially harmful insecticides. In this application note, we evaluate the effectiveness of surface enhanced Raman spectroscopy (SERS) to measure trace levels of imidacloprid, one of a class of insecticides linked to honeybee loss.

Background

Because of their role as pollinators, honeybees are a critical element of ecosystems worldwide, and contribute nearly $25 billion in crop value each year to agricultural economies in just the European Union and United States. Bee pollination from commercial honeybee colonies is crucial to growers of almonds, apples, blueberries, cherries and other fruits and vegetables. In the U.S., many growers rely on rented bee hives for successful planting seasons.

In recent years, high rates of honeybee loss have prompted investigation by government regulators and other researchers. Early in 2016, the U.S. Environmental Protection Agency cited the insecticide imidacloprid as a threat to commercial honeybee colonies[1]. Imidacloprid is widely used for pest control in agriculture, turf management and home protection applications.



Ball and spoke model of the neonicotinoid molecule, imidacloprid.

According to ongoing U.S. EPA studies, imidacloprid traces at concentration levels greater than 25 ppb are likely harmful to honeybees. Additional studies will provide a more definitive assessment of imidacloprid exposure and other factors affecting honeybees. Many are skeptical that imidacloprid alone is to blame for bee colony collapse, citing other pesticides, parasites and hive management practices as contributing to the decline.

SERS and Trace Level Pesticide Detection

In SERS, analytes are adsorbed on a three-dimensional gold, silver or gold-silver surface such as a glass substrate prior to analysis, inducing a plasmon resonance effect that boosts the Raman signal intensity. SERS substrates from Ocean Optics amplify very weak Raman signals by many orders of magnitude, making possible trace level detection of samples such as explosives and pesticides. With prior success using SERS to measure low concentrations of other insecticides, we anticipated similar results with imidacloprid.

Measurement Conditions

We tested the effectiveness of Ocean Optics gold and gold-silver nanosponge substrates, the former using 785 nm as the Raman laser excitation wavelength and the latter using 638 nm as the excitation wavelength. For the 785 nm Raman excitation setup we used a QE *Pro*-Raman spectrometer and for 638 nm excitation we used the IDRaman reader. Both configurations also included the Raman laser, a Raman probe and a sample holder.

For the measurements using gold substrates we prepared 1000 ppm, 100 ppm, 10 ppm and 1 ppm solutions of imidacloprid in acetone, added 10 µL of each solution per substrate, and let the substrate dry completely. For solutions preparation, faster-drying acetone is a better choice than water.

For the gold-silver nanosponge substrate measurements we prepared a 100 ppm solution of imidacloprid in acetone, added 10 µL of the solution per substrate, and let the substrate dry completely.

Experiment Results

We made a series of measurements using the gold (AU) substrates, in a setup with 785 nm Raman laser excitation at 15 mW of power and the spectrometer integration time set for 3 seconds (**Figure 1**). The gold substrates work best for imidacloprid concentrations >4 pg, primarily because the gold substrates have a stronger background signal, making lower concentration measurements challenging.

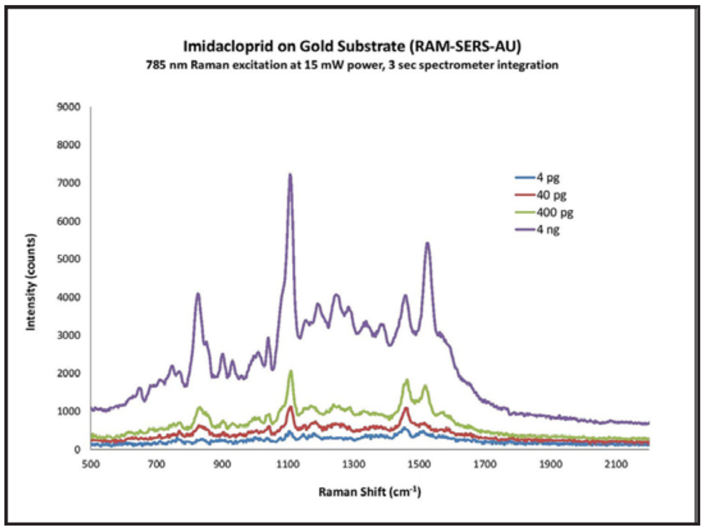


Figure 1. SERS substrates increase Raman signal intensity significantly. This graph shows results using gold substrates to measure the insecticide imidacloprid.

For very low level imidacloprid concentrations, our new gold-silver (SP) nanosponge substrates are most effective. These substrates are based on a plasma-phase deposition of the gold-silver alloy onto a unique glass surface, and are distinguished by high sensitivity with low background noise. The low background noise makes it easier to discern Raman peaks at very low concentration levels. To test this, we used the gold-silver substrates in a setup with 638 nm Raman excitation at 21.2 mW of power and the spectrometer integration time set for 1 second (**Figure 2**).

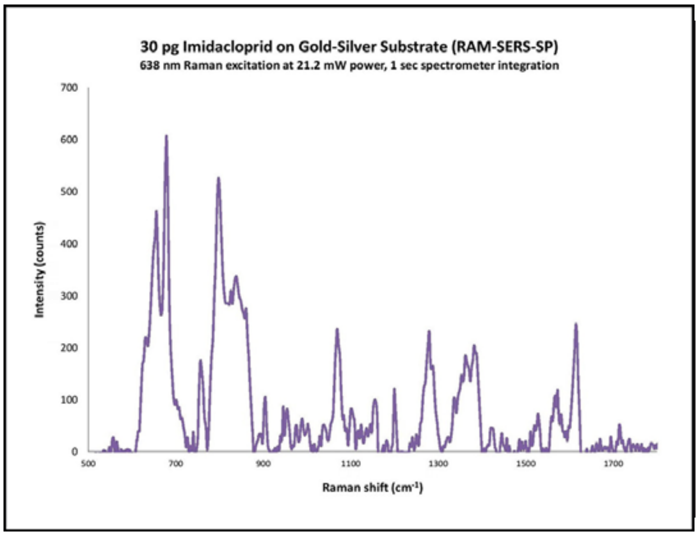


Figure 2. Gold-silver nanosponge substrates have less background signal, making them a good choice for measuring very low concentrations of insecticides such as imidacloprid.

The lowest imidacloprid concentration we measured was 4 pg, which converts to 0.4 ppb. This is well within the 25 ppb concentration level that the U.S. EPA reports is harmful to honeybee populations.

Also Notable

We reported our experiment results in mass amounts (picograms) versus quantity-per-quantity measures (ppb, ppt and so on). This approach provides a more accurate analysis by accounting for the volume of the analyte, the concentration of the analyte in solution, the area of the SERS substrate, and the spot size of the laser (in our experiments, spot size varied from 25 µm to 158 µm). Also, for purposes of our calculations, we assumed uniform coverage of the analyte after deposition and drying.

Summary

Raman is a useful technique for fast, non-destructive analysis, with the enhanced sensitivity provided by SERS substrates allowing detection of trace levels of samples such as insecticides. Already, Ocean Optics modular Raman spectrometers and SERS substrates have demonstrated good measurement results for pesticides including thiram, malathion, phosmet, chlorpyrifos and carbophenothion.

In our imidacloprid measurements, we observed some differences in Raman peaks between substrates, most likely the consequence of different binding mechanisms of the analyte with the substrate material (nanoparticles for the gold and thin film for the gold-silver alloy), but also because the chemistries enhance certain transitions differently. In addition, some molecules will exhibit shifts in their Raman peaks depending on how they are oriented on the SERS-active surface.

As our testing has demonstrated, SERS substrates are a viable option for trace level detection. And, unlike many existing SERS products on the market, Ocean Optics SERS substrates are easy to use, affordable and can be mass produced with high repeatability for routine deployment in the lab or field.

References and Resources

1. "Pesticide is threat to bees, EPA says," Los Angeles Times, January 7, 2016.

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