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.

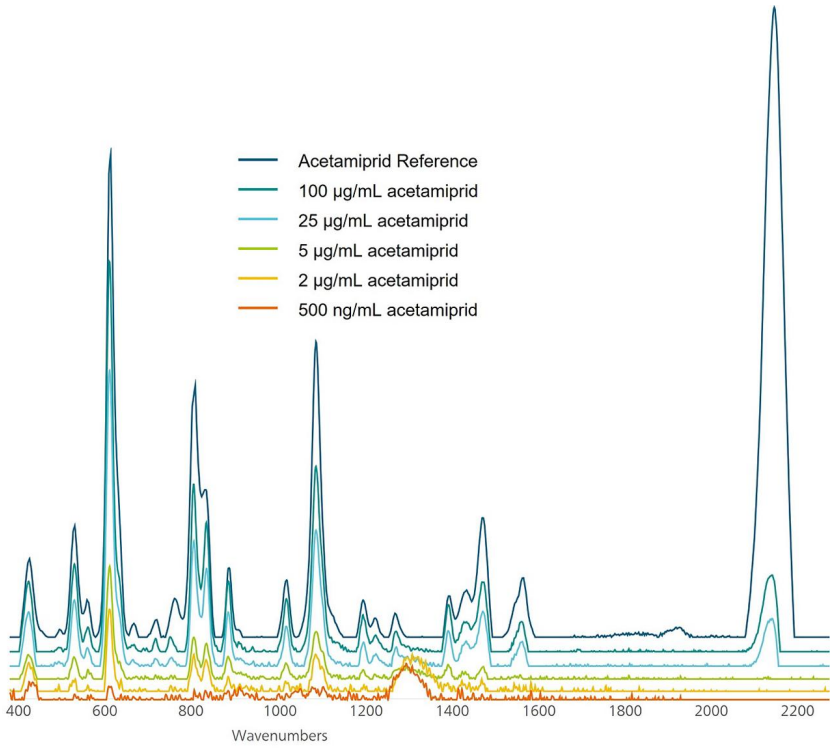

Figure 1. Raman spectra stack of acetamiprid reference and various concentrations (100 µg/mL down to 500 ng/mL).

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.

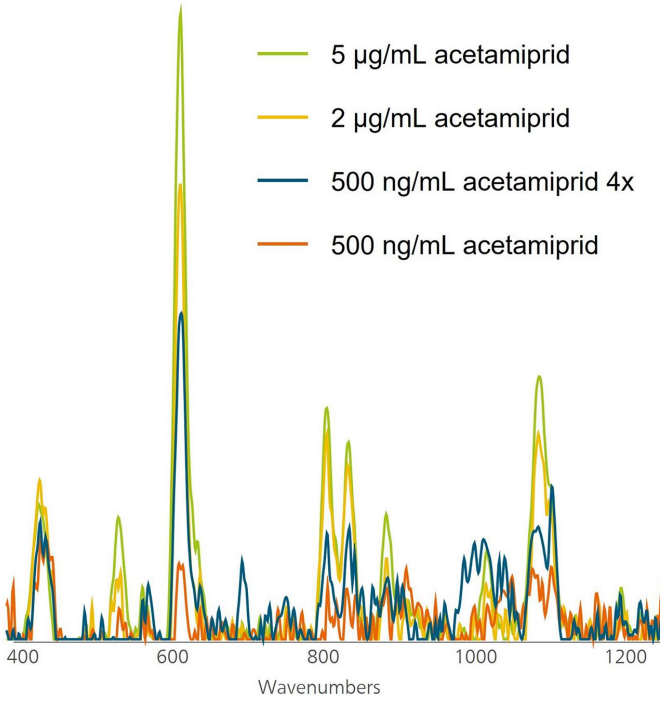

Figure 2. Very low concentration SERS spectra can be improved by combining multiple sample aliquots as seen here with a single 500 ng/mL acetaprimid aliquot (orange) compared to quadruple the 500 ng/mL acetaprimid sample evaporated to the same sample volume for analysis by MISA (blue).

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

1. *Raisin Grades & Standards | Agricultural Marketing Service*. https://www.ams.usda.gov/grades-standards/raisin-grades-standards (accessed 2022-07-26).
2. Group, E. W. *EWG's 2022 Shopper's Guide to Pesticides in ProduceTM*. https://www.ewg.org/foodnews/ (accessed 2022-07-26).
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.

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CONFIGURATION

MISA Advanced

Metrohm Instant SERS Analyzer (MISA) 是一款高性能、便携式分析系,可快速/定非法物、食品添加和微量食品染物。MISA 的特点是配了 Metrohm 独特的道光栅描 (ORS) 技的高效光。其空需求最小和并且池寿命有所延,是或移室用的理想。MISA 提供各 1 激光附件,可活取。分析可通 BlueTooth 或 USB 接行。

MISA Advanced 套件是一个完整套件,其作用是用能用 Metrohms 米粒溶液和 P-SERS 条行 SERS 分析。

MISA Advanced 套件包含了一个 MISA 小管附件、一个 P-SERS-附件、一个 ASTM 校正准件、一个 USB 迷、一个 USB 供元和用于行 MISA 器的 MISA Cal 件。随供了一个用来安全保管器和附件的固保箱。

MIRA XTR Advanced

MIRA XTR 是高功率 1064 nm 系的替代品。在先的人工智能和机器学的支持下,MIRA XTR 使用更敏的 785 nm 激光和 XTR 算法从品光中提取拉曼数据。

MIRA XTR 配有道光栅描 (ORS) 技,可更好地覆盖品,从而提高果的准性。

MIRA XTR Advanced 套件包括校正准件、智能通用附件、直角附件、品瓶附件和 Mira SERS 附件。用于任何型分析的完整套件。3B 操作。

50 mL

SERS 体溶液。用体能高效指示的潜在目分析物包括非法物、品、染料和。50 mL 装。