

# Near infrared spectra of beverages and threat liquids

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## Introduction

In response to the failed bombings of transatlantic flights in 2006, security in airports was tightened and now no more than 100 ml of a liquid is allowed to pass security points, especially for international flights.<sup>1,2</sup> Deregulation of this current condition of travel is desired; however, non-invasive detection of threat liquids concealed in a container is still challenging. It is for this reason that the development of a screening instrument for the identification of threat liquids in a sealed container is being pursued in many countries.

Our group has been investigating near infrared (NIR) spectroscopy as a new technology to distinguish threat liquids from commercial liquid products including beverages, liquid foods, cosmetics and shampoo.<sup>3,4</sup> NIR spectroscopy has several advantages: the screening time per sample can be less than a few seconds, the instrument can be small, the cost of construction is not expensive, the irradiation light is not harmful, the energy of the light does not detonate the liquid explosive, and determination of main chemical components in liquids is possible due to the acquisition of spectral information which is specific to molecules. However, there are some disadvantages: NIR spectroscopy cannot be used if the liquid is in a metal container and spectral resolution is not high in comparison with mid-infrared spectroscopy.

To identify threat liquids, such as flammable liquids and the raw materials of liquid explosives, it is necessary to have spectral data from commercial liquid products for comparison. However, the collection of spectral data from all the commercial products sold in the world is not realistic. The classification of liquids based on NIR spectral information could remove the need for such an extensive dataset. NIR spectra from beverages, including soft drinks and alcoholic drinks, were obtained and compared with the NIR spectra of threat liquids (hydrogen peroxide, nitric acid, gasoline, acetone and ethanol). A multivariate statistical classification model based on second derivative spectra was calculated to distinguish commercial beverages from threat liquids.

## Materials and Methods

### Samples

The samples were all commercially available: tea, coffee, carbonated beverages, red wine, white wine, fruit wine, vodka, gin, whisky, gasoline, vegetable oil, ethanol, acetone, and threat liquids: hydrogen peroxide (30%), nitric acid (30%), ammonia aqueous solution (30%), sodium hydroxide (30%) and hydrochloric acid (30%). The mixture of water and sucrose (50%) was prepared to compare the spectrum with soft drinks and alcoholic beverages. The mixtures of water and hydrogen peroxide (20%, 25%, and 30%) were prepared to establish the concentration dependence of peaks in the spectra. Table 1 summarises the 20 samples for which spectra are shown in Figures 1 and 2 although 31 samples were used for the principal component analysis (PCA).

**Table 1.** Samples studied in this work

Category	Name	No.	Category	Name	No.
Soft drinks	Water	1	Flammable liquids	ethanol	11
	mixture of water and sucrose (50%)	2		toluene	12
	green tea	3		acetone	13
	sweet carbonate	4		vegetable oil	14
	Cola	5		gasoline	15
	Coffee	6	Threat liquids	nitric acid (30%)	16
Alcoholic drinks	red wine	7		ammonia aqueous solution (30%)	17
	white wine	8		sodium hydroxide (30%)	18
	Vodka	9		hydrogen peroxide (30%)	19
	fruit wine	10	hydrochloric acid (30%)	20	

Reference paper as:

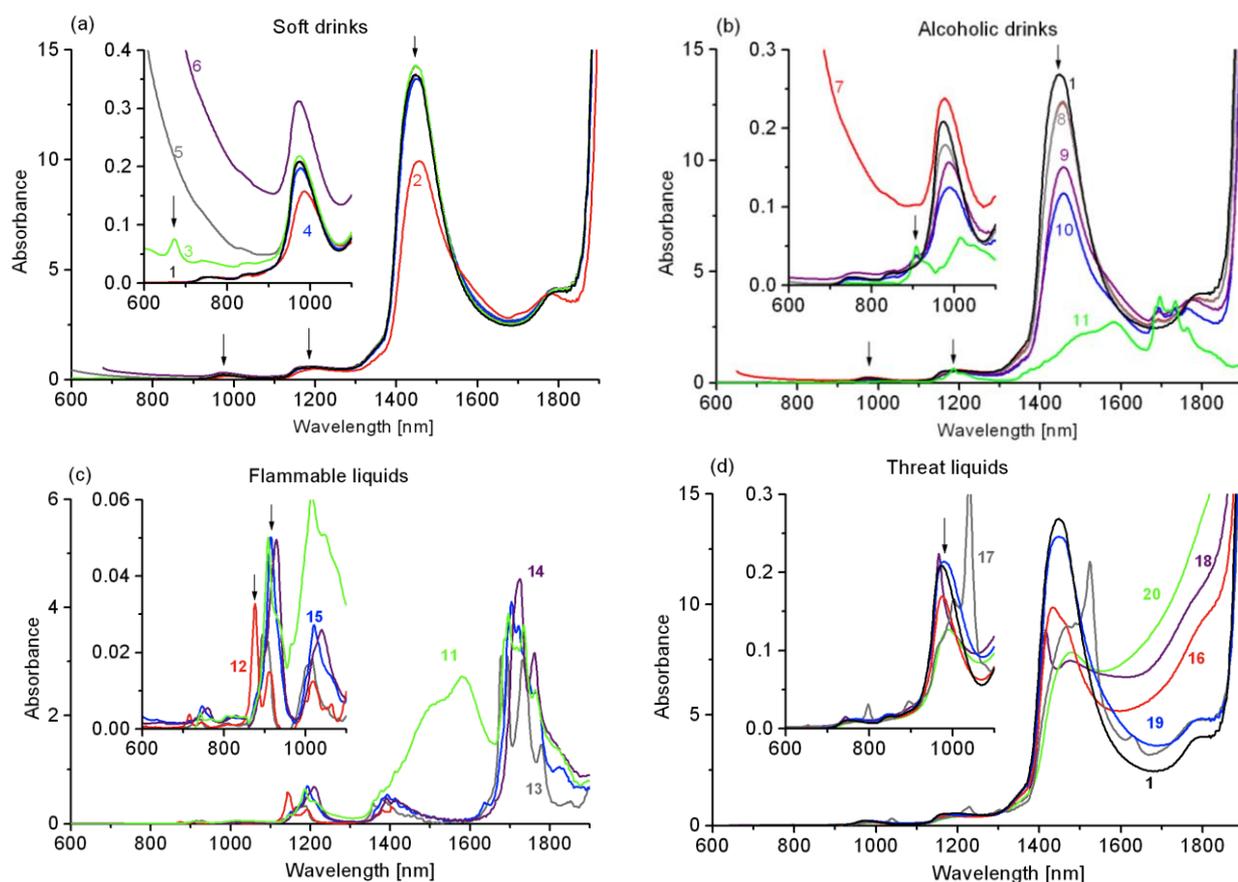
H. Sato-Akaba, R. Miyamura, D. Shirotani and H. Itozaki (2012). Near infrared spectra of beverages and threat liquids, in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGovern, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 228-231.

## Near infrared spectroscopy

NIR absorption spectra (600–1900 nm) were obtained in transmission using a Perkin Elmer Lambda 750 instrument. A 100 mm quartz glass cell was used for the region of 600 to 1000 nm while 10 mm and 1.0 mm quartz glass cells were used for the region of 1000 to 1300 nm and 1300 to 1900 nm, respectively. The absorption spectra were normalised against a light pathlength of 10 mm and the three spectra combined to give one continuous spectrum from 600 to 1900 nm. The resolution of the spectra was 2 nm. The second derivatives of the absorption spectra were calculated with numerical differentiation using 25-point gaps and all measurements were carried out at room temperature. Identification of the NIR peaks in the beverage spectra was based on NIR reference texts.<sup>5</sup> The spectra of beverages within 600 to 1000 nm are generally due to a mixture of the overtones of vibrational transitions and a tail of the absorptions due to electronic transitions.

## Classification method

PCA was carried out using The Unscrambler X (CAMO Software, Oslo, Norway). The second derivative absorption spectra were used for analysis to decrease the effect of the baseline differences between the spectra. The standard normal variate transform (SNV) was applied to the spectra prior to the PCA. The purpose of this treatment was to enhance the relatively weak spectra observed for organic solvents (when compared to those of aqueous liquids). In fact, the light pathlength varied between samples and therefore the spectral intensities varied even for the same liquids. The SNV treatment can also help to compensate for this difference of the spectral intensities within the same liquids.



**Figure 1.** NIR absorption spectra of liquids normalised to a light pathlength of 10 mm. Inset figures focus on the spectral region where whole bottle measurements are possible. (a) soft drinks: 1 - water, 2 - mixture of water and sucrose (50%), 3 - green tea, 4 - sweet carbonate soft drink, 5 - cola, 6 - coffee, (b) alcoholic drinks: 1 - water, 7 - red wine, 8 - white wine, 9 - vodka, 10 - liquor, 11 - ethanol, 12 - toluene, 13 - acetone, 14 - vegetable oil, 15 - gasoline, (c) flammable liquids: 11 - ethanol, 12 - toluene, 13 - acetone, 14 - vegetable oil, 15 - gasoline, (d) threat liquids: 1 - water, 16 - nitric acid (30%), 17 - aqueous ammonia solution (30%), 18 - sodium hydroxide (30%), 19 - hydrogen peroxide (30%), 20 - hydrochloric acid (30%).

Reference paper as:

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## Results and Discussion

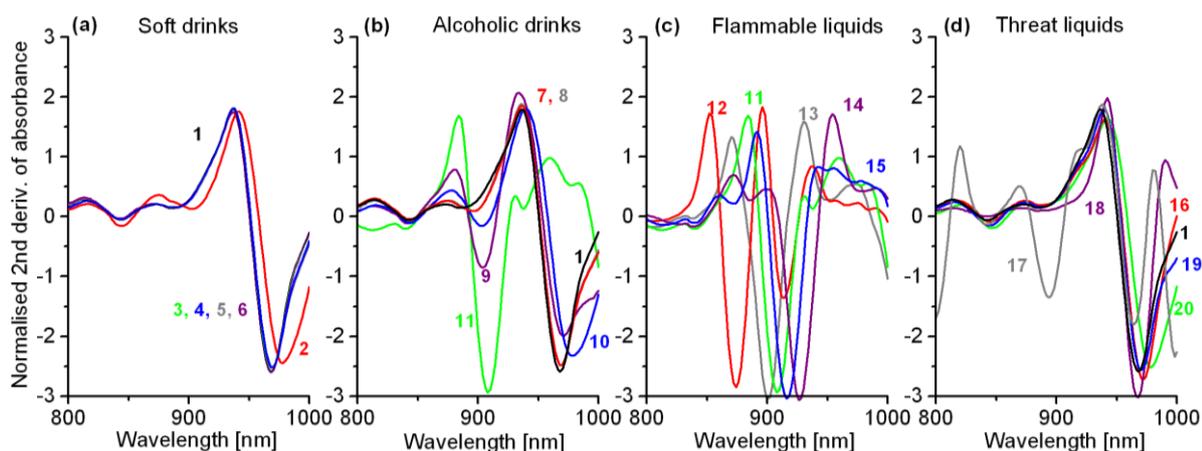
### NIR absorption spectra of beverages and threat liquids

NIR absorption spectra of commercially-available beverages were measured. Some of soft drinks are shown in Figure 1a. Vibrational absorptions due to water molecules were dominant: the second OH stretching overtone at 970 nm, the first OH combination band of stretching and bending at 1190 nm and the first OH stretching overtone at 1450 nm. Coloured drink spectra contained electronic absorptions, e.g. cola (#5) and coffee (#6). The absorption peak at 672 nm observed in green tea (#3) was due to the electronic transition of chlorophyll.<sup>6</sup> The peak at 986 nm for the mixture of sucrose and water (50%) (#2) was shifted from the second OH stretching overtone 970 nm; the second OH stretching overtone of sucrose is known at 990 nm. Therefore, the overtone of sucrose, which overlapped the overtone of water, led to the peak shift.

Spectra of several alcoholic drinks are shown in Figure 1b. The vibrational absorption due to water was dominant (970 nm, 1190 nm and 1450 nm). These peak intensities were dependent on the amount of water, which decreased as the amount of ethanol increased. The electronic absorption in red wine (#7) was strongly observed because of the colour of a red wine. However, the vibrational transition due to water in the 800–1000 nm region was clearly observed. The peak at 908 nm, which is the third CH stretching overtone of ethanol, was observed for all alcoholic drinks; this peak would be useful for the detection of ethanol and estimation of its concentration.

The spectra of flammable liquids (Figure 1c) were different from those of commercial beverages as the dominant peaks of water molecules were not present. The peak intensities within the flammable liquid spectra were at least three times smaller than those for water. Flammable liquids were clearly distinguished from aqueous solutions. The toluene (#12) peak around 876 nm was due to the third overtone of CH stretching in benzene ring. Peaks around 900 to 930 nm, which were observed for most of the organic liquids, were due to the third overtone of CH stretching in CH<sub>2</sub> group.

Figure 1d shows spectra of threat liquids, such as acid, base and hydrogen peroxide, all of which contained water molecules. The peak around 970 to 990 nm had different shapes for each of the samples and was due to the second overtone of OH stretching. The second and third overtones of NH stretching (790 nm and 1040 nm, respectively) were observed for aqueous ammonia solution (#17).



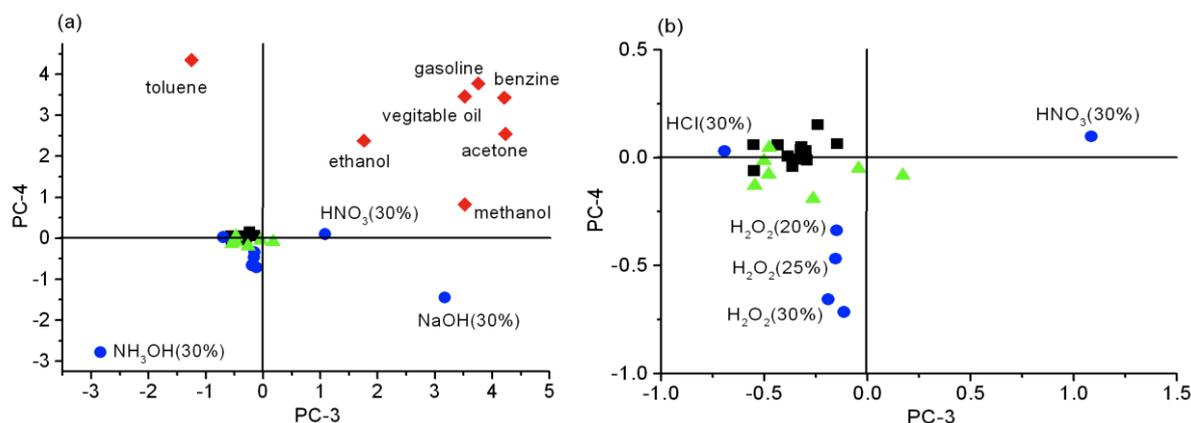
**Figure 2.** Normalised second derivatives of absorption spectra; only the region where whole bottle measurement is possible is shown. (a) soft drinks: 1 - water, 2 - mixture of water and sucrose (50%), 3 - green tea, 4 - sweet carbonate soft drink, 5 - cola, 6 - coffee, (b) alcoholic drinks: 1 - water, 7 - red wine, 8 - white wine, 9 - vodka, 10 - fruit wine, 11 - ethanol, (c) flammable liquids: 11 - ethanol, 12 - toluene, 13 - acetone, 14 - vegetable oil, 15 - gasoline, (d) threat liquids: 1 - water, 16 - nitric acid (30%), 17 - aqueous ammonia solution (30%), 18 - sodium hydroxide (30%), 19 - hydrogen peroxide (30%), 20 - hydrochloric acid (30%).

### Classification of the liquids

The spectral region for non-invasive screening of bottled liquids was limited by sensitivity. The light pathlength for bottle screening is generally around 50 to 500 mm. If there is strong absorption, the light rays do not reach to the detector. The strong absorption due to water molecules and sensitivity of the detector meant that the spectral region for use was below 1000 nm with a lower limit of around 800 nm, as decided by the presence of electronic absorptions from coloured bottles and liquids. However, the tail of the electronic absorption overlapped with the spectral region of 800 to 1000 nm. To solve this problem, the second derivatives of absorption spectra were used (Figure 2). Only the vibrational spectra remained in most cases.

Principal component analysis (PCA) was applied to the dataset of second derivative spectra (Figure 3). The third and fourth principal components (PC) allowed a distinction between the liquid groups to be made. The group of beverages was located near the origin while the samples of flammable liquids were scattered away from the origin. Hydrogen peroxide and nitric acid were separated from the beverage group and the concentration dependence of the hydrogen peroxide samples was observed. Hydrochloric acid (30%) was not separated from the group of beverages with using the scores of PC3 and PC4. A PCA applied to the dataset including only hydrochloric acid and beverages was able to separate these two groups.

These analyses indicated that the spectra of beverages are probably similar since the main components in beverages are limited to water, sugar and ethanol. Therefore, collecting a spectral dataset containing all possible beverages is not necessary.



**Figure 3.** Score plots of the principal component analysis of the total dataset: ◆ flammable liquids, ● threat liquids, ■ soft drinks, ▲ alcoholic drinks. (a) A map with all data points. (b) Enlargement of the area about the origin.

## Conclusion

NIR spectra of beverages and threat liquids were investigated. Absorption peaks related to water, ethanol and sugar were observed in the spectra of beverages. The variation associated with the beverage spectra was very limited; hence we conclude that collection of spectra from all possible beverages is not necessary. The distinction of flammable liquids and threat liquids from the beverages was possible with the aid of principal component analysis.

## Acknowledgements

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