Application Note AN-RS-030

Trace Detection of Fenthion in Olive Oil

Protecting consumer safety with Misa

Fenthion is a multi-purpose insecticide used in many countries for mosquito control. Although designated as moderately toxic to humans, fenthion is highly toxic to birds, fish, and aquatic invertebrates. To minimize human exposure and the unintentional poisoning of wildlife, the US EPA has classified fenthion as a restricted-use insecticide. However, the widespread spraying of olive orchards in Mediterranean countries results in olive oils that occasionally exceed the maximum residue limits established for olives.

Misa (Metrohm Instant SERS Analyzer) easily achieves sensitive trace detection of fenthion in spiked olive oil after a simple organic solvent extraction. This Application Note presents an excellent example of how the signal from SERS substrates can compete with the target signal at very low levels of detection. This is a common occurrence that Misa and Misa Cal address through peak assignment in Misa Cal's SERS libraries. This is just one of the built-in advantages that make Misa so user-friendly.

INTRODUCTION

This application note describes a simulated test procedure for detecting fenthion in olive oil. The assay is based on the acquisition of SERS-specific spectra for fenthion in acetonitrile extracts using Misa and gold nanoparticles (Au NPs).

REFERENCE MATERIAL AND LIBRARY CREATION

To establish a reference spectrum, pure fenthion standard at a concentration of 100 µg/mL in methanol was analyzed using Au NPs. The unique SERS spectrum shown in Figure 1 can be used to create a library entry for fenthion.

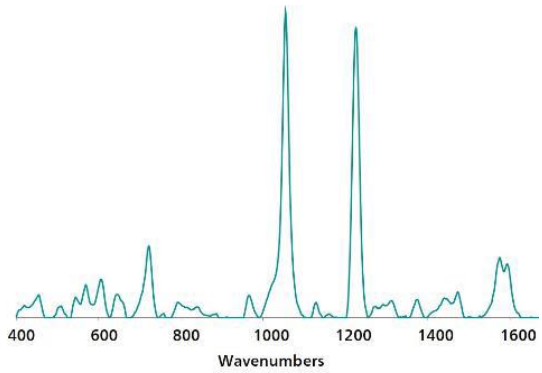

Figure 1. Standard Au NP SERS reference spectrum of fenthion.

EXPERIMENT

A stock solution of fenthion in methanol was used to spike olive oil, creating a range of test samples: 100, 10, 5, and 1 µg/mL, and 500 ng/mL. To each aliquot, 0.5 mL of cyclohexane was added, followed by 0.5 mL of acetonitrile and 50 µL of water. Contents were mixed by shaking, and each vial was rested for 10 minutes to allow phase separation. Using a pipette, 200 µL of the lower acetonitrile layer was carefully removed and transferred to a fresh vial. The acetonitrile was removed by evaporative heating. The dried residue was resuspended by the sequential addition of 450 µL of Au NPs and 50 µL of 0.5 mol/L NaCl, shaken to mix, and then inserted into the vial 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	6.07505.040	Averages	10
ID Kit - Au NP	6.07506.440	Raster	ON

RESULTS

Overlaid baseline-corrected spectra acquired for the concentration range of fenthion used to spike olive oil shows detection down to 500 ng/mL (Figure 2).

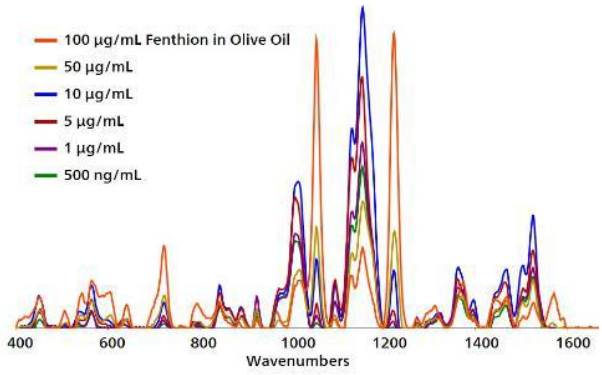

Figure 2. Au NP SERS concentration profile of fenthion extracted from spiked olive oil.

Upon careful consideration, Figure 2 appears to be a composite of two distinct moieties. It is well-known that trace detection capabilities come from signal enhancement through interaction of the target analyte with the SERS substrate. Each SERS substrate contributes its own signal to a spectrum, which may be distinct at these very low levels of detection. Closer inspection of the strongest peaks in this figure reveals the expected inverse relationship between increasing intensity of the fenthion peaks and decreasing signal from the substrate, seen in Figure 3.

Misa Cal's dedicated library entries include peak assignments for each substance, which permit identification of the target even in what appears to be a mixed spectrum.

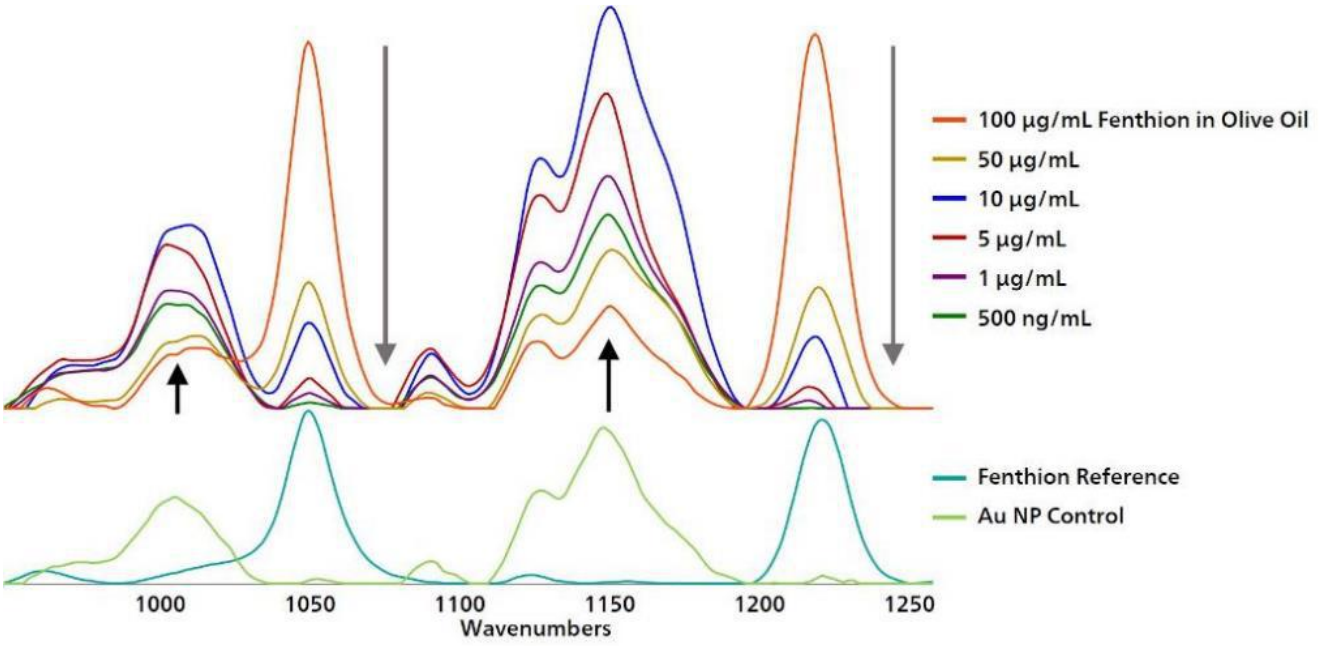

Figure 3. Inverse relationship between fenthion and Au NP SERS substrate signals at very low concentrations

FIELD TEST PROTOCOL

Detection of fenthion in the field

Using a pipette, add 4 drops of olive oil to a 2 mL vial. Fill the vial halfway with cyclohexane and shake until oil is in solution. Add acetonitrile until the vial is nearly full, shake, and let sit for 10 minutes. With a clean pipette, carefully decant a portion of the *bottom layer* into *clean vial*. Heat to remove the solvent. Add Au NPs to this vial until ~1/3 full, followed by 3 drops of NaCl solution. Cap and shake the vial gently to mix, then insert into vial attachment on Misa for measurement.

Table 2. Requirements for field test protocol

ID Kit - Au NP	6.07506.440
includes:	Gold nanoparticles (Au NP)
	Scoop
	Disposable pipettes
	2 mL glass vials
Reagents	
Cyclohexane	
Acetonitrile	
NaCl solution	3 g NaCl in 100 mL water
Test settings	Use ID Kit OP on MISA

CONCLUSION

The limit for fenthion in olive oil is 1 µg/mL in the US. Based on the simple protocol reported in this application note, Misa provides sufficient sensitivity for detecting fenthion at concentrations that meet the established limit for olives.

From automated workflows included in the ID Kit OP to one-touch operation to dedicated pesticide libraries, Misa Cal is a powerful companion to Misa in identification of trace-level food adulterants.

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