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 DS (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.

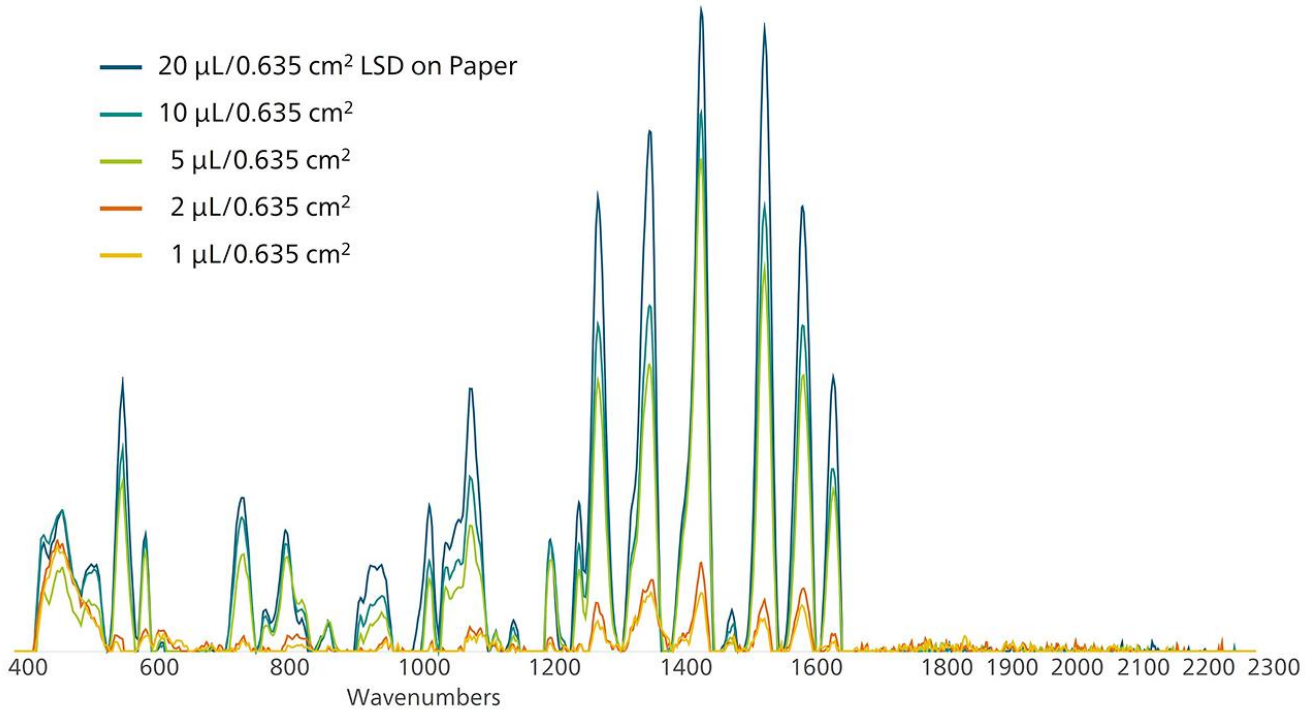


Figure 1. Reference LSD on chromatography paper concentration profile.

LSD ON COLORED PRINTER PAPER

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.

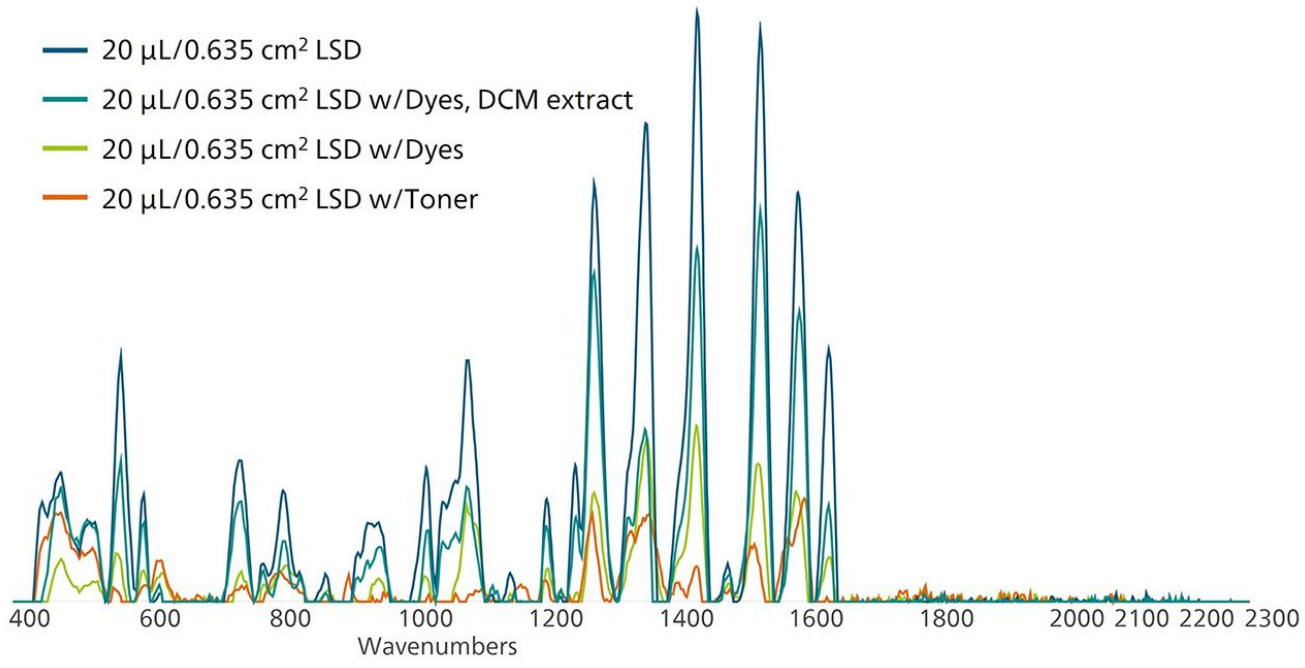
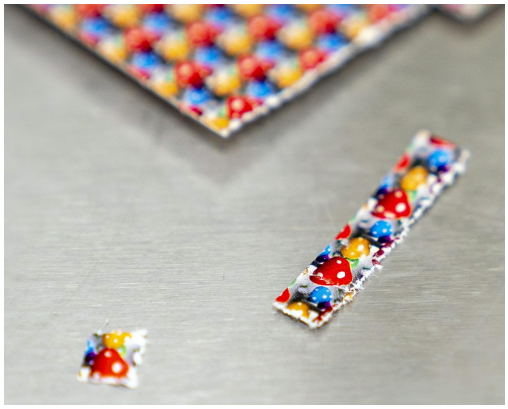


Figure 2. LSD reference (blue), as compared with samples taken directly from colored paper and samples that have been extracted.

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 Organic Chemicals v3 KnowItAll® Raman Spectral Library (Handheld) from Wiley 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.



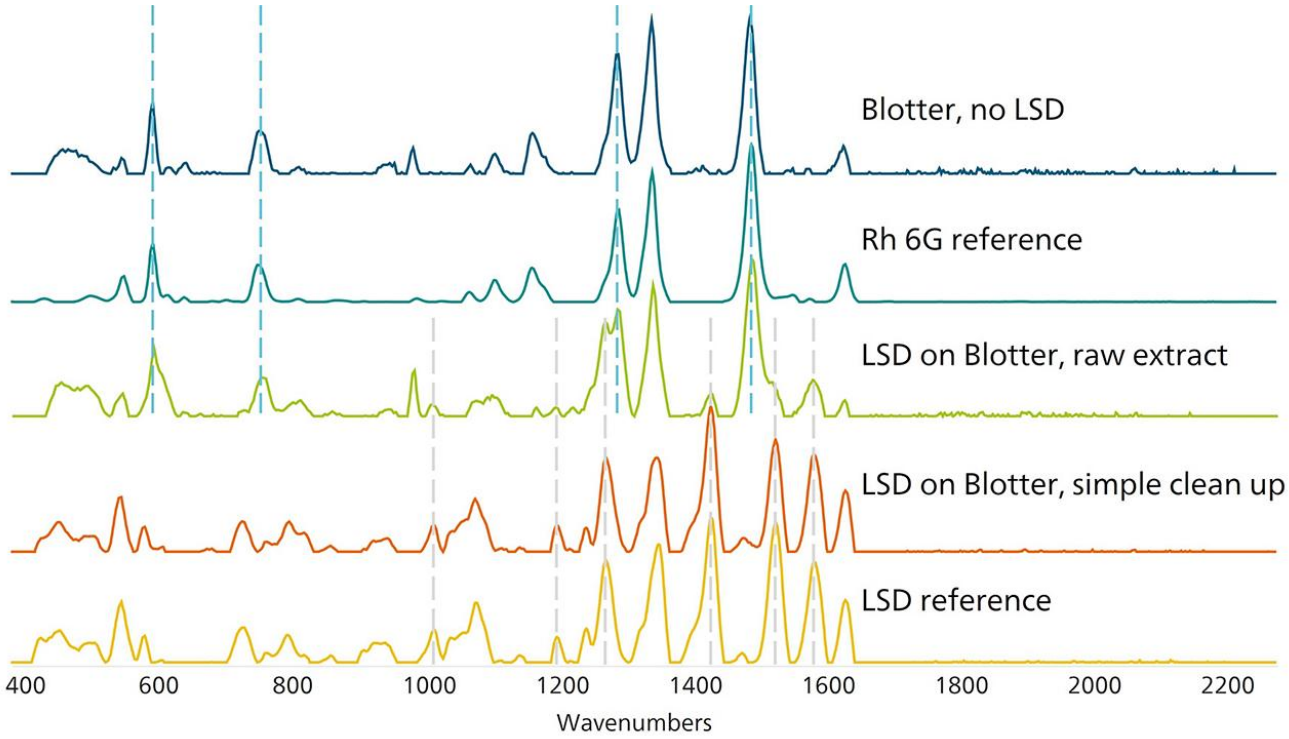


Figure 3. Ultimately, comparison of experimental spectra with two references demonstrates how effective a simple sample extraction step can be in the detection of LSD on paper substrate.

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) est un système d'analyse portable hautement performant pour détecter ou identifier rapidement des traces de substances illicites, d'additifs et de contaminants alimentaires. MISA possède un spectrographe très efficace doté de la technologie ORS (Orbital Raster Scan) unique de Metrohm. Son encombrement est minimal et la durée de vie prolongée de la batterie en fait le système d'analyse idéal pour les tests sur site ou les applications de laboratoire mobiles. MISA propose divers accessoires laser de classe 1 pour des options d'échantillonnage flexibles. L'appareil d'analyse peut fonctionner via la connectivité BlueTooth ou USB.

Le module MISA Advanced est un ensemble complet qui permet à l'utilisateur d'effectuer des analyses SERS avec les solutions de nanoparticules de Metrohm et des bandelettes réactives P-SERS.

Le module MISA Advanced contient un embout de flacon MISA, un embout P-SERS, un standard de calibrage ASTM, un câble USB mini, un bloc d'alimentation USB et le logiciel MISA Cal pour le fonctionnement de l'appareil MISA. Une mallette de protection robuste est également fournie pour ranger l'appareil et ses accessoires en toute sécurité.

MIRA XTR Basic

MIRA XTR est une alternative pour les systèmes haute puissance 1 064 nm. Piloté par un traitement informatique avancé, MIRA XTR utilise une lumière laser de 785 nm plus sensible ainsi que des algorithmes XTR pour eXTRaire les données Raman de la fluorescence de l'échantillon. MIRA XTR dispose également d'un balayage de trame orbital (ORS, Orbital Raster Scanning) pour fournir une meilleure couverture de l'échantillon, augmentant ainsi l'exactitude des résultats.

Le package de base est un module d'entrée de gamme qui contient les composants de base nécessaires au fonctionnement du MIRA XTR. Le package de base comprend le standard de calibrage, l'embout universel intelligent et la bibliothèque de substances illicites. Fonctionnement en classe 3B.

MIRA XTR Advanced

MIRA XTR est une alternative pour les systèmes haute puissance 1064 nm. Piloté par une IA et une technologie d'apprentissage machine (« Machine Learning ») avancées, MIRA XTR utilise un laser de 785 nm plus sensible ainsi que des algorithmes XTR pour eXTRaire les données Raman de la fluorescence de l'échantillon. MIRA XTR dispose également d'un balayage de trame orbital (ORS, Orbital Raster Scanning) pour fournir une meilleure couverture de l'échantillon, augmentant ainsi l'exactitude des résultats.

Le pack MIRA XTR Advanced comprend standard de calibrage, embout universel intelligent, embout à angle droit, support pour flacons et accessoire SERS MIRA. Un package complet pour tous les types d'analyse. Fonctionnement en classe 3B.

Kit d'identification – nanoparticules d'argent (Ag NP)

Le kit d'identification Ag NP comprend les composants nécessaires à un utilisateur Mira/Misa pour une analyse SERS avec une solution d'argent colloidal. Le kit se compose d'une spatule à usage unique, d'une pipette compte-gouttes, d'un petit flacon d'échantillon et d'un flacon d'argent colloidal.