UV/VIS NanoPhotometer® for authenticity testing of spirits

A new rapid, cost effective screening method




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Verification of authenticity of food plays an important role in official food quality control. The financial incentive to replace food by inferior products or to falsify it by mixing with poor quality or low-priced products is especially evident in premium quality, high-priced foods. Depending on the nature of the product added consumers may not only be misled, but health hazards originated from toxic ingredients may result. The latest "Methanol Case" in Eastern Europe in 2012 e.g. caused more than 30 deaths as a result of methanol-adulterated spirits.

Authenticity testing of spirits from open containers in restaurants, nightclubs or bars is a recurring routine task for food control authorities. Along with routine inspections, complaints from anonymous consumers reporting the suspicion of trademark counterfeiting require follow up and investigation.

For authenticity testing of spirits, various complex analytical examination procedures are currently available. In addition to the analysis of volatile components by gas chromatography, coupled also with mass spectrometry (GC-MS) and the determination of the stable isotope ratios of the alcohol molecule by carbon isotope mass spectrometry (^{13}C-IRMS) and deuterium nuclear magnetic resonance (^{2}H-NMR), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) is increasingly used. By comparing the ^{1}H-NMR profile of unknown samples with reference samples previously stored in a database, assertions can be made pertaining to the authenticity of spirits.

In addition to the aforementioned techniques, a new, mobile analytical measuring system based on UV/Vis spectroscopy, the Implen NanoPhotometer®, offers a quick cost effective method of checking the authenticity of spirits. With this technology a characteristic absorption spectrum (scan wavelength range of 200-900 nm) similar to a one-dimensional fingerprint can be obtained in a few seconds with just a drop of sample. This fingerprint can be compared with those of known brand products within seconds – in the laboratory or on-site.

As part of a case study, absorption spectra of authentic spirits were acquired and stored in a database. Various production batches of spirit brands were taken into account in order to create the best possible database for the recognition of unknown samples. For verification purposes, allegedly branded spirits were taken from open containers to compare the samples with the available database.

The Principle of Measurement

The Implen NanoPhotometer® is a UV/Vis spectrophotometer. The analysis time of only 3.5 seconds and a sample volume requirement of just 5 µl are great advantages of this affordable maintenance-free, portable device. With each sample measurement, a capillary film is formed between two scratch-resistant, metal-free quartz surfaces situated within the proprietary measurement head of the instrument. This patented measurement process eliminates sample evaporation, allowing reliable measurements of samples in volatile organic solvents in a single drop. The NanoPhotometer® can also be used as a standard photometer operating with a cuvette. No consumables are required for the measurement and cleaning is very straightforward requiring a simple swipe with a Kimtech Science Precision Wipe®. Due to its ease of use, the NanoPhotometer® can be operated by users lacking a sound laboratory background after only a short tutorial of the system. Implen's patented "Sample Compression Technology ™" and "True Path Technology ™", which allow

the reliable measurement of samples in the micro-volume range, are explained in more detail below.

SAMPLE COMPRESSION TECHNOLOGY ™

The NanoPhotometer® has an optical geometry, similar to a microscope slide and a cover glass used in microscopy. The sample is pipetted onto a pedestal serving as a "slide", while the reflector mirror in the lid acts as the "cover glass" enclosing the sample drop between two quartz surfaces. This creates a thin sample film of a precisely defined layer of thickness (pathlength). In addition, due to the enclosed environment, the sample liquid is protected against evaporation. For the measurement the sample is illuminated from below, the light beam passes through the sample and is reflected from the lid mirror back through the sample onto the detector.

TRUE PATH TECHNOLOGY ™

In standard spectroscopic procedures, a manual dilution step is generally necessary in order to obtain the optimum measurement range for a sample. This step is not only time consuming, but also error prone. The NanoPhotometer® virtually dilutes samples by adjusting the path length to the optimal measurement range. The device works with two precisely defined path lengths (0.07 mm and 0.67 mm) fixed by immobile anchor points. The correct pathlength is automatically selected depending on the concentration of the sample. With its enclosed optical concept and no internal moving components, the NanoPhotometer® does not require recalibration over the lifetime of the instrument. The NanoPhotometer® utilizes a xenon flash lamp with a lifetime of about 10 years (10^9 flashes). Slight change to the lamp's intensity will be experienced over time; this very minor change will not compromise the accuracy of the instrument over the entire lifetime of the lamp. Each time the instrument is powered on, the NanoPhotometer® performs an automatic self-calibration. The application menu of the device will only appear when instrument initialization is successfully completed. If quality assurance checks are required, an Installation Qualification (IQ) and Operational Qualification (OQ) package containing a certified Didymium glass filter and standard solutions can be utilized to verify wavelength and photometric accuracy of the unit. A set of documentation software is also available.

First tests to establish a database of spirit categories and brands

In order to create a database, three suitable absorption spectra (from a 10-fold measurement process) were selected for samples of different categories (i. e. whisky, brandy, tequila, rum) and brands of spirits; these spectra were then used as reference samples for each brand or batch of a brand respectively. A software algorithm developed by Implen compares the absorption spectrum of an unknown sample with the spectra stored in the database. As a result of the analysis, the spectrum of the reference sample which best matches the unknown sample is displayed. The percentage probability that the fingerprint of the unknown sample matches the brand name sample is also displayed. Figure 1 shows an example of the differentiation of four different brandies based on their absorption spectrum.

Verification of open samples from the gastronomy sector

Samples of different categories of spirits (whiskeys, brandies, bitter spirits, rum and vodka) taken from open bars in gastronomic establishments were compared with data from available reference samples in the database. It was found that both the spirit categories and the brands can be distinguished very reliably with the NanoPhotometer®. If the absorption spectrum of an open, alleged brand sample did not match the authentic product in the database, this was also evident from the classical analysis data obtained in routine laboratory analysis.

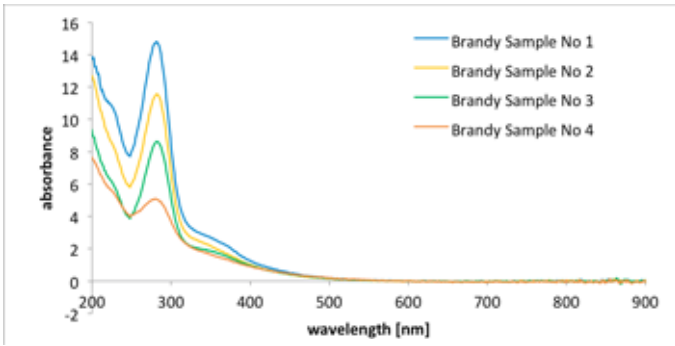
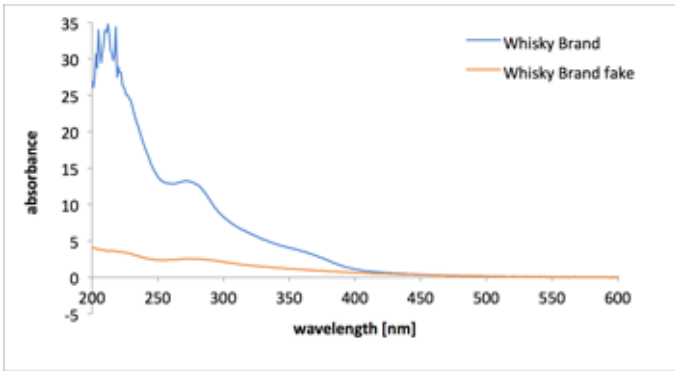


Fig. 1: UV/Vis spectra of four different brandies

In some cases absorption spectra of whiskey, brandy and rum brands did not show any or only slightly visible differences, which makes it difficult to identify unknown samples. For these cases even more refined algorithms are currently being developed, so that even very minor differences between samples will lead to better identification or differentiation in the future.

Examination of electronic commerce samples

Besides the sale of low-quality products as brand-name products in gastronomy establishments, electronical commerce becomes a growing potential marketing platform for counterfeit branded products. Several alleged brand products from internet retailing offered at a



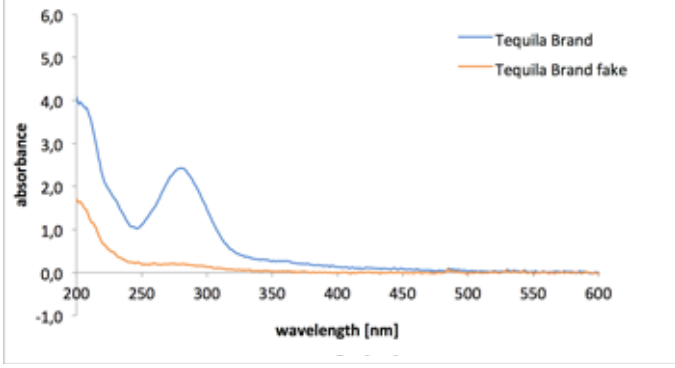


Fig. 2 and 3: UV/Vis spectra of electronical-commerce whisky and tequila compared to respective authentic brand products

suspiciously low price were as well analyzed at the Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe as part of a research project using ^{1}H-NMR and also tested with the NanoPhotometer®. The samples were identified as counterfeit at CVUA. The following figures show the alleged branded whisky and tequila clearly identified as counterfeits after matching the absorption spectra with the respective authentic samples using the NanoPhotometer®.

Examination of Denaturants

Another application of the NanoPhotometer® is the ability to detect denaturants. These are certain substances that are added to spirits to render them useless for consumption. Denaturation is a common tool used by tax authorities. Depending on the intended use of the alcohol various denaturants are introduced. If alcohol is rendered unusable by the addition of denaturants for consumption purposes, it may no longer legally be used as a foodstuff. If it is still used for the production of a spirit drink, the product becomes unacceptable for human consumption and is considered unsafe or dangerous. The following figure shows the analysis results of a vodka mixed with different proportions of denaturated alcohol containing methyl ethyl ketone (MEK) and the substance "Bitrex" (Denatonium benzoate). Additions of 5% denatured alcohol in a vodka sample can already be detected by the NanoPhotometer®.

Conclusion and Outlook

The first results of using the NanoPhotometer® to verify the authenticity of spirits and to differentiate brands have been very successful. The resultant data show this method has great efficiency for the rapid screening of unknown samples without the need for expensive, labor intensive and time consuming analysis in the laboratory. Due to the compact design and the simple operating concept of the device, even on-site use, e.g. in gastronomic establishments, is possible.

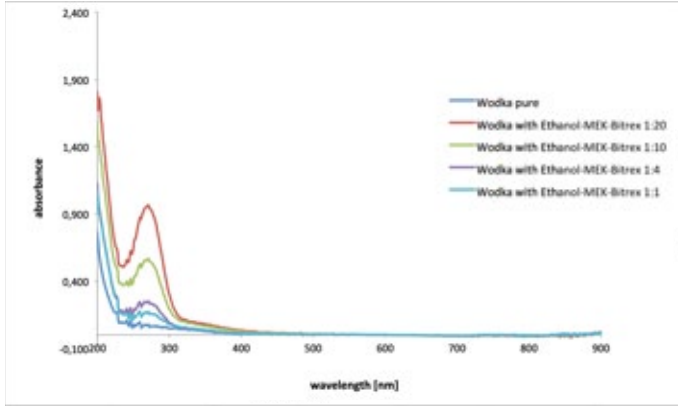


Fig. 4: Detection of various amounts of denaturated alcohol in vodka

In a follow-up project it will be examined how the identification of categories and brands of spirits can be achieved even more reliably. For this study the established data will be utilized together with the refinement of the algorithms developed for the NanoPhotometer®.

Literature:

Kuballa, T., Hausler, T., Okaru, AO, Neufeld, M., Abuga, KO, Kibwage, IO, Rehm, J., Luy, B. , Walch, SG, Lachenmeier, DW, Detection of counterfeit brand spirits using 1H NMR finger prints in comparison to sensory analysis, Food Chemistry 245, (2017), 112-118

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