



Application Note AN-RS-027

Trace Detection of Thiram on Apples

Protecting consumer safety with Misa

Thiram is used extensively as a fungicide and parasiticide to prevent disease in crops and as an animal repellent to protect trees and ornamental plants. However, extensive toxicological studies conclude that chronic, high-level exposure can cause considerable organ damage to land and aquatic species. While only moderately toxic to humans through skin exposure and ingestion, thiram is highly toxic if inhaled. To reduce its negative effects on health and the environment, the US defines maximum residue limits that vary for different food crops. In

contrast, the EU recently banned thiram and is moving to use pesticides that carry reduced health risks. Using Misa (Metrohm Instant SERS Analyzer), low level detection of thiram on apples is achieved with guided workflows adapted for use by diverse testers. Misa Cal software automatically processes results and achieves chemical identification by matching to either proprietary, user-created, or commercially available spectral libraries. Results can be geotagged and shared immediately with the accompanying chemical hazard information.

INTRODUCTION

This application note describes a simulated test procedure for detecting thiram residue on apple skin. The assay is based on the acquisition of SERS-specific

spectra for thiram using Misa and Metrohm Raman's proprietary silver P-SERS substrates.

REFERENCE SPECTRUM AND LIBRARY CREATION

To establish a reference spectrum, a pure thiram standard at a concentration of 500 µg/mL in ethanol was analyzed using silver (Ag) P-SERS strips. The

unique SERS spectrum shown in **Figure 1** can be used to create a library entry for thiram.

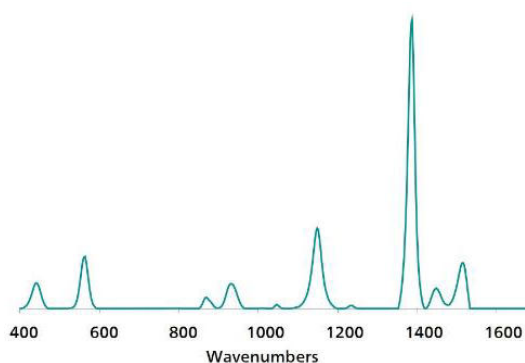


Figure 1. Standard SERS reference spectrum of thiram.

EXPERIMENT

To simulate rapid testing, 25 µL aliquots of 1000, 100, and 10 µg/mL thiram in ethanol were applied to 2 cm² sections of apple skins washed with water and dried. After thorough drying of the test sections, Ag P-SERS test strips were dipped in ethanol and immediately swabbed in a circular motion within treated sections on the apple skin. Each strip was dried for five minutes and then placed in the P-SERS attachment on Misa for measurement.



Table 1. Experimental parameters

Instrument		Acquisition	
Firmware	0.9.33	Laser Power	5
Software	Misa Cal V1.0.15	Int. Time	5 s
Misa Vial Attachment	6.07505.030	Averages	10
ID Kit - Ag P-SERS	6.07506.470	Raster	ON

RESULTS

Overlaid and baseline-corrected spectra acquired for swabs of an apple skin treated with different

concentrations of thiram show detection down to 10 $\mu\text{g/mL}$ (Figure 2).

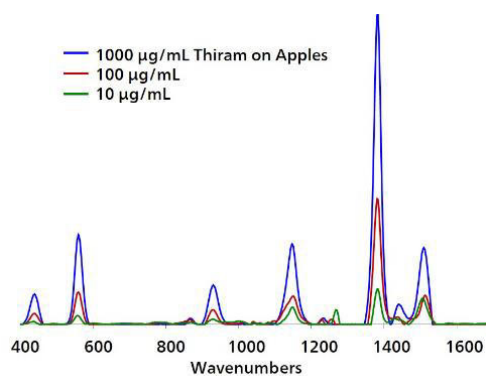


Figure 2. Overlaid baseline-corrected spectra acquired from Ag P-SERS swabs show detection of thiram on apple skins to 10 $\mu\text{g/mL}$.

FIELD TEST PROTOCOL

Detection of thiram in the field

Dip the printed end of a P-SERS strip into ethanol. *Touch only the unprinted back side of the swab with your gloved hands.* Use the moistened, printed side of the strip to swab the peel of an apple. Rub the strip in

a circular motion. After drying for 5 minutes, insert the Ag P-SERS strip, with the printed portion facing down and toward the instrument, into the P-SERS attachment for measurement.

Table 2. Requirements for field test protocol

ID Kit - Ag P-SERS	6.07506.470
includes:	Silver P-SERS
	Scoop
	Disposable pipettes
	2 mL glass vials
Reagents	Ethanol
Test settings	Use ID Kit OP on MISA

CONCLUSION

Misa is a highly sensitive, cost-effective system for the unambiguous identification of pesticide residue on fruit. Its user-friendly analyses paired with smart

software in a compact, portable format make it a powerful solution for field detection of food adulterants.

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CONFIGURATION



MISA Advanced

Metrohm Instant SERS Analyzer (MISA) is a high performance, portable analyzer system used for rapid, trace level detection / identification of illicit materials, food additives and food contaminants. MISA features a high-efficiency spectrograph equipped with Metrohm's unique Orbital-Raster-Scan (ORS) technology. It has a minimal footprint and extended battery life, perfect for on-site testing or mobile laboratory applications. MISA offers various Laser Class 1 attachments for flexible sampling options. Analyzer operation is available through BlueTooth or USB connectivity.

The MISA Advanced package is a complete package that allows the user to perform SERS analyses using Metrohm's nanoparticle solutions and P-SERS strips.

The MISA Advanced package includes a MISA Vial Attachment, a P-SERS Attachment, a ASTM Calibration Standard, a USB Mini Cable, a USB Power Supply and MISA Cal software for operating the MISA instrument. A ruggedized protective case is also provided to securely store the instrument and accessories.



ID Kit – Ag P-SERS

The ID Kit - Ag P-SERS contains the components a Mira / Misa user requires to perform a SERS analysis using silver P-SERS strips. The kit contains a disposable spatula, dropper, sample vials and 2 silver P-SERS strips.