



Identification and quality assessment of beverages using a long period grating fibre-optic sensor modified with a mesoporous thin film



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ABSTRACT

In this study, an optical fibre long period grating (LPG) sensor functionalised with a mesoporous thin film was employed for the identification and quality assessment of beverages. The principle of the discrimination of beverages using an LPG sensor is based on the measurement of the change in refractive index of a sensitive film, induced by the binding of the chemical compounds present in the beverage. The sensitive film deposited onto the LPG consisted of poly(allylamine hydrochloride) (PAH) and silica nanospheres (SiO₂ NPs) with diameters ranging from 40 nm to 50 nm. PAH imparts selectivity, while the SiO₂ NPs endow the film with high porosity and enhanced sensitivity. In this study, five different types of beverages, red and white wines, brandy, nihonshyu (sake, a Japanese rice wine), and shochu (a Japanese distilled beverage), prepared via distillation and fermentation, were used to assess the capability of the sensor to identify the origin of the beverages. In addition, a selection of red wines was used to evaluate the use of the sensor in the assessment of the quality of beverages. The results obtained were benchmarked against those obtained using gas chromatography–mass spectrometry for the determination of volatile compounds contributing to the flavours of a set of red wines. Principal component analysis (PCA) was employed for data analysis. This approach enabled both quality assessment of beverages and identification of the methods and materials used for their preparation.

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1. Introduction

There is a clear need for simple, rapid, and cost-effective techniques for an objective assessment of the quality of alcoholic beverages, their origin, and the substances used to make them to ensure adequate standards of production, uniformity within a brand, and to avoid falsification [1,2]. The chemical composition of an alcoholic beverage is determined typically by the method of preparation and the chemical composition of the primary products used for its production [3]. While ethanol and water are the main chemicals present in all alcoholic beverages, numerous volatile and non-volatile flavour compounds are also present [4]. Thus, the analysis of the chemical composition of the alcoholic beverages is a challenging task due to the complexity of the media and the presence of hundreds of different chemicals. Among the many factors that contribute to the typicity and quality of a wine, aroma is

probably the most important organoleptic characteristic and a key attribute for consumers. Several hundred chemically different flavour compounds, such as higher alcohols, aldehydes, ethyl esters of fatty acids, fatty acids, ketones, monoterpenes, and volatile phenols, have been found in wines [5]. They have slightly different chemical and physical properties, such as polarity and volatility, and their concentrations range from a few ng/L to more than 100 mg/L [6].

Standard methods and procedures for the quality assessment of alcoholic beverages are based on gas and liquid chromatography, often coupled with mass spectrometry for the structural identification of the individual components [7]. For the enrichment of the aroma substances, several methods have been used such as liquid–liquid extraction, column chromatography, solid phase extraction, and solid phase microextraction. The presence of a large variety of compounds that contribute to taste and flavour means that the analysis of the comprehensive spectral data on some wines is not sufficient for assessing their quality. Therefore, pattern recognition approaches have also been applied to the classification of “multi-component” wines and are useful for quality control evaluations [2,8]. In fact, pattern recognition methods for

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classification and identification are used increasingly in fields such as food chemistry, process monitoring, medical sciences, pharmaceutical chemistry, and social and economic sciences. Classification is one of the fundamental methodologies in chemometrics and basically consists of finding a mathematical model capable of recognising the membership of each object to its proper class. Once a classification model has been obtained, the membership of new objects to one of the defined classes can be predicted [8]. Sensory evaluation by trained experts is also employed, but it does not always provide an objective analysis of the consumer products and is an expensive procedure.

Recently, electronic noses and tongues, combined with statistical approaches, and chemometrics have been used intensively for food and beverage identification and ageing and quality assessments [8–12]. Typically, electronic noses and tongues mimic the human olfactory system and are based on an array of nonspecific sensors (or sensors with different selectivities) combined with pattern recognition software. Most electronic nose systems are based on metal oxide sensors or mass sensitive transducers that are inherently highly sensitive to water, making the detection of flavour chemicals present at low concentrations in alcoholic beverages extremely difficult.

In this regard, fibre optic sensors provide an alternative, universally adaptable sensing platform because of the inherent stability of the optical fibres, their high sensitivity, and the ability to multiplex sensors in series [13]. In particular, the combination of optical fibre devices and nanomaterials offers the prospect for the development of measurement techniques using an optical waveguide with a nanostructured coating layer that exhibits changes in its optical properties upon exposure to targeted chemical species. Recently, we have demonstrated a novel chemical sensor based on a layer-by-layer (LbL)-deposited mesoporous film composed of silica nanospheres (SiO_2 NPs) on an optical fibre long period grating (LPG) for the detection of organic compounds [14] and ammonia [15] and for the measurement of the refractive index (RI) of substances [16].

An LPG consists of periodic modulation of the refractive index of the core of an optical fibre with the period lying typically within the range from 100 μm to 1 mm [17]. It couples light from the forward propagating mode of the core of the fibre with a discrete set of co-propagating cladding modes at wavelengths governed by the phase matching condition, as shown in Eq. (1):

$$\lambda_{(x)} = (n_{\text{core}} - n_{\text{clad}(x)})\Lambda \quad (1)$$

where $\lambda_{(x)}$ represents the wavelength at which the coupling occurs for the linear polarised (LP_{0x}) mode, n_{core} is the effective refractive index of the mode propagating in the core of the fibre, $n_{\text{clad}(x)}$ is the effective index of the LP_{0x} cladding mode, and Λ is the period of the grating.

The presence of a coating layer with a sub- μm thicknesses, deposited via LbL film deposition techniques such as Langmuir Blodgett (LB), electrostatic self-assembly (ESA), and dip coating, modulates the transmission spectrum (TS) of the LPG and makes it highly sensitive to the external refractive index. Based on this principle, sensors for pH, humidity, and chemical and biological applications have been demonstrated [17].

Herein, we report the use of an LPG coated with a poly(allylamine hydrochloride)/ SiO_2 NPs (PAH/ SiO_2) film [14,18] for the identification and quality assessment of beverages. Five different types of beverages, red and white wines, brandy, sake (a Japanese rice wine), and shochu (a Japanese distilled beverage), prepared via distillation and fermentation were used to evaluate the use of the sensor for the determination of the origin of the beverages. In addition, the sensor was used to assess the quality of a selection of red wines. Furthermore, the performance of the sensor for the determination

of the volatile compounds contributing to the flavours of a set of red wines was benchmarked against that of gas chromatography–mass spectrometry (GC–MS). Principal component analysis (PCA) was employed for the data analysis, aiding the identification and quality assessment of the beverages. The new sensor enables evaluation of the quality of beverages and the determination of both the methods and materials used for their preparation. In addition, to the best of our knowledge, this method is the first example of the application of an optical fibre LPG chemical sensor that measures refractive index and determines chemical composition of the alcohol for the identification and quality assessment of beverages.

2. Experimental section

2.1. Materials

PAH (M_w : 200,000–350,000, 20% w/w in H_2O) was purchased from Tokyo Kasei, Japan. SiO_2 NPs (SNOWTEX 20L) was purchased from Nissan Chemical. Pure ethanol (EtOH, 99.5%) and acetic acid (99.5%) were purchased from Wako Chemicals, Japan. All of the chemicals were analytical grade reagents and used without further purification. Nihonshyu (sake), shochu, brandy, and a selection of white and red wines were purchased at the local supermarket (Table S1, Supporting information). For the red wine quality assessment, 24 commercially available red wine samples (Table S2) were purchased from a local store. Deionised water (18.3 M Ω cm) was obtained by reverse osmosis followed by ion exchange and filtration (Millipore, Direct-QTM).

2.2. LPG coating

An LPG with a period of 100 μm and a length 35 mm was fabricated in a single mode optical fibre (Fibercore SM750) with a cut-off wavelength of 670 nm using point-by-point exposure to the output from a UV laser source (frequency quadrupled Nd:YAG laser operating at a wavelength of 266 nm) [14–16]. A mesoporous thin film was deposited onto the LPG using an electrostatic self-assembly approach as previously described [14–16]. The LPG was fixed in a Teflon holder constructed with a compartment to accommodate a solution, Fig. 1b [19].

Briefly, the region of the optical fibre containing the LPG was rinsed with deionised water and immersed in a 1 wt% ethanolic KOH (ethanol/water = 3:2, v/v) solution for 20 min, leading to a negatively charged surface. The optical fibre was then immersed sequentially into a solution containing a positively charged polymer, PAH, and a solution containing negatively charged SiO_2 NPs for 20 min each, resulting in the alternate deposition of PAH and SiO_2 NPs layers on the surface of the fibre, Fig. 1a. The fibre was rinsed with distilled water, and dried by flushing with nitrogen gas after each deposition step. A (PAH/ SiO_2)₁₀ film deposited on the LPG, which was prepared by repeating the two-step sequence for 10 cycles, was previously shown to provide optimal sensor performance in terms of sensitivity and response time [16].

2.3. Beverage identification using the LPG sensor

Prior to analysis of the beverages, the LPG sensor was exposed to known concentrations of ethanol to calibrate its refractive index response, as described previously [16]. Briefly, LPG fibre modified with the PAH/ SiO_2 film was immersed into the ethanol solution. Ethanol concentrations ranging from 1% to 40% in increments of 5% were used to simulate the alcohol strengths of the beverages. For comparison, beverages were diluted using water in order to adjust the alcohol strength to the same values as those of the EtOH solutions. The LPG was then immersed in 500 μL of the final

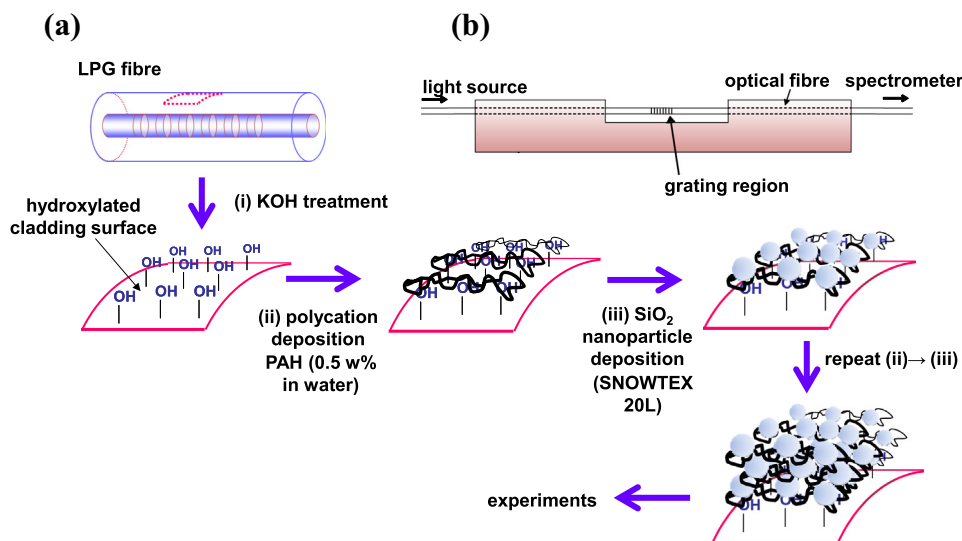


Fig. 1. (a) Schematic illustration of the electrostatic self-assembly deposition process and (b) a deposition cell with a fixed LPG fibre.

solution. The TS of the optical fibre was recorded by coupling the output from a tungsten-halogen lamp to the fibre and analysing the transmitted light using a fibre coupled charged coupled device (CCD) spectrometer. It is known that the refractive index of solutions depends on the concentration of the given solution. A hand-held refractometer (R-5000, Atago) was thus used to measure the RI of the given solutions at room temperature. For qualitative evaluation of the data, the experimental results were analysed using the principle component analysis (PCA) method (Statistical EXCEL add-in, V. 5.05 by Esumi Co. Ltd.) to reduce the multidimensionality of the obtained data.

2.4. Beverage identification via GC–MS

A Jms-Q1000G GC–MS system (JEOL, Japan) was used for the identification of the compounds using the mass spectral library (NIST Version 2.0 build 25.06.2008).

To determine comprehensively the chemical composition of the compounds present in each beverage, two samples were used for each GC–MS investigation; the evaporated volatile organic compounds (VOCs) adsorbed by a Tenax GR adsorption tube and the dry sediment (Fig. 2). Both samples were obtained by purging

ultra-pure helium at 300 ml/min for 2 min through a quartz tube containing glass wool as an absorber and 3 μ L of the beverage, as shown in Fig. 2. The quartz tube was connected to a Tenax GR adsorption tube for collection of the volatile compounds (mainly VOCs) in the wine sample. The remaining dry sediment was wrapped in ferromagnetic foil (pyrofoil, PF) after drying. There are several advantages to this sampling method, including the possibility of removing water that is not adsorbed in the Tenax GR and the use of exactly the same sample volume for each beverage, which enables the quantification of compounds after system calibration. After sample collection, the adsorption tubes were inserted into an automatic desorption device (Curie point injector JCI-22, Japan Analytical Industries, Japan) that was preheated, via induction heating, to 150 °C and then heated rapidly (in 0.2 s) to the Curie point temperature of the ferromagnetic foil of 280 °C for the tube containing the Tenax GR and 220 °C for the tube containing the dry sediment. Under the described conditions, fast and effective desorption of VOCs from the adsorbent was achieved [20]. Subsequently, all of the volatile compounds were injected into the GC column within 15 s with the aid of helium flow. The Curie point injector was coupled with the GC–MS for simultaneous sample injection and GC program start.

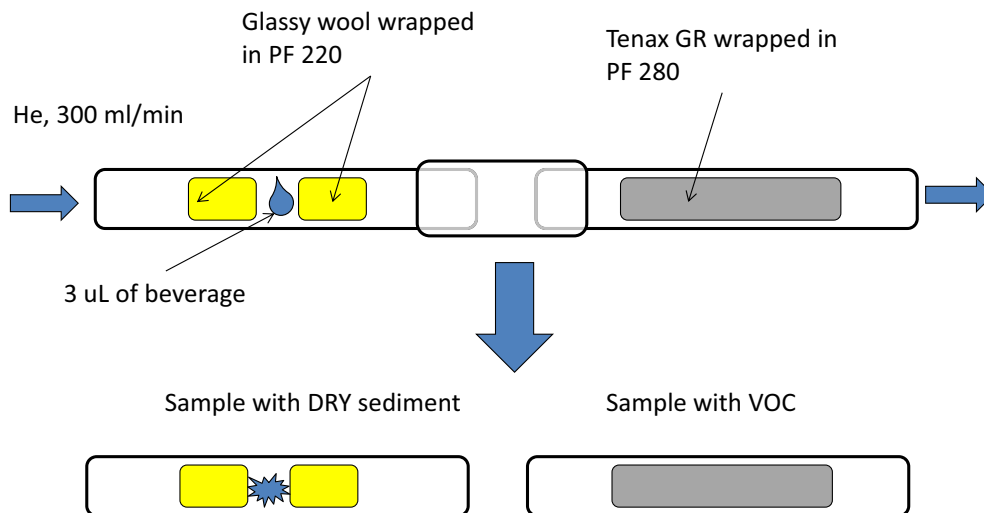


Fig. 2. Illustration of the sampling method used for the qualitative GC–MS analysis of the different beverages; PF, pyrofoil.

2.5. Wine quality assessment using the LPG sensor

Twenty-four commercially available red wines (Table S2) were purchased from a local supermarket. The protocol for wine quality assessment was developed in house; it should be noted that main purpose of this work was to demonstrate and test the applicability of the developed sensor to conduct real live experiments and not to develop new methods and procedures for beverage quality assessment. Before analysis, the wine samples were dialysed in a cellulose tube (Seamless Cellulose Tubing 18/32, Viskase Sales Corp., USA) and were diluted using certain volume of deionised water to remove any sediments and larger organic moieties. As a result, the dialysates were adjusted to 0.5% of the alcohol strength. Dilution and dialysis of the wine sample were required to obtain reliable and repeatable results, because the sensor response was saturated at higher concentrations and to avoid contamination of the sensitive film. Wine R1 (Table S2) was left open for several weeks until it was spoiled. After exposure and analysis of each sample to regenerate the properties of the PAH/SiO₂ film and remove any adsorbed analytes, the modified LPG sensor was washed in 0.1 wt% aqueous ammonia for 5 min [14]. All of the experiments were conducted using the same optical fibre modified with the same PAH/SiO₂ film.

2.6. Wine quality assessment via GC–MS

The VOCs were collected using the purge method through adsorption tubes packed with Tenax GR, as described in Section 2.4, with slight modification. In particular, for each wine sample, 3 µL was dried inside the quartz tube connected to the Tenax GR adsorption tube under a 50 ml/min flow of ultra-pure helium for 10 min and only the volatile components were analysed.

A Jms-Q1000GC (JEOL, Japan) GC–MS system consisting of an Agilent 7890A gas chromatograph coupled to a quadrupole mass spectrometer working in the positive electron ionisation mode (EI) at 70 eV was used for the analyses. The capillary column used for the separations was a DB-WAX (polyethylene glycol stationary phase, 30 m length, 0.25 mm inner diameter, 0.5 µm film thickness; Agilent J&W, part number 19091J-413). The GC inlet temperature was maintained at 230 °C and a splitless injection was done. The oven temperature program parameters are provided in Table S3. The total GC run time was 44 min.

3. Results and discussion

3.1. Deposition of the 10 cycle PAH/SiO₂ film

The change in the TS of the optical fibre LPG sensor in response to the deposition of the PAH/SiO₂ film has been described elsewhere [21]. It was found that for a 100 µm-period LPG, a 10-layer PAH/SiO₂ film (450 nm), (PAH/SiO₂)₁₀, provides a high sensitivity to RI changes, and therefore this film thickness was adopted for the current study [16]. Fig. S1 shows the evolution of the TS during the deposition of the (PAH/SiO₂)₁₀ film. The resonance band shifts linearly with the number of layers indicating that a uniform film is deposited onto the optical fibre LPG.

3.2. Beverage analysis

3.2.1. LPG sensor

Fig. S2 shows the dependence of the RI on the concentration of ethanol in pure ethanol solutions and in different beverages measured using a hand-held refractometer (R-5000, Atago). Interestingly, the value of the RI of the different beverages correlated very well with the RI of the ethanol solutions with the same

concentrations. Nihonshyu had slightly higher RIs of 1.343 and 1.347 at 15% and 20% ethanol, respectively, than those of the other beverages and the EtOH solution (RI = 1.3395_(15%) and 1.345_(20%)). In principle, these results indicate that it is impossible to discriminate between different beverages using the RI value alone; however, determination of the RI is a simple and reliable method for assessing the alcoholic strength of beverages. In other words, if the LPG is not coated with a film that changes its optical properties in response to the presence of particular chemicals, the identification of beverages and determination of their quality is not possible.

Typical TS changes and the dynamic response of the LPG coated with the (PAH/SiO₂)₁₀ film when immersed in EtOH solutions of differing concentrations are shown in Fig. 3a and b. These results are similar to previously reported values and are described thoroughly elsewhere [16]. The response time of the proposed system estimated from these results is within 10 s (Fig. 3b).

Behaviour similar to that observed with the pure EtOH solutions was observed when the LPG was immersed in beverages with different alcohol concentrations (Figs. S3–S7). However, the amplitude of the change differed depending on the nature of the beverage, the substances each contained, and the method of preparation. In particular, the first resonance band at 665 nm shifted to the blue region by ca. 16 nm when the brandy concentration changed from 0% to 40% (Fig. S3a), and thus was ca. 2.6 times greater than that for the EtOH solution in the same concentration range (Fig. 3a). In addition, the response time for brandy was much longer than for the EtOH solution and followed a Langmuir adsorption-type curve (Fig. S3b, response to 5%). These differences in the spectral and dynamic responses between the brandy and EtOH solution cannot be explained based on the RI measurements, because the RIs of the EtOH solution and of the brandy were identical at a given concentration (Fig. S2). It is possible that this difference may be due to chemical interactions between the (PAH/SiO₂)₁₀ film and the chemicals present in brandy. Previously [14], we showed that an LPG coated with a PAH/SiO₂ film was very sensitive to aromatic carboxyl acids, and similar spectral behaviour and time scales were observed when the device was exposed to these types of compounds.

In contrast to the results obtained for the brandy, the spectral changes observed for the shochu were similar to those observed for the EtOH solutions, both qualitatively and quantitatively (Fig. S4). The first resonance band underwent a 4 nm shift when the EtOH concentration in the shochu changed from 0% to 25%, which is similar to the change for the EtOH solution (3.5 nm) over the same concentration range. The dynamic transmission change, measured at 820 nm, was also identical, indicating that there is no chemical interaction between the PAH/SiO₂ film and the chemical compounds in the shochu.

The differences in the responses on immersion of the LPG in shochu and brandy, which are both distilled products, may lie in the origin of the materials from which these beverages are made, i.e., wheat and grapes, respectively.

Further evidence that the different responses of the LPG coated with the PAH/SiO₂ film to different beverages are due to the different chemical compositions of these drinks was obtained when additional liquors produced in a similar manner but from different materials were measured. Thus, two different types of drinks produced via fermentation, nihonshyu from rice and red and white wines from grapes, were evaluated using the LPG coated with the PAH/SiO₂ film.

Figs. S5a and S5b show the transmission spectra and dynamic transmission changes of the LPG coated with (PAH/SiO₂)₁₀ obtained when it was immersed in nihonshyu with different alcohol concentrations. It can be seen in the figure that the trends in the spectral and dynamic changes for the nihonshyu were very similar to those observed for the EtOH solutions and shochu (Figs. 3

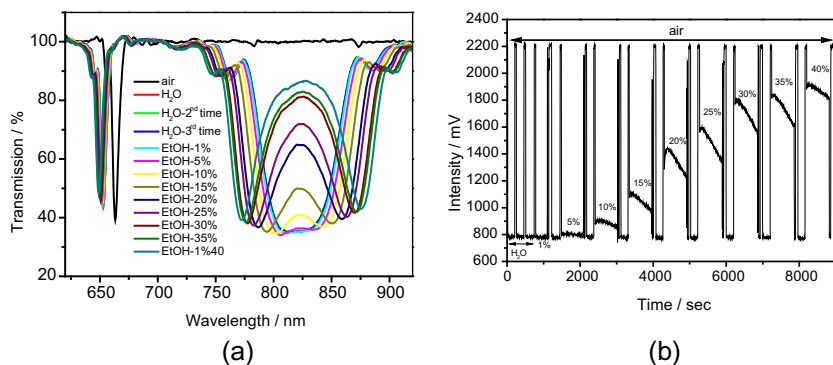


Fig. 3. (a) Transmission spectra of the LPG coated with the $(\text{PAH}/\text{SiO}_2)_{10}$ film when immersed in EtOH solutions of concentrations ranging from 1% to 40%. The legend indicates the concentration at which each spectrum was obtained; the TS measured in air provides a reference (b) Transmission changes recorded at 820 nm when the LPG was immersed in EtOH solutions with differing EtOH concentrations.

and S4, respectively). In contrast, when the white (Fig. S6) and red (Fig. S7) wines were analysed their responses were similar to those observed for the brandy (Fig. S3).

To summarise, Fig. 4a compares the spectra obtained at 10% alcohol strength for the different beverages and Fig. 4b shows the wavelength shifts as a function of EtOH concentration for the beverages and the EtOH solution. As can be seen from these results, the LPG device showed the highest response to red wine. Next, to determine which variables could be used for beverage identification, PCA was used to analyse the data.

The variables used for the PCA analysis are summarised in Table S4, and the PCA plot of the variables listed in Table S4 is presented in Fig. 5. This plot reveals that the different beverages can be classified into three main groups, such as wine of good quality, wine of poor quality, and ethanol-like drinks. The PC1 values can be used to separate wine based and non-wine drinks, while the PC2 values can be used to separate the high quality and low quality beverages because the red wine was spoiled and was similar to vinegar.

These results suggest that grape-based beverages (brandy, and red and white wines) contain higher concentrations of organic carboxylic acids. These conclusions were confirmed by the GC–MS analysis, which indicated that the grape-based liquors had higher total concentrations of carboxylic acids than the other beverages.

3.2.2. GC–MS measurements of volatile compounds

The total aromaticity graph, indicating the total area under the curve (AUC) for all of the peaks that were accounted for under the selected masking parameters (intensity 10^5), is shown in Fig. 6. From this diagram, it can be seen that a significant loss of information about the beverage content occurs only if the headspace of the beverage (i.e., only the volatile samples collected

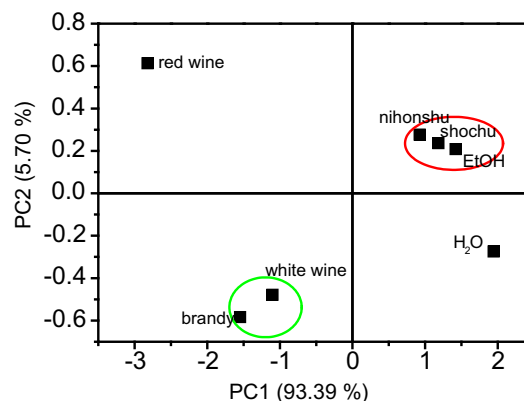


Fig. 5. PCA performed using the data obtained with the LPG sensor and the parameters listed in Table S4.

using the Tenax GR adsorption tube without the dry sediment) is analysed.

Using the NIST library data, all of the compounds contained in the beverages were divided into classes, and the results are shown in Fig. 7. From this diagram, some distinctive features of the tested alcoholic beverages can be seen, such as the prevalence of aldehydes in the nihonshu and carboxylic acids in all of the drinks made from grapes (the brandy and wines). The percentages of the different classes of organic compounds in the different beverages evaluated in this study, excluding EtOH, are summarised in Table S5. Interestingly, the GC–MS results confirmed that the grape-based beverages (brandy and red and white wines) contained higher concentrations of organic carboxylic acids. Consequently, it can be

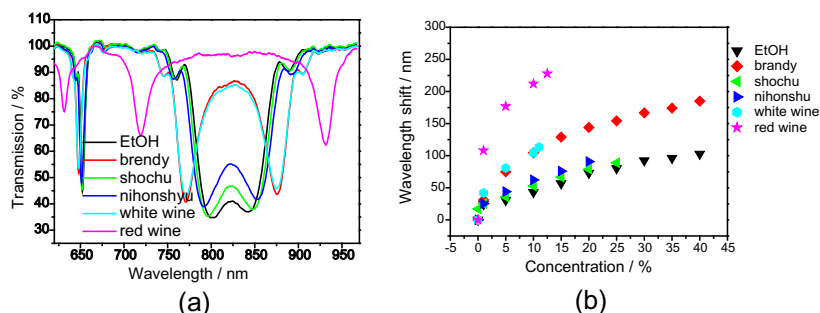


Fig. 4. (a) Evolution of the transmission spectra for the LPG fibre coated with the $(\text{PAH}/\text{SiO}_2)_{10}$ film immersed in different beverages with the alcohol concentration adjusted to 10%; black line, EtOH; red line, brandy; green line, shochu; blue line, nihonshu, cyan line, white wine; and magenta line, red wine. (b) Wavelength shift vs. EtOH concentration; wavelength shift is calculated as difference between 2 resonance bands in Fig. 4a. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

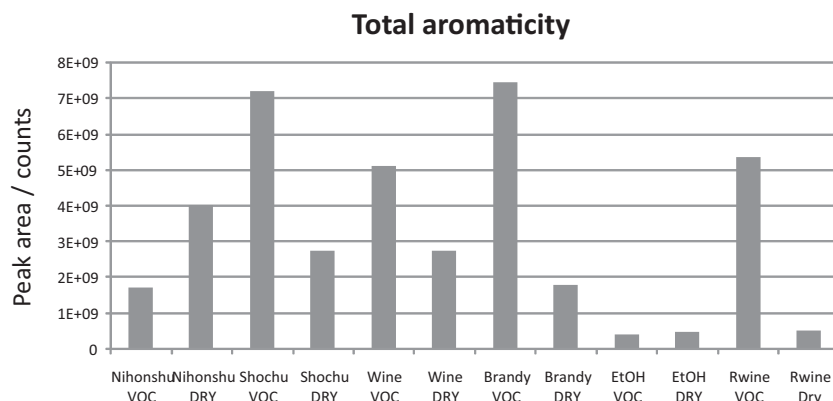


Fig. 6. Total aromaticity graph indicating the total AUC for selected peaks.

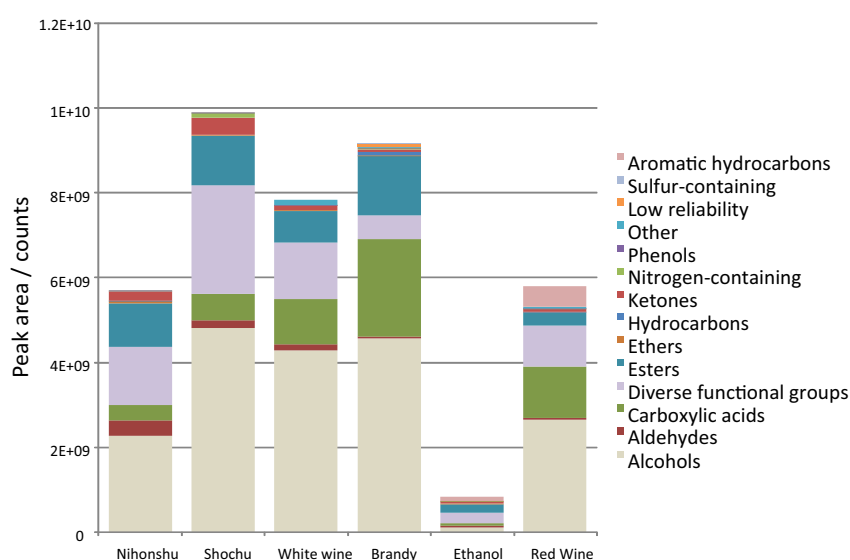


Fig. 7. Contribution of different classes of organic compounds to different beverages flavours.

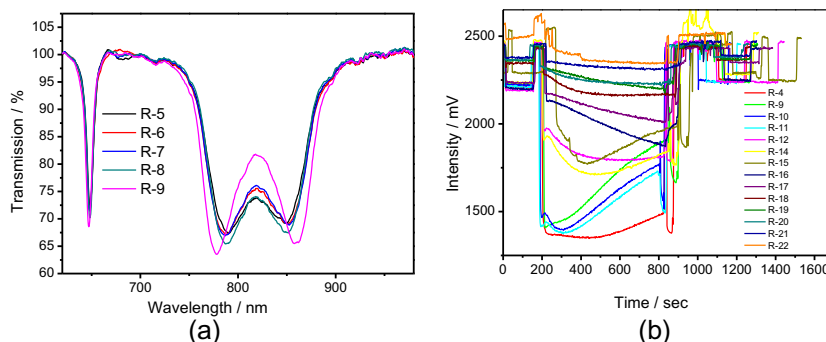


Fig. 8. (a) TS of the LPG fibre modified with the (PAH/SiO₂)₁₀ film and (b) dynamic changes measured at 820 nm in different dialysed red wines: the alcohol strength of each sample was adjusted to be 0.5%.

concluded that the LPG sensor is highly sensitive and selective for organic carboxylic acids in these beverages.

3.3. Wine quality assessment

3.3.1. LPG sensor

To evaluate the possibility of employing the LPG sensor for the determination of wine quality, it was exposed to 24 red wine samples, one of which was spoiled. Fig. 8a and b shows the typical

evolution of the TS and the dynamic response recorded at 820 nm, respectively, for the LPG sensor immersed in different wines.

It should be noted that the same LPG sensor was used to analyse all of the wine samples and that the sensor response was refreshed using a 0.1 wt% aqueous solution of NH₃ between each analysis. The TS and dynamic change in water were recorded after each NH₃ rinse to confirm sensor recovery (Fig. S8). Fig. 9 presents the PCA plot of the results for the different red wines. It can be seen that the spoiled wine R1 is clearly separated from all of the other

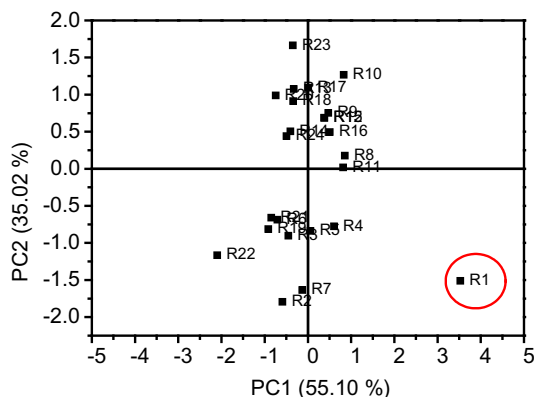


Fig. 9. PCA plot of red wines measured using the LPG fibre. The circled data point indicates the result for the spoiled wine.

groups of wines, indicating that it is possible to determine the quality of wine using an LPG sensor functionalised with a PAH/SiO₂ thin film. The same type of wine was also measured before it was spoiled and the results are shown as R4 in Fig. 9.

Next, to determine which chemical compounds were present in the unspoiled and spoiled wines, both were analysed using GC–MS and the results are presented in Fig. 10 and summarised in Table 1. These analyses revealed that acetic acid was present at an elevated concentration in spoiled wine, (Table 1). It is a well-known fact that the spoilage of wines leads to the increase of carboxylic acids, in particular lactic and acetic acids [22]. Similarly, the current GC–MS analysis confirmed that spoiled wines possess increased acetic acid contents (ca. 830 mg/L); however, these were still within normal levels, and were lower than the international standard range (1.2–1.3 g/L).

To achieve a higher level of insight regarding wine quality, the GC–MS data were then analysed using the PCA contribution plot with the purpose of determining and comparing the extent to which each variable (compound) contributed to the flavour pattern observed for a given wine variety. From the total list of compounds present in the wines, the 24 that were present at considerable levels and thus were likely the main contributors to the quality and flavour were selected for the analysis, and the results are shown

Table 1

Quantitative assessment of acetic acid content in red wine samples. Bold value represent the highest value.

Sample	Average concentration, mg/L	Sample	Average concentration, mg/L
R1	827	R13	530
R2	288	R14	528
R3	N/D	R15	486
R4	572	R16	520
R5	552	R17	407
R6	678	R18	536
R7	503	R19	255
R8	455	R20	384
R9	511	R21	507
R10	511	R22	454
R11	491	R23	344
R12	453	R24	576

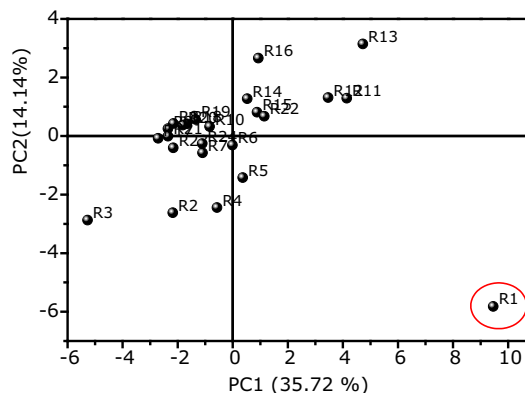


Fig. 11. PCA plot of the GC–MS data obtained for 24 selected compounds that were present in the red wines analysed in this study. The red circle indicates the spoiled wine sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Fig. 11. Notably, this PCA plot obtained using GC–MS data is similar to the PCA plot prepared using the LPG data.

These results indicate that the LPG sensor was reacting to the presence of acetic acid, which belongs to a class of carboxylic acids, at elevated concentrations in the spoiled wine sample, and thus suggest that the LPG sensor may potentially be applied for

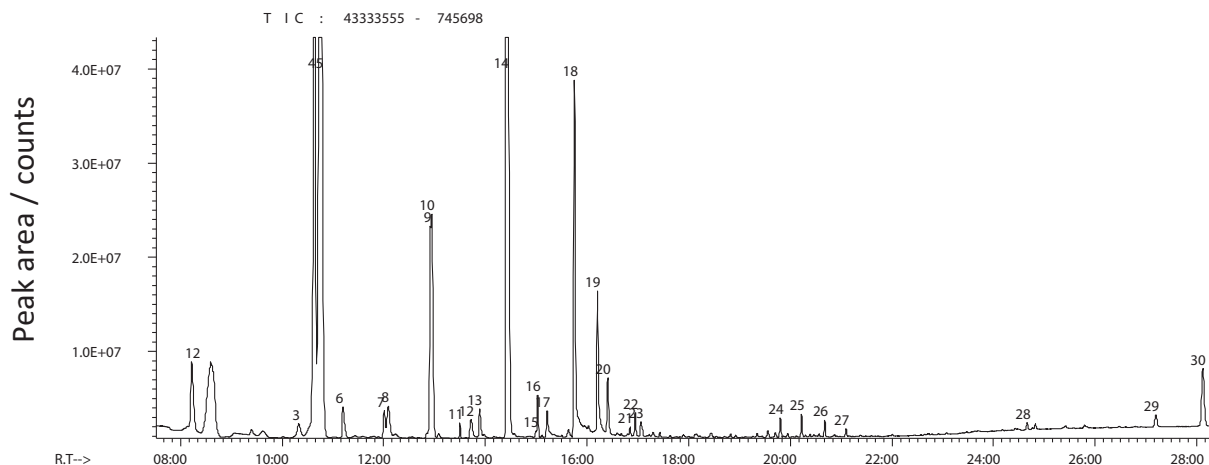


Fig. 10. Typical total ion chromatogram of a wine sample (R2). Peak numbers (1, 2) isobutanol (1-propanol, 2-methyl-); (3) D-limonene; (4, 5) isoamyl alcohol (1-butanol, 3-methyl-); (6) siloxane (bleed compound); (7, 8) 2-butanone, 3-hydroxy-; (9, 10) ethyl lactate (propanoic acid, 2-hydroxy-, ethyl ester); (11) siloxane (bleed compound); (12) nonanal; (13) ethanol, 2-butoxy-; (14) acetic acid; (15) siloxane (bleed compound); (16) 1-hexanol, 2-ethyl-; (17) decanal; (18, 19) 2,3-butanediol, [R-(R*,R*)]-; (20) propylene glycol (1,2-propanediol); (21) ethanol, 2-(2-ethoxyethoxy)-; (22) silanediol, dimethyl-; (23) butyrolactone; (24) benzyl alcohol; (25) phenylethyl alcohol; (26) 1-dodecanol; (27) phenol; (28) 1-tetradecanol; (29) n-nonadecanol-1; and (30) octacosyl trifluoroacetate.

beverage quality assessment. The mechanism of the determination of the spoiled wine is based on the interaction of amine functional groups of the PAH polymer present in the PAH/SiO₂ film and a carboxylic functional group of acetic acid. Further investigation is required to deduce which other compounds might be present in spoiled wines at elevated concentrations.

4. Conclusions

An LPG with a 100 µm grating period and coated with a porous thin film shows promise as a sensor for beverage analysis. When the PCA method was applied to the results obtained for various types of beverages, it was possible to identify drinks made from grapes and other materials. The sensing mechanism is based on the interaction between the organic carboxylic acids and the functional groups of the PAH/SiO₂ film on the LPG fibre. The GC–MS analysis confirmed that the different types of beverages contained different chemical compounds. In particular, carboxylic acids were present at elevated concentrations in the grape-based beverages (brandy and red and white wines). The LPG sensor was also used successfully to identify spoiled wine. In addition, a series of GC–MS experiments was performed to identify the different compounds that contribute to the flavour of 24 different wine samples. It was then demonstrated that the LPG sensor offers promise for the determination of compounds that are present in wines at high concentrations (1–1000 mg/L (ppm)) using a small sample volume (3 µL). Because many of these compounds contribute directly to the odour of wines and can be detected by consumers, it is important to at least determine if they are present. Furthermore, in addition to the qualitative patterns of wines that can be obtained using the LPG sensor, the evaluation method can be adjusted for the quantification of selected compounds, as was demonstrated for acetic acid.

Conflict of interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.sbsr.2014.06.001>.

References

- [1] W. Cynkar, R. Damberg, P. Smith, D. Cozzolino, Classification of Tempranillo wines according to geographic origin: combination of mass spectrometry based electronic nose and chemometrics, *Anal. Chim. Acta* 660 (2010) 227–231.
- [2] L. Lvova, R. Paolesse, C. Di Natale, A. D'Amico, Detection of alcohols in beverages: an application of porphyrin-based electronic tongue, *Sens. Actuat. B: Chem.* 118 (2006) 439–447.
- [3] IARC Working Group, Chemical composition of alcoholic beverages, additives and contaminants, *IARC Monogr. Eval. Carcinog. Risks Hum.* 44 (1988) 71–99.
- [4] R. Perestrelo, A. Fernandes, F.F. Albuquerque, J.C. Marques, J.S. Camara, Analytical characterization of the aroma of Tinta Negra Mole red wine: identification of the main odorants compounds, *Anal. Chim. Acta* 563 (2006) 154–164.
- [5] E. Miklosy, Z. Kalmar, V. Polos, Z. Kerenyi, Study of volatile aroma components in young Tokaji Aszu wines by GC–MS, *Chromatogr. Suppl.* 51 (2000) S305–S308.
- [6] International methods of analysis of wines and musts, International organization of vine and wine, Paris, 1962–1972. <<http://www.oiv.int/oiv/info/en/methodesinternationalesvin?lang=en>>.
- [7] D. Ballabio, T. Skov, R. Leardi, R. Bro, Classification of GC–MS measurements of wines by combining data dimension reduction and variable selection techniques, *J. Chemometrics* 22 (2008) 457–463.
- [8] J.A. Ragazzo-Sanchez, P. Chalierb, D. Chevalier, M. Calderon-Santoyo, C. Ghommidh, Identification of different alcoholic beverages by electronic nose coupled to GC, *Sens. Actuat. B: Chem.* 134 (2008) 43–48.
- [9] J. Lozano, T. Arroyo, J.P. Santos, J.M. Cabellos, M.C. Horrillo, Electronic nose for wine ageing detection, *Sens. Actuat. B: Chem.* 133 (2008) 180–186.
- [10] V. Parra, A. Arrieta, J.A. Fernandez-Escudero, M. Iniguez, J.A. de Saja, M.L. Rodriguez-Mendez, Monitoring of the ageing of red wines in oak barrels by means of an hybrid electronic tongue, *Anal. Chim. Acta* 563 (2006) 229–237.
- [11] C. Apetrei, I.M. Apetrei, I. Nevares, M. del Alamo, V. Parra, M.L. Rodriguez-Mendez, J.A. De Saja, Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods: correlation between electrochemical signals and analytical parameters, *Electrochim. Acta* 52 (2007) 2588–2594.
- [12] C. Di Natale, F.A.M. Davide, A. D'Amico, P. Nelli, S. Groppelli, G. Sberveglieri, An electronic nose for the recognition of the vineyard of a red wine, *Sens. Actuat. B: Chem.* 33 (1996) 83–88.
- [13] K.T.V. Grattan, B.T. Meggitt, *Chemical and Environmental Sensing*, Kluwer, Boston, Dordrecht, 1999.
- [14] S. Korposh, T. Wang, S.W. James, R.P. Tatam, S.-W. Lee, Pronounced aromatic carboxylic acid detection using a layer-by-layer mesoporous coating on optical fibre long period grating, *Sens. Actuat. B: Chem.* 173 (2012) 300–309.
- [15] S. Korposh, R. Selyanchyn, W. Yasukochi, S.-W. Lee, S. James, R. Tatam, Optical fibre long period grating with a nanoporous coating formed from silica nanoparticles for ammonia sensing in water, *Mater. Chem. Phys.* 133 (2012) 784–792.
- [16] S. Korposh, S.W. James, R.P. Tatam, S.-W. Lee, Refractive index sensitivity of fibre optic long period gratings coated with SiO₂ nanoparticle mesoporous thin films, *Meas. Sci. Technol.* 22 (2011) 075208s.
- [17] S.W. James, R.P. Tatam, Optical fibre long-period grating sensors: characteristics and application, *Meas. Sci. Technol.* 14 (2003) R49–R61.
- [18] D. Viegas, M. Hernaéz, J. Goicoechea, J.L. Santos, F.M. Araujo, F. Arregui, I.R. Matias, Simultaneous measurement of humidity and temperature based on an SiO₂-nanospheres film deposited on a long-period grating in-line with a fiber Bragg grating, *IEEE Sens. J.* 11 (1) (2011) 162–166.
- [19] S. Korposh, S. Kodaira, S.-W. Lee, W.J. Batty, S.W. James, Nano-assembled thin film gas sensor. II. An intrinsic high sensitive fibre optic sensor for ammonia detection, *Sens. Mater.* 21 (4) (2009) 179–189.
- [20] R. Selyanchyn, S. Korposh, T. Matsui, H. Matsui, S.-W. Lee, Purge and trap sampling coupled to Curie point thermal desorption for the detection of parts per trillion 2,4,6-trichloroanisole in water, *Chromatographia* 71 (2009) 317–321.
- [21] S. Korposh, S.W. James, S.-W. Lee, S.M. Topliss, S.C. Cheung, W.J. Batty, R.P. Tatam, Fiber optic long period grating sensors with a nanoassembled mesoporous film of SiO₂ nanoparticles, *Opt. Express* 18 (12) (2010) 13227–13238.
- [22] G.H. Fleet, Yeast interactions and wine flavour, *Int. J. Food Microbiol.* 86 (1–2) (2003) 11–22.



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