

Portable Raman spectrometer – design rules and applications

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Abstract. Raman spectroscopy has become more popular due to its new prospective field applications in forensic sciences, war against terrorism, environment protection and other field chemical analysis. Raman spectrometers can be miniaturised to portable devices and their price is decreasing due to development of optoelectronics components. Unfortunately, this technology has still numerous limitations that influence their design and limit the scope of possible applications. The conception and design of the portable Raman spectrometer is described, including discussion of performance and limitations of representative components of such device available on the market. An enhanced portable Raman spectrometer using two lasers, one emitting at 355 nm and the other at 785 nm, and employing advanced signal acquisition and data processing methods is presented. Advantages of such system are outlined and example measurement results acquired using equivalent hardware are presented. Data processing flow for identification of chemicals is also described.

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

1. Introduction

At present, portable Raman spectrometers are offered by a few independent companies [1–4]. They become increasingly 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 and no requirement for special sample preparation [5]. Therefore, such devices can be efficiently applied in forensic sciences, war against terrorism, environment protection and other field chemical analysis without resorting to time-consuming equipment-intensive analysis methods [6]. Raman spectroscopy can be used in identification of forensic traces at crime scene in the field, in fast identification of unknown substances at airports or government buildings (e.g. post or customs offices), in field identification of smuggled or controlled substances (e.g. alcohols, fuels, drugs) as well as in detection of pollutants in water or soil. Raman measurements can be performed on very small samples (down to a few micrometers across) and the measurement time does not exceed a few minutes. An important advantage of this technique is its ability to make measurements on substances enclosed in transparent containers, such as bags or vials, without opening them.

The two main factors that prevent widespread adoption of portable Raman spectroscopy devices are high price of such devices and lack of reliable automated detection capabilities of chemical substances of interest, based on acquired Raman spectra. In this paper we would like to outline some compromises that can result in developing contemporary solutions for portable Raman spectrometers.

2. Design of Raman spectrometer

2.1. Typical setup of Raman portable device. The most common Raman setup, shown in Fig. 1, consists of a narrow-band laser, a spectrometer based on a CCD linear image sensor, connected to an electronic control unit that interacts with the user via keyboard and display, controls the measurement process and executes detection algorithms. Most of portable devices available on the market are equipped with limited display used only for selection of measurement parameters and presentation of results of measurements and preliminary identification.

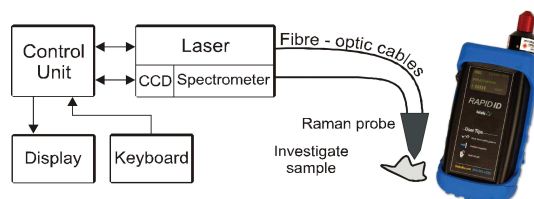


Fig. 1. Block diagram of a Raman spectrometer and example market product of Intevac Photonics after Ref. 3

The most serious problems in design of the Raman spectrometers come from low level of the useful Raman signal and existence of strong interfering optical signals, mainly external illumination and fluorescence induced by the laser beam. Influence of these problems significantly depends on excitation laser wavelength, size of the sample and optical properties of investigated materials. Therefore, selection of proper excitation laser is crucial in Raman spectroscopy. Moreover, lasers for portable Raman spectrometers should

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have sufficient output power, narrow bandwidth of emission line, robust construction as well as small weight, size and moderate power consumption. Thus, diode lasers are the best solution, while diode-pumped solid-state lasers (DPSSLs) can also be considered in some cases.

At present, state-of-the-art portable Raman spectroscopic devices use the diode laser of the wavelength equal to 785 nm working in CW (continuous wave) mode as an excitation source. This near-infrared excitation wavelength, enabling quite efficient fluorescence reduction, is recognized as an industry standard, also this laser has sufficient output power (a few hundreds milliwatts), compact size, long lifetime (at least 10 000 h) as well as a relatively low price. Moreover, there are databases with a large number of Raman spectra measured at this laser excitation wavelength for various substances. Such databases can be purchased from a few independent vendors and used as a standard library for detection aims. However, such devices have also various drawbacks that limits their accuracy and restricts possible scope of application. Firstly, the Raman signal is adversely affected by CCD noise and etaloning as well as other interfering signals, especially during field operations. Secondly, the Raman signal induced by a 785 nm laser is too weak in some applications. It is reasonable to consider shorter wavelengths to increase intensity of the Raman signal and to reduce interferences. Therefore, a modified setup that would utilize the latest advances in optoelectronics and more advanced measurement techniques should be developed.

2.2. Proposal of setup improvement. Portable Raman spectrometers available on the market require modifications aimed at improving their performance, especially reliability of automated detection of chemical substances. These modifications would consist of adding another laser and spectrometer, enhancement to the data processing hardware and the use of new data acquisition and processing methods.

The primary source of such modified system would still be a laser emitting at 785 nm with FWHM of emitted spectrum less than 0.15 nm and signal-to-noise ratio better than 40 dB. The optical output power would reach 400 mW, keeping the laser within a safety class IIIb, while being sufficient for Raman spectra measurements. At present such lasers weight about 100 g, consume only a few Watts and are available below 10 000 \$.

A compact spectrometer with thermo-electrically cooled CCD of resolution 1024 pixels would be used to detect Raman spectra. This choice results in lowering background noise and theoretical spectra resolution around 6 cm^{-1} for Raman wavelength of range $100\div 3500\text{ cm}^{-1}$. In practice, the resolution and the Raman range depend not only on CCD dimensions but also on laser bandwidth, its temperature stability as well as on parameters of diffraction grating used in the spectrometer and filters in the optical probe. Typically, resolution of $8\div 10\text{ cm}^{-1}$ can be attained within Raman shift range $200\div 3500\text{ cm}^{-1}$. These values are a good compromise between requirements of data processing algorithms and limitations on the weight and size, since increasing the resolution would require not only

replacing the CCD detector with one with more pixels, but also increasing the size and weight of the spectrometer.

Electronics that controls spectrometer, laser and display can use a Digital Signal Processor (DSP), a Field Programmable Gate Array (FPGA), an embedded microprocessor or a standardized Single-Board Computer (SBC) running either a real-time operating system (QNX, OS-9) or embedded version of a standard operating system (Embedded Linux, Windows XP Embedded).

Especially the last solution is attractive, due to availability of low-power credit card-size SBCs featuring 1 GHz class mobile processor implementing Intel x86 architecture, a gigabyte of memory as well as complete set of peripherals (VGA and touch screen controller, USB/SATA/Serial ports) needed to run a desktop PC operating system or its embedded version from attached Solid State Disk (SSD). Consuming only about 10 W and running Windows XP Embedded, such SBC can implement advanced measurement methods, such as synchronous detection, and execute complex detection algorithms, written in MATLAB or other generic tools, thereby improving identification accuracy. A VGA-resolution, LED-backlit 5÷6 inches in touch-screen would be used for interaction with the user.

The low-level control of measurements as well as power management of the system would be performed by a dedicated circuit controlled from the SBC, thus obviating the need for a hard real-time operating system. This circuit, connected to the SBC by an RS232 or USB connection, controls lasers and triggers spectrometers. The lasers can work in the constant output power mode or with their output power modulated by sine or rectangle function to enable synchronous detection. Additionally, the circuit manages power resources of the system by switching on/off spectrometers' cooling and additional pointing green or red lasers that are necessary due to security standards for class IIIb lasers [7].

Further improvement in portable Raman spectrometer can be achieved by using a second laser of a wavelength shorter than the present standard – 785 nm. A similar solution has been recently available but is focused on laboratory applications [8]. Intensity of the Raman signal is inversely proportional to the wavelength to the power of four and numerous Raman bands can be intensified because of Raman resonance effect. Moreover, silicon CCD arrays, which are the most convenient detectors for portable spectroscopic devices, are sensitive in the wavelength range extending from 350 to 1000 nm.

However, lasers working in UV-VIS range can induce strong interfering fluorescence signal when numerous organic materials are investigated. For a VIS excitation laser the fluorescence appears in the same spectral band that the Raman signal, thus saturating detector and disabling Raman signal detection. These signals can be spectrally separated if excitation in deeper UV (wavelength shorter than 280 nm) is applied, but use of such excitation is connected with a large size and high price of equipment, low sensitivity of some detectors (e.g. CCD arrays) and risk of unwanted photochemical reactions.

In such circumstances it is necessary to use the excitation wavelength for which the fluorescence is at least reduced and

compact lasers that have adequate performance and acceptable price are available. At present, such wavelength is 355 nm, for which compact Diode-Pumped Solid State Lasers (DPSSLs) working in CW mode are available. Emitting about 10 mW, these lasers consume more power than a 785 nm diode laser because they use a non-linear process (third harmonic generation) to obtain radiation at 355 nm from the pumping laser working at 1064 nm. Although the 10 mW of power emitted at 355 nm may seem to be too small, the Raman signal produced by such excitation laser should have intensity comparable to the Raman signal produced by signal induced by 785 nm excitation laser having power of 200 mW.

2.3. Sensitivity enhancement. Typically, Raman spectroscopy can identify substances at concentration higher than 1% w/v. When an investigated sample comprises a lower concentration of the identified substance, the Surface Enhanced Raman Spectroscopy (SERS) provides a unique solution for easy increase of detection sensitivity by many orders of magnitude without excessive power consumption of the portable device. This technique has been known since thirty years but due to the poor reproducibility of the handmade substrates its routine application was strongly limited. Recently, however, substrates of gold-coated textured silicon manufactured using methods of the semiconductor industry has become available, keeping Raman signal variation below 10% for excitation wavelength 785 nm [9]. The two main drawbacks of this technique are necessity of taking sample of investigated substance in order to place it on the SERS substrate and relatively high cost of the substrates.

2.4. Data processing. Raman spectrometer needs a dedicated software that can perform effectively measurements and further data processing. Spectra have to be processed at different stages to detect automatically, or with very limited operator involvement, various substances or mixtures.

The process of Raman spectra recognition, shown in Fig. 2, comprises three main stages. Initially, a background signal has to be removed from the spectrum [10]. This signal is a result of fluorescence, background noise of CCD detector and other light sources present in field measurements [11]. Subsequently, the spectrum signal should be smoothed to reduce its random error and random spikes. Among various algorithms proposed in literature, the Savitzky and Golay smoothing filter seems to be a good choice [12, 13]. Then, the preliminary processed spectrum is parameterized to get a set of parameters (positions of the spectra peaks, their relative amplitudes and widths) that gives essential information about the spectrum, necessary for detection of the investigated chemicals.

Detection algorithms that are used in Raman spectroscopy employ various methods that recognize similarity of the estimated parameter set to the set established for reference spectra. Overview of these methods can be found in literature [10, 12, 14]. The methods can be divided into two main groups: one used for identification of chemicals and the other applied for determination of composition of chemicals mixtures.

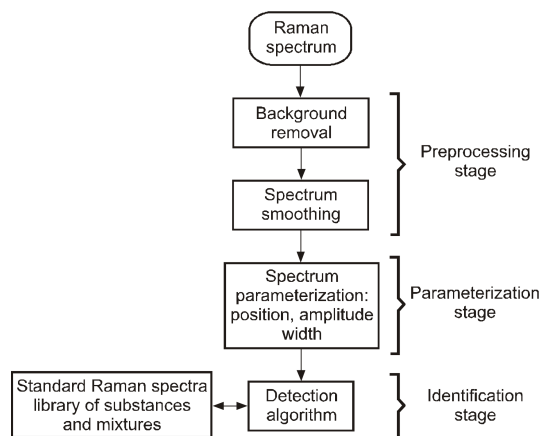


Fig. 2. Block diagram of algorithm for spectra pre-processing and substances identification using Raman spectra

The identification process is based on comparing the Raman spectrum of the investigated sample with Raman spectra of chemicals stored in a database. The investigated sample is assumed to contain the substance whose spectrum the most closely matches that of the sample. This means that detection process depends not only on accuracy but also on the content of the reference database and can give often ambiguous results when identification process is performed automatically, without ensuring adequate quality of input Raman spectrum, especially sufficient signal to noise ratio. Requirements for computations performed during spectrum parameterization are moderate and this task can be done by an ordinary PC in few seconds. We expect that more time-consuming is a process of comparison of these parameters within a database that can consist of tens of thousands spectra.

3. Tests of the device model

A model of portable Raman spectrometer utilizing two excitation wavelengths: 355 nm and 785 nm was set up and tested. The system consisted of a 10 mW UV laser, a 400 mW NIR laser, dedicated Raman fibre-optic probes (up to 5 meters long) and a miniaturized spectroscopic modules with a TE-cooled back-thinned CCDs controlled via USB.

Exemplary Raman spectra registered in such system are shown in Fig. 3. The main sources of observed interferences are noise of the CCD and laser-induced fluorescence. The background noise can be reduced by the cooling of the CCD, but in the portable device only one-stage cooling can be applied (that provides CCD temperature $\sim -15^{\circ}\text{C}$) not to exceed acceptable power consumption and weight.

In practice, at field measurements there are also other factors that can significantly influence the Raman signal acquisition process. Firstly, the laser light should be focused on the investigated chemical to obtain sufficient energy concentration that assures strong Raman signal. This is difficult to obtain when measurements are made by a Raman probe kept in hand. Secondly, when the measurements are performed through the plastic or glass package we can expect some interference signal coming from the package material.

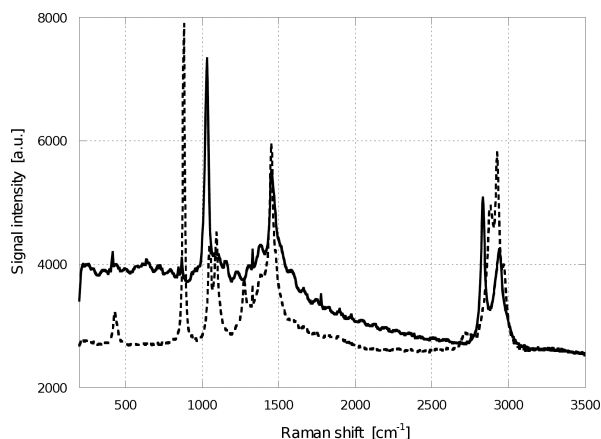


Fig. 3. Raman spectra of methanol (continuous line) and ethanol (dotted line) measured at room temperature using excitation laser wavelength 785 nm and 1024-pixel CCD (detector temperature fit to -15°C)

These problems are illustrated in Fig. 4, which shows the Raman spectra measured by Raman probe placed at various distances from the tested liquid (mixture of 80% methanol and 20% ethanol). The differences are clearly visible and we can expect that applied algorithms cannot always handle this problem to assure accurate and fast identification irrespective of the quality of acquired spectra.

Good quality of the spectra is important. For example, we observed for data presented in Fig. 4 that the same algorithm identified the main peaks with a shift of up to 10% variation between the presented measurement results. Even greater variation, up to 25%, was observed between relative amplitudes of these peaks. But the greatest differences were noticed at peak widths estimation. The estimated peak width was up to three times greater in some cases than normally.

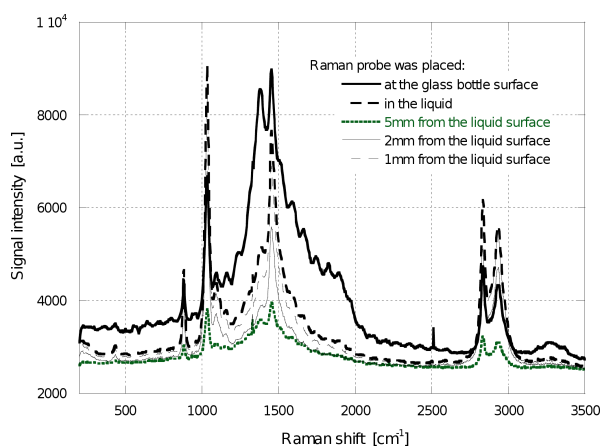


Fig. 4. Raman spectra of a mixture 80% methanol and 20% ethanol measured at excitation laser wavelength 785 nm having optical output power 300 mW and acquisition time of 40 s; the CCD of 1024-pixel working at temperature equal to -15°C was applied

The aim of another test was to compare Raman spectra recorded using two excitation wavelengths. Common medicine – Polopiryna S – commercial form of acetylsalicylic acid was used as an investigated sample. Results of measurements car-

ried out with excitation of 785 nm are shown in Fig. 5, while those obtained with excitation of 355 nm are shown in Fig. 6.

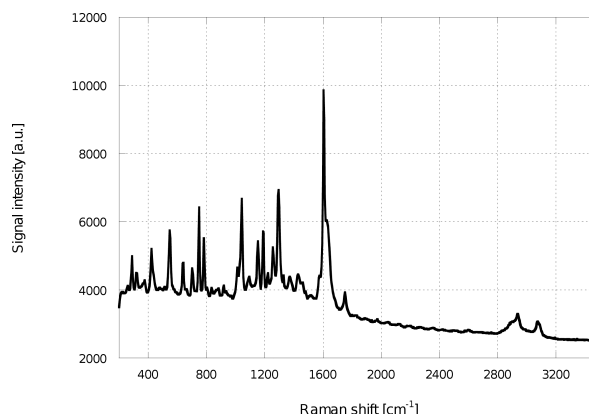


Fig. 5. Raman spectrum of Polopiryna S measured at excitation laser wavelength 785 nm having optical output power 300 mW and acquisition time of 40 s; the CCD of 1024-pixel working at temperature equal to -15°C was applied

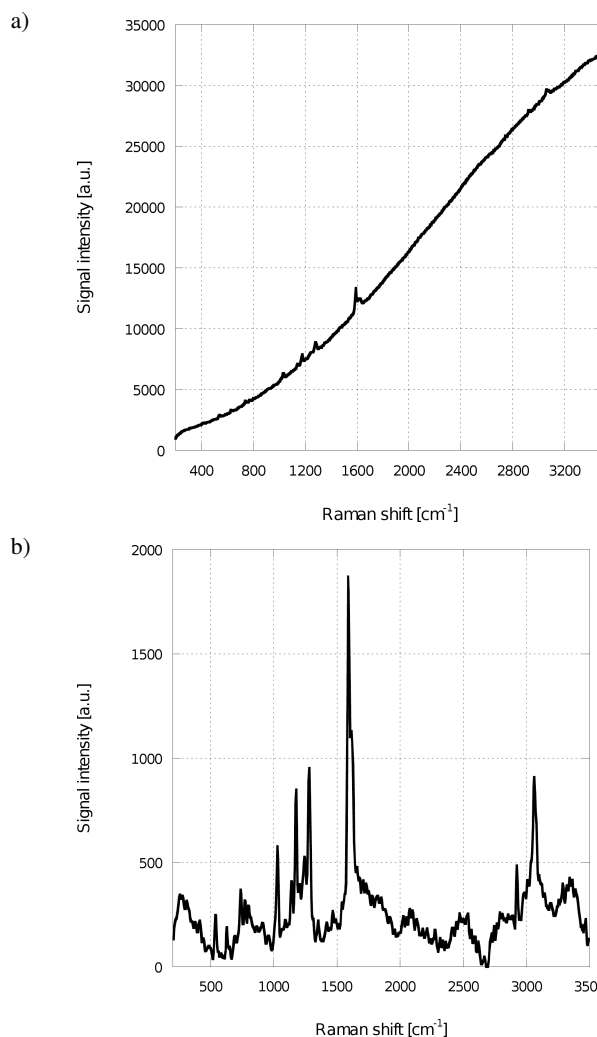


Fig. 6. Raman spectra of Polopiryna S measured at laser wavelength 355 nm having optical output power 3 mW and acquisition time of 80 s; the CCD of 1024-pixel working at temperature equal to -15°C was applied: a) recorded spectrum, b) pre-processed spectrum

It can be noticed that the Raman bands in the spectrum shown in Fig. 5 are strong and the spectrum is only slightly influenced by the optical background. Conversely, the spectrum recorded with use of 355 nm laser contains strong fluorescence signal (see Fig. 6a). Fortunately, the fluorescence is not strong enough to saturate CCD array, which enables extraction of Raman signal by algorithms of data pre-processing presented above: spectrum smoothing and background removal (offset correction and baseline correction). Results of the pre-processing performed with use of spectroscopic software Thermo Fischer Scientific Inc. GRAMS/AI are presented in Fig. 6b.

The comparison of the spectra presented in Fig. 5 and Fig. 6b shows that set of strong Raman bands at 539 cm^{-1} , 628 cm^{-1} , 741 cm^{-1} , 1031 cm^{-1} , 1176 cm^{-1} , 1614 cm^{-1} , 1242 cm^{-1} , 1591 cm^{-1} , 1614 cm^{-1} , 2926 cm^{-1} , 3063 cm^{-1} required for proper identification of acetylsalicylic acid can be seen in both spectra. Although 355 nm laser induces a strong fluorescence signal, its important advantage is ability to generate a measurable Raman signal with the use of low power on sample (\sim single milliwatts).

4. Conclusions

This paper outlines the design of a portable Raman spectrometer. The design process requires some compromises to achieve a product that is affordable for many users and sufficiently accurate. We conclude that a system with an excitation laser source of 785 nm wavelength can be built with reasonable costs. The addition of the second excitation source - the 355 nm laser is more expensive and results in preparing a more bulky device but its portability still can be assured. Usage of the second laser enables measurements with low power on sample and selection of appropriate excitation wavelength for samples requiring Raman signal enhancement (e.g. by resonance effect). The tests of the device model confirmed that it can make measurements via transparent walls with a slight jitter of the probe focusing, common in field measurements. A proper design of the spectrometer together with efficient data pre-processing algorithms enables efficient collection of Raman signal and optical background removal.

Presented systems must collect spectra of various substances and perform their identification. That latter process can be problematic when the system is used in various conditions in the field applications. The key problem, as discussed in the paper, is ensuring adequate quality of acquired spectra and reduce any spectral components caused by the wall of a container through which the measurement is performed.

The described enhanced portable Raman spectrometer is a compromise between price, weight and accuracy that covers numerous applications, to name a few: forensic traces analysis, explosives and drug detection during police and customs officers work, environment pollution detection, control of octane level and pollutants in petrol as well as plastic classification at recycling process.

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