APPLICATION NOTE PA301

Identification of cocaine abuse from human hair samples with
Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS)

A novel approach combining different techniques, including FTIR spectroscopy, photoacoustic detection with an interferometric cantilever microphone and principal component analysis (PCA) with a proper data preprocessing procedure, was applied in the investigation of hair samples for cocaine abuse. Gasera PA301 photoacoustic detector for solid, semi-solid and liquid samples was used to successfully discriminate between cocaine overdose patients and a cocaine-free reference group based on their hair samples.

Application

Cocaine is difficult to detect by quick observation and expensive blood or urine tests are always needed for certainty. Cocaine has several infrared absorption bands, with two characteristic bands around 1750 and 720 cm^{-1}, which can be used for identification. Drugs can enter the hair via the bloodstream, sebaceous and eccrine secretions and external contamination. Hair has some advantages over the more commonly used blood or urine samples in drug testing. Hair has a longer detection window of substances and it can be used for studying a person's drug history. Hair samples are also noninvasively collected and do not suffer from preparation and storage problems.

Hair is a problematic sample material for common infrared spectroscopic techniques. Lack of sensitivity and difficult sample preparation procedures of transmission-based

Fig. 1. PA301 and its accessory box

infrared techniques, attenuated total reflectance (ATR) spectroscopy, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) lead to low reproducibility of the measurement.

In cantilever-enhanced PAS, an interferometric silicon cantilever microphone is used as a pressure sensor instead of the condenser microphone, which is used in most of the commercial photoacoustic detectors. Cantilever-enhanced PAS has many advantages over the more commonly used transmission or reflection-based infrared techniques, which makes it ideal for measuring hair fibers:

• High sensitivity
• No sample preparation is needed
• Depth profiling can be performed for layered samples
• Technique is nondestructive and suitable for opaque samples

Measurement results

12 hair samples from cocaine-overdose patients along with 12 reference hair samples from subjects with no cocaine abuse were measured with Gasera PA301 connected to Bruker Tensor 37 FTIR spectrometer. The measurement setup is shown in Fig. 2, and the parameters are presented in Table I. 20 – 30 mg of hair material was used per measurement to obtain a good average. Carbon black was used in the normalization of the spectra and helium was used as a carrier gas in the photoacoustic cell. Hair fibers consist mostly of keratin, which is a general name for fibrous proteins consisting of long amino acid chains, along with water, lipids, pigment and trace elements. The cocaine content in hair samples varied between 1.5 and 38 ng/mg.
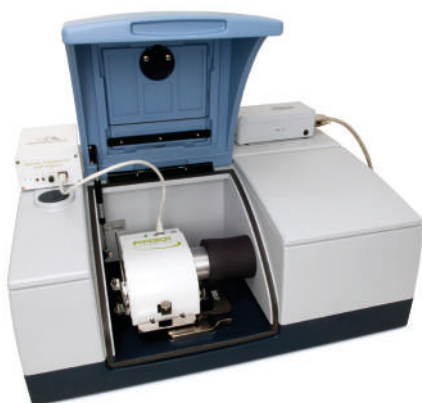

Fig. 2. PA301 installed as an external detector to the FTIR spectrometer.

Table I. FTIR spectrometer measurement parameters

Measurement time	90	s
Mirror velocity	2.2	kHz
Resolution	8	cm^{-1}
Spectral range	400 - 4400	cm^{-1}
Aperture	6	mm

The averaged spectra of hair samples from the cocaine users and the reference group are shown in Fig. 3. The discrimination between the two groups cannot be performed with a visual inspection, and therefore, data processing is needed. The spectral pre-processing contained four different steps: selecting of the optimal spectral range, normalizing the intensities, taking the second derivative and mean centering. The selection of the optimal spectral range is important because the discrimination of spectra is done according to the cocaine content, and this requires the effects of natural variance among different hair samples to be as low as possible. The selected spectral range is shown in Fig. 3.
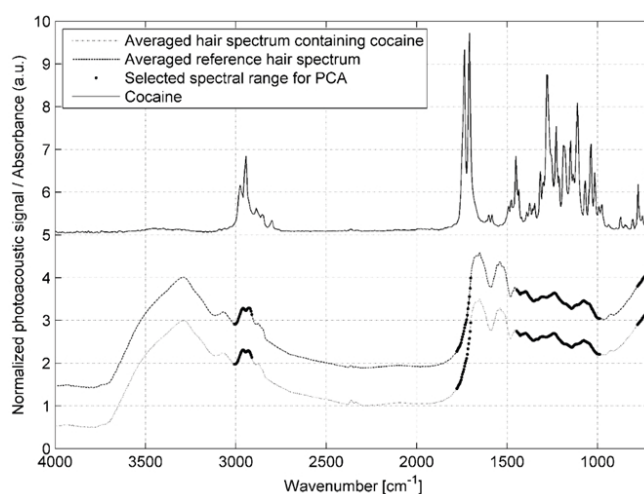

Fig. 3. Average photoacoustic spectra for hair samples of cocaine users and reference group, and a library FTIR spectrum for pure cocaine.

The result of the PCA algorithm performed on the pre-processed spectra is shown in Fig. 4. The samples separated into two groups in the principal component (PC) 1 and 2 plot according to their cocaine content. Even though ten PCs were calculated, the first two were enough for the discrimination of the two classes of hair samples.
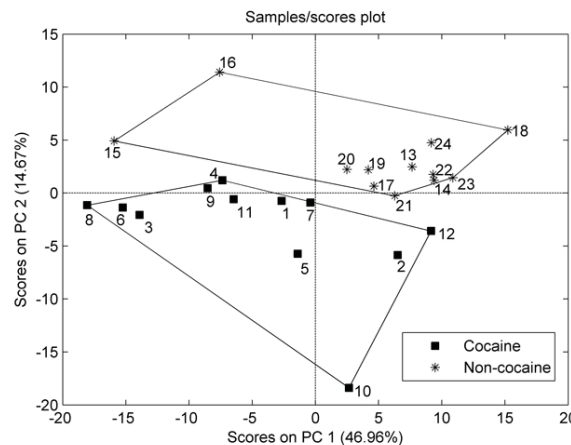

Fig. 4. Cocaine users and non-cocaine users separated with PCA based on the photoacoustic measurement and data pre-processing.

The measurement technique can be further developed using microsampling techniques in photoacoustic spectroscopy to measure single hair fibers with a length of only a few millimeters. The precision can also be improved by the use of tunable laser source for a greater and more controlled sampling depth.