Application Note AN-RS-039

Trace Detection of Acetamiprid on Raisins

Protecting Consumer Safety with MISA

Recent test studies conducted by the USDA [1] and the NVWA in Europe [2] have shown that raisins, the popular snack food made from dried grapes, are at the top of the list of fruits and vegetables that have been shown to contain unacceptably high levels of pesticide residues. 80% of imported raisins in the Netherlands are contaminated with an average of 11.3 different pesticides per sample, and nearly all marketed brands of raisins in the US contain at least two different pesticide residues [3]. The fundamental health concern is that the long-term, cumulative effects of consuming a variety of pesticides are unknown. Clearly, this challenges the assumption that raisins provide a child-friendly, healthy alternative to processed snack foods. To address such food safety concerns, there is a need for rapid and accurate testing to screen food samples for potentially hazardous substances. In this Application Note, MISA (Metrohm Instant SERS Analyzer) from Metrohm Raman excels in the detection of the pesticide acetamiprid on commercially sold raisins. MISA is a viable alternative to analytical laboratory testing in the quest to prevent contaminated foods from reaching and harming consumers.

INTRODUCTION

Acetamiprid is a highly effective systemic neonicotinoid insecticide. Although toxicity to humans and other mammals is low, it is moderately to highly toxic for birds and aquatic life, posing a potential threat to wildlife and the food chain. This Application Note demonstrates the rapid and sensitive detection of acetamiprid extracted from raisins using the Metrohm Instant SERS (Surface-Enhanced Raman Scattering) Analyzer.

SERS DETECTION OF ACETAMIPRID ON RAISINS

As direct point-and-shoot Raman spectroscopy is unsuitable for trace analyte detection, SERS was used in this experiment. Dilutions of 1 mg/mL acetamiprid in methanol were pipetted onto individual 1 g portions of raisins, yielding samples containing 100, 25, 5, and 2 µg/mL (ppm) and 500 ng/mL (ppb) acetamiprid. Each sample was dried and placed in a vial with 0.2 mL of dichloromethane (DCM). Each tube was vortexed for two minutes and rested for 30 minutes, and then the supernatant was transferred to a clean vial for evaporative drying. After 0.9 mL of silver colloid was added, each vial was vortexed for one minute. This was followed by the addition of 0.1 mL of 500 mmol/L NaCl and gentle agitation of the contents. Each vial was inserted into the vial holder attachment of MISA for measurement.

RESULTS AND DISCUSSION

As shown in Figure 1, SERS spectra for DCM extracts of acetamiprid on raisins are identical to the reference spectrum for pure acetamiprid (in dark blue). The highly resolved signature peaks tend to correlate in intensity to analyte concentration.

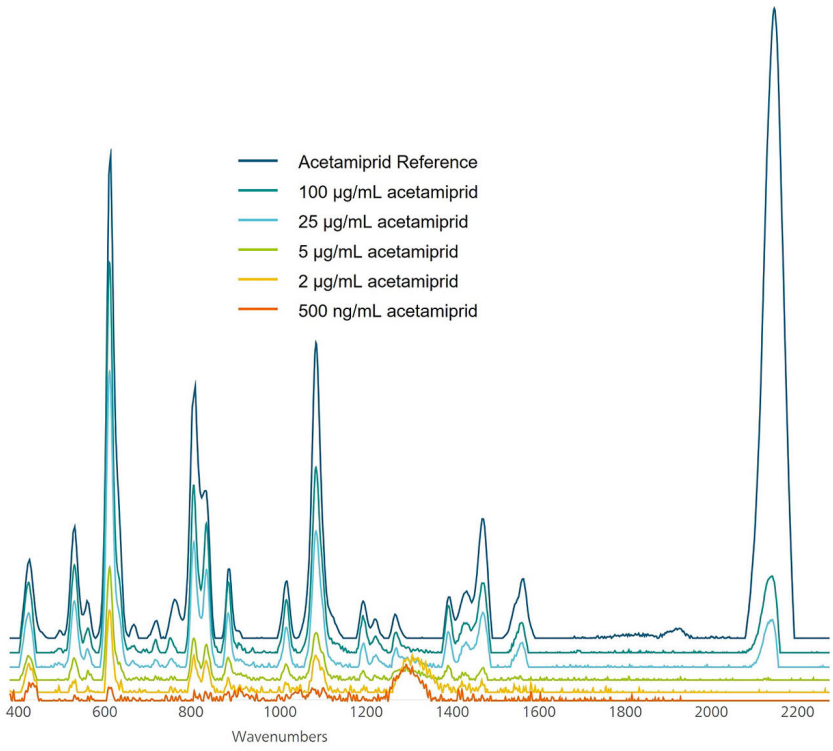

Figure 1. Raman spectra stack of acetamiprid reference and various concentrations (100 µg/mL down to 500 ng/mL).

IMPROVING SERS SENSITIVITY

Information content from Raman spectra is greatest at higher analyte concentrations. Some poorly resolved signature peaks in Figure 1 persist at 500 ng/mL (ppb), yet sensitivity at this level is essential because it corresponds to the maximum residue level accepted for acetamiprid in Europe.

At very low concentrations, the following two strategies may improve SERS detection:

1. Combine multiple extract aliquots into one test sample. In this case, three to four 0.2 mL DCM aliquots (from the same test batch of raisins) would be combined into one vial before evaporative drying.
2. Longer integration times on the instrument may improve sensitivity. The Auto Integration feature on MISA is adequate for higher concentrations; lower concentrations may require manual setting of integration times to four to eight seconds, for example.

Figure 2 overlays spectra for samples containing one aliquot of 5 µg/mL, 2 µg/mL, and 500 ng/mL acetamiprid with a sample that contains four aliquots of 500 ng/mL acetamiprid. This figure provides visual confirmation for improved signal through combined aliquots.

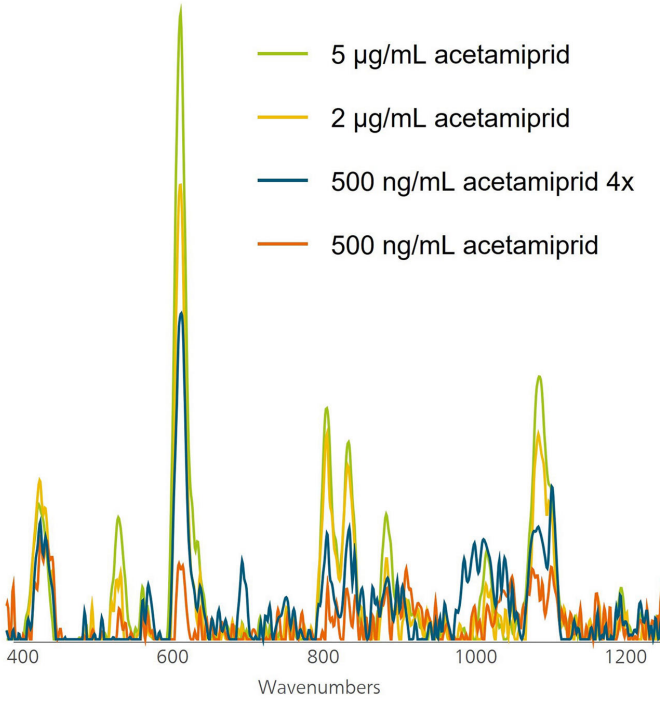

Figure 2. Very low concentration SERS spectra can be improved by combining multiple sample aliquots as seen here with a single 500 ng/mL acetaprimid aliquot (orange) compared to quadruple the 500 ng/mL acetaprimid sample evaporated to the same sample volume for analysis by MISA (blue).

CONCLUSION

MISA is a compact, user-friendly, state-of-the-art analytical tool for ensuring food safety. It facilitates informative decision making when screening food samples suspected of containing pesticide residues. Dedicated SERS substrates and a well-developed library of proven pesticides, herbicides, fungicides, and potentially harmful food additives make MISA a powerful tool for trace-detection applications.

REFERENCES

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3. Authority (EFSA), E. F. S. National Summary Reports on Pesticide Residue Analysis Performed in 2020. *EFSA Support. Publ.* 2022, *19* (3), 7216E. https://doi.org/10.2903/sp.efsa.2022.EN-7216.

CONTACT

Metrohm Portugal
R. Frei Luis de Granada 14G
1500-680 Lisboa
vendas@metrohm.pt