High Resolution Spectroscopy of Sweeteners

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Abstract: The identification of sophistication in beverage and food products has an increasing role in modern society. Different techniques are currently used for qualitative assessment of food stuff and beverages. Among them high resolution spectroscopy shown to be able to identify different types of sweeteners such as fructose, glucose, maltose, sucrose and aspartame. To this purpose, a reliable, fast and easy-to-use screening method for the optical characterization of these substances was developed. In the present work the Infrared Laser Photo-Acoustic Spectroscopy was used to record high resolution infrared absorption spectra of common sugars in the fingerprint region, not previously reported in literature at our knowledge. Spectral data were obtained by a CO_2 laser based optical apparatus. These preliminary results are the key toward a further analysis of sweeteners in a complex matrix devoted to detecting adulteration of commercial fruit juices and light drinks by low cost sweeteners.

1 INTRODUCTION

Nowadays the food safety and consumer protection requirements are to increase the food and beverage quality and to adopt faster and easier methods for the quality determination. In the field of fruit juice adulteration most of frauds are based on the addition of water and low cost sweeteners to the product. The chromatographic methods GC and HPLC are currently used as accurate reference techniques to successfully determine fruit juice authenticity by oligosaccharide profiling (Pan 2002). Unfortunately they are time consuming, expensive and difficult to implement in an on-line setting (Leopold 2009).

The Fourier Transform Infrared (FTIR) spectroscopy approach considers the entire sample composition and is widely used to identify and study chemicals by measuring vibrational/ roto-vibrational frequencies of the excited molecules. Absorption bands in the MIR range are characteristic of the bonds and functional groups of a molecule, so the overall spectrum acts as a fingerprint for a given compound. This made it possible to apply FTIR spectroscopy to authenticity issues and composition profiling (Kelly 2005).

In the field of infrared spectroscopy, the high resolution spectroscopy based on a laser source may compete with the FTIR spectroscopy in order to quantify simultaneously the Fructose, Sucrose and Glucose content in a juice used as authenticity biomarkers. A laser spectroscopic techniques can offer a significant chance in detecting specific spectral signatures of sugars, and organic compounds in general, at trace concentration. Among different possible laser spectroscopic methods, high resolution Laser Photoacoustic Absorption Spectroscopy (LPAS) was selected for identification of sugars in the solid phase. LPAS (Michaelian 2003) is characterized by roughness, high sensitivity and high selectivity. The LPAS is an indirect absorption spectroscopy technique based on the Photoacustic effect in solid, which was discovered by Alexander Bell in 1880. Bell showed that when a periodically interrupted beam of sunlight illuminates a solid in an enclosed cell, an audible sound could be heard by means of a hearing tube attached to the cell. The sunlight energy absorbed by the sample is transformed into kinetic energy in the course of energy exchange processes. This results in local heating and consequently a pressure wave is generated. The sound obtained in this way represents the Photoacoustic signal. By measuring the sound at different wavelengths, a Photoacoustic spectrum of a sample can be recorded. To this purpose, modern LPAS systems employ the intensity modulation of a laser beam in order to allow the generation of acoustic waves in a resonant photo-acoustic cell.

In the present study, commercial standard samples of sugars (Fructose, Maltose, Sucrose, Glucose) and sweeteners (Aspartame) were analyzed

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by LPAS. The experimental results were reported in the paper. A PCA statistical treatment was applied to the experimental spectra in order to classify the examined substances. The present paper is the preliminary step toward the development of a easy-to-use technique for a real time detection of the mentioned fraud.

2 MATERIALS AND METHODS

To analyze the sugar samples by LPAS technique we adopted an optical apparatus realized in ENEA Frascati Research Centre with a grating tuned 2 Watts line tunable CO_2 laser source (Model Merit-G from ACCESS LASER), a two-channel power meter (Rk-5720 model by Laser Probe), a 3 cc volume Photoacoustic (PA) cell, and a lock-in amplifier (SR 830 model, Stanford Research Systems). The CO_2 laser emission was square wave modulated by a digital signal generator (SFG 830 by INSTEK) at the resonant frequency (40 Hz) of the PA cell, with a 50% duty cycle. The PA signal generated inside the PA cell was detected by a miniaturized sensitive microphone (Model EK 3033 by Knowles Electronics Inc., USA) and sent to the lock-in amplifier, which communicates to PC via GPIB interface. Data were acquired in the frame of a software developed in Labview environment. A general scheme of a LPAS experiment is shown in the Figure 1. More information on the LPAS system employed in the present work have been reported in previous papers (Giubileo et al. 2012, Puiu et al. 2014).

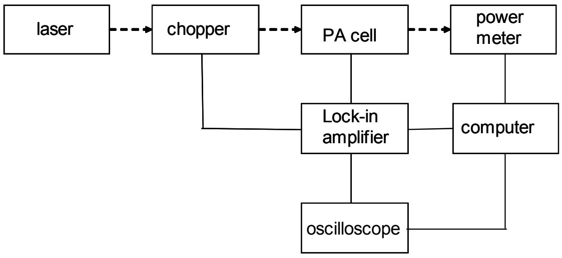

Figure 1: LPAS set-up schematic view.

The sweeteners for the study were purchased as commercial standard preparation from the suppliers reported in the Table 1. The sample of sweetener to be analyzed was placed inside PA cell at RT, without any pre-treatment. Measurable PA signals were obtained from a few milligrams of pure samples, depending on the investigated substance. The measurements were repeated 10 times for each one of the 55 laser lines emitted from the laser source at wavelengths falling in the 9.2 to 10.8 µm spectral range. For each kind of substance, four different samples were analyzed. The laser beam power interacting with the sample was set between 50 mW and 500 mW on the strongest laser lines with the purpose to maintain the sample temperature lower than the melting point.

Table 1: List of sugars analyzed in this paper.

Sweetener	**Chemical formula**	**m.p. (°C)**	**Supplier**
Fructose	$C_6H_{12}O_6$	100	Merk
Glucose	$C_6H_{12}O_6$	146	Merk
Maltose	$C_{12}H_{22}O_{11}$	360	Sigma
Sucrose	$C_{12}H_{22}O_{11}$	186	Baker
Aspartame	$C_{14}H_{18}N_2O_5$	249	Fluka

3 RESULTS

For each one of the analyzed substances, measurable PA signals were detected in the investigated spectral range, while the background signal was verified to be neglectable with respect to the sample signal. This allowed to plot a Photoacoustic spectrum for every analyzed sweetener, without the necessity to subtract the background signal. The resulting LPAS infrared absorption spectra of Fructose, Maltose, Sucrose, Glucose and Aspartame are reported in the Figures 2 to 6.

Each spectrum in these figures represents the average of four different PA spectra of the same type of substance.

The error bars on the graphs come out from the standard deviation (*sd*) after averaging multiple spectra. The recorded *sd* was under 3%, which means a very good reproducibility of data and a high stability of the system.

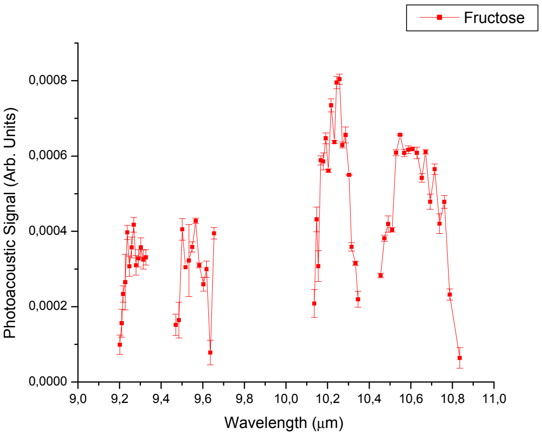

Figure 2: IR photoacoustic spectrum of fructose.

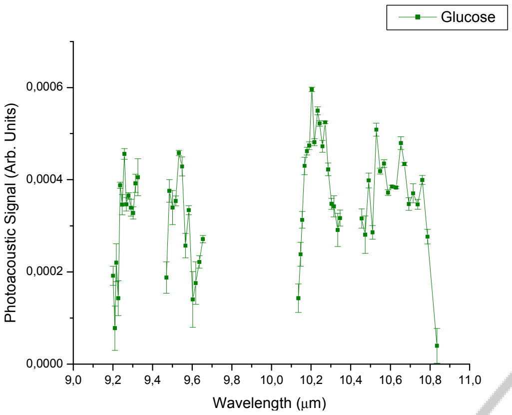

Figure 3: IR photoacoustic spectrum of glucose.

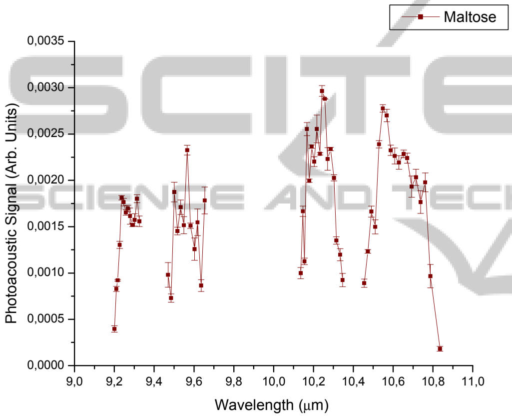

Figure 4: IR photoacoustic spectrum of maltose.

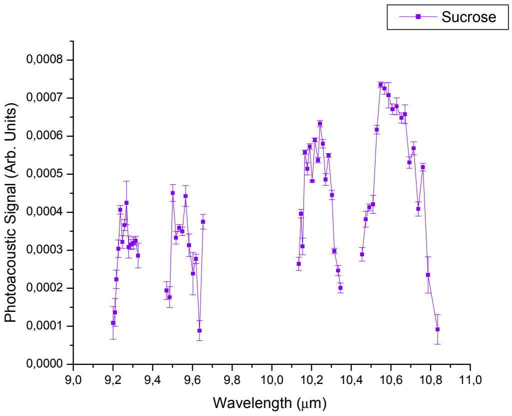

Figure 5: IR photoacoustic spectrum of sucrose.

Absorption data have been processed in order to make the experimental data not dependent on the local measurement settings, nor on the sample adopted amount. In particular, the absorption data have been normalized to the laser beam power. An independent record of the laser emission power spectrum is shown in the Figure 7.

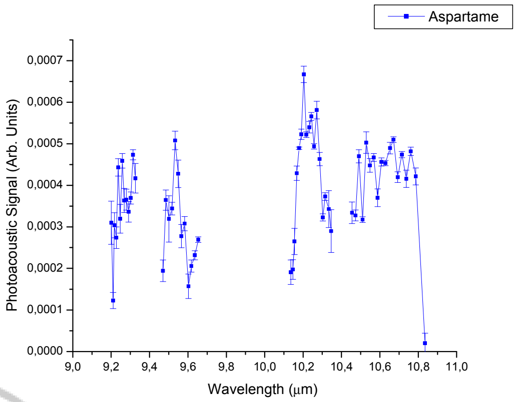

Figure 6: IR photoacoustic spectrum of aspartame.

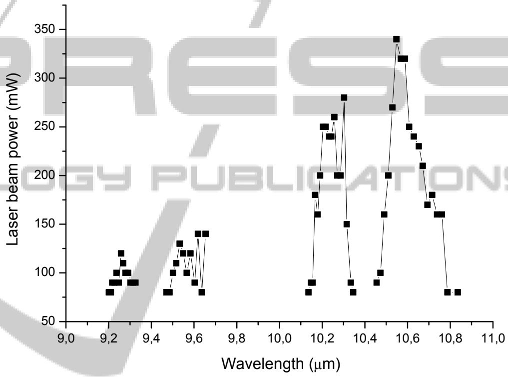

Figure 7: Spectrum of the laser emission power.

4 DISCUSSION

The present paper was not thought as a detailed study of the sweeteners IR absorption molecular transitions. Really it was intended as a first step of a work aimed to realize a new real-time methodology for the mentioned fraud detection to be applied on field. Consequently, the vibrational rotational transition lines assignment was not approached in the present paper.

From the graphs reported in the Figures 2 to 6 it appears that every substance shows a characteristic spectral pattern, nevertheless a rapid direct comparison among the spectra is difficult to achieve. For this reason, a data treatment based on Principal Component Analysis (PCA) was applied to the spectral data as a demonstration of the system capability to distinguishing among different standard sweeteners.

PCA is a calculation algorithm that allows to reduce dimensionality of a data set and make it evident statistical differences eventually present among the analyzed samples. PCA is a powerful statistical instrument described for the first time in the year 1901 (Pearson 1901). The PCA algorithm finds hypothetical variables (called Principal Components, PC) accounting for as much as possible of the variance in the multivariate data (Davis 1986, Harper 1999); the new variables are the results of a linear combination of the original variables, where every descriptor has an own "weight", or loading. Generally the first few new variables retain most of the variation of original variables. The use of PCA appears extremely suitable for the spectroscopy analysis discussed in this work. It allows to make it clear the grade of similarities or differences among the spectra and point out the most involved emission lines (loading). The PCA calculations operated on the above spectral data produced the sample distribution reported as a 3D chart in the Figure 8.

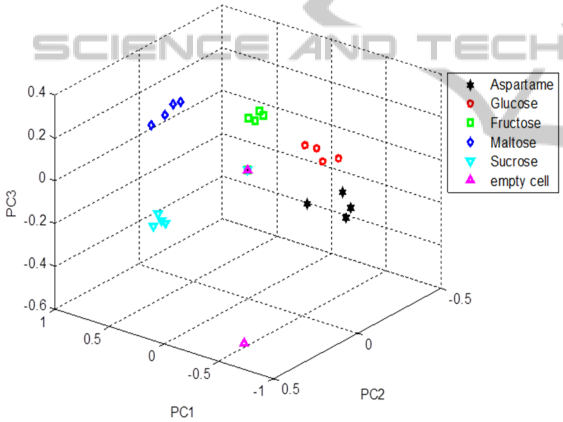

Figure 8: 3D representation of PCA.

The infrared absorption data have been normalized to their maximum peak value, in order to make them directly comparable with each other. For the PCA calculations, also the PA signal from the empty cell was taken into account.

On each axis, the respective value of one of the first three principal components is reported: PC1, PC2 and PC3.

Taking into account the respective contribution of each principal component to the substances classification (see the Figure 9), it appears that the first three PCs can explain 80% of the overall spectral differences. Moreover, due also to the same minor impact given by PC2 and PC3, we reduced the PCA graph to the 2D representation reported in the Figure 10 that brings out five different groups corresponding to the analyzed types of sweeteners.

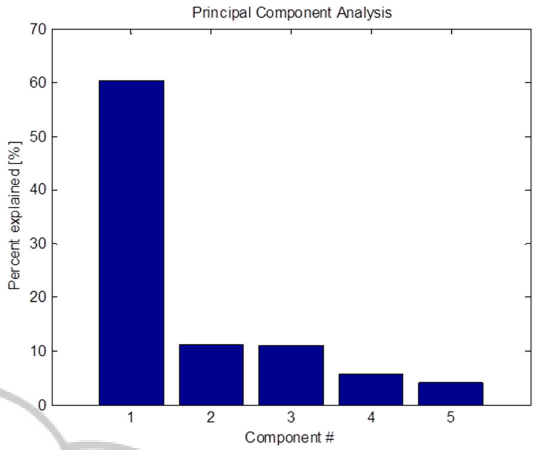

Figure 9: Weights of the principal components.

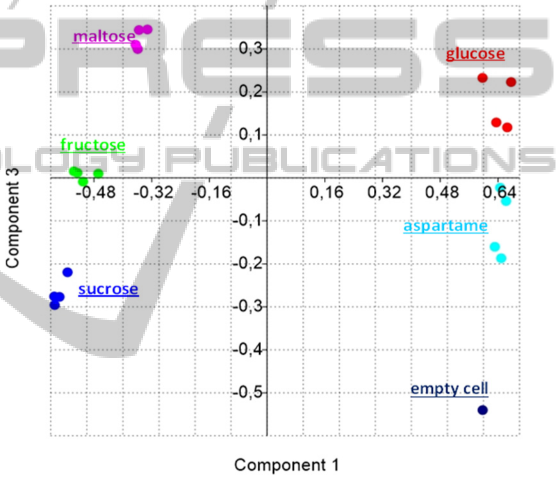

Figure 10: 2D graph of PCA.

5 CONCLUSIONS

In the present paper, the LPAS technique was applied to collect the high resolution infrared absorption spectra of Fructose, Maltose, Sucrose, Glucose and Aspartame in the 9.2 to 10.8 µm spectral region. To our knowledge, the high resolution infrared absorption spectra shown in this paper have been reported for the first time in literature.

Further that, we have also shown that the joint application of LPAS and Chemometrics can be used to unambiguously classify the analyzed substances without mis-assignments. This result makes the method promising for a simple identification of sophistication in beverage and food products.

The data here reported will be useful in the future realization of a fast and easy-to-use screening apparatus for detecting the presence of unwanted sweeteners in juices and light beverages. Consequently, the next step will include the LPAS analysis of sweeteners mixtures and fruit juices to check the capability of the optical technique to probe the quality of a unknown sweetener and detect frauds.

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