Near infrared spectroscopic analysis of single malt Scotch whisky on an optofluidic chip

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Abstract: Standardization and quality monitoring of alcoholic beverages is an important issue in the liquor production industry. Various spectroscopic techniques have proved useful for tackling this problem. An ideal sensing device for alcoholic beverages should be able to detect the quality of alcohol with a small amount of sample at a low acquisition time using a portable and easy to use device. We propose the use of near infra-red spectroscopy on an optofluidic chip for quality monitoring of single malt Scotch whisky. This is chip upon which we have previously realized waveguide confined Raman spectroscopy. Analysis on this alignment-free, portable chip may be performed in only 2 seconds with a sample volume of only 20 µl. Using a partial least square (PLS) calibration, we demonstrate that the alcohol content in the beverage may be predicted to within a 1% prediction error. Principal component analysis (PCA) was employed for successful classification of whiskies based upon their age, type and cask. The prospect of implementing an optofluidic analogue of a conventional fiber based spectroscopic probe allows a rapid analysis of alcoholic beverages with dramatically reduced sample volumes.

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1. Introduction

Quality standardization is an essential task in the liquor production industry. There have been several techniques used for standardization based on the various physical and chemical properties of alcoholic beverages. In the case of Scotch whisky the major parameters that have been used for assessing quality are alcohol content, color consistency and congener profile. Congeners are the organic compounds that are formed during fermentation and amount to less than 1% of the total volume. However it is the congener profile that dictates the flavor of the whisky [1].

Several optical detection techniques have been reported in the last two decades for analyzing the quality of alcoholic beverages, particularly for analyzing Scotch whisky. Ethanol content is one of the main parameters that determines quality. In authentic whisky, the concentration of ethanol must be more than 40% of the volume. Spectroscopic calibration of ethanol concentration in alcoholic beverages has been previously achieved using a fiber optic probe [2]. Other laboratory based analytical techniques have been proposed which utilize infrared (IR) spectroscopy to determine ethanol content [3–7]. Ethanol concentration has also been measured using a non-optical technique which determines the density of samples through a flow injection-pervaporation method [8]. However distillation is required to implement this technique which makes it time consuming compared to optical methods. Another approach used mass spectroscopy to authenticate whisky samples [9,10]. In contrast to the laboratory based analytical studies mentioned previously there have been attempts to implement portable analytical devices. One of these was a handheld UV-vis-IR spectrometer combined with a flow cell for Scotch whisky authentication [11]. A separate study compared Near Infrared (NIR) fluorescence spectroscopy with NIR Raman. In this study it was observed that Raman spectroscopy performed better for concentration calibration, although the same paper raised concerns about implementing laser based Raman spectroscopic detection in a production line using free-space Raman detection devices [12]. Recently the same group reported an analytical technique to detect counterfeit whisky samples using attenuated total reflectance with a diamond-tipped immersion probe for mid-IR spectroscopy [1].

All of this literature and research demonstrates that spectroscopic techniques, when combined with multivariate analysis, form a powerful tool to authenticate whisky samples (or indeed other alcoholic beverages). However, the majority of these are laboratory based

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techniques which require significant sample preparation [1,5,9,10]. Also, the typical acquisition times needed ranges from 10s of seconds to several minutes and sample volumes in the range of milli-liters. A solution to these limitations would be to move this analytic technique into an optofluidic platform. The field of optofluidics, which has emerged from the marriage of microfluidics with photonics technologies, enables faster chemical analysis with reduced sample volumes in miniaturized portable devices [13,14].

In this paper, we propose the use of a fiber based optofluidic chip for NIR spectroscopic analysis of Scotch whisky. The very same device was recently shown to yield what we termed Waveguide Confined Raman Spectroscopy (WCRS) within an optofluidic chip. This offered alignment-free Raman spectroscopic detection of analytes with very low sample volumes (in the order of few microliters) accompanied with relatively short acquisition times (1-2 seconds) [15–17]. WCRS microfluidic chips can be considered as microfluidic analogues to fiber optic Raman probes [18,19]. This makes this optofluidic device compatible for use within a portable NIR Raman system. We remark that this chip may not only record Raman spectra of the sample but naturally picks up fluorescence present as well. This fluorescent component may be removed using modulation methods for example [16]. However in this study our data exploits both the Raman and fluorescent information from the sample. The optofluidic chip presented here was fabricated in polydimethylsiloxane (PDMS) using soft lithography and does not require any micro- optical filters. This makes the manufacturing cost of this chip is up two orders of magnitude less than that of a typical fiber based Raman probe. Although the low manufacturing cost makes this chip suitable as a disposable one, it is possible to reuse the chip by following a simple rinsing procedure with water between loading each sample. Orthogonal collection geometry was employed in the WCRS chip to ensure maximum collection of Raman photons, discarding the majority of the forward scattered Rayleigh photons. It was possible to perform analysis of various whiskies with just 20 µl of sample without any special sample preparation. This is shown in Fig. 1. A standard fiber Raman probe based detection would not readily allow analyte detection with such low sample volumes. Also, since the sample to be detected is confined within the microfluidic channel, any variation due to ethanol evaporation was avoided.

As a proof of principle to demonstrate the usefulness of this optofluidic device for analyzing alcoholic beverages, we have analyzed different brands of Scotch whiskies available on the market. Raman spectra of these whisky samples were obtained and various multivariate techniques were used to achieve both ethanol concentration prediction and classifications of the different types of Scotch whisky tested. Partial Least Square (PLS) calibration was performed to obtain the ethanol concentration and, principal component analysis (PCA) was used to classify various brands based on flavor, age and type of cask.

2. Experimental

The microfluidic chip was fabricated in PDMS using soft-lithography with pre-defined fiber insertion channels as detailed in [15]. Two ultra-low OH multimode optical fibers with core sizes of 200 µm (Polymicro Technologies) were embedded into the chip for the excitation and collection of Raman signals. The fused silica in ultra-low-OH fibers contain a lower hydroxyl component resulting in reduced fluorescence excited in the fiber.

The procedure for acquiring Raman spectra of each sample is detailed in Fig. 1. Whisky samples were directly loaded into the microfluidic chip without any special preparation; 20 µl of whisky was placed at the sample inlet of microfluidic chip using a micropipette. This drop of sample was then introduced into the microfluidic chip by creating a negative pressure inside the channel using a 1 ml syringe attached to the outlet of the microfluidic chip. Once the sample was sucked into the signal detection region Raman spectra of the sample was recorded with a 2 s acquisition time. After Raman acquisition, any remaining liquid at the sample inlet was wiped off and 40 µl of deionized water was passed into the microfluidic channel to rinse the system. This rinsing procedure was sufficient to avoid any cross contamination between samples. With a 2s acquisition time, the total time required to acquire

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a Raman spectrum from the sample was less than 1 minute, which includes the sample loading procedure as described.

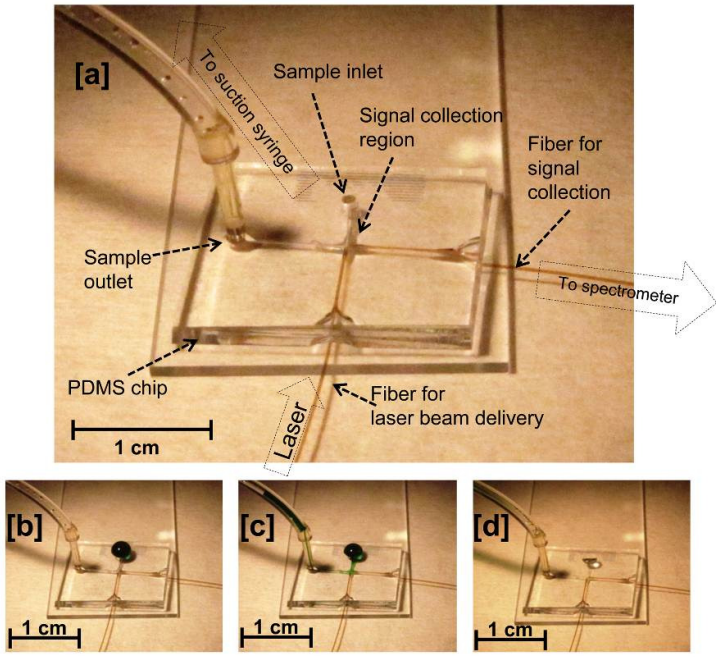

Fig. 1. [a] Photograph of the WCRS based microfluidic chip for whisky analysis. [b-d] Sample loading and Raman spectrum acquisition procedure; a food coloring agent has been used as the sample for better photographic contrast. [b] 20 µl of the sample is placed at the sample inlet of the microfluidic channel [c] The sample is introduced into the microfluidic channel by creating a negative pressure within the channel using a 1 mL syringe attached to the sample outlet port of the chip, followed by Raman acquisition of the analyte for 2s [d] After removing the remaining sample at the inlet, 40 µl of deionised water is sucked into the microfluidic channel to rinse and to avoid contamination while analysing the next sample.

Raman excitation was performed with 200 mW of laser power coupled to a multimode excitation fiber through an SMA adaptor from a diode laser (Laser2000 (UK) Ltd., maximum power 450 mW, wavelength 785 nm). The other end of the collection fiber coupled the collected Raman photons into a spectrometer (Shamrock SR-303i, Andor Technology) through a telescopic system to match the F-number of the fiber to that of the spectrometer. The spectrometer employed a 400 lines/mm grating, blazed at 850 nm and was equipped with a deep depletion, back-illuminated and thermoelectrically cooled CCD camera (Newton, Andor Technology) for the detection of Raman signals [17].

Six commercially available Scotch whisky brands and their variants were used in this study. For the ethanol concentration calibration experiment, ethanol samples with known concentration were prepared by mixing 100% pure ethanol (Sigma Aldrich) with de-ionized water. To avoid experimentalist bias, four sets of samples with percentage volume ethanol concentrations varying from 36% to 43% with a step size of 1% were prepared by two different persons. Five spectra from each of the sets for each of the concentration were acquired with an acquisition time of 2s each, providing 20 spectra for each concentration. For the concentration prediction 5 spectra each from 4 sets of samples were acquired with an acquisition time of 2s from seven types of whiskies. For the classification experiments, it is important to note that the fluorescent background was also taken into consideration along with the Raman signals. To avoid the effects of photo-bleaching from skewing the classification results spectra were acquired only after ensuring that the samples were already photo-bleached. This was achieved by irradiating the sample with the excitation laser for 5 minutes.

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This additional step of photo-bleaching was performed to obtain multiple spectra from a single sample. However in practice where only one acquired spectrum would be used to classify the sample, the photo-bleaching step can be avoided. In the classification experiments, four sets of 50 Raman spectra were obtained from each of the photo-bleached whisky samples. A series of Raman spectra from non-photo-bleached samples were also obtained for 800 s, each with 2s single acquisition time, to classify whisky samples from the same brand but with different flavors that are otherwise impossible to classify.

3. Results and discussions

The Raman spectra of the whisky samples are dominated by the peaks which correspond to the 40% ethanol. In addition to ethanol, whiskies contain other organic compounds such as organic acids, higher order alcohols, esters and aldehydes which are usually called congeners. Extractives from the wood of the cask where whisky was matured are also present. These extractives are usually tannin, acid and coloring matters. These congener components which include the congeners and the secondary products from the cask result in the distinct flavor of a particular whisky brand. However these congener components only amount to less than 1% of the total whisky volume [20].

The acquisition parameters used in this experiment were not sufficient to obtain specific Raman peaks corresponding to the congener components. Figure 2 shows three typical Raman spectra obtained from three different brands of whiskies. It can be seen from the spectra that while the Raman peaks remain same, the broad fluorescence background in the spectra is different for different samples. Since it is the congener components that make a specific whisky brand distinct, this variation in the fluorescence background may be due to the variation in the congener profile in different types of whisky samples. Combining the fluorescence background information with the Raman peaks was crucial in successfully classifying the different types of whiskies, as will be explained later in this section.

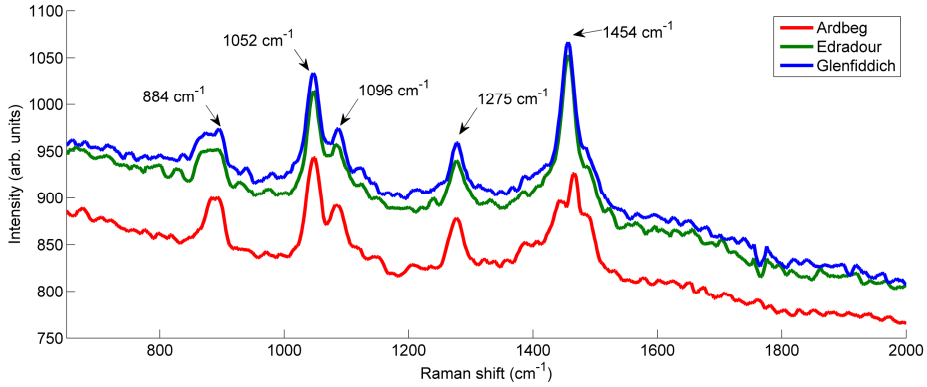

Fig. 2. Representative Raman spectra of three different whisky samples (2s acquisition time, 200 mW excitation power). The prominent Raman peaks of ethanol within the fingerprint region are marked.

3.1 Concentration prediction

A PLS model was used to predict the concentration of ethanol in each whisky sample. The model was built based on the Raman spectra from 655 cm^{-1} to 1720 cm^{-1} of samples, each with a known ethanol concentration. The model was built using 20 Raman spectra for each concentration. The Raman spectra were smoothed using a Savitzky–Golay smoothing filter with a smoothing width of 8 and at degree 3. To remove the fluorescence background from the data, baselines were estimated using polynomial fitting and optimized it with iterative modified polynomial fitting (impf) algorithm [21]. The estimated baseline was then subtracted from the obtained spectra. The model was validated with the leave one out cross validation

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method as shown in Fig. 3. When six parameters were used for prediction, the root mean square error of prediction (RMSEP) was 1.17% [22].

The validated PLS model was then used to predict the ethanol concentration of 7 types of whiskies. The model successfully predicted the ethanol concentration of the samples within a 1% error when compared to the concentration claimed by the manufacturers on the product label, as shown in Fig. 4. From this result it is clear that the PLS model works well for predicting ethanol concentrations of whisky samples. Ethanol concentration is an important parameter in the assessment of the quality of whisky. The ethanol concentration must be more than 40% for authentic whisky samples [1], hence this calibrated technique may be used for the rapid detection of counterfeit whisky.

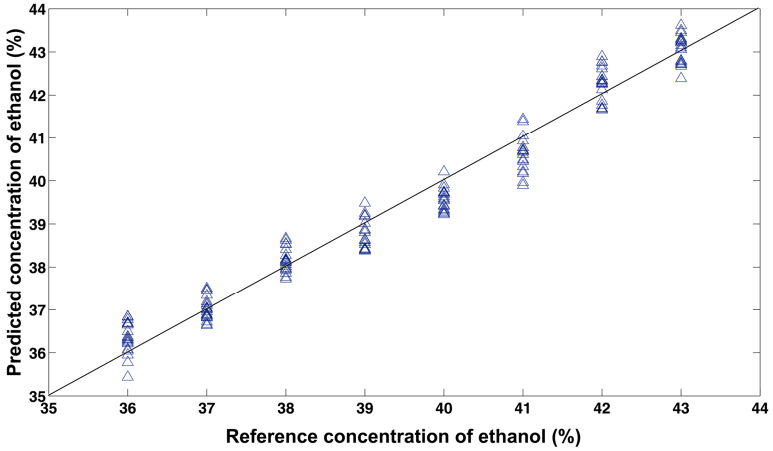

Fig. 3. Validation of the PLS model, using leave one out cross validation. To avoid cross-correlation, while validating a data point corresponding to a particular concentration, other data points with the same concentration was not included while building the PLS model.

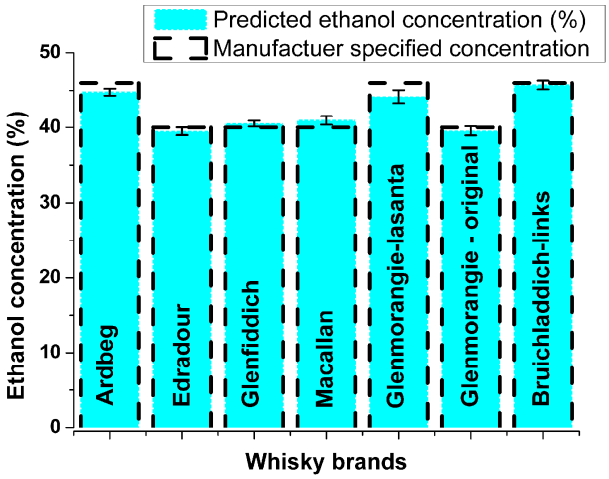

Fig. 4. Prediction of ethanol concentration in various whisky brands using a PLS model. The error bar gives the standard deviation of predicted concentration for 20 Raman spectra acquired from the same whisky type.

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3.2 Classification of whisky samples

As discussed previously, although the acquired Raman spectra of whisky contain only the Raman peaks that correspond to ethanol, the fluorescent background was markedly different for different types of whisky. This difference may result from the varying contributions of the congener components that are responsible for the colour of the whisky. For the ethanol concentration prediction, the fluorescence background was removed by performing a baseline subtraction on the data. However, the fluorescence background proved very useful for categorizing different types of whisky. Hence for the classification of the whisky samples we performed PCA on the acquired NIR spectra just after the Savitzky-Golay smoothing with a smoothing width of 8 and degree of smoothing 3. PCA is a multivariate technique which can be used for dimensionality reduction. In the case of analysing and classifying spectra, each pixel in the obtained spectra can be considered as each parameter, which may or may not be correlated to each other. PCA transforms this multidimensional space into a set of orthogonal co-ordinates (principal components) in such a way that the first principal component would contain maximum variance of the data set. The following principal component would contain the next significant variance and so on. Once this transformation has been done more than 90% of the variance would be captured within first few principal components. Hence the remaining principal components may contain negligible variance among data points and hence they may be discarded, resulting in significant dimensionality reduction for the data set [23]. In this study to demonstrate the classification of various whisky samples, we have plotted the first two principal components against each other to show the distribution of the data set.

There are various types of classifications proposed for single malt Scotch whiskies based on flavour, geographical location of origin, age, and cask. We used PCA based multivariate analysis to cluster the Raman spectra obtained from different types of whisky samples. Different brands were clustered and the result was compared to a popular classification of single malt whisky based on their aromatic features [24]. Various brands of Scotch whiskies were classified into 10 distinct clusters. There is a smooth transition in the quality of whiskies from cluster A to cluster J whose details can be found in [24]. This means the aromatic features of brands in cluster A and B would be similar and that those of cluster A and J would be very different. We applied PCA on the spectra acquired from five 10 year old whisky brands. After performing PCA, the data was plotted in a graph of principal component 1 (PC1) vs. PC2 as shown in Fig. 5. The samples used were from clusters A, B, H, I and J. It was observed that each sample formed a cluster distinguishable from each other. Also the samples which correspond to the clusters H, I and J closely clustered when compared to the samples corresponding to A and B. This shows that the acquired spectra show a trend to clustering based on the aromatic feature of the whisky sample.

Another key criterion to classify whisky is its age. The aging process changes the congener profile and thereby color of the whisky. We applied PCA to Raman spectra obtained from three whisky samples of the same brand (‘Glenfiddich’) with different ages. As can be seen in Fig. 6, the Raman spectra of the samples corresponding to different ages are clearly distinct.

We have also performed classification of whisky samples based on their cask. We chose 4 types of 10 year old “Glenmorangie” where the whisky was kept in different cask for the final 2 years of the maturing process. The difference in the cask also alters the congener profile. Clustering was performed as explained previously and the results are shown in Fig. 7. These exhibit a clear distinction between the samples with different cask types in the PC1 vs. PC2 plot.

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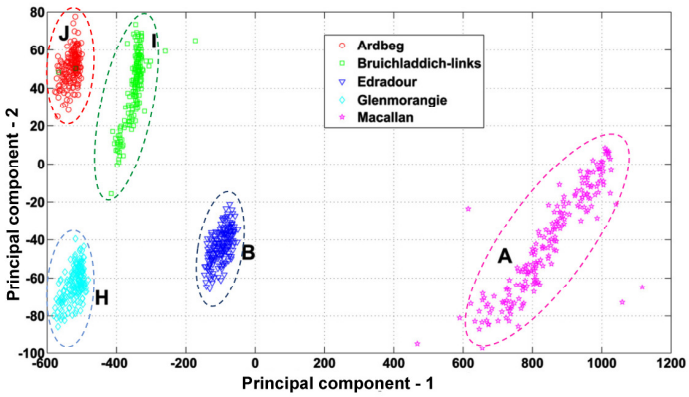

Fig. 5. PC1 vs. PC2 cluster plot of Raman spectra of various whisky samples. Each type consists of 200 spectra acquired from photo-bleached whisky samples. The letters in bold face near to each cluster corresponds to the category to which that particular brand belongs to when the brands are classified based on their aromatic features [24].

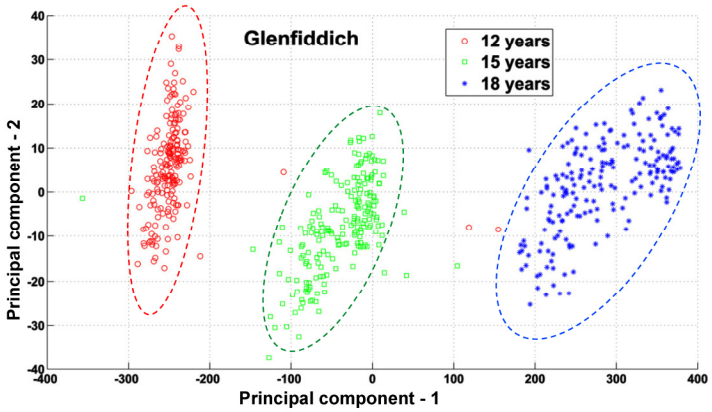

Fig. 6. PC1 vs. PC2 cluster plot showing clear differentiation for same brand of whisky samples with different ages.

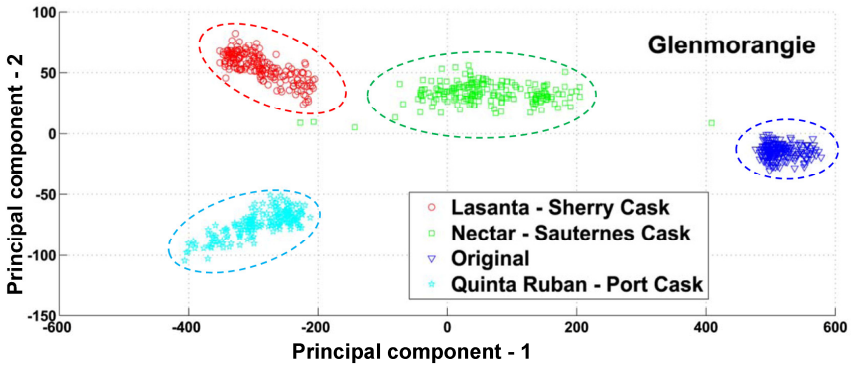

Fig. 7. PC1 vs. PC2 cluster plot showing clear differentiation for same brand of whisky samples matured in different casks.

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3.3 Effect of photo-bleaching

We tried to classify another set of samples of same brand ("Bruichladdich") with different aromatic features as shown in Fig. 8. It can be seen that "Links" and "Peat" are not distinguishable using PCA based clustering. This means the information from the Raman spectra and fluorescent background was not sufficient to distinguish between these two types of whiskies, even when information of higher principal components were used.

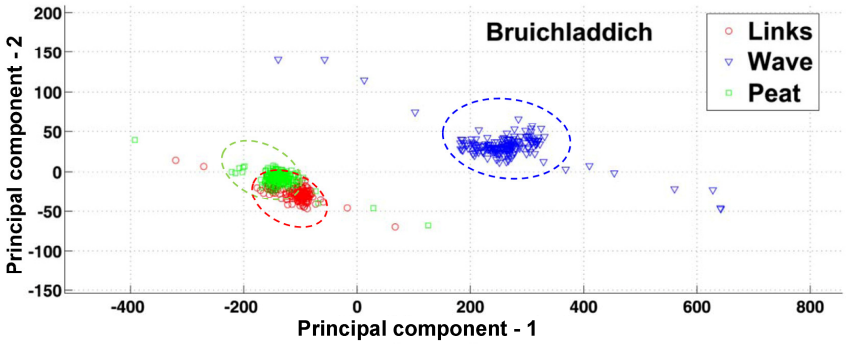

Fig. 8. PC1 vs. PC2 cluster plot for the same brand of whisky with different aromatic features.

However it was observed that the fluorescence background from the sample was reduced and eventually the sample photo-bleached if the sample was exposed to the excitation wavelength for longer duration in the order of minutes. The fluorescence decay rate was used as an additional parameter to distinguish between samples which have similar fluorescence and Raman signatures. To obtain this information, a series of Raman spectra were acquired, with 2s single exposure times, for 800 seconds each for every samples. The fluorescence decay due to photo-bleaching was obtained by plotting the average signal level in the region between 740 cm^{-1} to 750 cm^{-1} where no Raman peak is present. The obtained curve was fitted to a single decaying exponential to obtain the decay constant, as shown in Fig. 9. It can be seen that the decay constant corresponding to "Links" is one order greater than that of "Peat". Compared with previous methods, where sample detection was possible with a 2s acquisition time, obtaining a decay constant is time consuming and requires an acquisition time of ~6 minutes. However, this measurement provides additional information which helps to achieve a more accurate classification. The variation in photo-bleaching rate might be due to the variation in the congener features of different whisky samples.

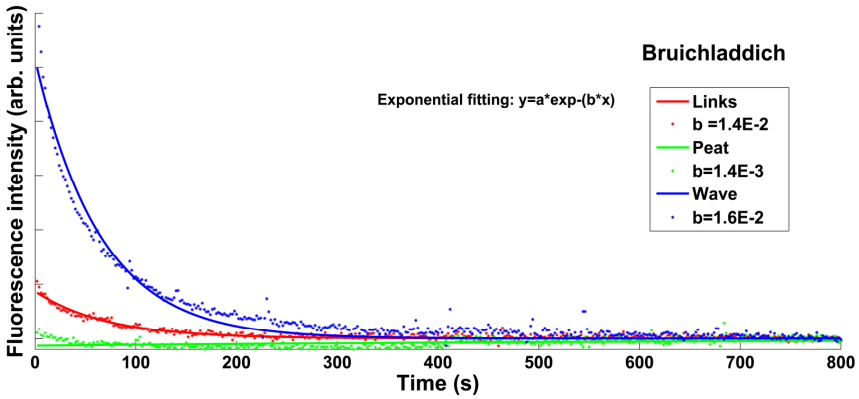

Fig. 9. Variation in the effect of photo-bleaching for three types of whisky samples. A decaying exponential was fitted to obtain the decay constant.

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3.4 Reproducibility

Reproducibility of the data is another important aspect when such optofluidic devices are used for practical applications. The reproducibility in the whisky differentiation results have been verified by classifying a query data set of Raman spectra recorded one week after the measurement of a training data set. Classification of whisky samples based on age was chosen for this study. The training data set containing 200 spectra of each class were recorded with the protocol used for recording data for the previous classification studies. Using the same chip, a similar set of data was recorded as query data one week later. PCA was performed in these data sets and first five principal components were selected for both data sets. Mahalanobis distances (MD) from each class in the training data set were estimated for each spectrum in the query data set. Each query data point was then classified into the class yielding minimum value of MD [25]. Table 1 shows the outcome of the classification as a confusion matrix which shows a sensitivity of ~98%.

Table 1. Confusion matrix showing classification Raman spectra of whisky samples based on their age

		Predicted class		
	Glenfiddich	**12 years**	**15 years**	**18 years**
Actual Class	**12 years**	197	1	2
	15 years	1	198	1
	18 years	0	0	200

This proves that the acquired data is reproducible over a time period if the same chip and similar experimental conditions such as excitation power, acquisition time and other spectrometer parameters are maintained. However clear deviation in the data was observed when spectra were acquired from different chips. This is mainly due to the variation in the quality of cleaving the fiber tip prior to embedding it into the microfluidic chip. In the future, employing an automated cleaving procedure may help to overcome such deviation, offering inter chip reproducibility as well. We believe the pre-aligned nature of the collection optics in this optofluidic device makes the result more reproducible than data collected using a free-space system, since drift within the system over time is a critical issue for free-space systems.

4. Conclusion

We have shown the use of a completely alignment-free optofluidic device for Scotch whisky analysis. By harnessing the advantages of optofluidics, our presented microfluidic chip offers portability and fast detection of analyte with relatively low acquisition times (2s) with very low sample volumes (20 µl). In this device, which is an optofluidic analogue to a fiber based Raman probe, samples can be analysed without the requirement for any special sample preparation. A PLS model was built to predict of the concentration of ethanol in the various whisky samples, and was successful in predicting the concentration in an accuracy of 1%. Furthermore, it has been shown that the combination of Raman spectra and the fluorescent background information was used to classify different types of whiskies using PCA. Whisky classification based on aromatic features, age and cask type was achieved. It was also demonstrated that the fluorescence decay constant can be also used as another parameter to distinguish whisky types which are otherwise non-distinguishable otherwise although this required a longer acquisition time. Finally it was shown that the classification data obtained is reproducible over one week. The results show that this optofluidic probe is well suited for developing portable devices to authenticate alcoholic beverages. The low acquisition time also offers the potential development of devices for online process monitoring in production lines of liquors.

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