Application Note AN-RS-038

Detection of LSD on blotter paper

Raman, SERS, and drug enforcement

Lysergic acid diethylamine (LSD), or «acid» as it is popularly known, is a Schedule 1 controlled substance responsible for potent euphoria-inducing and sensory-altering properties. Long lasting psychopathological consequences, such as auditory/visual hallucinations and psychoses, have been documented in vulnerable LSD users. LSD is typically spotted on colorful, absorbent «blotter» papers for sublingual and oral administration. Convenient detection of LSD requires a flexible system capable of trace detection of the target compound in the presence of potential interferents—including dyes, substrates, and solvents—with minimal sample processing. This Application Note describes real-world test simulations using SERS (surface-enhanced Raman scattering) materials and test samples consisting of ink-printed and color dyed paper matrices spiked with LSD. Simple extraction procedures are highlighted to lift the target compound and remove fillers, inks and dyes that fluoresce or otherwise confound identification of LSD.

MISA (Metrohm Instant SERS Analyzer) and MIRA XTR (Metrohm Instant Raman Analyzer) are ideal solutions for rapid field identification of a range of illicit and dangerous chemical substances. Easy-to-use test kits and flexible sampling allow rapid and accurate interrogation of suspect materials with minimal time, training, and expense.

INTRODUCTION

Raman spectroscopy is a superior method for detection of bulk materials and chemicals, although it lacks sensitivity for trace detection. When LSD-saturated paper products are interrogated with Raman, the spectrum is dominated by the substrate signal. SERS, however, is sensitive enough to detect the active ingredient in typical single-dose street samples containing 20–400 µg of LSD.

LSD ON CHROMATOGRAPHY PAPER

SERS measurements of LSD samples extracted from unprinted chromatography paper were collected. Serial dilutions of 1 mg/mL LSD in methanol were pipetted onto individual squares of paper, yielding test LSD concentrations of 20, 10, 5, 2, and 1 µg/0.635 cm^2. Once dry, each square was placed in a glass vial, shaken with 500 µL of Ag colloid and rested for five minutes to facilitate extraction. The paper was removed, and 100 µL of 0.9% NaCl was added to the vial. This mixture was gently shaken and allowed to rest for one minute before the vial was inserted into the vial holder attachment on MISA and measured using the ID Kit OP.

Figure 1 shows the concentration profile of LSD on chromatography paper, indicating efficient and rapid aqueous extraction of the target compound. Of note is the absence of spectral interference from the paper substrate. Inspection of the concentration profile suggests a LOD (limit of detection) of approximately 1 µg LSD, which is sufficiently sensitive for confident screening of confiscated drug samples.

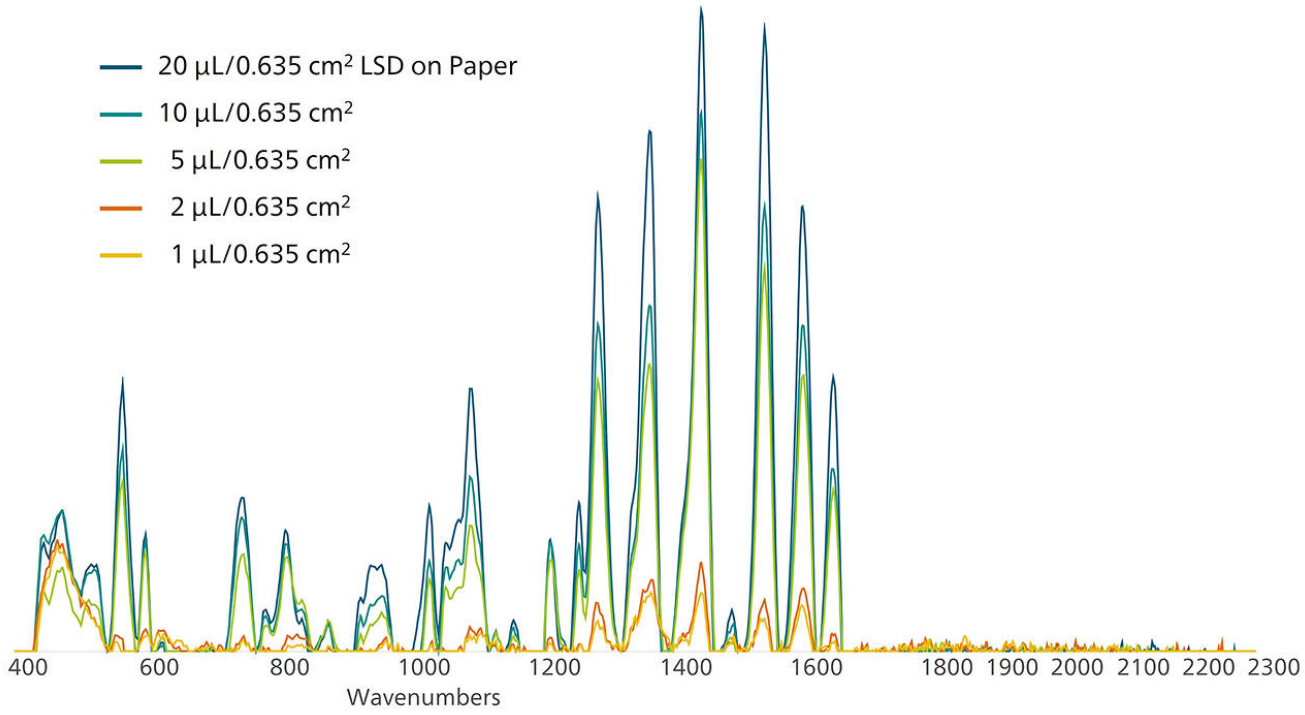


Figure 1. Reference LSD on chromatography paper concentration profile.

To evaluate the effects of colorants on SERS identification of LSD extracted from paper, the procedure outlined in the previous section was replicated with both paper laser-printed with colored toner and paper coated with a mixture of food dyes. As the bottom two spectra in Figure 2 show, both treatments significantly reduce the intensity and resolution of the LSD signal. This is largely due to the fluorescence emissions of colorants, which serve to lower the signal-to-noise (S/N) ratio of signature peaks.

A simple sample clean-up procedure based on liquid-liquid extraction improved signal intensity dramatically. In this modification of the extraction procedure, dried LSD-saturated paper was added to a glass vial containing 500 µL of water and 10 µL of 1 mol/L NaOH. This mixture was shaken gently, 500 µL of dichloromethane (DCM) was added, and the subsequent mixture was shaken again. After phase separation, the (bottom) DCM layer containing LSD was carefully pipetted to a fresh vial, the solvent removed by evaporation, and the remaining solid resuspended in a solution of 500 µL Ag colloid, 10 µL of 1 mol/L HCl, and 50 µL of 0.9% NaCl. The contents were gently mixed and measured with MISA.

This procedure converts LSD into its free base form, which is selectively solvated in DCM and can be separated from water-soluble toner and food dye interferents.

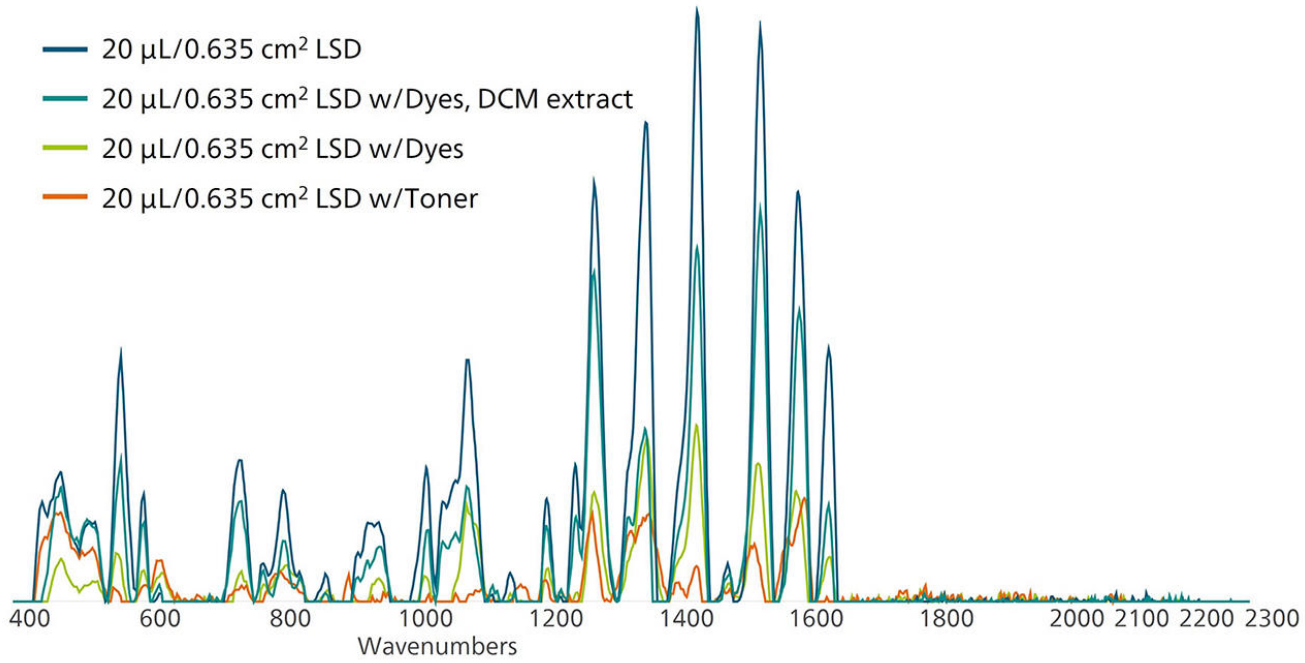
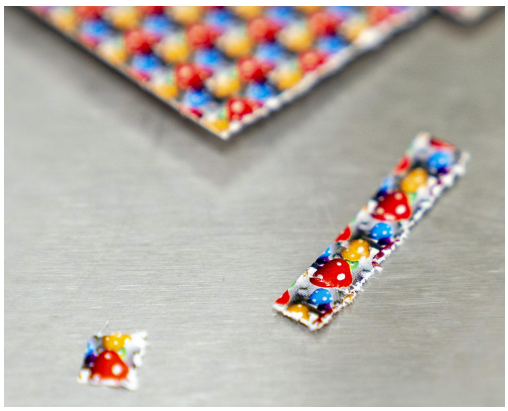


Figure 2. LSD reference (blue), as compared with samples taken directly from colored paper and samples that have been extracted.

LSD ON ARTWORK BLOTTER PAPER

Simulated real-life detection of LSD was conducted with commercially available sheets of perforated artwork blotter paper. Again, 0.635 cm^2 squares of blotter were saturated with 20 µL of 1 mg/mL LSD solution. Initial aqueous extraction of LSD-saturated blotter squares revealed a complex spectrum that appeared to be a mixture of LSD and another compound (green spectrum in Figure 3). Aqueous extraction of an untreated blotter square and library matching within the SERS Library - Illicit Materials indicated correlation with high confidence (HQI = 0.79) to rhodamine 6G. Rhodamine 6G is a fluorescent dye that is used in inks and sometimes as a colorant in counterfeit foods (see AN-RS-014 for more information). It is strongly Raman/SERS-active and can obscure the LSD signal.



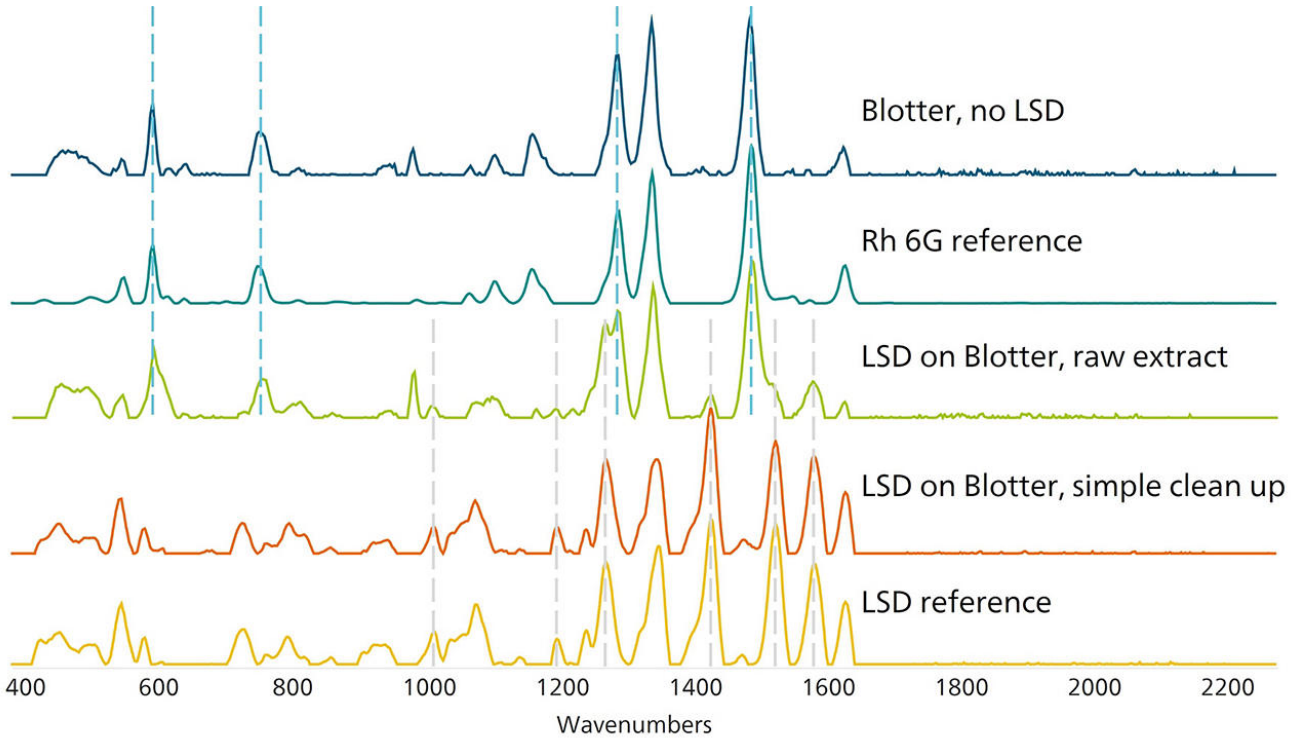


Figure 3. Ultimately, comparison of experimental spectra with two references demonstrates how effective a simple sample extraction step can be in the detection of LSD on paper substrate.

To separate LSD from rhodamine 6G, a blotter square was placed in a glass vial and shaken with 500 µL of water, next with 20 µL of 1 mol/L tartaric acid, and then with 0.5 mL DCM. The aqueous phase (top layer) was pipetted into a separate vial containing 500 µL Ag colloid and 50 µL 0.9% NaCl for SERS measurement. Treatment with tartaric acid results in formation of the tartrate salt of LSD which is soluble in water and can be separated from rhodamine 6G, which remains in the DCM layer. This simple clean-up procedure resulted in a very strong and clean LSD signal (orange spectrum in Figure 3). This experiment demonstrates that colored interferents on commercial blotter sheets may be easily removed for sensitive SERS detection of LSD.

EXTRACTION SUMMARY

The two procedures below illustrate the appropriate selection of solvent for the separation of LSD from different types of colorants that may hinder detection. In a real-world scenario, a wide variety of dyes may be present. The best approach for each sample may involve experimentation with both of extraction summaries included here:

LSD with water-soluble colorant

1. Shake with dilute NaOH and DCM
2. Carefully remove (bottom) DCM layer to a separate vial and evaporate solvent
3. Resuspend sample in colloid, HCl, and NaCl
4. Measure SERS

LSD with solvent-soluble colorant

1. Shake with dilute acid and DCM
2. Carefully remove (top) aqueous layer to a separate vial
3. Add colloid and NaCl
4. Measure SERS

CONCLUSION

SERS capabilities on MISA and MIRA XTR DS provide rapid onsite identification of LSD in suspect street samples with simple, user-friendly procedures. Uniquely, this application provides alternative extractions as a way of addressing real-world situations while keeping sample clean-up as simple as possible. This provides a rapid and portable alternative to conventional analytical laboratory testing procedures and their associated expenses for time, materials, and personnel. Metrohm's state-of-the-art test solutions continue to support detection and regulation of illicit substances.

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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.

MIRA XTR Basic

MIRA XTR is an alternative for high power 1064 nm systems. Powered by advanced computational processing, MIRA XTR uses a more sensitive 785 nm laser light along with XTR algorithms to eXTRact the Raman data from the sample fluorescence. MIRA XTR also features Orbital Raster Scanning (ORS) to provide better coverage of the sample increasing the accuracy of the results.

The Basic package is a starter package that contains the basic components required for operating the MIRA XTR. The Basic package includes a Calibration Standard and Intelligent Universal Attachment. Class 3B operation. MIRA XTR supports Metrohm handheld Raman libraries.

MIRA XTR Advanced

MIRA XTR is an alternative for high power 1064 nm systems. Powered by advanced computational processing, MIRA XTR uses a more sensitive 785 nm laser along with XTR algorithms to eXTRact the Raman data from the sample fluorescence. MIRA XTR also features Orbital Raster Scanning (ORS) to provide better coverage of the sample increasing the accuracy of the results.

MIRA XTR Advanced package includes a Calibration Standard, Intelligent Universal Attachment, Right-angle Attachment, Vial Attachment, and MIRA SERS Attachment. A complete package for any type of analysis. Class 3B operation. MIRA XTR supports Metrohm handheld Raman libraries.

ID Kit - Ag NP

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