Application Note AN-RS-036

藏红花中有毒染料的痕量检测

Protecting consumer safety with MISA

Saffron, a precious spice comprised of dried stigmas from the purple Crocus sativa flower, is prized for its many health benefits and for its distinctive color, aroma, and delicate flavor. It is the most expensive spice in the world by weight, due to the labor- and time-intensive process of collecting individual filaments by hand. Saffron quality in the international trade market is certified under ISO 362-1. However, illicit producers sell low-grade or counterfeit saffron to unsuspecting consumers and reap substantial profits. The challenge in authenticating saffron is due to the variety of strategies used to mimic a pure product, including dyes and the inclusion of flower parts from different species. Successful methods for authentication of saffron typically require complex analytical methodologies in combination with chemometric methods, which does not address the rising demand for cost-effective, on-site analysis and interdiction of counterfeit saffron in the field. SERS (Surface-Enhanced Raman Scattering) detection of a toxic dye (Sudan 1) used to adulterate saffron demonstrates the power of MISA (Metrohm Instant SERS Analyzer) for simple, portable food authentication in this Application Note.

AUTHENTICATION OF SAFFRON

The most common form of saffron adulteration is the marketing of dyed and dried stamens and stigmas from other flower species to imitate saffron's distinctive visual and sensory properties. In this application, crocin, a carotenoid ester that is primarily responsible for saffron's distinct coloration, is extracted and compared with Sudan 1, an orange-red azo dye and a known carcinogen. Sudan 1 is banned for use in foods worldwide, yet is frequently used for the illicit coloring of costly spices. In a manner consistent with saffron counterfeiting, non-saffron flower parts are dyed and mixed with authentic saffron for this application. This mixture is extracted and compared to both saffron and Sudan 1 standards to demonstrate the ability of SERS to differentiate these strongly colored compounds.

MATERIALS AND METHODS

High-quality Negin saffron from Iran was purchased from a commercial supplier. Plant material used for simulating saffron adulteration with biological material consisted of dried stigmas and stamens harvested from flowers purchased at a local grocer. Sudan 1 was sourced from a chemical supplier. Raman spectra were collected directly from purchased saffron, placed in a glass vial, and inserted into the vial holder on MISA. A SERS reference spectrum for saffron required extraction of 100 mg of pure saffron with 1 mL of methanol, then addition of 100 µL each of extract and 0.5 mol/L NaCl to 800 µL of Au nanoparticles in a glass vial. The SERS sample was mixed, inserted into the vial holder, and analyzed with the SERS OP on MISA. SERS analysis of saffron adulterated with Sudan 1 consisted of a 1:1 (w/w) mixture of pure saffron and flower parts which had been soaked in a 1 mg/mL solution of Sudan 1 in methanol and dried. Extracts for analysis were prepared as for pure saffron above.

RESULTS AND DISCUSSION

Saffron can be detected directly with Raman analysis, although authentication would likely require a combination of Raman and chemometrics. This is primarily because highly colored materials, such as the crocin compounds that lend their color to authentic saffron and the dyes used in counterfeit products, can exhibit fluorescence that overwhelms the Raman signal.

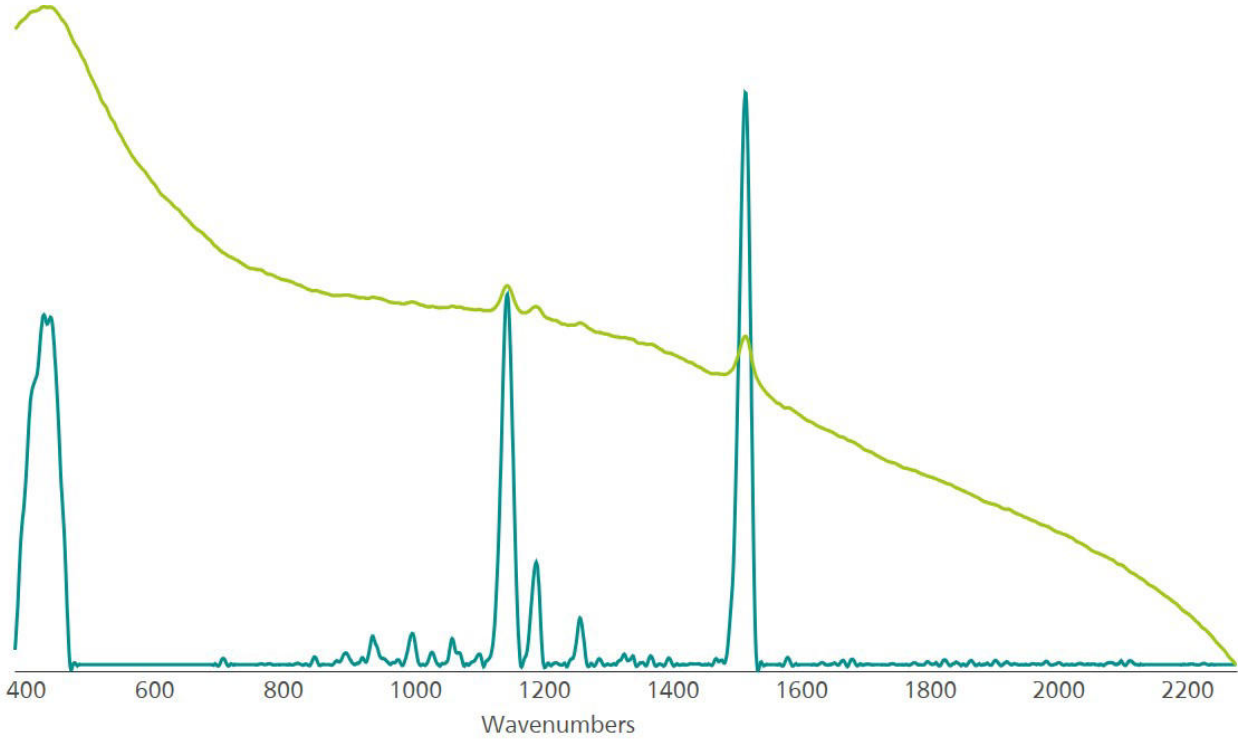

Figure 1. Saffron's distinctive Raman spectrum: unaltered (top) and baselined (bottom).

This is demonstrated in Figure 1, where the unaltered Raman spectrum of saffron (top) displays the broad, distinctive signal of fluorescence. The baselined spectrum (bottom) contains signature peaks from crocin, but of low intensity. This is a classic example of an application where SERS can more sensitively evaluate a specific analyte, because fluorescence has less of an influence on the SERS spectrum.

The SERS spectrum for pure saffron provides a useful standard for evaluating the authenticity of saffron, as shown in the bottom spectrum in Figure 2.

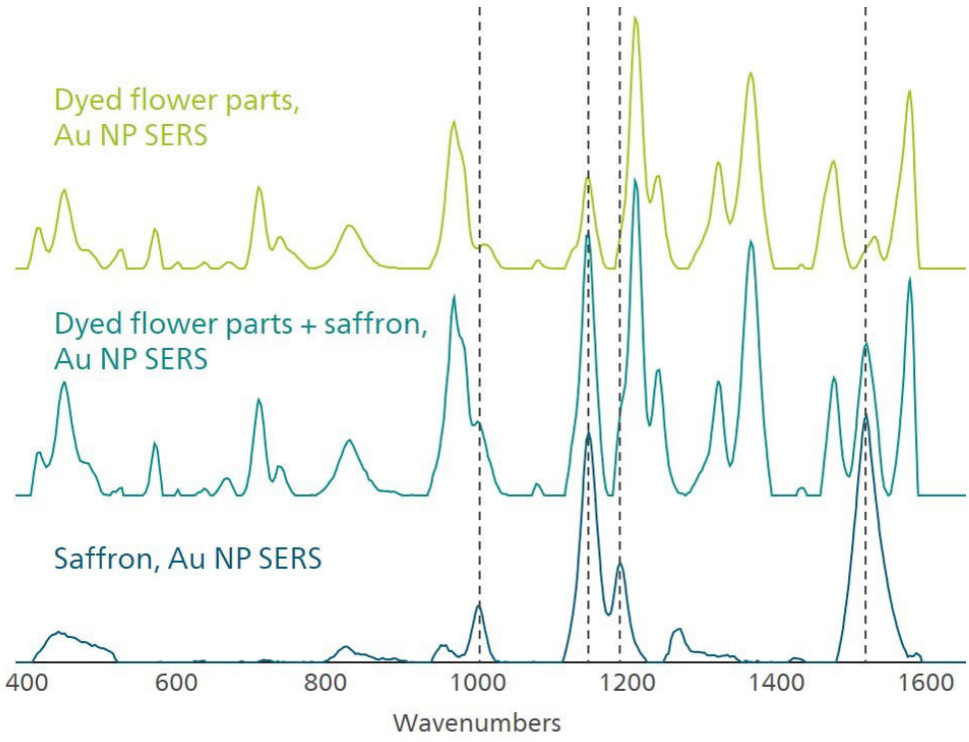

Figure 2. Visual confirmation in the SERS spectra of Sudan 1 (top), Saffron (bottom), and an experimental mixture of both.

The acquired peak profile agrees with reported spectra of crocin extracted from saffron. Sudan 1 at a concentration of 0.01 mg/mL also has a distinct and complex SERS spectrum, as seen in the top spectrum in Figure 2. When these distinct spectra are overlaid with the SERS spectrum of a mixture of pure and counterfeit saffron, both pure saffron and Sudan 1 can be distinguished. Finally, detection limits are important for any trace detection application with SERS. Serial dilutions of 1 mg/mL Sudan 1 dye stock solution in methanol were used to demonstrate detection of Sudan 1 at concentrations as low as 500 ng/mL (Figure 3). With this level of sensitivity, the use of virtually any amount of this dye for saffron authentication can be detected with MISA.

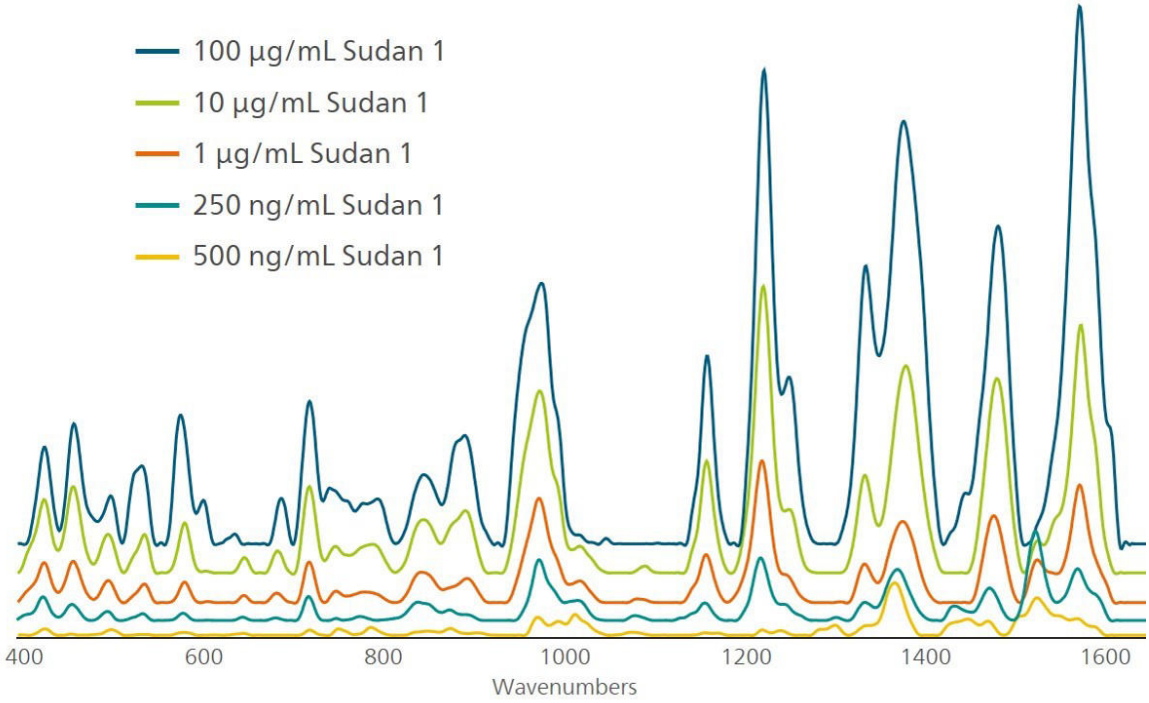

Figure 3. Concentration profile for Sudan 1, demonstrating MISA's detection capabilities down to 500 ng/mL.

CONCLUSION

Herein, saffron is authenticated and Sudan 1 is detected by SERS in a demonstration of the growing potential of portable Raman spectroscopy for the frontline defense of food safety and integrity. Given the strong SERS response of chemical structures common to dyes and artificial food colorants, this application is likely to extend to other coloring agents used to enhance spices and mask inferior product. MISA from Metrohm Raman holds great promise as a versatile tool for protecting food safety.

CONTACT

瑞士万通中国
北京市海淀区上地东路1号
院1号楼7层702
100085 北京
marketing@metrohm.com.cn

CONFIGURATION

MISA Basic

Metrohm Instant SERS Analyzer (MISA) 是一款高性能、便携式分析系统,可快速检测/鉴定非法物质、食品添加剂和微量食品污染物。MISA 的特点是配备了 Metrohm 的轨道光栅扫描 (ORS) 技术设备的光谱仪。其空间需求小和并且电池寿命有所延长,适用于现场测试或移动实验室应用。MISA 提供各种 1 级激光附件,可灵活选择取样。该分析仪可通过 BlueTooth 或 USB 连接运行。

MISA Basic 套件的作用是让用户能够根据自己的需要调整 MISA。这是一个入门级套件,其中包含使用 Metrohm 的纳米颗粒溶液进行 SERS 分析所需的基本组件。

MISA Basic 套件包含了 MISA 仪器、一个 MISA 小管附件、一个 USB 迷你电缆、一个 USB 供电单元和用来运行仪器的软件 MISA Cal。

MISA Advanced

Metrohm Instant SERS Analyzer (MISA) 是一款高性能、便携式分析系统,可快速检测/鉴定非法物质、食品添加剂和微量食品污染物。MISA 的特点是配备了 Metrohm 的轨道光栅扫描 (ORS) 技术设备的光谱仪。其空间需求小和并且电池寿命有所延长,适用于现场测试或移动实验室应用。MISA 提供各种 1 级激光附件,可灵活选择取样。该分析仪可通过 BlueTooth 或 USB 连接运行。

MISA Advanced 套件是一个完整套件,其作用是让用户能用 Metrohms 纳米颗粒溶液和 P-SERS 试剂条进行 SERS 分析。

MISA Advanced 套件包含了一个 MISA 小管附件、一个 P-SERS-附件、一个 ASTM 校正标准件、一个 USB 迷你电缆、一个 USB 供电单元和用于运行 MISA 仪器的 MISA Cal 软件。还随供了一个用来安全保管仪器和附件的坚固保护箱。

Misa

与 15 x 26 mm 大小的玻璃样品瓶适配。Misa 样品瓶附件可用于测量 Metrohm 的金银材质 SERS 纳米颗粒。搭配 1 级激光器使用。