Application Note AN-RS-050

Trace detection of mercaptans in fuel

Safe, rapid detection of mercaptans with Raman spectroscopy

Mercaptans are organic sulfur compounds with the general formula R–SH. They naturally occur in crude oil and cannot be effectively removed through the distillation process [1,2]. Elevated concentrations of mercaptans are corrosive and can reduce the thermal stability of fuels, leading to problems with engine health, performance, and increased pollution. Consequently, ASTM D1655 sets the maximum allowable concentration of mercaptans in jet fuel at 30 mg/L (ppm) [3].

Mercaptans are Raman active and at high concentrations they can be identified and quantified by analyzing their Raman spectra. However, the trace amounts of mercaptans found in fuels are generally below the limit of detection (LOD) of standard Raman spectroscopy. To overcome this limitation, Surface-Enhanced Raman Scattering (SERS) can be employed, which significantly enhances the Raman signal and enables the detection and quantification of mercaptans at trace levels.

CURRENT METHODS FOR MERCAPTAN ANALYSIS

Standard methods such as potentiometric titration (ASTM D3227), ultraviolet fluorescence (ASTM D5453), gas chromatography (GC), and high-performance liquid chromatography (HPLC) are used to quantify low concentrations of mercaptans. However, these methods are time consuming and costly, require skilled personnel that can perform complex procedures, and generate chemical waste. Conversely, Raman spectroscopy is an easy to use, cost-effective analytical technique with quick results.

MERCAPTAN ANALYSIS WITH SERS

SERS (Surface-Enhanced Raman Scattering) is ideal for trace materials below the LOD of traditional Raman spectroscopy, such as mercaptans found in fuels. SERS amplifies the Raman signal of molecules bound to nanoparticles through electromagnetic field enhancement generated from the excitation laser-nanoparticle interaction. This enhanced signal exceeds the sensitivity of standard Raman techniques and enables rapid identification and quantification of trace amounts of chemicals.

Additionally, SERS requires minimal training, it uses very small sample volumes (typically less than 20 µL), and it improves safety by minimizing exposure risks and waste disposal concerns.

SAMPLE PREPARATION

Methyl mercaptan (MM; 2,000 mg/L in toluene) was serially diluted with paraffin oil. Dilute samples (5 µL) were applied to Metrohm's silver paper SERS (Ag P-SERS) substrates and allowed to rest for five minutes. After resting, SERS data was collected with MIRA XTR (**Figure 1**). Experiment samples and conditions are summarized in **Table 1**.

Figure 1. SERS is easily implemented on any 785 nm Raman instrument with dedicated substrates. Metrohm's MIRA XTR and P-SERS substrates are a convenient, portable, and sensitive solution.

Table 1. Samples and experimental conditions for the SERS determination of trace MM in fuels.

Instrument	MIRA XTR		
Software	Vision		
Calibration Samples	Conc.	0.00, 0.05, 0.10, 0.25, 0.50, 1.00 mg/L (ppm)	
	Method	Laser: Time: Averages:	100% (~50 mW) 1 sec 10
Validation Samples	Conc.	0.00, 0.05, 0.10, 0.25, 0.50, 1.00 mg/L (ppm)	
	Method	Laser: Time: Averages:	100% (~50 mW) 1 sec 3

RESULTS

The Raman spectrum of the MM standard solution only displays peaks attributed to toluene, the solvent matrix. No mercaptan-specific peaks are observed, indicating that a concentration of 2,000 mg/L (ppm) is too low for detection by standard Raman spectroscopy (**Figure 2a**). However, after analysis with Ag P-SERS, the Raman band at 675 cm – 1 associated with S–C stretching becomes detectable even at 100 ppm (**Figure 2b**) and was observable down to 0.05 ppm (50 ppb; **Figure 2c**). This result suggests that SERS enables the detection of mercaptan at trace levels significantly below the ASTM limit of 30 ppm [**3**].

A calibration curve for low-concentration MM was developed and validated against samples measured by different data collection methods (**Figure 3**). With an R^2 of 0.975, the model effectively captures the relationship between peak intensity and concentration. The model's PRESS (predicted residual error sum of squares) value of 0.0632 is high in order to distinguish subtle concentration changes between 0.00 and 0.05 ppm (50 ppb) but is sufficient for differentiating samples with increments of >0.05 ~ 0.10 ppm. The calibration model predicts the concentration of validation sets with good accuracy, achieving an R^2 of 0.962 and a PRESS value of 0.053. The validation curve was adjusted for bias and slope using Vision software, optimizing sample validation. These results confirm that MIRA XTR, coupled with Ag P-SERS substrates, can be effective for quantitative analysis of low-concentration MM.

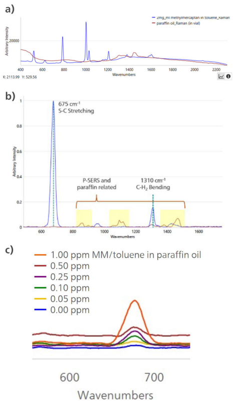

Figure 2. Raman spectra of a) the MM standard and paraffin oil, b) Ag P-SERS substrates with 0.00 and 100.00 mg/L (ppm) MM, and c) Ag P-SERS substrates with 0.00, 0.05, 0.10, 0.25, 0.50, and 1.00 mg/L (ppm) mercaptan.

A calibration curve plateau above 1 ppm (data not shown) suggests that the adsorption efficiency of MM on the Ag substrate declines at higher concentrations. This, combined with the low detection limit, indicates a high affinity of mercaptans for the Ag P-SERS substrate. Thus, dilution may be required to accurately quantify higher mercaptan concentrations, such as fuels containing 30 ppm mercaptans.

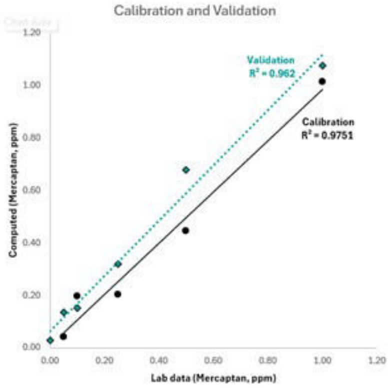

Figure 3 Calibration and Validation curves of MM across the concentration range of 0.00–1.00 mg/L (ppm).

CONCLUSION

Coupling MIRA XTR with Ag P-SERS substrates permits detection of trace mercaptan concentrations down to 0.05 ppm (50 ppb). This very low detection limit exceeds that of traditional methods and enables detection of mercaptan concentrations well below the ASTM standard [**3**]. A simple, fast analysis with SERS provides a safe, efficient, and highly sensitive solution for mercaptan analysis in complex fuel matrices.

REFERENCES

1. Carroll, J. J. *Natural Gas Hydrates: A Guide for Engineers*; Gulf Professional Pub., 2003.
2. *Shale Oil and Gas Handbook*; 2016.
3. *D1655 Standard Specification for Aviation Turbine Fuels*. https://www.astm.org/d1655-22.html (accessed 2025-02-03).

CONTACT

117702
100085

marketing@metrohm.com.cn

CONFIGURATION

MIRA XTR Advanced

MIRA XTR 是高功率 1064 nm 系的替代品。在先的算理的支持下,MIRA XTR 使用更敏的 785 nm 激光器和 XTR 算法从品光中提取 Raman 数据。MIRA XTR 配有道光栅描 (ORS) 技,可更好地覆盖品,从而提高果的准性。

MIRA XTR Advanced 套件包括校正准件、智能通用附件、直角附件、品瓶附件和 Mira SERS 附件。用于任何型分析的完整套件。3B 操作。MIRA XTR 支持瑞士万通手持式拉曼功能。

SERS Discovery Kit

SERS 分析入套件,包含金和 P-SERS 以及体。