



Application Note AN-RS-039

Trace Detection of Acetaminiprid 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 $\mu\text{g/mL}$ (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.

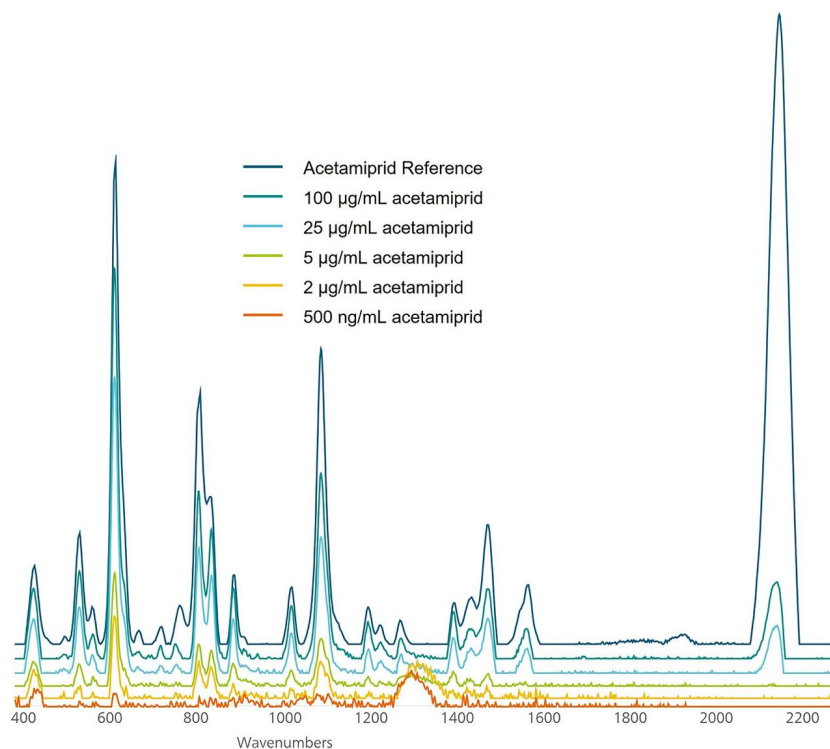


Figure 1. Raman spectra stack of acetaminophen reference and various concentrations (100 µg/mL down to 500 ng/mL).

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 acetaminophen 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 acetaminophen with a sample that contains four aliquots of 500 ng/mL acetaminophen. This figure provides visual confirmation for improved signal through combined aliquots.

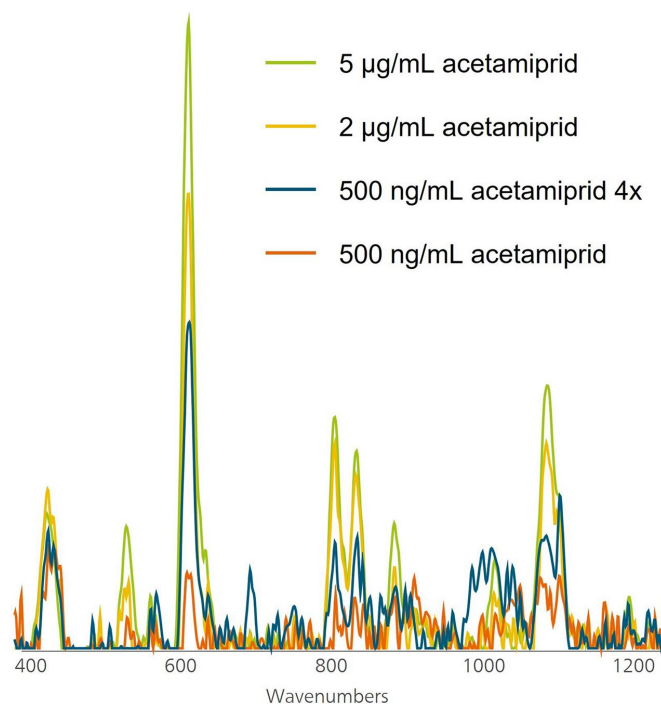


Figure 2. Very low concentration SERS spectra can be improved by combining multiple sample aliquots as seen here with a single 500 ng/mL acetamiprid aliquot (orange) compared to quadruple the 500 ng/mL acetamiprid sample evaporated to the same sample volume for analysis by MISA (blue).

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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CONFIGURATION



MISA Advanced

Metrohm Instant SERS Analyzer (MISA) は、微量レベルでの違法物質、食品添加物、および食品汚染物質の迅速な検出 / 同定のための高性能な携帯可能分析システムです。MISAは、Metrohm 独自の軌道ラスタースキャン技術 (Orbital Raster Scan Technologie, ORS) を備えた高効率の分光器を有しています。これは省スペースで、より長いバッテリー寿命を持ち、現場やラボでの移動式用途にも完璧に適しています。MISA ではフレキシブルなサンプル採取を可能にする、レーザークラス1の様々なアタッチメントをご利用いただけます。アナライザーはBluetoothまたはUSBコネクタを介して操作可能です。

MISA Advanced ハッチケースは、ユーザーに Metrohmのナノ粒子溶液とP-SERSストリップを用いたSERS分析を可能にするコンフリートハッチケースです。

MISA Advanced ハッチケースには、MISAハイアルアタッチメント、P-SERSアタッチメント、ASTM校正標準、USBミニケーブル、USB電源装置、ならびにMISA装置を操作するためのMISA Calソフトウェアが含まれます。装置と付属品を安全に保管するための頑丈な保護ケースも同梱されています。



MIRA XTR Advanced

MIRA XTRは、高出力1064 nmシステムに代わる装置です。高度な AI と機械学習により、サンプルの蛍光発光からのラマンテータを抽出するのに、MIRA XTR は XTR アルコリスムと共により感度の高い 785 nm のレーザー光を使用します。MIRA XTR はまた、サンプルの包括域を拡張して結果の精度を高めるための軌道ラスタースキャン (Orbital Raster Scanning、ORS) を特徴としています。MIRA XTR Advanced package には、校正標準、インテリシエントなユニバーサルアタッチメント、ライトアングルアタッチメント、ハイアルアタッチメント、MIRA SERS アタッチメントが含まれています。あらゆるタイプの分析に対応する完全なパッケージです。クラス3B操作。



50 mL

SERS活性銀コロイド溶液。銀コロイドによってより良い性能を示す可能性のある対象分析物には、違法ドラッグ、医薬品、着色料、ならびにアミンが挙げられます。50 mLパッケージ。