Lightnovo

APPLICATION NOTE

Quantification of toxic methanol in vodka

INTRODUCTION

Methanol is a deadly poison contents in low quality or counterfeit alcoholic drinks. It's a serious problem can be harmful or even lethal. Poisonings by toxic chemicals as methanol occur all over the world.
In this situation it is advantageous to have a reliable and rapid method for methanol identification and quantification.
Raman spectroscopy is a powerful method for material identification that enables rapid, noncontact and non-destructive analysis that can be performed through the glass.

TECHNOLOGY

Raman spectroscopy provides a unique opportunity to study the chemical composition of materials at the microscale.
Such capabilities come at the cost of extremely high requirements for instrumentation: lasers with stabilization of wavelength and power, low noise spectroscopic sensors, and a large clear aperture of spectrometer's optics. Therefore, demanding Raman spectroscopy and microscopy applications usually require high-end, bulky, and costly Raman instrumentation.
Lightnovo ApS found possible solutions to the most critical Raman miniaturization challenges: need for laser temperature and power stabilization, reduction of sensor dark noise, compensation on pixel-to-pixel quantum efficiency (QE) variation, laser optical isolation and achieving high spectral resolution.

As result a novel optics miniaturization strategy allows us to create **compact Raman spectrometers and microscopes** based on non-stabilized laser diodes, densely-packed optics, and non-cooled small pixel size sensors.
Lightnovo ApS proposed miniaturization concept based on real-time calibration of Raman shift and Raman intensity using an in-built reference channel that collects the Raman spectrum of polystyrene located in the spectrometer. We have demonstrated the miniaturization of the whole device dimensions down to several centimeters and achieved excellent sensitivity, low power consumption, perfect wavenumber and intensity calibration combined with high spectral resolution of around 7 cm^{-1} within the spectral range of 400-4000 cm^{-1}.

Details for miniRaman MRs patent

MATERIALS, SAMPLE PREPARATION AND MEASUREMENTS

Methanol, ethanol and water with the purity of 99.9%, 99.8% and 99.9% were used in this research (manufactured by Sigma-Aldrich , CAS Numbers 67-56-1, 64-17-5 and 7732-18-5, respectively). The temperature of the liquid samples was 25±0.4˚C. The solution of vodka was prepared at concentration ratio 40:60 for ethanol and water. The concentration of components in the methanol-vodka solutions was changed from 0% to 40% of methanol (in volume %). Diluted samples at concentrations 0, 0.1, 0.25, 0.5, 1, 5, 10, 20, 40% with ±0.1% dilution error were prepared with the usage of Eppendorf Pipette Research Plus (volume 100-1000µL). Each sample was stored in glass vials with a screw cap (volume 1.5ml). The whiskey bottle used in the studies was produced by Johnnie Walker, Red Label. Whiskey contains 40% of ethanol. The thickness of glass bottle at the measurement area was ~2.7mm.

Figure 1. Photograph of miniaturized Raman spectrometer measuring whiskey content through the glass bottle

RESULTS

In order to demonstrate the sensitivity and quantification performance of our miniaturized Raman spectrometer we performed measurements of vodka samples with different concentrations of methanol. The raw Raman spectra of water-ethanol solutions with different concentrations of methanol (variation between 0-40%) in the range 400-2300cm^{-1} and 2750-4000cm^{-1} are shown respectively in Figure 2b, 2e. Results of PLS calibration for methanol quantification demonstrate LoD = 0.07%, and LoQ = 0.25% (Figure 2l-2p). To the best of our knowledge, the lowest previously reported LoD that was obtained by research grade Raman spectrometer with deep cooling CCD was 0.23–0.39%[1]. However, according to European regulations, methanol concentration in vodka products should be below 0.5%[2]. This means that LoD should be below 0.1% to perform routine methanol quantification through the bottle with vodka. Now, such methanol control becomes possible with our highly sensitive miniaturized Raman spectrometer.

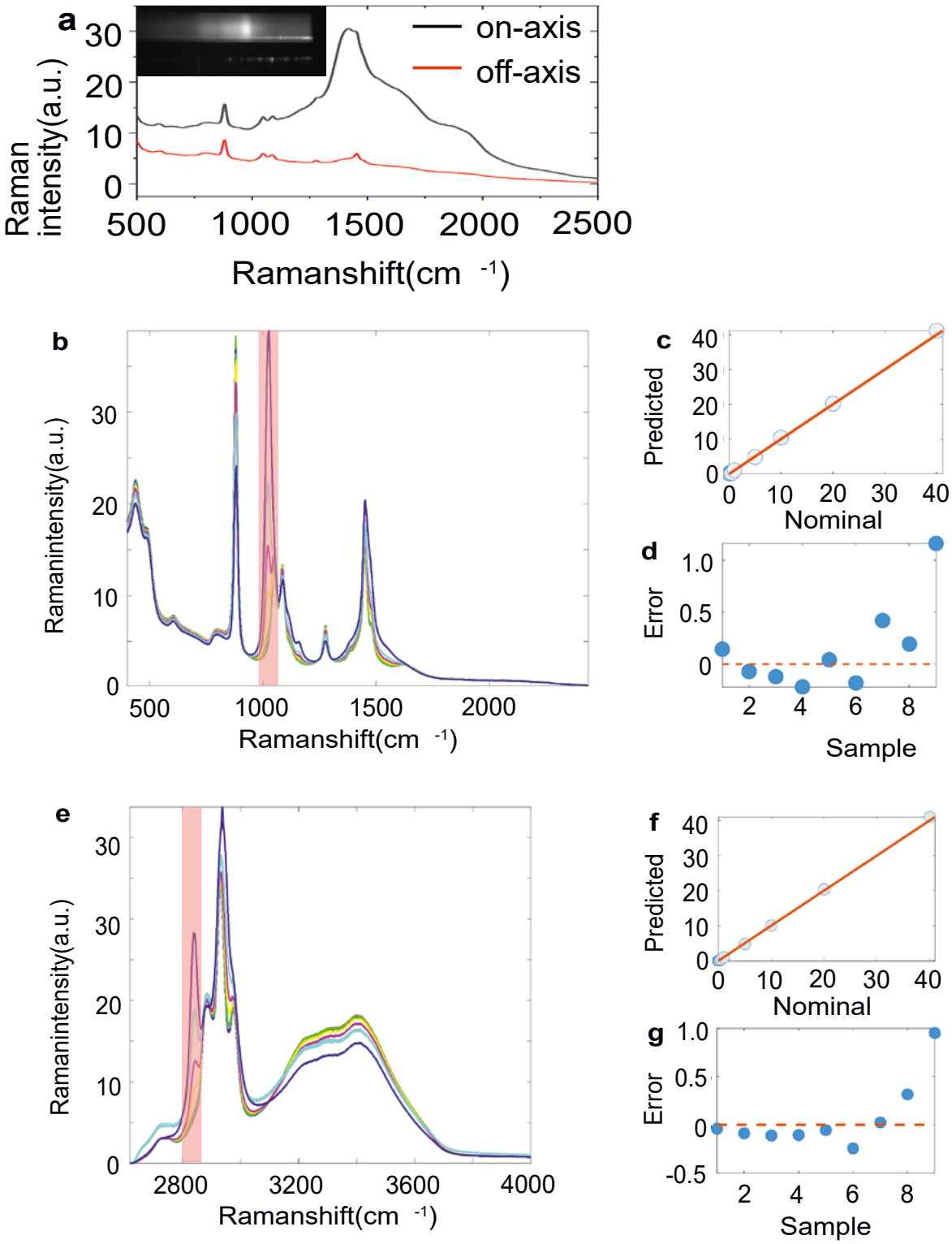


Figure 2.

a) Raman spectrum of whiskey measured by miniaturized Raman system through the glass bottle with on-axis (black curve) and off-axis (red curve) laser beam delivery that demonstrates SORS benefit to avoid the contribution of fluorescence from glass bottle (upper right image is a screen shot from CMOS sensor in the case of off-axis laser beam delivery),

b), e) Raman spectra of water-ethanol solution (40% of ethanol) with different concentrations of methanol (variation between 0-40%) in the range 400-2300cm^{-1} (b) and 2750-4000cm^{-1} (e),

c), d) result of PLS calibration for methanol quantification based on the Raman data in the range 400-2300cm^{-1},

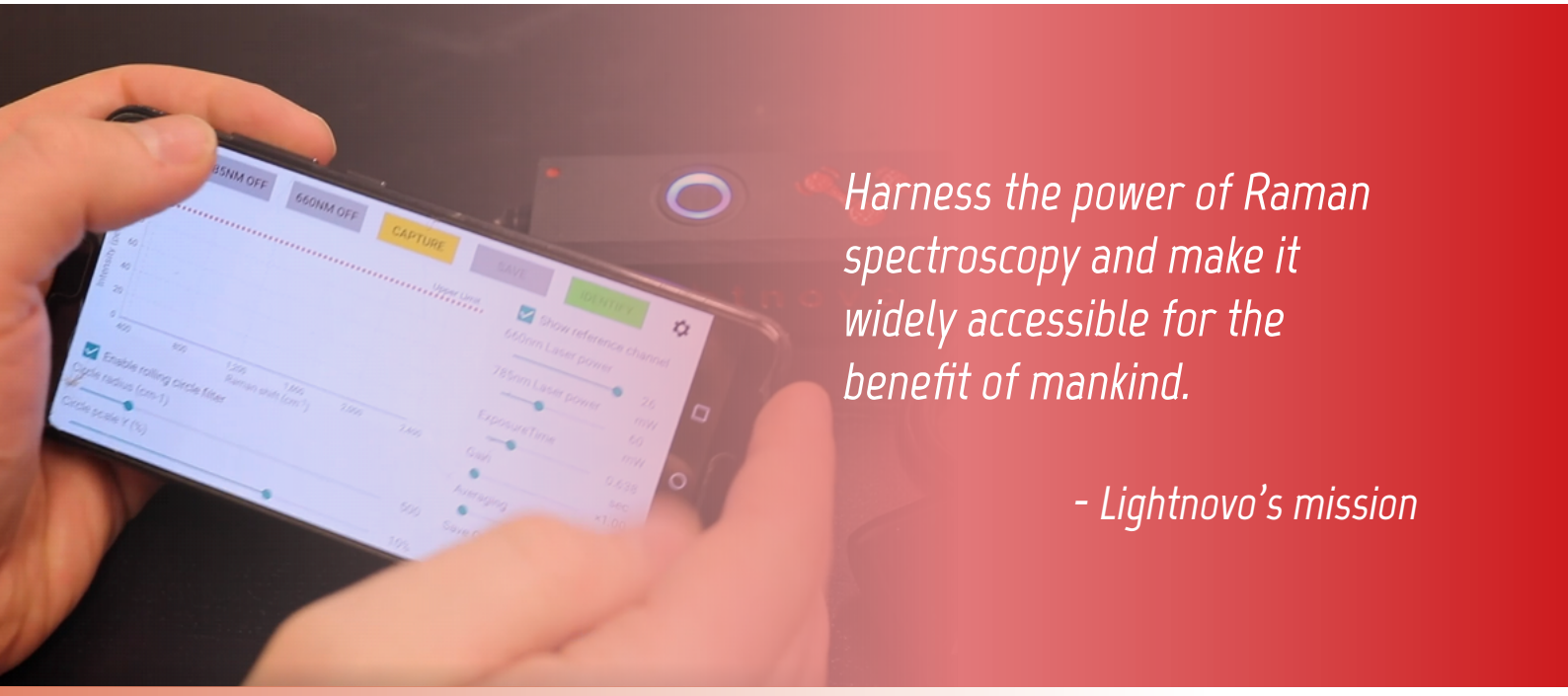
f), g) result of PLS calibration for methanol quantification based on the Raman data in the range 2750-4000cm^{-1}.

CONCLUSION

Lightnovo`s strategy allowed to miniaturize Raman spectrometer down to several centimeters and have achieved excellent sensitivity and premium performance for quantitative analysis.
Lightnovo ApS demonstrated technology for both miniaturizing and democratizing Raman spectrometers, making Raman spectroscopy more accessible to researchers as well as consumers.

LITERATURE

1 Ellis DI, Muhamadali H, Xu Y, Eccles R, Goodall I, Goodacre R. Rapid through-container detection of fake spirits and methanol quantification with handheld Raman spectroscopy. *Analyst* 2019; **144**: 324–330.
2 Paine AJ, Dayan AD. Defining a tolerable concentration of methanol in alcoholic drinks. *Hum Exp Toxicol* 2001; **20**: 563–568.



Harness the power of Raman spectroscopy and make it widely accessible for the benefit of mankind.

- Lightnovo's mission

Lightnovo

Lightnovo ApS
Blokken 15, 1. tv.
3460 Birkerød
Denmark (DK)
CVR: 40979603

+45 71 37 04 10
info@lightnovo.com
https://lightnovo.com