Application Note AN-RS-025

Trace Detection of Paraquat in Tea Leaves

Protecting consumer safety with Misa

Paraquat is a highly effective herbicide used to manage weeds in agricultural operations. It is also exceptionally toxic, causing debilitating health effects that can result in delayed death after exposure. In China alone, it is estimated that over 5000 deaths each year are attributed to exposure during application and production of paraquat. In recognition of paraquat's danger, the EU and several other countries have banned its use for any application. The US EPA permits limited use of paraquat by licensed applicators. Despite tight regulation, paraquat continues to be produced and is liberally used as an herbicide in over 100 countries without regulatory oversight.

Testing for paraquat typically requires involved sample processing and analysis by trained chemists using expensive laboratory instruments such as HPLC, CE, and LC/MS. Misa achieves trace level detection of paraquat residue in tea leaves in a fully integrated, portable, smart system for easy on-site testing by non-technicians.

This application note describes a simple procedure for trace detection of paraquat on tea leaves, based on the acquisition of SERS spectra of paraquat in chloroform extracts using Misa and gold nanoparticles (Au NPs).

REFERENCE SPECTRUM AND LIBRARY CREATION

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

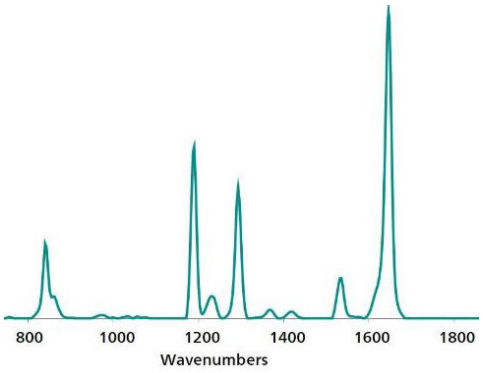

Figure 1. Standard reference SERS Au NP spectrum of paraquat.

EXPERIMENT

Serial dilutions of paraquat in water were added to 0.1 g aliquots of finely ground tea in glass vials to yield a concentration range of spiked test samples: 50, 25, 10, 5, and 1 µg/g, 100 and 50 ng/g. These samples were dried at 80 °C, and 1 mL of chloroform was added each vial. Each sample was shaken for thorough wetting of the ground tea leaves and rested for 15 minutes to facilitate settling and extraction. After waiting the required time, 10 µL of chloroform extract was decanted to a fresh vial, dried briefly, and resuspended in 450 µL of Au NPs and 50 µL of 0.5 mol/L NaCl. Sample vials were gently shaken and immediately placed 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	1 s
Misa Vial Attachment	6.07505.040	Averages	10
ID Kit - Au NP	6.07506.440	Raster	ON

RESULTS

Overlaid Au NP SERS spectra acquired for a range of paraquat-spiked tea samples demonstrate detection down to 1 µg/g (Figure 2). Spectra were baseline-corrected and background-subtracted with Misa Cal software.

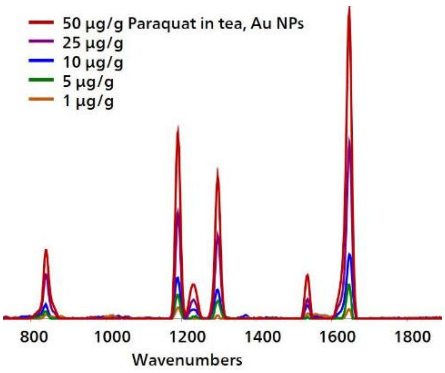

Figure 2. SERS spectra for a concentration range of paraquat in tea.

FIELD TEST PROTOCOL

Detection of paraquat in the field

If tea leaves are very large, then grind, crush, or chop them. Using the large end of the scoop, add 3–4 scoops of sample to a 2 mL vial. Add chloroform to the vial until halfway full. Cap and shake the vial gently to mix, then let sample rest for 15 minutes. Fill a clean vial ~1/2 full with Au NPs. Using a pipette, add 2 drops of chloroform extract to a *clean vial* and remove the solvent with evaporative heating. Fill this vial halfway full with Au NP solution, add 1 drop of NaCl solution, and shake gently to mix. 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	
Chloroform	
NaCl solution	3 g NaCl in 100 mL water
Test settings	Use ID Kit OP on MISA

CONCLUSION

The level of detection reported here for paraquat on tea leaves is significantly lower than the permissible levels of residue allowed for most vegetable, herb, and fruit crops. Sampling with Misa is simplified with onboard operating procedures that automate acquisition parameters, sample processing, and results reporting. Misa's dedicated software, Misa Cal, can be used for spectral processing, library matches, and results sharing.

CONTACT

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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 – Au NP

The ID Kit - Au NP contains the components a Mira / Misa user requires to perform a SERS analysis using gold colloidal solution. The kit contains a disposable spatula, dropper, sample vials and a bottle of gold colloid.