

COMPACT RAMAN (CLS) SPECTROMETER FOR ACTIVE TEST OF LIQUID AND SOLID SAMPLES

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Raman (CLS- Combinational Light Scattering) spectroscopy is a technique used to study vibrational, rotational, other low-frequency modes in a system and takes advantage of the inelastic scattering of laser light by molecules. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Since different molecules show different energy changes, the Raman (CLS) effect have found a wide application as a qualitative or quantitative analysis method.

In this article the results of homemade compact Raman (CLS) spectrometer for remote detection of liquid and solid samples are presented. The spectrometer is intended for active analyses of liquid and solid samples in different environmental conditions, including food samples checking, narcotics and explosives spreading.

The spectrometer consists of the block for spectral analysis, two lasers, two fiber-optical sensors and sampling probe and can work with two types of laser sources without reconfiguration the optics and lasers. ($\lambda_1 = 532 \text{ nm}$; $\lambda_2 = 785 \text{ nm}$)

Scattered radiation via fiber enters the spectral block. Raman (CLS) spectrum is separated in 4096 receiver components (pixels) by help of the TEC- regulated CCD array. Developed spectrometer can operate also by accumulator battery and is considered as portable. The spectrometer is capable to detect the spectral coverage in the range between 150 and 4000 cm^{-1} and may be used for liquids (including water solution, alcohol, different types of gasoline) and solids (including pills, powders, explosives and drugs) analysis. The spectral resolution of developed system is not worse than 8 cm^{-1} .

Range of applications of the developed Raman system includes: forensics; pharmaceuticals; gemotology; recycling; semiconductors; microwave assisted synthesis and other.

1. INTRODUCTION

There are many analytical technologies available for chemical identification in the field situations, particularly. Fourier transform infrared spectroscopy (FTIR) using attenuated total reflection (ATR) [1], gas chromatography/mass spectrometry and Raman (or combinational light scattering - CLS) spectroscopy, ion mobility spectroscopy, Laser Induced Breakdown Spectroscopy (LIBS), colorimetric tests (reaction of specific chemicals with an unknown compound), Raman spectroscopy (RS) and other [2]. Some of these methods are very effective tools for the analysis of unknown materials but can be used in the laboratory settings only because of large dimensions, big mass, long time of analysis and other disadvantages.

Detection techniques based on optical methods possess a reasonable resolution, high quality and purity, easily movable. Moreover several methods such as Raman (CLS) analysis have radiation that penetrates the walls of glass and clear plastic, eliminating necessity to open containers and greatly reducing the risk of exposure.

In this work we present compact homemade Raman (CLS) spectrometer for active test of liquid and solid samples.

Raman (CLS) scattering of light (see fig. 1) [3,4] represents inelastic scattering of radiation by molecules of substance, being the combination of frequencies of incident radiation and own frequencies of a molecule (vibration and rotational).

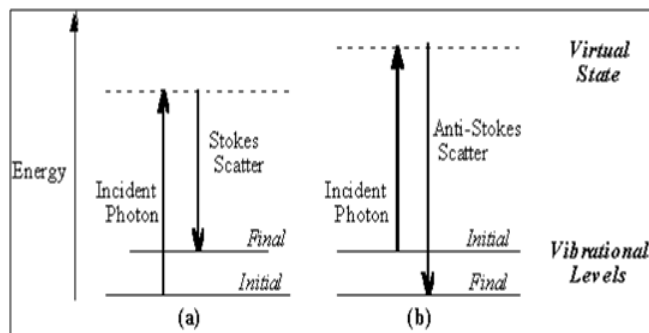


Fig.1. Energy level diagram for Raman (CLS) scattering; (a) Stokes Raman (CLS) scattering (b) anti-Stokes Raman (CLS) scattering.

Frequencies of molecular fluctuations depend on weights of the atoms constituting a molecule, and normally is one order of magnitude less than frequency of visible light. Molecules of the substance, which are taking place in various excited conditions, scatter the photons with addition or subtraction of energy, forming Stokes and anti-Stokes components of a spectrum, respectively.

Advantages of Raman spectroscopy are as follow:

- non-destructive check and research of samples;
- quick inspection;
- no frequency-tuned radiation source is required for revealing of spectral lines of vibration-rotational spectrum for observation of whole spectrum of substance, as in a case of absorption spectroscopy. Practically whole vibration-

rotational spectrum of a researched molecule is observed in a narrow site of a visible range, where there are maxima of sensitivity of photo detectors of optical radiation;

- water does not cause the troubles for Raman spectra measurements, when comparing with IR spectra;
- for packing the samples it is possible to use the glass and quartz, which are transparent for exciting and scattered radiations.

Disadvantages of Raman (CLS) spectroscopy:

- RS spectra have rather small intensity of signals (scattering section 10^{-31} - 10^{-29} $\text{cm}^2\text{molec}^{-1}$), therefore the additional measurements on increasing of energy potential of the device are required for detection of displaying substances with sensitivity on a level of threshold concentration, and even lethal, for some substances with weak lines of radiation;
- frequently meeting unpredictable fluorescence with size of some orders of magnitude higher than Raman (CLS) signal. Fluorescence is observed, when the virtual energy level blocks an external electronic level so, that laser energy becomes higher (shorter wave length). Latter results to increase the probability of fluorescence;
- a problem of suppression of elastically scattered light (Rayleigh scattering). The use of the selective filter blocking the wave length of the exciting laser is possible for its elimination.

Differently, there is a rigid connection between the structure of a molecule and the frequency of the spectral components appearing in scattering. Therefore the number of such components and their position in a spectrum allow to determine a composition and structure of molecules. Thus, not frequencies of emission lines but their shift relative to frequency of exciting light are the major characteristic of RS-spectra.

Since different molecules show different energy changes, the Raman (CLS) effect have found a wide application as a qualitative or quantitative analysis method. In general in Raman (CLS) spectrometer a registration of spectra is carried out in Stokes band (positive Raman (CLS) shift).

Raman (CLS) spectrometers are widely used in criminalities, for detection of drugs and explosives, for analysis of contents of mail items, and also at the control of burning temperature.

The main aim of the present work is to develop and build a portable Raman (CLS) spectrometer for active tests of liquid and solid samples.

2. EXPERIMENT

In Fig. 2 the overview of our compact Raman (CLS) spectrometer for active test of liquid and solid samples is represented. The spectrometer consists of exciting laser, fiber-optics sensor, probe cavity, block for spectral analysis and exploitation packing.

Radiation of exciting laser (535 or 785 nm, 0, 5 W) goes through a fiber-optical sensor to the sampling probe where passes through the notch filter and is focused by lenses on a sample. The sampling probe (SP) has several endings - to be able to focus on different depth from the sample surface, and to calibrate the spectrum with known material.

Light scattered from the sample is collected and passed to the spectral block. Then it is reflected by the mirror 1 and directed onto the diffraction grating and on the receiver (registration system) CCD passing optical system - mirror 3 and cylinder 4.



Fig 2 Pictures of the Raman spectrometer

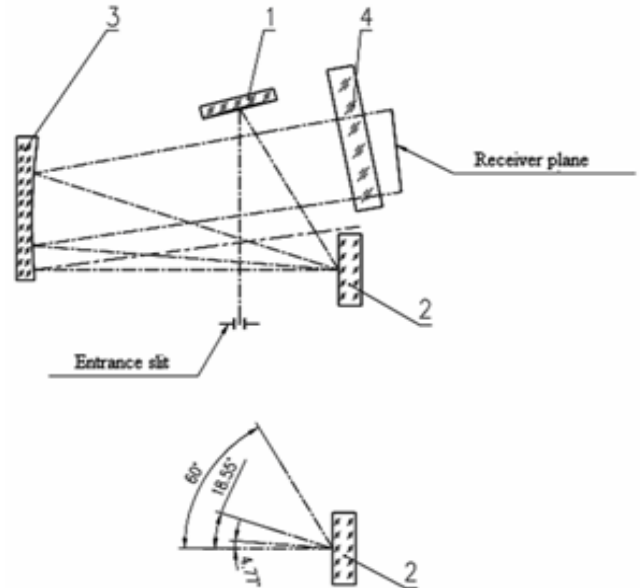


Fig.3. Optical scheme of developed system.(upper scheme) Maximal grating turning angle (below scheme). For details see text.

Continuous spectrum in the range of sensitivity of CCD 4...50 μm is separated in 1000 receiver components (pixels). Data reading from detector to computer is produced through the USB cable. If spectrometer operates on accumulator battery and notebook is used then device is considered to be portable.

In accordance with basis of Raman(CLS) spectroscopy each chemical compound has the specific spectrum of scattering. Relevant different wave numbers pixels register changes of intensity that correspond to displayed spectra.

Further comparison of received spectra and spectral database is carried out.

Detected spectrum is observed in working interface window of special program software. Using special program it is possible to set control parameters of spectrometer (integration time, laser power, smoothing passes etc.). After recording the spectrum, it is possible to find spectral peaks and modify spectrum in other programs (Excel etc.).

It is very important for Raman (CLS) spectrometer to have high resolution. Latter allows to distinguish certain spectral features required to be fully resolved with the aim for identifying the components in an organic liquid samples.

3. RESULTS AND DISCUSSION

In Figure 4 the spectrum of three grades of gasoline are depicted. One can clearly see the aromatic fraction in the 1000 cm⁻¹ region fully distinguishable from the olefinic background of the fuels indicated by the 1450 cm⁻¹ band. With increasing of fuel grades (from 87 to 93) these lines shift to high frequency side (see Fig.5).

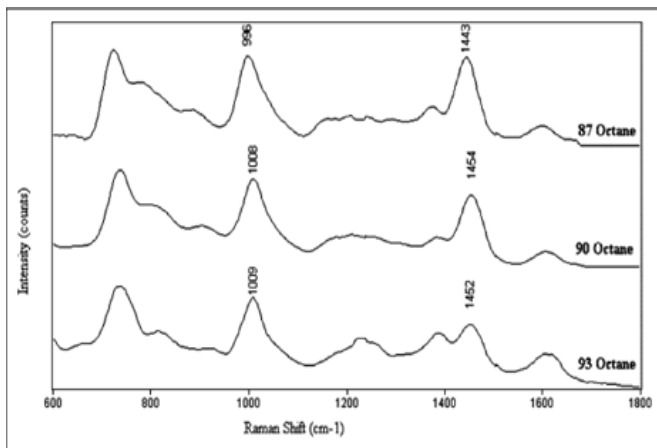


Fig 4 Raman (CLS) spectra of commercial gasoline's.

Fig 5 shows differences between gasoline grades. During the registration of A-92 regular motor gasoline and AI-95 regular motor gasoline definitive Raman (CLS) lines at 725 sm⁻¹, 784 sm⁻¹ and 1000 sm⁻¹ are observed. Depending on gasoline grades different relative intensity of spectral lines 725 sm⁻¹ and 784 sm⁻¹ were detected in our experiments.

The software of the Raman (CLS) spectrometer allows to determine composition of many component mixtures. For these aims the modified algorithm of registration analysis is used [5].

The basic algorithm of the regression analysis for processing a signal consists of the following. There are measurements of spectral curve $x_i(t_j)$ known substances (t_j -frequency or energy, $i = \overline{1, k+1}$); the spectrum of the researched sample containing 1st,...,k+1 substances, is measured, however the percentage of it is unknown. Then the spectrum of a sample $x(t_j)$ supposes representation

$$x(t_j) = \theta_1 x_1(t_j) + \dots + \theta_k x_k(t_j) + \theta_{k+1} x_{k+1}(t_j),$$

and $\theta_1 + \dots + \theta_{k+1} = 1$, $\theta_i \geq 0$, $i = \overline{1, k+1}$, where θ - vector of unknown parameters $\theta_1 \dots \theta_k$.

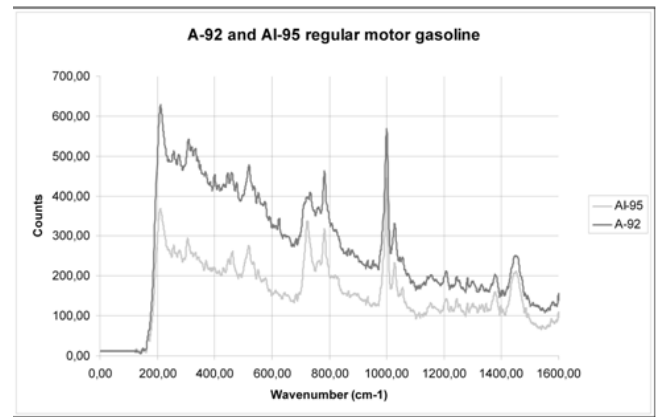


Fig.5. Spectra of A-92 and AI-95 regular motor gasoline.

Thus, the task of definition of a percentage of a mix leads to a model

$$\bar{\varphi} = X\bar{\theta}, \quad (1)$$

where $\bar{\theta} = (\theta_1, \dots, \theta_k)^T$ - vector of parameters (factors of regress), X - matrix (n×k), j-th column of which represents values of j-th controllable variable in 1-st..., n-th measurements, $\bar{\varphi} = (\varphi_1, \dots, \varphi_n)^T$ - vector of math waiting of observable value y (response) in 1-st..., n-th measurements.

Nonlinear model

$$\bar{y} = \bar{\varphi}(x, \bar{\theta}) + \bar{\varepsilon}, \quad (2)$$

where ε - the random error, sometimes is reduced to linear by suitable functional transformation.

So, if

$$\varphi(\bar{x}_i, \bar{\theta}) = \prod_{j=1}^k \exp\{\theta_j x_{ij}\},$$

then transition to (1) is carried out by taking the logarithm. Generally definition of parameters of nonlinear model reduces to the decision of sequence of linear tasks, linearising function φ in (2) and using iterative.

So, let

$$y = X * \theta + \varepsilon \quad (3)$$

If the law of distribution of mistakes is random (but is known), optimum on efficiency (at big n) estimations among all unbiased can be found on a method MP. These estimations $\bar{\theta} = \bar{\theta}(\bar{y})$ will not be linear on \bar{y} , despite of linearity (3). If to be limited by a class of linear estimations $\bar{\theta} = A\bar{y}$, irrespective on the law of distribution of mistakes of an estimation with optimum properties turns out at the set kind of a matrix.

Let's search for such estimation $\bar{\theta}$ of a vector of parameters that at its substitution in (3) sum of squares of

deviation experimental \bar{y} from predictable $\bar{y} = X * \bar{\theta}$ was minimal. Thus we assume that:

1. $E\bar{\varepsilon} = \bar{0}$;
2. $cov(\bar{\varepsilon}, \bar{\varepsilon}) = \sigma I_n$;
3. $rank X = k$;
4. Mistakes ε_i are independent.

Minimization on $\bar{\theta}$ of expression

$$Q = \sum_{i=1}^n (y_i - \sum_{j=1}^k X_{ij}\theta_j)^2 = (\bar{y} - X\bar{\theta})^T (\bar{y} - X\bar{\theta}) \quad (4)$$

leads to research of decisions of system

$$X^T X \bar{\theta} - X^T \bar{y} = 0 \quad (5)$$

By virtue of a condition 3 determinant of matrix $X^T X$ not equal to 0, so the system of the normal equations (5) has the unique decision

$$\bar{\theta} = (X^T X)^{-1} X^T \bar{y} \quad (6)$$

It is obvious, that it corresponds to a minimum (4), as at $\theta_i \rightarrow \pm\infty$ Q grows unlimited. The way of a finding of an estimation of a vector of parameters from a condition of a minimum (4) refers to *as a method of the minimal squares* (MMS), and an estimation (6) - *an estimation of a method of the minimal squares* (MMS estimation).

Let's consider geometrical interpretation of a method of the minimal squares. Let E_n - n-dimensional Euclid's space. Supervision of y_1, \dots, y_n determine in E_n end of a vector \bar{y} , which has been lead from the beginning of coordinates. Columns of matrix X, being by virtue of a condition 3 independent n-dimensional vectors x_1, \dots, x_k , generates in E_n linear variety E_k of vectors $\bar{y} = \bar{\theta}_1 \bar{x}_1 + \dots + \bar{\theta}_k \bar{x}_k$. In general, \bar{y} does not belong to this variety. Vector $\bar{\varepsilon} = \bar{y} - X\bar{\theta}$ represents a line from the end of \bar{y} to a point $X\bar{\theta}$ of variety. Minimizing

$$\bar{\varepsilon}^T \bar{\varepsilon} = (\bar{y} - X\bar{\theta})^T (\bar{y} - X\bar{\theta}) \quad (7)$$

in (4), we solve a task of finding a line with minimal length, i.e. construction of a perpendicular from \bar{y} on a plane E_k . At a corresponding choice of $\bar{\theta}$ vector $\bar{\varepsilon}$ is perpendicular to E_k , i.e., it is orthogonal to any of \bar{x}_j , $j = \bar{1}, \bar{k}$, : $\bar{x}_j^T (\bar{y} - X\bar{\theta}) = 0$, therefore $X^T (\bar{y} - X\bar{\theta}) = 0$, i.e. we received the normal equations (5). By virtue of linear independence $\bar{x}_j rank(X^T X) = k$, follows (6).

At essential noise level in a signal the method of direct regression analysis leads to essential mistakes, especially at definition of substances with small concentration. Such substances can be not recognized on a background of noise.

For their reliable definition and verification it is offered to use algorithm with artificial noise.

Essence of algorithm is an artificial adding of noise to initial signal and definition after that structure of a diagnosed mix with definition of concentration. This procedure is carried out repeatedly and as a result those components from a database which appear steady against brought hindrances are defined. Stability to hindrances can be defined as the attitude of the minimal and maximal concentration of the given substance for all cycle of calculations. If this attitude is great, that is during casual adding of noise the level of determined concentration strongly varies, most likely, that the given substance in a mix is absent. If the attitude is close to 1 the given substance is steady against hindrances and is considered present in a mix. Other components which at the direct analysis have been determined as present in a mix, but eliminated as a result of artificial adding of noise are considered false.

The common algorithm of this method is shown in Fig. 6.

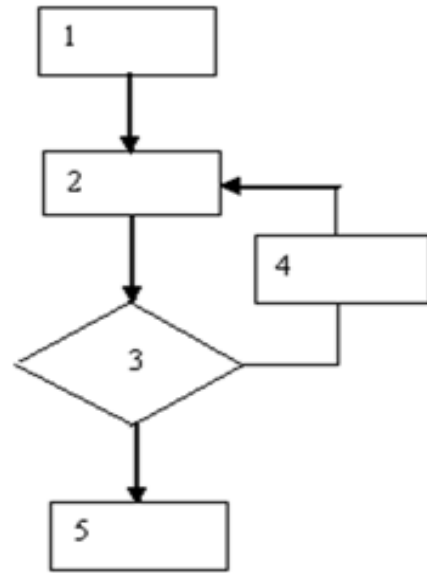


Fig. 6. Algorithm of a method of regression analysis with artificial noise: 1 – depicts the input of the received signal; 2 – calculation of a vector of concentration of substances by using equation (6); 3 – the conditional operator of an exit from a cycle of calculations with artificial noise (the counter of cycles); 4 – generation of random noise and its imposing on a spectrum of a signal; 5 - output of results of calculation of structure of a mix and concentration of the certain substances, definition of calculated value of a signal / noise ratio, a calculated error of calculations.

4. CONCLUSION

We developed and produced compact Raman (CLS) spectrometer for active test of liquid and solid samples as gasoline, drug, explosives and other. The range of practical applications of this device is wide.

5. ACKNOWLEDGMENTS

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- [1]. *A. S. Boreisho, E. V. Bertceva, S. Yu. Strakhov, V. S. Korepanov, A. V. Morosov, A. V. Savin*, Detection of explosives traces on documents by attenuated total reflection method, Proceedings of SPIE, 6733, 67331W.1 (2007).
- [2]. Committee on the Review of Existing and Potential Standoff Explosives Detection Techniques, National Research Council, Existing and Potential Standoff Explosive Detection Techniques (National Academies Press, N.W. Washington, DC, 2004).
- [3]. *C. M. Hodges, J. Akhavan*. The use of Fourier Transform Raman spectroscopy in the forensic identification of illicit drugs and explosives, Spectrochimica Acta, 40A, 303 (1990).
- [4]. *Patrick Hendra*, Sampling for FT Raman Spectrometry, Int. J. Vib. Spect., 1, 1.4, (1996).
- [5]. *E.V.Bertceva, S.L Druzhinin, S.Yu.Strakhov, N.I.Pahomkova*. The analysis of techniques of processing a LIDAR signal based on the algorithms of correlation and regression analysis, Proceedings of SPIE, 6594, 65940G (2006).