

Development of a Raman detector for hyphenation with high-temperature liquid chromatography and isotope ratio mass spectrometry



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Application Note

Introduction

Due to criminal statistics, product and trademark piracy have raised dramatically in recent years. The critical numbers of fake articles in foodstuffs, pharmacy and cosmetics exhibit potential risks for public health.

Product piracy can be identified by determining the origin and authenticity of the chemical compounds that are part of fake articles. After applying a separation by high-temperature high performance liquid chromatography (HT-HPLC) origin and authenticity of analytes are revealable by isotope ratio mass spectrometry (IRMS). The sole linkage of HT-HPLC and IRMS can be used if the composition of samples is known. The analysis of samples with unknown composition additionally requires the identification of the separated compounds. Especially for this experimental approach we developed a detector based on Raman spectroscopy. The principle of measurement is shown in Figure 1:

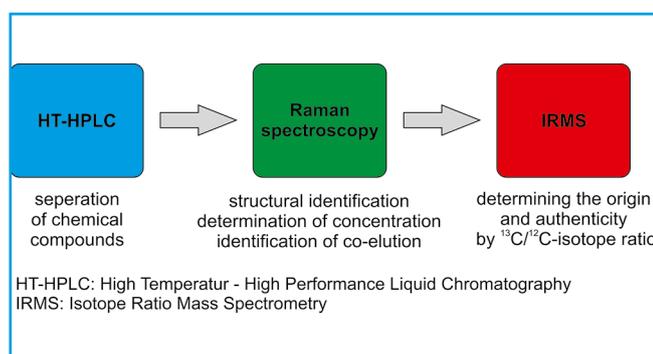


Figure 1: Principle of measurement; determining the origin and authenticity of chemical compounds by linking different analytical techniques.

Experimental setup

The hyphenation of HT-HPLC, Raman detector and IRMS is displayed in Figure 2. The Raman device was set between HT-HPLC and IRMS and operated like a flow cell for online detection. The laser light was guided by the optical fibre 1 to the T-piece 1 which coupled the HT-HPLC capillary tubing, the liquid core waveguide and the optical fibre 1.

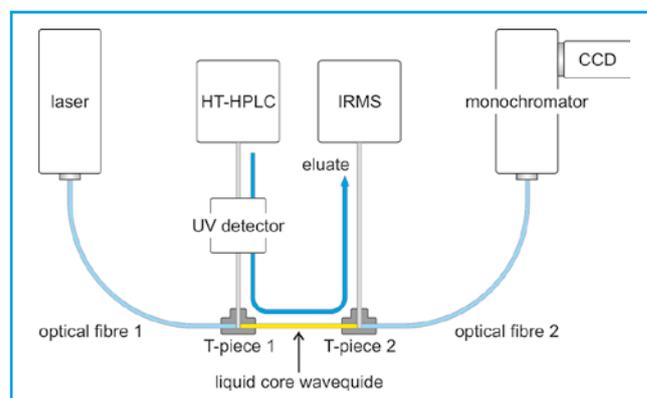


Figure 2: Experimental setup; hyphenation of HT-HPLC/Raman/IRMS.

Raman signals were generated within the liquid core waveguide. The Raman light was collected by optical fibre 2 that directed the scattered light to the monochromator and CCD detector (HoloSpec f/1.8 from Kaiser Optical Systems and Newton DU920P-BV from Andor Technology, Figure 3) for the spectral analysis.

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Results

The applicability of the described setup was tested with a mixture of sulfathiazole and sulfamerazine. The analytes were solved in a 50:50 mixture of water and methanol with a concentration of 100 mg·L⁻¹ for each substance. The injection volume on column was 20 µL. With a laser power of 2 W and a detection time of 10 s we could observe Raman spectra that are displayed in Figure 5.

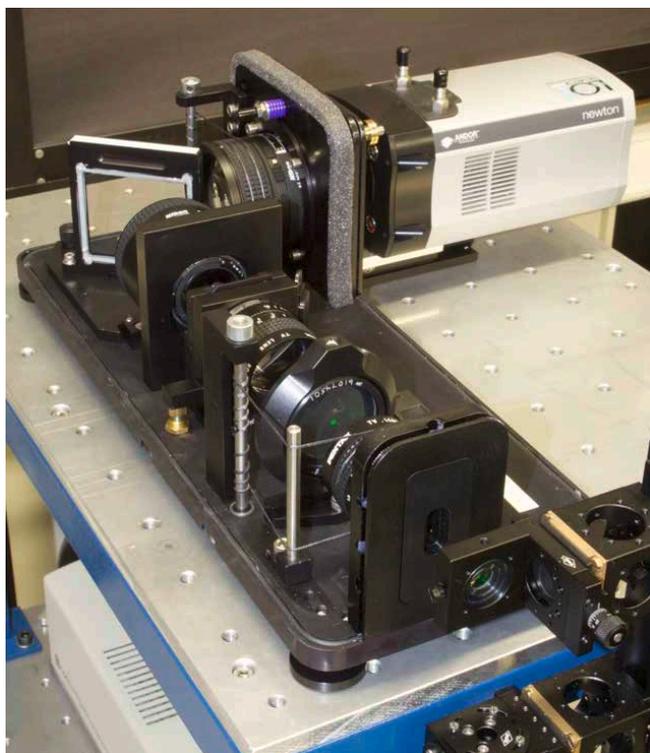


Figure 3: Kaiser HoloSpec monochromator (open view) and Andor Newton CCD detector.

Figure 4 shows a photo of the flow cell device and the liquid core waveguide during Raman measurement.

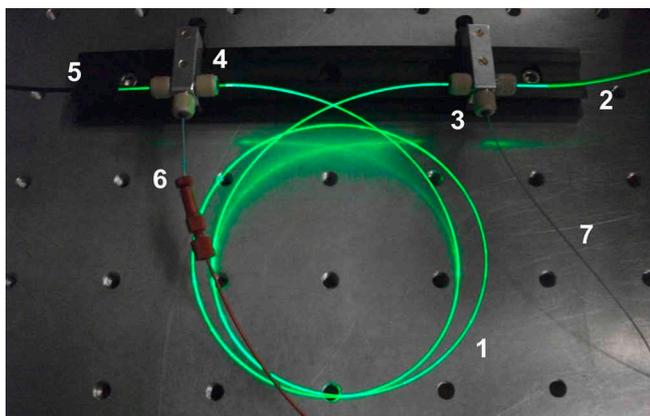


Figure 4: Flow cell device during Raman measurement, excitation wavelength: 532nm, 1: Liquid core waveguide with ID=250µm, length=1m, 2: Optical fibre 1, 3: T-piece 1, 4: T-piece 2, 5: Optical fibre 2, 6: Capillary tubing from HT-HPLC, 7: Capillary tubing to IRMS.

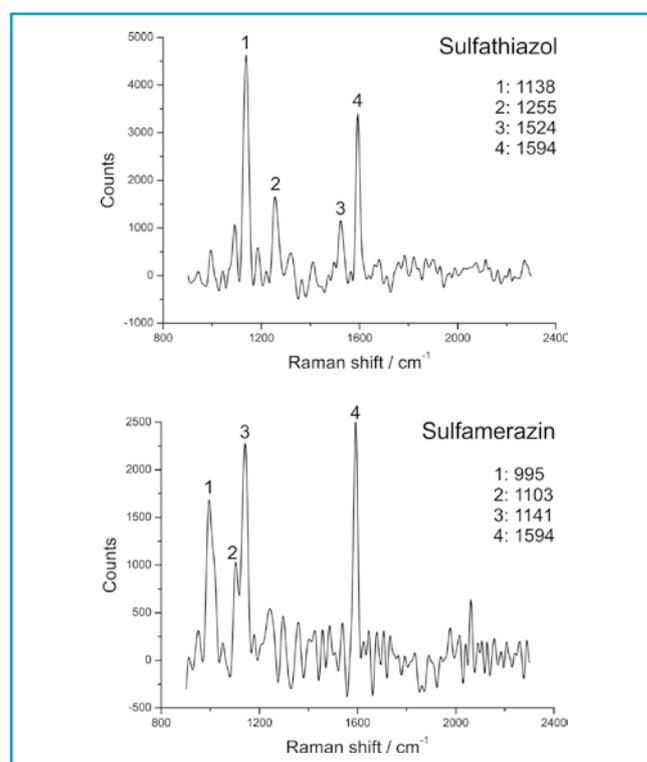


Figure 5: Online Raman measurement of sulfathiazole and sulfamerazine after separation by HT-HPLC.

Conclusion

Raman spectroscopy is ideally suited as a novel on-line detection technique for the hyphenation of high-temperature liquid chromatography with isotope ratio mass spectrometry. Analytes can be unambiguously identified by their characteristic Raman spectra. Addicted to the Raman scattering cross section of the analysed substance we currently achieved a limit of detection between 1 – 4 mg·L⁻¹ (< 10⁻⁵ M).

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