Detection of illicit chemicals by portable Raman spectrometer

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Abstract. The Raman spectrometers can be built as the portable devices and can be used in various places to detect illicit chemicals. This method has become popular due to deficiency of other fast methods that could be applied against terrorist attacks or could help police at their work. The Conception of a portable Raman spectrometer has been presented. The Description enclosures the presentation of the prepared device and its possible applications by presenting exemplary detection results.

Key words: Raman spectroscopy, chemical detection, lasers, detection efficiency.

1. Introduction

At present, portable Raman spectrometers are offered by a few companies that produce various optical systems or propose advanced security systems [1–7]. They become more popular due to the unique advantages they offer, compared to other analytical techniques: nondestructive and non-contact method of obtaining the fingerprint spectrum of materials without any special sample preparation [6, 7]. There are numerous applications reported in the literature where such technique can be used to scan unknown materials or to identify traces (e.g. drugs smuggled in alcohol beverages, drugs identified in drivers saliva, explosive detection) [8–12].

Recently, due to reasonable price and limited size, diode lasers of the wavelength equal to 785 nm have been the most common excitation sources in Raman portable devices. Unfortunately, in some applications, such excitation is not sufficient to get visible peaks in the spectrum due to influence of fluorescence or weakness of the peaks. A solution of this problem is a use of the laser having different wavelength. It is known that application of UV lasers give better results in some explosives identification than use of traditional 785 nm lasers [13, 14]. Therefore, the presented device comprises two independent sources, having wavelength of 785 nm and 355 nm, respectively. The latter wavelength was selected due to potential improvement in explosives detection and reasonable dimensions of the applied laser for its portable application.

The device consists of unmovable optics with variable optical probes that can be selected according to the relevant needs. The prepared software assures adjustment of various parameters during measurements and performs the detection process. Devices can be operated by a person who gets yes/no answers as a detection result or can perform a more in-depth analysis of the measured Raman spectrum by applying various algorithms that demand to adapt a few parameters and require more thorough knowledge.

2. Raman spectrometer design

The prepared Raman spectrometer comprises two independent lasers together with the corresponding optical spectrometers that aquire spectra from one stage cooled CCD detectors arrays of 1024 pixels resolution. The cooling is required to reduce noise of the detectors [15]. All optical components of the applied spectrometers (e.g. optical filters, diffraction gratings) are fixed mechanically to assure high resistance against harsh conditions with mechanical stress and intense vibrations present at working place.

The device is controlled by a PC board computer having a touch screen (Fig. 1). Optical signals are transmitted into the device by optical fibres, independently for two excitation wavelengths. Such design enables application of optical probes dedicated for various measurement conditions. The exemplary optical probe comprises two independent modules (Fig. 1): emitting laser light and receiving the Raman signal generated by the laser-irradiated sample under investigation. The device can use other optical systems, like wide area illumination probes (for bottles screening), telescopic probes (for distant measurements), SERS surface (for trace identification using Surface Enhanced Raman Spectroscopy technique), spatially offset Raman probes (for tissue investigation) [16].

The device uses class IIIB lasers so fulfilement of safety regulations is needed. Firstly, the system is turned on by a key and a safety switch can turn off the lasers immediately. Additionally, beeping and lighting signals inform about laser light emission as is required by the industry standards [17].

The device has been equipped with a dedicated software that can be used to measure Raman spectra at various measurement conditions and can identify the sample by comparing its spectrum with the library spectra (Fig. 2). The software enables setting laser power and measurement time as well as exclusion of influence of the plastic or glass packages. Moreover, synchronous detection can reduce influence of outside irradiation when the measurements are performed in field. All

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the measured spectra can be included into the library or external libraries can be downloded into the device database by the USB interface. The applied spectrometers measure Raman spectra (Fig. 3) with a resolution of $8 \div 10$ cm^{-1} that is sufficient for various chemicals identification.
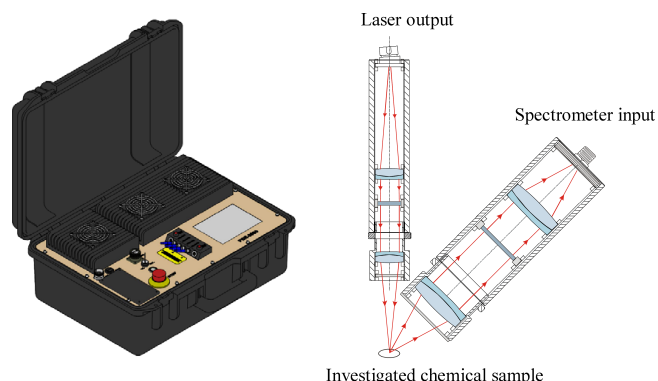

Fig. 1. Visualization of the prepared Raman spectrometer (left) and a basic diagram of the Raman optical probe (right); red colour lines mean the extreme rays

Fig. 2. Front panel of measurement parameters adjustment (top) and the window during the measurement process (bottom)

Two types of the methods that compare Raman spectra are applied. The first group bases on estimating correlation between the meas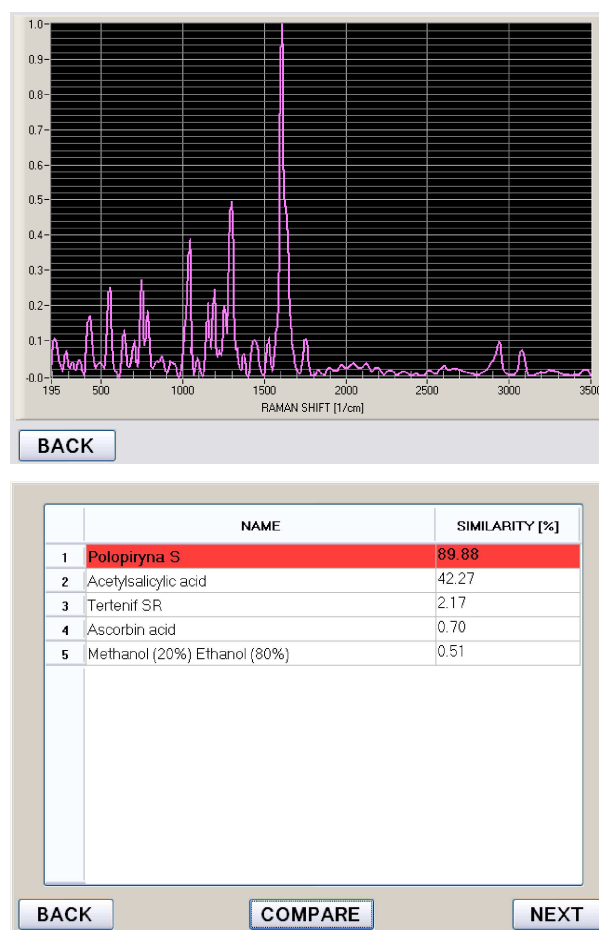ured spectrum and the library spectra. That group is sensitive to various ingredients/pollutants which are usually present in the investigated samples. Another method bases on peak matching and is much less sensitive to the ingredients different from the investigated one. The latter method can detect presence of illicit chemicals. These algorithm can work in two modes. One mode gives a list of the most correlated library spectra (Fig. 3). Such mode is available for the qualified staff. Another possible mode can detect whether the Raman spectrum of the investigated chemical sample responds to one of the spectrum within the specific group (e.g. drugs, explosives) or not. This means a mode of yes/no answer for the operator that do not need to be highly qualified.

Fig. 3. The Raman spectrum of the pill Polopiryna S measured by 785 nm laser by CCD sensor cooled to -15°C within 5 s (top) and the window of its identification results (bottom)

The software can utilize other methods that are applied to establish percentage composition of the investigated chemical samples at their given composition by applying the support vector machine algorithm [18]. That algorithm utilizes non-linear regression model that gives better results than ordinary linear regression.

3. Effectiveness of the selected chemicals detection

Two selected examples of measurements are presented to show efficiency of detection and to underline good points of the prepared device. The first one presents results of the popular explosive RDX (hexogen) identification by comparing Raman spectra obtained for both available excitation lasers (Fig. 4). Some selected peaks are more intensive for the 355 nm laser excitation than for 785 nm one, that helps to identify the investigated sample. The effect of the selected peaks amplification was reported in literature and resonance phenomena are presumably responsible for that effect [13]. Such spectra are observed for some common explosives but not all of them demonstrated this features.
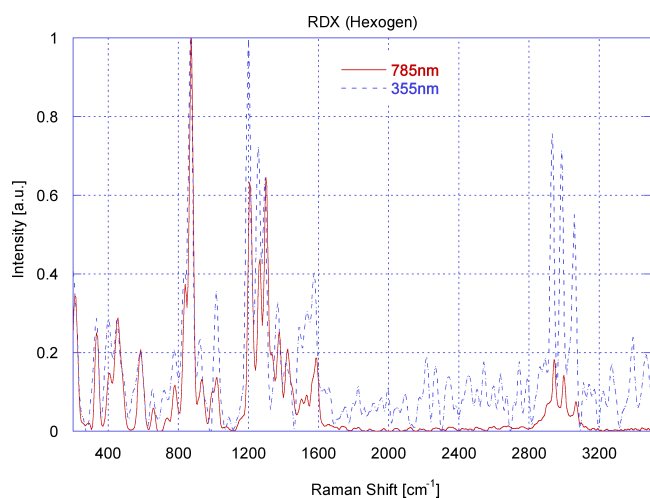

Fig. 4. The Raman spectra of the RDX (hexogen) explosive measured at laser excitation of 785 nm (350 mW) and 355 nm (10 mW) within the same measurement time of 20 s

It is worth to underline that the observed advantage of UV laser application was not diminished by fluorescence that was diminished by applying algorithms of a background removal to the recorded spectra. This conclusion means that the selected 355 nm excitation laser is a good compromise between fluorescence observed in the recorded Raman spectra and device portability that is strongly limited for the bulky lasers having shorter wavelengths. Another important advantage of the applied laser is the much lower optical power that irradiates sample when compared with the 785 nm laser. This protects the investigated samples from excessive overheating during the measurements.

Another interesting application of the presented device is a very fast detection of alcohol beverages that could be prepared from the contaminated ethanol to avoid excise on spirits. This illegal procedure is common in Poland and creates serious budget losses. Ethanol is often contaminated by adding bitrex (denatonium benzoate) to avoid consumption. Bitrex is the bitterest chemical compound and therefore is used to contaminate ethanol. Usually, a concentration of about 20 mg/l is used for the contamination. Bitrex can be neutralized at home by adding sodium hypochlorite (NaClO) that is popular in some household cleaning products. The Raman spectrum of the pure bitrex has visible peaks (Fig. 5) [19]. Some of these peaks are preserved in the remains of ethanol contaminated by bitrex and next cleaned by adding NaClO. The measurements were performed using a few drops of the suspicious alcoholic beverage that evaporated on the SERS layer leaving some remains of the contaminants. Preparation time of the investigated liquid sample and the measurement time takes only a few minutes together and can be done anywhere.
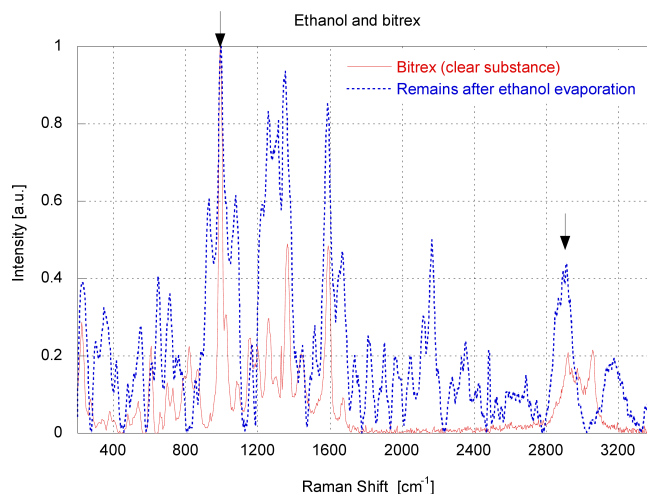

Fig. 5. The Raman spectra of the bitrex crystals and remains of the contaminated ethanol after its evaporation using SERS technique at laser excitation of 785 nm (350 mW) within the same measurement time of 120 s; the black arrows point at the peaks present during both measurements

4. Conclusions

This paper enclosures possibility of various illicit chemicals detection by the prepared portable Raman spectrometer. The device can work in harsh environment due to isolated encasement against humidity and dust. The prepared software can work in two modes, dedicated for advanced staff or for yes/no detection used by less experienced operator. Two examples of the possible Raman spectrometer applications are presented. The advantages of the laser 355 nm applications were confirmed for some explosives. Another interesting use of the device for identification of alcoholic beverages of doubtful origin was also mentioned.

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