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Development of a compact Raman spectrometer for the real-time analysis of chemical substances

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Abstract

Due to its numerous possible applications, optical spectroscopy has become a cross-sectional technology experiencing a steady growth in various disciplines. This trend is accompanied by the desire to develop more efficient and yet more compact devices. Especially, the integration of spectrometers into decentralized point-of-care applications is a driving force behind the miniaturization. In addition to the lack of compactness, high purchase prices inhibit a final entry into the market. In order to solve this problem, a compact Raman spectrometer for the analysis of chemical substances is presented. Although Raman spectroscopy is considered a rather complex technology, it offers the possibility of fast, non-destructive analyses of small concentrations. For the realization of a miniaturized low-cost spectrometer, highly efficient components were used allowing a miniaturization and correction of aberrations due to optical folding and curved surface structures. The main optical components of the system are a curved diffraction grating (grating period ≤1 µm) and a toroidal mirror enabling a precise imaging on the detector. The optical components were manufactured using a modified ultra-precision machine (LT-ULTRA MMC 1100). In addition, special light traps were implemented in order to reduce the scattered light. The system performance was analysed using a laser with an excitation wavelength of 785 nm (analysis range: 780 to 1050 nm). Since the developed system is to serve as a prototype for the detection and analysis of chemical drugs, γ-Butyrolactone of different concentrations was used for the laboratory measurements. The system was able to detect concentrations up to 5.6 %. Regarding this, an automated evaluation algorithm using fast Fourier transformation was implemented. In order to prospectively access further application areas and to meet the need of low prices, improvements are made with regard to replication methods.

Miniaturized spectrometer, Raman spectroscopy, micro optics, chemical analysis

1. Introduction

As part of the optical analysis, optical spectroscopy is a cross-sectional technology that is experiencing a steady growth in various markets such as energy technology, environmental analysis or medical technology. In this course, Raman spectroscopy is commonly used e.g. to provide information about chemical bonds or biological tissues [1]. Raman scattering is based on the interaction of an electromagnetic wave of a laser beam and a molecule, whereby changes in the polarizability of the electron lead to an inelastic scattering of the incident beam [2]. Since each molecule has a unique chemical structure, substances can be identified from the characteristic spectral patterns ("fingerprinting"). Moreover, the amount of a substance in a sample can be determined quantitatively or semi-quantitatively [3]. Samples can be analysed in a variety of physical states, e.g. as solids, liquids or vapours [1].

Raman spectroscopy offers the advantage of a broad information content and short evaluation times compared to conventional methods for the identification of chemical or biological substances [4]. For example, it is possible to rapidly detect dangerous drugs such as γ-Hydroxybutyrate (GHB), also known as "liquid ecstasy", and to determine the concentration. In order to avoid the unintentional consumption of that sort of drugs in liquids, special devices are required giving fast and reliable warnings [5]. Compact Raman spectrometers could help to solve such use cases. The need for miniaturization is accompanied by the trend towards price constraints. To meet these requirements, cost-effective and flexible manufacturing methods are required that meet the high-quality requirements of optical analysis [6-7]. Ultra-precision diamond machining is one approach for the production of master structures such as curved diffraction gratings. These must be replicated in order to provide cost-effective end products. However, optics produced in this way can cause scattered light effects and grating ghosts, which must be avoided. This paper presents an exemplary prototype for the investigation of chemical substances using a compact Raman spectrometer. In addition, possible methods for reducing the costs of hand-held devices are shown.

2. Development of the compact Raman spectrometer

2.1. Spectrometer setup

The developed spectrometer consists of both commercially available components and specially manufactured optical components (see *Figure 1*). A light source (Thorlabs) with an excitation wavelength of 785 nm and an analysis range of 780 nm to 1050 nm, a Raman probe (StellarNet Inc.), a STM32 microcontroller (STMicroelectronics) as well as a TCD1304DG CCD line image sensor (Toshiba) were purchased. Moreover, the self-produced light trap and housing were anodized and coloured in order to increase the light absorption. The Rayleigh scattering was eliminated by a long pass filter and only the Stoke scattering (Raman lines) was detected.

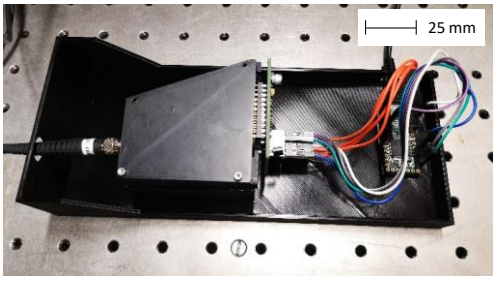

***Figure 1**: Specially developed prototye of the compact Raman spectrometer.*

2.2. Manufacturing of the optical components

The dispersive spectrometer built consists of a spherical optical grating and an imaging element in order to realize the imaging. By using curved diffraction optics, which combine imaging and dispersion properties, it is possible to realize more compact optical designs with a reduced interfacial number [7].

The optical components were manufactured by ultra-precision manufacturing. The grating and a toroidal mirror were manufactured with a modified ultra-precision milling machine (LT-ULTRA MMC 1100). The extension of the machine by a tilting and rotating module adds two additional rotation axes and enables the targeted adjustment and adaptation of the blaze angle to the shape of the surface. A defined chip formation at low forces is decisive for the production of the grating in order to achieve optimum surface quality in addition to high dimensional accuracy [6]. It was possible to set the grating period to ≤1 µm. The diffraction efficiency was reached to >95 % of physical limits. The structures were generated by the use of specially shaped monocrystalline diamond tools that must be free of break-outs or unevenness in the nanometre scale regarding their cutting edges.

3. Experimental results

In order to evaluate the functionality and accuracy of the spectrometer, a krypton (KR) calibration source was initially used. The measurements were performed with a conventional spectrometer as well as with the prototype. The results of the calibration for both systems are shown in *Figure 2*. These were compared to the expected spectrum of the krypton source. Additionally, the comparison of the two signals with the expected KR spectrum shows no false-light phenomena.

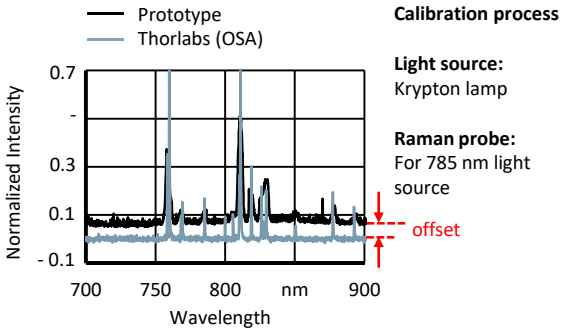

***Figure 2**: Comparison of the spectra gained from the KR calibration source.*

Furthermore, various chemical substances such as ketamine, 1,5-pentanediol and γ-Butyrolactone (GBL), which were dissolved in water or in alcohol (ethanol) beforehand, could be identified. GBL was used for the analyses due to its high structural similarity to GHB. *Figure 3* shows the spectrum of a GBL-water solution with a concentration of c_{GBL} = 564 mg/ml, measured with a commercial spectrometer (Thorlabs) and with the prototype. It becomes clearly apparent that the signature peaks of GBL are similar for both spectrometers, allowing an identification of the substance with high accuracy. Algorithms were written in Matlab and Python to create an automated data evaluation. Part of the algorithms was to integrate the data for 10 s, to then use a fast Fourier transformation to immediately decompose the Raman signals into their frequency components and, consequently, to identify them correctly. By this, concentrations of GBL up to 5.6 % could reliably be detected.

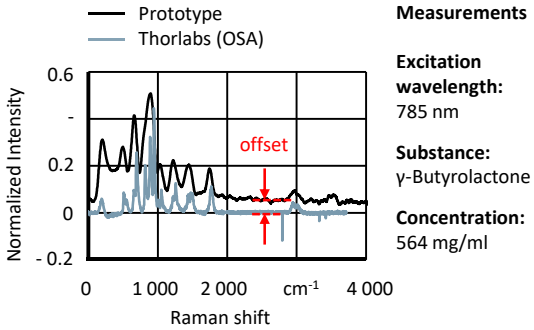

***Figure 3**: Raman spectrum of γ-Butyrolactone (564 mg/ml) in water measured with a Thorlabs spectrometer (OSA) and the prototype.*

4. Conclusion and outlook

Ultra-precision machining makes it possible to produce optical elements like curved gratings for the use in miniaturized Raman spectrometers that are free of false-light phenomena. The developed prototype represents the first step towards a hand-held system tailored to detect compromising substances in beverages. The experiments carried out show a high degree of accuracy in matching the respective substances.

However, there is still a need to improve the chemometric models and to set up a specific database in order to be able to detect a larger variability of substances at even lower concentrations. In the course of further development, maintaining laser safety will strongly be forced. A further aspect is the development of a low-loss replication process to replace the manufacturing of high-priced precision optics with inexpensive replicates. First successful tests using a UV-nanoimprint lithography (UV-NIL) process have already been carried out. By this, entering the consumer market of modern spectroscopy will prospectively be possible, enabling many people to protect themselves against the consumption of harmful substances. Moreover, the setup can easily be adapted to analyse different substances in other applications.

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