

Application Note

KEYWORDS

- Honeybee die-offs
- Imidacloprid
- Pollination

TECHNIQUES

- Surface Enhanced Raman Spectroscopy (SERS)

APPLICATIONS

- Pesticide detection
- Trace level analysis

Pesticide Detection using SERS Techniques

SERS Detects Insecticide Associated with Loss of Honeybee Colonies

by Anne-Marie Dowgiallo, Ph.D., R&D Sensor Scientist

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.

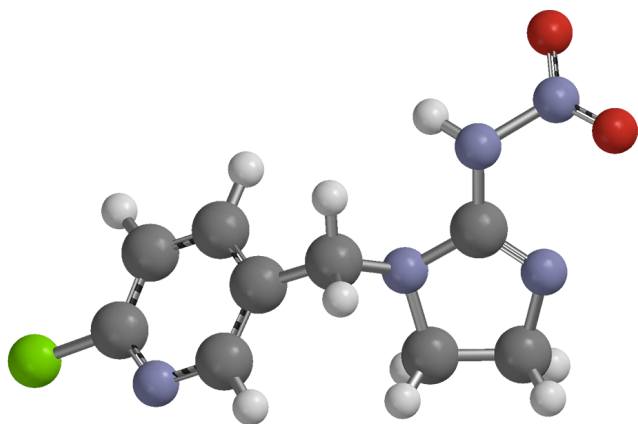


Background

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 colonies¹. 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 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-di-

mensional gold surface prior to analysis, inducing a plasmon resonance effect that boosts the Raman signal intensity. SERS substrates from Ocean Insight amplify very weak Raman signals by many orders of magnitude, making possible trace level detection of samples such as fungicides 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 Insight gold substrates, using 785 nm as the Raman laser excitation wavelength. For the 785 nm Raman excitation setup we used a QE *Pro*-Raman spectrometer. Configurations 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 μ L of each solution per substrate, and let the substrate dry completely. For solutions preparation, faster-drying acetone is a better choice than water.

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.



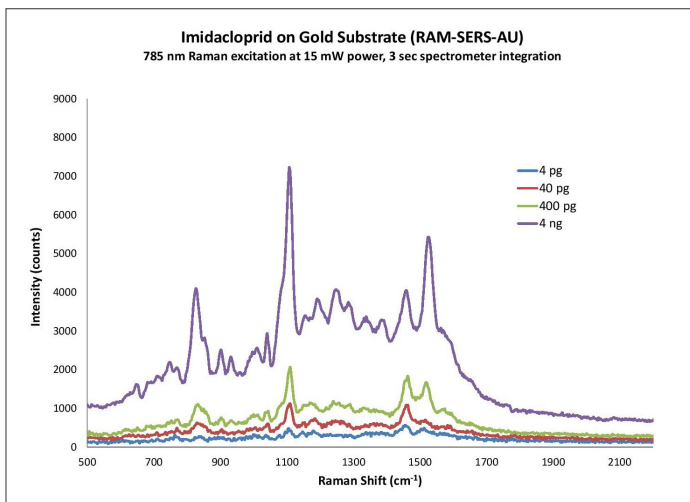


Figure 1. SERS substrates increase Raman signal intensity significantly. This graph shows results using gold substrates to measure the insecticide imidacloprid.

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 Insight modular Raman spectrometers and SERS substrates have demonstrated good measurement results for pesticides including thiram, malathion, phosmet, chlorpyrifos and carbophenothion.

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 Insight 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.

- European Commission, Health and Food Safety – analysis of honeybee health at https://ec.europa.eu/food/animals/live_animals/bees_en
- National Pesticide Center – imidacloprid fact sheet at <http://npic.orst.edu/factsheets/imidagen.html>
- The bees killer imidacloprid insecticide: a vibrational characterization, Sociedade Brasileira de Química (<http://www.s bq.org.br/38ra/cdrom/resumos/T1768-1.pdf>)

www.gmp.ch

GMP SA
GMP SA

Main office: Avenue des Baumettes 17
Büro Zürich: Dübendorfstrasse 11a

CH-1020 Renens
CH-8117 Fällanden

Tél. 021 633 21 21
Tel. 044 825 34 00

Fax. 021 633 21 29
Fax. 044 825 34 01

info@gmp.ch
info@gmp.ch