

Using Anton Paar's Cora 5001 Raman spectrometer to detect methanol contamination in alcoholic beverages

Relevant for: Food & Beverage

As methanol, a common by-product of fermentation processes and adulterant of alcoholic beverages, poses a risk to consumers health its detection in even low concentration is important. This is easily possible using the Cora 5001 Raman spectrometers.



1 Introduction

Anton Paar's Cora 5001 Raman spectrometer can be used to detect contaminants in alcoholic beverages. One of the most prominent contaminants of such beverages is methanol (MeOH) which has toxic effects and thus poses a risk to consumers health. After ingestion methanol is metabolized to highly toxic compounds such as formaldehyde and formic acid which can cause permanent blindness as it harms optical nerves and can even be fatal after ingestion of about 30 mL. [1, 2, 3, 4] Every year there are several cases of death or blindness due to methanol poisoning all over the world ranging from 20-800 victims per outbreak with approx. 30 % fatality rate. [2, 5]

In some spirits methanol cannot be totally avoided as it is a by-product during fermentation processes and cannot be fully removed by distillation procedures due to its volatility. [4, 5] Such spirits are usually based on potato or fruit origin as those are rich of pectin of which methanol is recovered during fermentation. [4, 5] However, methanol is also known to be intentionally added as it is similar to ethanol in its properties and taste and thus used as adulterant. [4] To prevent health risks there are several standards, regulations and guidelines established. However, regulations vary depending on the country and on the type of spirit. [4] Thus, the maximum levels of methanol that are allowed

vary in a range of about 0.05 -15 g/L related to 100% ethanol. [1, 4]

Cora 5001 offers a fast and non-destructive measurement of spirits which is possible through glass. This enables uncovering of methanol contamination without the need for transportation to analytical facilities and without opening the bottle. If sampling is preferred, e.g. for additional characterization methods or archiving, Cora 5001 Direct offers additional advantages. It is a laser class 1 instrument requiring no laser safety precautions and the implemented autofocus routine facilitates measurements even for untrained personal.

2 Instrumentation and Experimental

As model an ethanol-water mixture was adulterated with methanol. The ethanol-water mixture had an alcohol content of 45 % (v/v) representing beverages like e.g. raki, rum or vodka. The methanol content was varied between 0.05 % and 10 % (v/v). The mixtures were filled and stored in crimped standard glass vials (4 mL; N13). Each mixture as well as reference samples without methanol were prepared in triplicate.



Fig. 1: Cora 5001 with sample compartment is an easy-to-use instrument due to its laser safety class 1, the implemented autofocus routine and its intuitive software

Table 1: Examples of maximum methanol limit for selected spirits and regulations of the European Union, USA and China. [1, 6]

| Type of spirit | Maximum MeOH limit | Ref. |
|---|--------------------|-------|
| Ethanol of agricultural origin | 0.3 g/L* | EU |
| Grape marc spirit, fruit spirit, cider spirit, and perry spirit | 10 g/L* | EU |
| Fruit marc spirit | 15 g/L* | EU |
| Imported brandy | 0.35 % (v/v) | USA |
| Spirits from fermented potatoes | 2.0 g/L* | China |

* expressed in relation to pure ethanol

The samples were measured in random order using a Cora 5001 with sample compartment (see Fig. 1). Focus optimization was performed on the reference sample of the ethanol-water mixture using the autofocus-option. All samples were measured at this position in horizontal rotor orientation within the vial holder accessory. The measurements were performed using an excitation wavelength of 785 nm with a laser power of 450 mW at a constant exposure time for all sample. The exposure time was determined for the sample with the highest ethanol content (reference sample) using the auto-exposure option. Each vial containing a mixture was measured three times. Reference samples were measured ten times per vial. The subtract background option was activated and data was baseline corrected for further analysis.

3 Results

3.1 Quantification of methanol content

Raman spectra obtained from all mixtures are shown in a close-up in Fig. 2 to highlight changes resulting from the varying methanol content. The presented region is the spectral range of interest used for the analysis. For data analysis a python script was applied. However, the implemented custom model "Simple Quantification Tool" can be used as well.

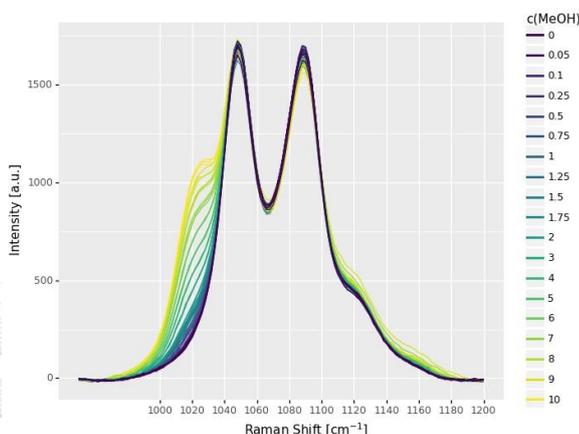


Fig. 2: Raman spectra of samples adulterated with methanol in a concentration range of 0.05 %-10 %. With increasing methanol content, the Raman signal at 1020 cm⁻¹ rises

For quantification the peak height ratios of signals at 1020 cm⁻¹ and 1050 cm⁻¹ were calculated. The peak (or in low concentrations the peak shoulder) around 1020 cm⁻¹ originates from the symmetric C-C-O stretch vibrations of methanol. [6] Compared to pure methanol whose most prominent Raman signal is at 1036 cm⁻¹ the peak is shifted to lower wavenumbers due to hydrogen bond interactions between C-C-O groups and water molecules which are part of the mixture. Depending on the ethanol content of the spirit of interest or consequently its water content the position of this peak can be shifted. The signal at 1050 cm⁻¹ originates from the asymmetric C-C-O stretch vibration of ethanol. [6] Thus, this calculation relates the methanol to the substance of interest in spirits to which limits in regulations refer. There is no need to take the water content which is barely visible in the Raman spectra into account. This makes the calculation of methanol easily transferable to different kinds of spirits. The resulting calibration curve is presented in Fig. 3. There is a linear correlation between the methanol content and the peak height ratio (quantification metric used in this case) which can be used to quantify the methanol content.

3.2 Limit of detection and limit of quantification

To evaluate the capabilities of this analysis the limit of detection (LoD) and the limit of quantification (LoQ) were determined as well. For the calculation of LoD and LoQ the following equation was used [7]:

$$limit = \frac{a \cdot \sigma_{s,ref}}{m}$$

$a = 3$ for LoD

$a = 10$ for LoQ

$\sigma_{s,ref}$ = standard deviation of quantification metric of reference measurements

m = slope of linear calibration curve

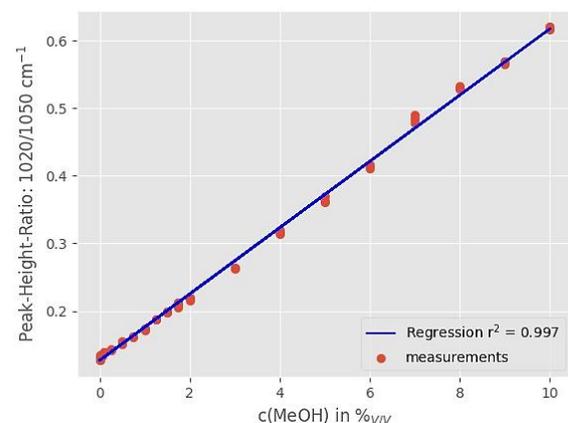


Fig. 3: Linear Correlation of methanol content to the quantification metric, the peak height ratio of the methanol signal at 1020 cm⁻¹ and the ethanol signal at 1050 cm⁻¹

For this experiment a LoD of 0.08 %(v/v) and a LoQ of 0.27 %(v/v) were determined. Taking the ethanol content of the used mixtures into account this corresponds to 1.44 g/L and 4.82 g/L, respectively. Those values are expressed in relation to 100% ethanol content as listed in the EU regulation 2019/787. [1] Although the LoD is above the regulated limit of methanol for ethanol of agricultural origin in the EU it is below the regulated limit of several other groups of spirits such as fruit marc spirits, imported brandy or others as listed in Table 1. Besides, as methanol poisoning often is a result of intentional adulteration, Raman spectroscopy can help to avoid health risk for consumers even for those spirits whose limits are below the detection limit as spirits with health threatening methanol contents can be uncovered.

4 Conclusion

The Cora 5001 Raman spectrometer of Anton Paar offers a fast and non-destructive analysis of contaminated alcoholic beverages to uncover toxic components such as methanol. As the concentration of methanol linearly correlates with changes in the Raman spectrum even a quantification of this adulterant is possible using the peak height ratio of methanol and ethanol signals with calculated LoD and LoQ values in relation to 100% ethanol of 1.44 g/L and 4.82 g/L, respectively. Thus, this technique enables to measure methanol contents below regulated limits for a lot of spirits, especially those which are known to contain methanol due to its production process like spirits of

potato or fruit origin. Even for those spirits whose limits set by governmental regulations are below the detection limit, Raman spectroscopy can be a useful pre-screening tool to avoid severe methanol poisoning.

5 References

- [1] „Regulation (EU) 2019/787 of the European Parliament and of the Council of 17 April 2019,“ *Official Journal of the European Union*, 2019.
- [2] World Health Organisation, „Methanol poisoning outbreaks,“ *information note*, July 2014.
- [3] G. Botelho, O. Anjos, L. M. Estevinho und I. Caldeira, *Processes*, 8, p. 1609, 2020.
- [4] X.-N. Pang, Z.-J. Li, J.-Y. Chen, L.-J. Gao und B.-Z. Han, *J. Food Prot.*, 80 (3), pp. 431-442, 2017.
- [5] E. I. Ohimain, *Springer Plus*, 5, p. 1607, 2016.
- [6] H. Vaskova, *Int. J. Biol. Biomed. Eng.*, 8, pp. 27-34, 2014.
- [7] K. Danzer, H. Hobert, C. Fischbacher und K.-U. Jagemann, *Chemometrik-Grundlagen und Anwendungen*, Springer-Verlag, 2001.

Contact Anton Paar GmbH

Tel: + 49 511 40095-0 | www.anton-paar.com
application-optotec@anton-paar.com