Light-Assisted Detection of Methanol in Contaminated Spirits

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***Abstract*—The growing market of artisanal alcoholic beverages have faced challenges to assess the quality of the commercialized products. Contaminated beverages, resulting not only from an uncontrolled production process but also from deliberate adulteration, may contain nonsafe amounts of methanol leading to risks for consumers. Ethanol and methanol share similar physical-chemical properties. Both are colorless, soluble in water, and they have very close values of density. Although analytical laboratorial methods can precisely determine the alcoholic composition, rapid distinction between them is a conundrum. This paper proposes and compares two methods that can be used to fast detect the contamination of alcoholic beverages with methanol. Despite the proximity between densities of methanol and ethanol, as well as the close refractive indexes of methanol and water, it is shown that these macroscopic parameters can be used together to analyze the beverage composition. Additionally, using the fingerprinting molecular analysis provided by Raman spectroscopy and a statistical procedure based on principal component analysis, it is shown a rapid method for the detection of methanol presence in beverages above a pre-established level, without the need for addition of any standard to the sample. The performances of both methods were tested and validated with samples containing different amounts of water, ethanol, and methanol and beverages deliberately contaminated with methanol.**

***Index Terms*—Contaminated beverages, methanol contamination, Raman spectroscopy, refracto-densitometry.**

I. Introduction

ALONG the past years, not only the market for artisanal alcoholic beverages have experienced a worldwide expansion, but also the number of reported cases of intoxication by contaminated products. In the specific case of methanol, ingestion of contaminated beverages may cause health problems from simple nausea and vomit to serious blindness and even death. Consumption of methanol amounts ranging from 0.3 to 1 g per kilogram of body mass is considered lethal. However, there is a risk of intoxication even for the ingestion of methanol amounts far below this high level [1]. Considering the lethal amount and a person with a mass of 70 kg, this limit represents the ingestion of 200 ml of a contaminated beverage containing 70 g of methanol.

Owing to the serious risks to the citizens' heath, limits of methanol content in alcoholic drinks are established in different countries and must be followed by the industries.

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In Brazil the maximum allowed concentration of methanol is 0.2 g/L of alcohol [2] while in the United States it would be 2.8 g/L [3]. Depending on local law, distilled beverages with alcoholic content in a predefined range can be considered a spirit. In Brazil, for example, this range lies between 38 °GL and 54 °GL – the percentage of alcohol per volume. All distributed products must be registered and have their processes controlled by the Ministry of Agriculture, Livestock and Supply [2]. Depending on the stage of the product lifecycle, from registration and classification to production control and inspection, standard tests are applied. Such set of rules are followed by the industries that produce drinks under rigid quality criteria. However, methanol concentration in illicit and even artisanal beverages may exceed the safe limit. In order to elevate the alcohol content, checked by densitometry, unscrupulous enterprises deliberately add methanol to alcoholic beverages. Methanol is used to tamper with the beverages, due to its similar density and lower price when compared to ethanol [4].

Besides, the manufacturing technologies employing traditional distillers in the production of home-distillated spirits may result in high levels of methanol content in the beverage [5]. Since methanol has a lower evaporation temperature (65 °C) than the ethanol (78 °C), depending on the fermentation that took place, the number of distillation cycles and the characteristics of the distiller apparatus and raw ingredients, as much as 10% of the yield (the first 10%) can be methanol. The heterogeneity in post separation batches could incur in concentrations higher than 10% in the final product. Low sampling rates for quality testing and the lack of appropriate laboratories and skilled personnel may introduce an additional setback for the adoption of corrective procedures. In such a scenario, many governments have warned their citizens, mainly the travelers, to the danger of drinking home-distilled spirits.

The required accuracy of the test used in the spirit analysis is highly dependent on its purpose. Several methods for alcohol analysis involving colorimetry with auxiliary chemicals, as well as demanding techniques employing cumbersome equipment for gas or liquid chromatography, rely on complex and/or time-consuming sample handling processes.

Considering that an unambiguous characterization often requires specialized laboratories and skilled manpower, not always readily available at the production or consume sites, a rapid method to assess the toxicity of beverages regarding the presence of methanol is of great concern for the sector.

Among the standardized methods used for a rapid assessment of conformity of alcohol-water based mixtures, are the densitometry and the refractometry. Densitometry is, for example, widespread used to determine the alcoholic content of ethanol fuel. Alcoholmeters give the total alcoholic content based on

density, measured by weight and volume and corrected by temperature tables. This method brings disadvantages such as the high volume needed and the waste of samples. In the field of artisanal beverage fabrication, the fast assessment of the ethanol content is achieved by the measurement of the sample refractive index with a handheld refractometer. The main drawback of both methods relies on the similarity between water and methanol refractive indexes and between ethanol and methanol densities, which may mask the presence of methanol in the blend. Additionally, both methods demand a rigid temperature control. Association of Official Agricultural Chemists standardizes such methods, and a comprehensive list can be found in the literature [6], [7].

On the other hand, Raman spectroscopy have been used successfully for nondestructive check of food quality [8], [9] and it can also give quantitative information regarding an analyte [10], [11]. The Raman scattering spectrum can reveal, in the visible or near infrared spectral region, the molecular fingerprint of the substance under analysis. Raman spectroscopy was applied for the quantification of ethanol and methanol in distilled alcoholic beverages with high accuracy and low uncertainty [12]. Nevertheless, the efficiency of this proposed method depends on the addition of a standard to the sample. Additionally, the determination of the methanol concentration in the beverage is related to the ethanol concentration. Therefore, the application of the method requires an internal reference and a rigorous sampling and data processing.

Despite the difficulties, as Raman spectroscopy is based on scattering of a laser light source, the optical apparatus can be set to analyze samples even without opening the containers [13]. This feature is interesting for a fast and easier assessment of beverages already bottled.

This work discusses two methods, which can be used to verify the toxicity of artisanal alcoholic beverages, regarding the presence of methanol. The first method consists of refractometric and densitometric (refracto-densitometry) measurements, whereas the second one relies on principal component analysis (PCA) [14] and Raman spectra of the samples [15]. Instead of determining with high accuracy and low uncertainty the methanol concentration, as described in the Raman-based method reported by Boyaci *et al.* [12], we focus on the rapid detection of methanol in the blend above a pre-set threshold. The performance of both methods was tested and validated with samples containing different quantities of water, ethanol and methanol and beverages deliberately contaminated with methanol. Within a pre-set 25% v/v of methanol content in the beverages, both methods resulted in equivalent results.

II. Materials and Methods

A. Physical Samples

Experimental measurements were carried out by using different classes of physical samples: pure alcohols, ternary mixtures, beverages, and beverages deliberately contaminated with methanol.

Ternary samples were prepared to simulate contaminated and uncontaminated beverages with total alcohol content of 38 °GL, 40 °GL and 42 °GL. Contamination was simulated by adding methanol to the samples in proportions ranging from 0 to 22% v/v. The base for the blends was ethanol 99.85%, methanol 99.85% and distilled water ($<$ 18 Mohms) kept in three 25 mL burettes (0.1 mL resolution).

To validate the methods proposed for the rapid detection of methanol contamination, were used five artisanal alcoholic beverages with different nominal alcohol content (39 °GL, 40 °GL, 47 °GL and two with 42 °GL). Anhydrous methanol (99.85%) was also added to these beverages in concentrations of 11, 20, 33, 43, and 50% v/v to produce contaminated samples. A set of 55 samples (35 ternary, 3 pure substances, 5 spirits, and 12 contaminated spirits for validation) was prepared just before the experiments and maintained in closed 50 mL vessels in order to minimize the evaporation since both ethanol and methanol are highly volatile.

B. Density and Refractive Index Measurements

The samples' densities were obtained by the ratio of mass to volume measured with a picnometer $(9.682 \pm 0.001\mathrm{mL})$ and an analytical scale (Shimadzu AUW220D, resolution of 0.0001g). The room temperature was maintained at (20.0 ± 0.5) °C during the measurements. Refractometric measurements were done by an Abbe refractometer (Atago, DR-A1, 0.5×10^{-4} resolution, 589.3 nm, nD 1.3000 to 1.7100). Sample temperature was kept at (20.00 ± 0.01) °C with a thermostatic bath (Lauda - Ecoline Staredition E200, 0.01 °C resolution) connected to the refractometer. For each sample, three measurements of mass and five measurements of refractive index were taken under repeatability conditions.

C. Raman Spectra Measurements

The experimental setup for Raman spectroscopy consists of a spectrometer (Horiba, iHR550, diffraction grating with 1200 l/mm blazed at 600 nm, Horiba Synapse CCD) which measures the light of an Argon ion laser at 488 nm (Coherent, Innova 70-2, 488 nm single-line, 6 GHz spectral linewidth, TEM_{00} operation at 10 mW of optical power, long-term power stability of $\pm$ 0.5 %) scattered by the sample. The setup uses a 4 mL quartz cuvette and an optical fiber GRIN lens coupled cuvette holder (Ocean Optics CUV-ALL-UV) connected to the spectrometer by a 200 μm optical fiber. Polarization of the exciting laser on the sample was adjusted by employing a λ/4 wave plate plus a linear polarizer.

The total spectral range of Raman shifts between 2714 and 3747 cm^{-1} resulted from the data acquisition under the optical pumping at 488 nm using a spectral span window centered at 580 nm and an integration time of 10 s. For each sample, three data acquisition cycles were performed at (20.0 ± 0.5) °C under repeatability conditions with an integration time of 10 s and 5 averages. With the adopted procedure, the signal from the 1024 pixels CCD is recorded without moving the spectrometer diffraction grating, so further spectral corrections were not necessary [16]. A spectral resolution of 0.5 nm corresponding to approximately 11 cm^{-1} resulted from the used 0.25 mm input slit.

D. Principal Component Analysis

Raman spectra acquired by the *SynergJY*, which controls the spectrometer, are exported by a script in *LabTalk* and processed

by the *MATLAB*. The first step is the conversion from wavelength in nanometers (nm) to wavenumber shift (cm^{-1}). This procedure is necessary for the area calculation as both the baseline reduction and normalization are related to energy or frequency intervals and not to wavelength. Then, the *msbackadj* from the bioinformatics *Matlab* toolbox removes the baseline of each spectrum. Spectra are normalized regarding to the area below the curve using (1), where $I(\nu)$ is the intensity over the smallest frequency band the spectrophotometer generates.

$$I(\nu) = I(\nu)/\sqrt{\sum I(\nu)^2}. \tag{1}$$

The baseline removal tool fits a spline to remove wideband fluorescence. This procedure also removes wide band vibrations such as the OH stretching band centered around 3400 cm^{-1} that could be used to quantify the alcohol content in the sample. This limitation, however, does not impose any serious drawback since the method focus on ethanol and methanol narrow bands to classify the samples.

For the analysis it was selected the spectral range from 2800 to 2986 cm^{-1}, related only to the ethanol and methanol molecules. The rotation matrix was calculated using an input space corresponding to the spectra of 200 samples. These spectra were mathematically obtained by linearly combining artisanal alcoholic beverage and methanol spectra, plus an adequate level of noise.

Initially, in order to give the same weight to all the dimensions in the analysis, from each one of the 176 dimensions of the matrix A, which corresponds to a spectral channel normalized in the band, was subtracted the mean of the sample space as in (2). Depending on the dataset under analysis, it is usual to standardize the data by dividing the point value by the standard deviation of the data set. However, as the adopted methodology emphasizes the use of spectral regions with more features, such procedure was not used here.

$$B_i = A_i - \bar{A}. \tag{2}$$

As each spectrum from 2800 to 2986 cm^{-1} contains 176 points, a 176×176 matrix is calculated by the *princomp* function of the statistical *MATLAB* toolbox. It determines the rotation matrix C for the input sample space, so that the highest variances are in the first components. The rotated vectors representing the spectra in another vector space were obtained multiplying the transposed input vectors B^T by the C matrix following (3).

$$P = B^T \cdot C. \tag{3}$$

The rotation matrix is then applied to the physical samples, giving (in one dimension) information about eventual contamination or adulteration.

III. Results and Discussion

A. Refracto-Densitometric Measurements

Using laboratory grade equipment such as a picnometer and an ABBE refractometer at controlled temperature, a classification as contaminated and uncontaminated beverages is possible. This classification requires setting a threshold for the level of contamination.

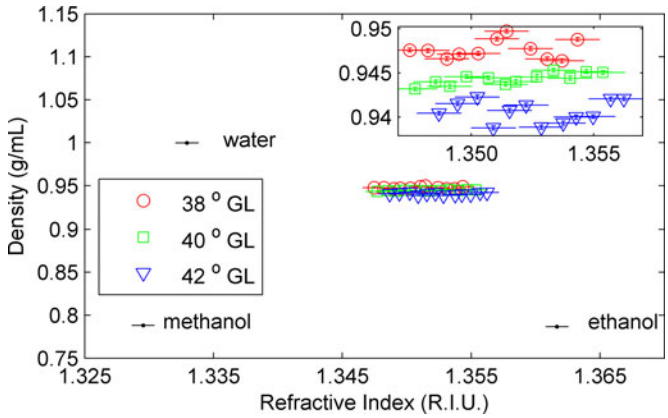

Fig. 1. Refracto-densitometry of the pure and ternary samples, containing water, ethanol and methanol, with total alcohol content of 38 °GL, 40 °GL and 42 °GL. The inset shows in details data from the ternary samples.

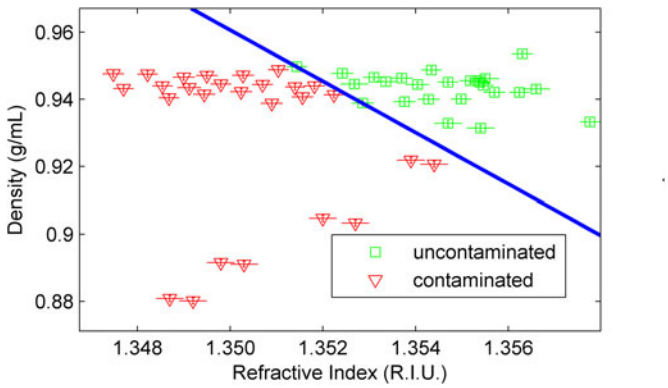

Fig. 2. Classification by the refracto-densitometric method of the ternary mixtures and artisanal beverages deliberately contaminated.

Fig. 1 shows a refracto-densitometry scatter plot of the prepared ternary samples, together with pure water, ethanol and methanol.

The inset shows with further details the dispersion of the data set. The shape of the obtained distribution, together with the fact that the replacement of ethanol by methanol in the sample shifts its data towards the origin of the Cartesian coordinate system, suggests the possibility of establishing a classification criterion.

By considering the previously mentioned lethal dose corresponding to 70 g of methanol in a 200 mL drink, a 25% v/v methanol level was adopted. This corresponds to a methanol volume of 1/4 of the total alcohol volume, independently of the alcohol concentration.

A linear function (4), could be the considered as a discriminator for the pre-set threshold of 25% v/v of methanol in the sample, as shown in Fig. 2.

$$d = -7.641n + 11.276. \tag{4}$$

Table I summarizes the results for the contamination status based on this linear discriminator.

This method of classification could be easily applied in loco once kits composed by a densimeter and a handheld refractometer are easily available, together with a calculation tool based on tables to determine the total alcohol concentration. Although

TABLE I
LINEAR DISCRIMINATOR AND PCA RESULTS FOR THE SET OF TEST SAMPLES

	Methanol concentration % (v/v)		Refracto-densitometric			Raman-PCA assisted	
Sample 42 °GL	In sample volume[(a)]	In alcohol volume[(b)]	Refractive index ($\pm 2.9 \times 10^{-4}$)	Density (g/mL) ($\pm 9.0 \times 10^{-4}$)	Decision: Contaminated	PC1	Decision: Contaminated
1	0	0	1.3563	0.95353	No	−0.010	No
2	0	0	1.3558	0.94306	No	−0.010	No
3	0	0	1.3552	0.94553	No	−0.010	No
4	0	0	1.3553	0.94559	No	−0.010	No
5	0	0	1.3577	0.93325	No	−0.010	No
6	0	0	1.3566	0.94306	No	−0.010	No
7	11	22.9	1.3554	0.93141	No	−0.010	No
8	20	37.3	1.3544	0.92067	Yes	+0.004	Yes
9	33	54.3	1.3527	0.90329	Yes	+0.005	Yes
10	43	64.1	1.3503	0.89106	Yes	+0.010	Yes
11	50	70.4	1.3492	0.88012	Yes	+0.015	Yes
12	0	0.00	1.3555	0.94617	No	−0.010	No
13	11	22.9	1.3547	0.93284	No	−0.005	No
14	20	37.3	1.3539	0.92185	Yes	+0.003	Yes
15	33	54.3	1.3520	0.90471	Yes	+0.005	Yes
16	43	64.1	1.3498	0.89156	Yes	+0.010	Yes
17	50	70.4	1.3487	0.88083	Yes	+0.015	Yes

Error bars relates to the worst case found for the previously measured samples. (a) Refers to methanol concentration in the total sample volume, whereas (b) is the methanol content face to the nominal (42 °GL) alcohol concentration in the sample.

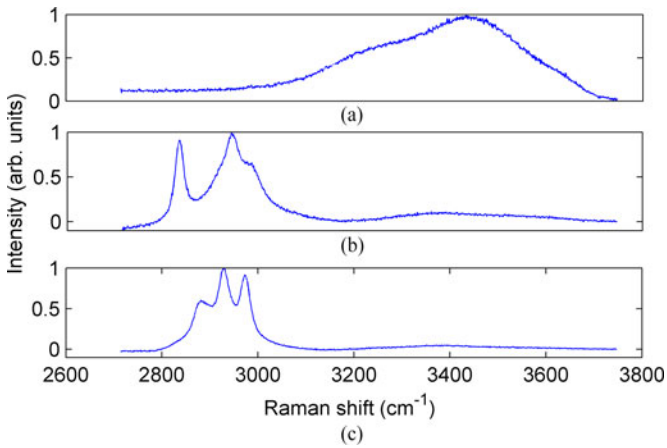

Fig. 3. Raman Spectra of: (a) pure water, (b) methanol and (c) ethanol.

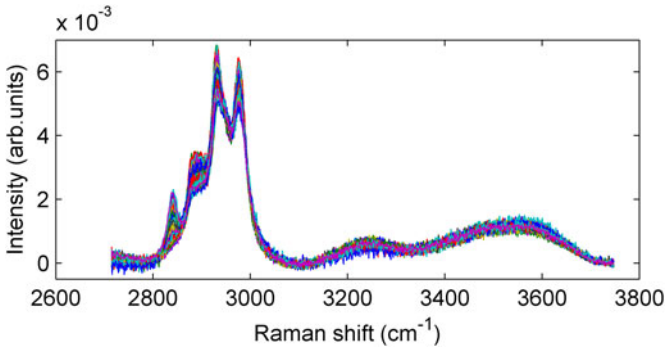

Fig. 4. Raman Spectra of the 35 prepared ternary mixtures.

representing a useful tool for the classification of samples regarding the methanol presence above a pre-set threshold, the method has a few limitations for field applications. The most important one is the strong dependence of these parameters with

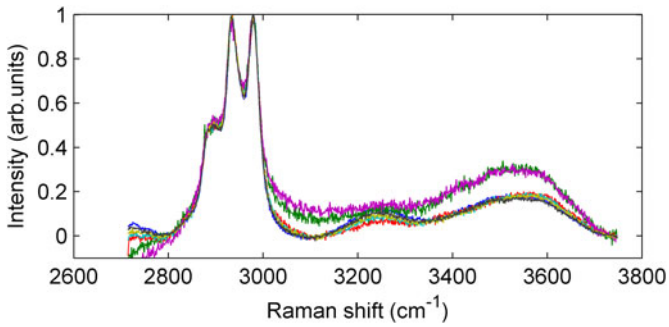

Fig. 5. Raman shift spectra for the five artisanal beverages.

the temperature. Even small changes of temperature can compromises the classification as the presence of methanol in the water-alcohol mixture is not considered in the standard calibration tables. Furthermore, the measured density for the ternary mixtures does not consider the densification by clustering that occurs in such cases [17], giving densities that are higher than a simple linear combination of its constituents [18]. In order to overcome the mentioned drawbacks, a dissimilar technique can be needed for the cases with dubious classification.

B. Raman Spectroscopy Assisted by PCA

1) Preprocessing of the Raman Spectra: The pumping laser beam wavelength λ_L, as well as the chosen spectral window, is a trade-off between the intensity of the Raman scattering, which is proportional to $(1/\lambda_L)^4$, and the presence of fluorescence. That means the high intensities of the Raman scattered photons at short wavelengths are masked by the fluorescence. The used baseline removal tool, which fits a polynomial spline and subtracts it from the dataset, proved to be functional but must be

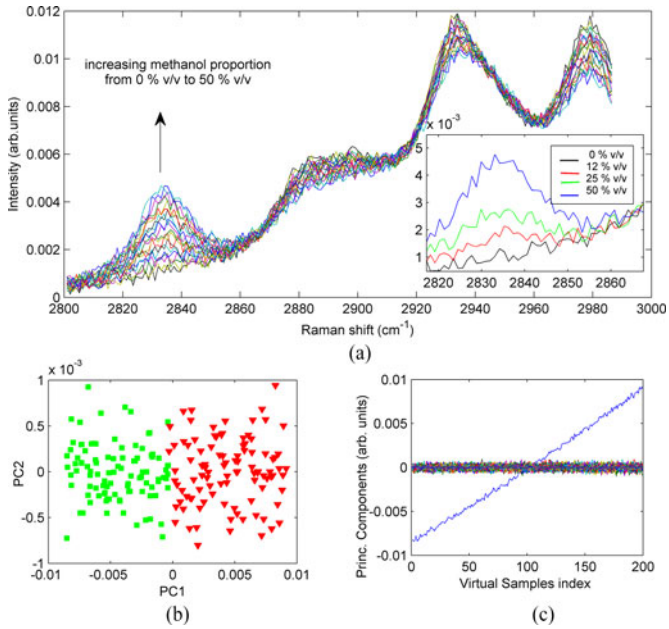

Fig. 6. (a) Raman spectra for the input space (200 virtual samples) used in PCA (inset shows details for four concentrations), (b) PCA scatter plot for PC1 and PC2 components, and (c) spectra as rotated representation for maximum variance.

reconfigured for any different pumping wavelength, and consequently different spectral windows for the same Raman shift.

Fig. 3 shows the Raman spectra for the water (a), methanol (b) and ethanol (c), and Fig. 4 shows the processed spectra obtained for the ternary mixtures.

Both figures make clear the spectral overlap between the bands of the three components in the mixture. Small differences in the spectra of Fig. 4 contain significant information, not only about the constituents of the sample but also about their concentrations, that can be accessed by the PCA.

Fig. 5 shows measured Raman spectra of five different artisanal beverages after the preprocessing step, comprised of the characteristics bands of ethanol as well as the wide OH band centered at around 3400 cm^{-1}, present in all main components of the blend, water, ethanol and methanol. It is important to notice that these spectra were normalized by the area under the curve; therefore, the intensities are not indicative of the relative concentrations. This procedure also compensates fluctuations in the pump laser power, misalignments in the cuvette reinsertion and other sources of systematic error. It can be seen that in the chosen spectral window for the PCA (from 2800 to 2986 cm^{-1}), the Raman spectra is quite similar for all the beverage samples.

The classification method based on Raman spectroscopy has some advantages in comparison with the refracto-densitometric method. Despite the possibility of using Raman spectroscopy for indirect measurement of temperature [19], for the selected spectral range, small temperature changes close to the room temperature do not represent a problem. The spectra of pure ethanol and methanol were measured within a temperature range from 16 to 27 °C and no important difference was detected for the chosen bands. Additionally, unlike the macroscopic parameters, any clustering occurring in the blend [17] does not influence the molecular information present in the Raman spectrum at the selected spectral range.

2) Input Sample Space and PCA Results: From the Raman spectra obtained for the methanol and one of the beverages, it was created an input sample space composed of 200 virtual samples with methanol content from 0 to 50 % v/v. However, as the two alcohols - ethanol and methanol - have different cross sections for Raman scattering, a correction factor of 0.66 had to be applied to the spectra previously to the sample space formation. This factor was determined after the baseline subtraction, from the ratio between the areas under the spectra, acquired between consecutive removals and re-insertions of the cuvette in the holder.

The PCA was then applied to the input sample space in accordance with the previous described procedure.

Fig. 6(a) shows the Raman shift of the 200 virtual samples mathematically obtained by the linear combination of the artisanal beverage and methanol spectra, whereas Fig. 6(b) shows the PCA scatter plot for components PC1 and PC2 of these samples. These resulting principal components are a subset from the product of the sample space by the rotation matrix and represent 99% (noise and application dependent) of the variance in the input sample space. Samples represented by triangles are considered contaminated as the methanol content is above the pre-set threshold of 25% v/v; squares depict uncontaminated samples. Fig. 6(c) shows all the spectra as a rotated representation. The abscissa corresponds to the index of the virtual samples with increasing methanol concentration, whereas the ordinate axis represents the superimposed intensity of each rotated spectral component. It can be seen that all changes in the spectral components are concentrated in one dimension represented by the diagonal line.

The same rotation matrix previously calculated was applied to the spectra of the physical ternary mixtures, preprocessed by the baseline removal and area under curve normalization tools. Fig. 7(a) shows the Raman spectra for the physical samples and Fig. 7(b) shows the scatter plot for components PC1 and PC2, where the triangles indicate classification as contaminated and the squares indicate classification as uncontaminated. Like in the case of virtual samples, one principal component, represented by the saw tooth line in the rotated spectral representation of Fig. 7(c), depicts the methanol concentration because the vector samples were ordered in groups of different alcoholic graduation. This also confirms the hypothesis of linear combination in the composition of Raman scattering spectra.

The pattern recognition, in this case, is similar to a calibration curve but it takes into account, simultaneously, the contribution of all spectral features in the analyzed band, instead of only the most pronounced ones.

3) Test Stage Using Physical Beverage Samples: In order to test the methods with the real beverage samples, the spectra of the stock and contaminated samples were rotated and the classification criterion was applied. Fig. 8(a) and (c) show raw acquired spectra, whereas (b) and (d) are the preprocessed signals. It can be seen that the sample in Fig. 8(a) presents a much higher level of fluorescence, which results in a much lower signal-to-noise ratio after the preprocessing, showed in Fig. 8(b).

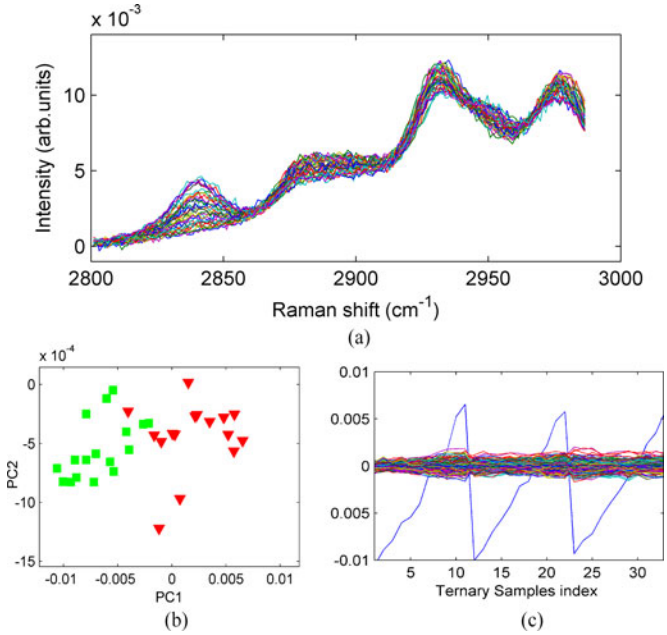

Fig. 7. (a) Raman spectra for the input space (physical ternary samples) rotated by PCA determined matrix, (b) scatter plot for PC1 and PC2 components, and (c) spectra as rotated representation for maximum variance.

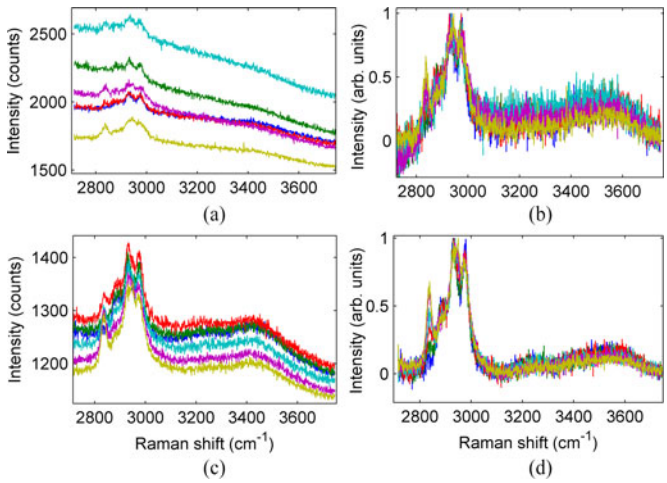

Fig. 8. Raman shift for the set of test samples: (a) and (c) raw spectra; (b) and (d) after preprocessing.

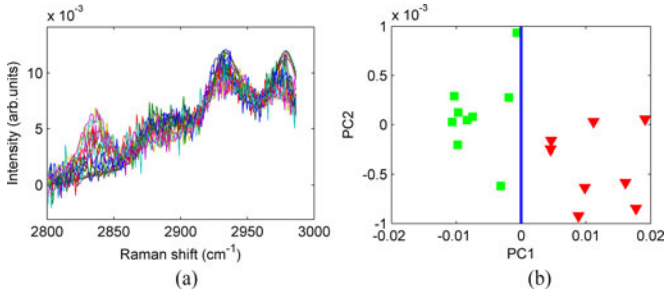

Fig. 9. (a) Raman spectra and (b) PCA scatter plot for the test samples of physical beverages.

TABLE II
SUMMARY OF THE COMPARISON BETWEEN THE PROPOSED RAPID DETECTION METHODS

Method	Refracto-densitometric	Raman-PCA assisted
Sample quantity needed	10 mL, accuracy depends on this volume (picnometer volume)	Depends on the optics, for micro cuvettes less than 1 mL (no sample waste if a back-scattering probe is used)
Operator dependency	High	Low
Equipment robustness	Density based on breakable glassware	Field grade Raman Portable spectrometer
Environmental conditions influence	Dependent of temperature variations, corrected tables are required	Independent of temperature for ambient conditions between 16 and 27 °C

Fig. 9(a) shows the Raman spectra for the set of 17 test samples, with methanol concentrations from 0 to 50% v/v, whereas Fig. 9(b) shows the PCA scatter plot for components PC1 and PC2 of these samples. By keeping the same decision threshold (PC1 $>$ 0), eight (depicted by triangles) among seventeen samples were classified as contaminated.

Table I also summarizes the obtained results based on PCA analysis regarding the contamination status. As the spectral window chosen for the analysis is influence-free from the Raman scattering of OH (close to 3400 cm^{-1}), the proportion of methanol face the nominal ethanol content in the sample can be estimated based on the alcoholic graduation. The similarity between both methods can be verified by the equivalent decision about the contamination status. Table II summarizes the main comparative aspects of both methods.

IV. CONCLUSION

We described two methods that can detect the presence of methanol in alcoholic beverages: a refracto-densitometric and a Raman-PCA assisted. Both methods rely on the pre-establishment of an acceptable threshold for methanol content in the beverage. For this work, this value was 25% v/v chosen by considering the lethal dose of methanol for an adult. However, such level can be adjusted for regulations that are more restrictive. The final classification regarding contamination can still include an uncertainty level, depending on the systematic and statistical errors inherent in the process. On the other hand, for both methods there is no need for the addition of a standard to the beverages, averting the consequences of sample manipulation. Although a linear discriminator was used for the classification, an artificial neural network (ANN) can be employed, depending on the final distribution of the samples in the scatter plot, as already reported in literature [20]. For cases, when the spatial entanglement of the components is high and a classification is not evident, training the ANN with the PCA results can lead to an improved classification. Regarding the challenges of field deployment an optical fiber Raman spectrometer, which in terms of miniaturization can be built with OEM modules [21], CCDs and holographic gratings, can be used to measure the Raman scattering spectrum when pumped by radiation generated by a laser LED in the visible spectral

region [22], [23]. It also can be built using emerging consumer product based technologies such as Smartphones Spectrometers [24]. Together, refracto-densitometric and Raman-PCA assisted methods provides a versatile platform for assessment of beverages regarding methanol contamination in a fast field procedure.

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