

Application of laser photothermal spectroscopy for standoff detection of trace explosive residues on surfaces

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Abstract. Laser photothermal methods of standoff detection of trace explosive residues on surfaces are considered. The analysis is restricted to the most promising methods: photoacoustic spectroscopy, deflection spectroscopy, and IR photothermal imaging of objects under resonant irradiation. Particular attention is paid to the choice of radiation sources and detectors. Comparative analysis of the existing standoff detection methods for explosive particles on the object surface is performed. Prospects of laser photothermal spectroscopy in this field are discussed.

Keywords: laser photothermal spectroscopy, explosives, standoff detection.

1. Introduction

Detection and identification of trace amounts of explosive residues are of great practical importance for national safety [1–6]. The most generally accepted methods for detecting trace explosive residues (in particular ion mobility spectrometry [7, 8] and gas chromatography [9, 10]) are used to detect them in the gas phase and have a local

character. Unfortunately, the vapour pressure of many known explosives is extremely small at room temperature (Fig. 1); moreover, using simple techniques of masking explosives (for example, putting them into a plastic bag), one can reduce the explosive concentration in environmental air by three more orders of magnitude [11].

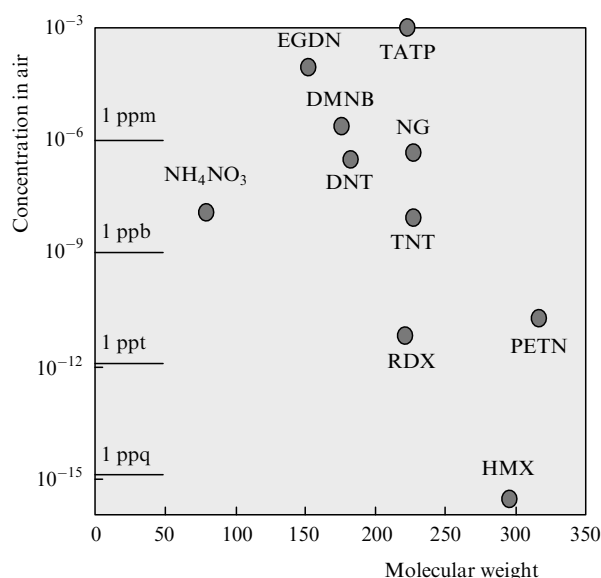


Figure 1. Concentrations of some highly efficient explosives in air at 25 °C [25].

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The extremely low vapour pressure of most explosives gave many researchers an idea of detecting their traces on surfaces of materials rather than as vapour-based detection. The investigations showed that successive fingerprints left on surfaces of some objects by a person who had dealt with explosives led to contamination of these surfaces by explosive particles with a mass from one milligram (in the first contact) to few nanograms (after 40–50 contacts) [12]. It is important that most explosives are well attached to the surfaces of materials with a high surface energy (for example, metals and their oxides); i.e., are strongly bound with them by adhesion forces.

In particular, only one grain of RDX (also known as hexogen or cyclonite) with a size of 5 μm and mass of ~ 90 pg contains ~ 300 billions of molecules; i.e., the same number as in the gaseous phase in 1 L of air under normal conditions [2]. Thus, it is quite feasible to detect trace amounts of this explosive using distant sensing of the surface of the object studied.

In contrast to local (point) analysis, in the case of distant detection of explosives both the operator and the equipment necessary for analysis remain at a safe distance from the object. In the literature, this method for detecting trace amounts of analytes is referred to as standoff detection [5, 13]. It should be distinguished from the other distant method for detecting explosives: remote detection, where only the operator is at a safe distance [5]. In the latter case a robotic platform with equipment is in the immediate vicinity of suspicious object.

There is good reason to believe that the standoff methods, which are characterised by rapid analysis, high sensitivity and selectivity, and capability of detecting and identifying many known explosives, should be based on laser techniques [4, 5, 14]. Currently, the most widespread laser methods for detecting trace explosive residues are the cavity ring-down spectroscopy (CRDS) [15], Raman spectroscopy [15, 16–18], photofragmentation–laser-induced fluorescence (PF–LIF) spectroscopy [15, 19, 20], laser-induced breakdown spectroscopy (LIBS) [15, 21–24], infrared spectroscopy [25], and active IR imaging based on backscattering spectroscopy [26].

Currently great interest is shown in the methods of photothermal spectroscopy, which has been developed for a long time and has a wide range of application [27–31]. Nevertheless, only relatively recently this technique has been recognised as an alternative to standoff applications [32–37], which explains the absence of critical analysis of the possibility of its use for detection of trace explosive residues (on the surfaces of objects located at a safe distance from the operator) in the literature.

The development of standoff sensors appears to be the most complex problem in detection and identification of trace explosive residues in view of the requirements for these devices. The basic requirements are as follows:

- (i) high sensitivity (10–100 ng) [21];
- (ii) high selectivity of analysis;
- (iii) low false alarm probability (10^{-6}) [38];
- (iv) simultaneous detection and identification of several explosives in a multicomponent mixture;
- (v) long-range detection (10–100 m, depending on the problem to solve) [4];
- (vi) monitoring in real time;
- (vii) no harm for human eye and skin;
- (viii) hidden examination.

There are no sensors that would completely satisfy all these requirements. In this context, the development of new methods for detecting trace explosive residues and improvement of the known methods are still urgent.

In this review we analyse the state of the art of the investigations in this field and estimate the prospects of further development of photothermal spectroscopy for standoff detection and identification of trace explosive residues on surfaces.

For brevity, the results will be presented in condensed form, and references to original studies will be given for more details. We will also indicate a number of full-range reviews and monographs, which contain a large amount of data on individual aspects of the problem of detecting trace explosive residues.

2. Spectral features of explosive molecules

Widespread explosives, such as trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), pentaerythritoltetranitrate (PETN), etc., are known to contain hydrogen, carbon, nitrogen, and oxygen [6]. Explosives are characterised by high nitrogen content, which exceeds several times that in conventional materials (silk, polyurethane, nylon, etc.). Most explosive mixtures, including the aforementioned ones, contain either nitro (NO_2) or nitrate (NO) groups. The vibrational frequencies of these groups depend on the type of the atom to which a given group is attached in the explosive molecule, and the absorption cross sections at these frequencies are fairly high. For example, a typical peak value of the absorption cross section σ_m for stretching vibrations of the NO_2 group in widespread explosives is $(1–10) \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$ [2].

The fundamental vibrational–rotational transitions in molecules of almost all known explosives lie in the mid-IR range from 2500 cm^{-1} (4 μm) to 1100 cm^{-1} (9 μm) [38]. Generally the room-temperature absorption spectra of large organic molecules consist of one or several wide (several gigahertz) bands [39]. The vibrational–rotational absorption spectra of explosive molecules have many specific features, which are determined by their symmetry and chemical composition. Thus, one can identify individual absorption spectral lines with high accuracy.

That is why the methods of IR laser spectroscopy are of practical interest for detecting and identifying explosives. Moreover, currently only laser techniques can be a real base of standoff detection of trace explosive residues on the surface. At the same time, simple estimates show that conventional absorption IR spectroscopy cannot provide the necessary sensitivity ($\sim 100 \text{ ng cm}^{-2}$) [27].

3. Laser photothermal spectroscopy

Laser photothermal spectroscopy is an alternative to the conventional absorption spectroscopy methods. Photothermal methods are based on direct measurement of the radiation energy absorbed by an irradiated object [27–31]. Absorption of light in a sample and a subsequent change in its thermal state (temperature and other thermodynamic temperature-dependent parameters) are general processes for all photothermal methods. Therefore, eventually all photothermal methods are based on measuring variations in temperature, pressure, or density that are caused by light absorption in a medium.

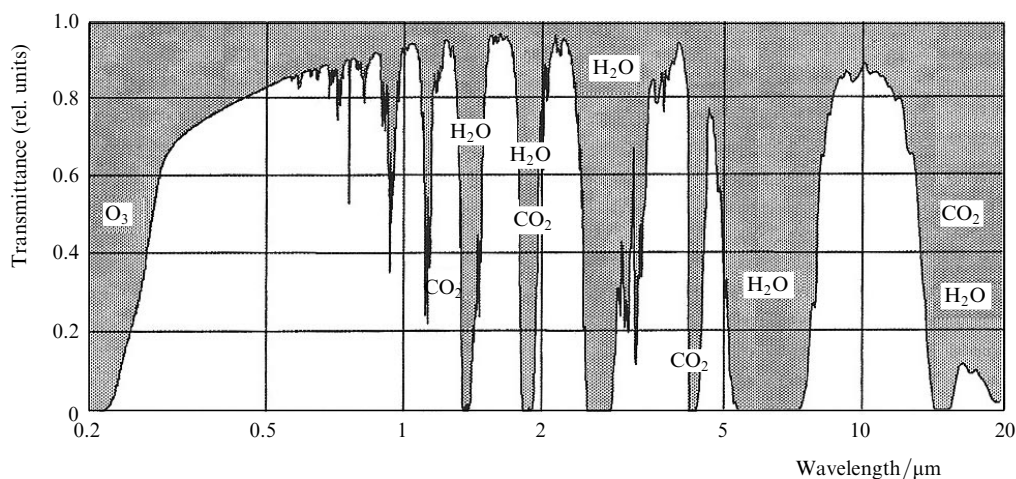


Figure 2. Transmission of atmosphere calculated using the MODTRAN code under the conditions of subarctic summer in pure atmosphere (meteorological visibility 23 km) at a height of 1 km [4]. The absorption bands of H₂O and CO₂ molecules are indicated.

Photothermal methods are active, nondestructive, and (in most cases) contactless. Generally, a material is heated by amplitude-modulated laser radiation. A characteristic feature of all photothermal methods is the collection of information about the properties and composition of the medium under study based on direct detection of absorbed power from the related changes in the physical and thermodynamic parameters of the medium. Hence, the characteristic features of these methods are as follows: (i) zero-reference measurements (in the absence of absorption the output signal is zero), (ii) an increase in sensitivity with increasing the radiation power (up to the absorption saturation), and (iii) fundamental limitation on the sensitivity by thermal fluctuations in the medium under study.

There are many methods for monitoring the thermal state of materials, which differ in the way of photothermal signal detection. The methods based on direct calorimetric or temperature measurements use temperature sensors. In photoacoustic spectroscopy the change in pressure in a medium upon heating is monitored using pressure sensors. Photothermal interferometry, photothermal deflection spectroscopy, thermal-lens method, photothermal diffraction spectroscopy, and photothermal reflection spectroscopy are based on measuring the variations in the refractive index upon sample heating. IR detectors are used in laser photothermal radiometry to record changes in the IR emission spectrum that are caused by periodic sample heating. Details of laser photothermal spectroscopy can be found in the original papers [40–47], as well as in reviews and monographs [27–31].

Practical application of photothermal methods in combination with tunable lasers turned out to be especially efficient for studying and monitoring weakly absorbing media [27, 28, 41, 44–46]. In particular, the methods of laser photothermal IR spectroscopy are used in a very important application: detection and identification of trace explosive residues in the gas phase [38]. In this case, most absorption measurements were performed using mid-IR lasers on molecular rotational or vibrational–rotational transitions.

Below we will be focused on the latest results obtained by photothermal spectroscopy for standoff detection and identification of trace explosive residues on surfaces. We

believe the methods of photoacoustic and deflection spectroscopy, as well as IR photothermal imaging of objects exposed to resonant irradiation, to be very promising for these purposes.

4. Specific features of standoff spectroscopy

Standoff technique appears to be one of the most widespread methods for detecting trace explosive residues [4, 5]. However, a number of difficulties must be overcome to implement it. First, the laser intensity at the detector input is inversely proportional to the squared distance to the object. Hence, both the radiation source power and detector sensitivity should be sufficiently high. Second, large-distance measurements must be performed taking into account the real state of atmosphere and the related dependence of light absorption and scattering on the laser wavelength, as well as the presence of transparency windows in the atmosphere (Fig. 2). In addition, the standoff technique imposes additional limitations on the laser wavelength and power density: both must be safe for human eye and skin.

Distances of 10–100 m are assumed to be quite safe to apply standoff detection of explosives that are, respectively, in possession of suicide terrorists or transported [4, 5, 34]. Standoff detection can be very efficient in places jammed with people (airports, railroad stations, underground stations, cinemas, etc.) (Fig. 3). An important advantage of



Figure 3. Example of possible application of the method of standoff detection and identification of trace explosive residues on the object surface [32].

this technique is the absence of intermediate stages (selection of tests and their transport to sensitive detector), due to which the examination time is significantly reduced in comparison with the local analysis, and examination can be performed in real time.

High-resolution laser spectral analysis (in particular, laser photothermal spectroscopy) can be used to implement highly sensitive standoff detection of explosives, both in the gas phase and in the form of microparticles on the surface of various materials. In this case, the necessary sensitivity, selectivity, and accuracy of analysis are provided by the high-precision measurement of resonant absorption of laser radiation within the profiles of individual vibrational–rotational lines in the spectra of molecules.

Under real conditions a significant problem in the analysis of trace explosive residues is the overlap of the vibrational–rotational absorption spectra of the material under study and interfering gases [15, 38, 48]. The overlap of the vibrational–rotational spectra obscures the object analysed and significantly affects the very important characteristic of explosive sensor: false alarm probability [38, 48]. In the standoff analysis these limitations are typical of almost entire IR range, which is characterised by a high density of weak absorption bands of H₂O, CO₂, and some other atmospheric gases (Fig. 4). In this case, quantitative concentration analysis is generally performed on the basis of the data of multispectral measurements using the spectral line databases, for example, HITRAN [49]. There are many studies on this special issue [38, 48, 50–57], which is to a greater extent a mathematical problem; therefore, we will not dwell on it and only note that the analysis of mutual position and characteristics of lines in vibrational–rotational bands of materials under study and interfering gases makes it possible to preliminary estimate the effect of their overlap in different spectral ranges and tune the analytical device to the most favourable range. This approach could be implemented due to the development of tunable quantum-cascade lasers (QCLs) with a narrow lasing line. Application of these lasers makes it possible to choose practically any spectral range in the entire mid-IR region [58, 59].

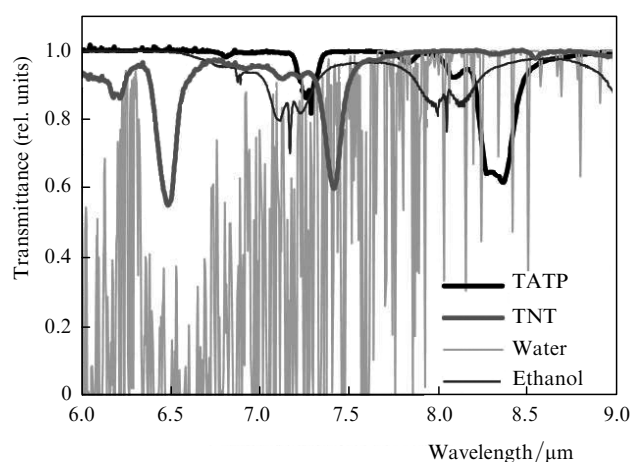


Figure 4. IR spectra of acetone triperoxide (TATP), trinitrotoluene (TNT), water vapour, and ethanol, which illustrate the overlap of vibrational–rotational absorption spectra of the detected materials and interfering gases [25].

5. Lasers for standoff photothermal spectroscopy

Currently, most often used IR sources for photothermal spectroscopy are lasers. When they are applied as sources of tunable monochromatic radiation for spectral analysis in the standoff regime, their main spectral characteristics are of primary importance. They are as follows:

(i) operation in the spectral range that provides the best detection conditions for the chemical compounds under study (as was noted above, this is almost entire mid-IR range, from 4 to 9 μm);

(ii) position of the laser wavelength in the atmospheric transparency window (in order to provide detection at large distances) (Fig. 2);

(iii) sufficiently high radiation power (more than 0.1 W) and low noise to ensure a low detection threshold for trace explosive residues;

(iv) single-mode radiation with a narrow lasing line (less than $\sim 0.001 \text{ cm}^{-1}$), which makes it possible to completely resolve spectral features of objects under study;

(v) wide band of smooth frequency tuning of laser radiation, which provides detection of materials under consideration in real multicomponent media (no less than 100 cm^{-1});

(vi) quality and rate of radiation frequency tuning, sufficiently high to provide reproducible scanning in a chosen spectral range;

(vii) stability and reproducibility of radiation parameters.

Recently low-pressure CO₂ and CO gas lasers were main radiation sources in the mid-IR range. None of them is truly tunable. They generate a set of discrete lines in the ranges of 9–11.5 and 5.0–7.5 μm, respectively, which fall in the range of fundamental vibrational–rotational transitions in molecules of some well-known explosives (TNT, RDX, PETN, etc.) [38]. These lines are spaced by $\sim 1 \text{ cm}^{-1}$. Application of these lasers in the detection of trace explosive residues is efficient for large (heavy) molecules, with characteristic broad absorption bands lying in the above-mentioned spectral region. At the same time, in the case of light molecules, which have narrow absorption lines, the detection efficiency depends on the coincidence of the laser wavelength with the absorption line for the gas analysed. Unfortunately, since CO₂ and CO lasers cannot be smoothly tuned, the selectivity of photothermal spectroscopy based on these sources is rather limited for explosive detection. This drawback can be overcome using a high-pressure CO₂ laser, where pressure-induced broadening leads to overlap of individual lasing lines; as a result, smooth tuning in the wavelength range of 9–11 μm can be performed [60]. However, the entire detection system becomes more bulky and complex.

Molecules whose characteristic absorption bands are not overlapped with the lasing lines of the above-mentioned lasers are detected using other radiation sources, for example, tunable spin-flip Raman lasers [61–63], lithium niobate parametric oscillators [64–66], and cw semiconductor lasers [67, 68].

Conventional semiconductor lasers generally operate in the near-IR region; therefore, they can be used to record only weak overtones of vibrational–rotational fundamental absorption bands. In this case, the sensitivity of photothermal spectroscopy is insufficient, because, on the one hand, the semiconductor laser power in the near-IR region is

relatively low, and, on the other hand, the absorption of molecules in the range of fundamental absorption band overtones is rather weak. For example, tunable semiconductor distributed-feedback lasers (radiation wavelength 1.55 μm) are used as radiation sources in acousto-optic sensors, which are applied in agricultural engineering to detect ammonia. Their sensitivity is 40 ppb in comparison with 20 ppt, which is characteristic of devices based on CO_2 lasers [69, 70].

High radiation powers for semiconductor laser diodes were obtained using optical fibre amplifiers [71, 72]. The narrow lasing line allows one to tune exactly to the absorption line of the material under study, thus providing a high selectivity. In turn, modulation of the laser diode radiation wavelength suppresses the effect of background signal and mechanical vibrations. Nevertheless, the acousto-optic sensors based on near-IR laser diodes, even using optical fibre amplifiers, cannot be considered as promising for detecting trace explosive residues.

Note that near-IR semiconductor lasers with radiation wavelengths up to $\sim 2 \mu\text{m}$ have been successfully developed for a long time in view of their importance for communication systems. The operation of semiconductor lasers in the shorter wavelength IR range is based on interband transitions in the semiconductor. These lasers belong to bipolar devices based on recombination of conduction-band electrons with valence-band holes. However, their wavelengths do not overlap the spectral range ($\lambda > 2 \mu\text{m}$), which includes the fundamental vibrational-rotational transitions of the large explosive molecules we are interested in. At the same time, the absorption spectra of the most important explosive molecules, as was noted above, lie in the wavelength range above 4 μm .

A very important long-wavelength IR range can be overlapped using unipolar semiconductor lasers of new type, which involve intraband transitions of carriers (for example, electrons in the conduction band): quantum cascade lasers (QCLs) [38, 58, 59]. They are based on multilayer InGaAs-InAlAs heterostructures, where lasing is due to the cascade intraband transitions. The QCL lasing wavelength is determined by the thickness of heterostructure layers and, therefore, can be set by heterostructure growth conditions. Lasers of this type can operate in the wavelength range of 3.5–24 μm [58, 59]. In the single-mode regime QCLs have a lasing line width of 1–3 MHz, whose frequency can be tuned in a wide spectral range due to the changes in temperature and pump current; the radiation power reaches few hundreds of milliwatts at room temperature [38]. The first experimental QCL demonstration dates back to 1994 [73]. Commercial production of QCLs began in 1997 (Alpes Lasers, Switzerland). Now there are many manufacturers in the market (NanoPlus GmbH, Alpes Lasers, Fraunhofer IAF, Daylight Solutions Inc., etc.).

Surely, with a further improvement in technology and parameters, QCLs will play a more important role in standoff detection of trace explosive residues. The recently developed cw QCLs, which are characterised by a high radiation power at room temperature, are used in photoacoustic gas sensors [26]. More details concerning the physical principles of QCLs, their lasing parameters, and areas of their application can be found in reviews and original papers [58, 59, 74–79].

6. Detectors for standoff photothermal spectroscopy

Recently significant progress has been made in the detection of photothermal signals. For example, the results of studying photoacoustic systems with application of laser diodes or QCLs in combination with microcantilever-based signal-recording system were reported in a number of studies [80–85].

A microcantilever is an element of physical, biological, or chemical sensors that measure changes in its bending or resonant frequency shift under various external effects [81–84]. The microcantilevers used in photothermal spectroscopy are generally composed of two materials with different thermal expansion coefficients. Upon heating microcantilever becomes bent under thermal stress, and this bending is generally measured optically, as, for example, in atomic-force microscopes [85]. The laser beam reflected from the microcantilever surface arrives at a position-sensitive detector, whose output signal is proportional to the bending value (Fig. 5). In turn, as a result of some processes (for example, adsorption), the bending of microcantilever is accompanied by a change in its mass, which is detected by a change in its resonant frequency [82]. The high sensitivity of microcantilevers, their small dimensions, and possibility of designing multielement linear arrays of sensitive elements make them promising elements of sensors for standoff detection of trace explosive residues by photothermal spectroscopy [84].

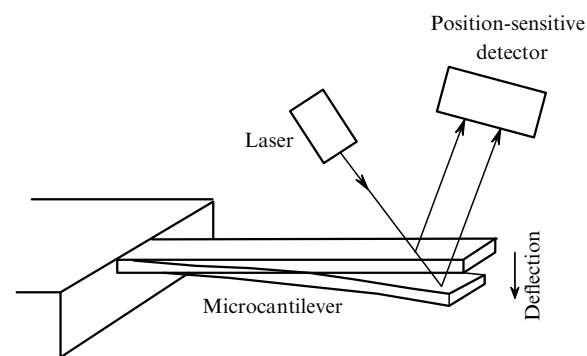


Figure 5. Microcantilever with laser measurement of displacement [85].

The results of [86] indicate that microcantilevers are highly sensitive. The equivalent (normalised to noise power) sensitivity of the acousto-optic system based on a compact laser Michelson interferometer and a silicon microcantilever was $1.4 \times 10^{-10} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$. This value exceeds that for conventional systems with a capacitance microphone by a factor of 100. Currently, microcantilevers are considered to be the main sensitive elements for standoff deflection laser spectroscopy.

Another promising sensitive element for standoff photothermal spectroscopy is a quartz tuning fork [87–90], which has some advantages over other optical detectors. For example, its Q factor, which depends on the environmental pressure, may reach $\sim 10^5$ in vacuum and $\sim 10^4$ in open air, and its frequency sensitivity is about 0.1 Hz [32]. The high Q factor makes the quartz tuning fork a highly sensitive acoustic detector. According to the estimates, the sensitivity

of a photoacoustic system based on this detector may reach $\sim 10^{-9} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$ [89]. For this reason, the quartz tuning fork is insensitive to external acoustic noise, and this circumstance is extremely important for standoff measurements using open photoacoustic systems [26]. It is also important that detectors of this type are nonsaturable.

Finally, in the systems for standoff detection of explosives, which are based on IR imaging under resonant object excitation by a tunable laser, uncooled microbolometer arrays are generally used as radiation detectors; the sensitive element in these microbolometers is a vanadium oxide film [35–37]. The noise-equivalent temperature difference (NETD) of microbolometers is $\sim 100 \text{ mK}$; this value is worse than that for cooled photoelectric detectors by approximately an order of magnitude [35]. Therefore, for the problems requiring high response speed and sensitivity, photoelectric detectors have all advantages.

7. Analysis of standoff methods of laser photothermal spectroscopy

7.1 Standoff laser photoacoustic spectroscopy

Photoacoustic spectroscopy was applied for the first time to locally detect explosives in the gas phase in [91], where TNT, RDX, and PETN molecules were identified in atmosphere at partial pressures of $\sim 10^{-6}$ Torr and lower; i.e., with concentrations on the order of few ppb. Note that significant progress has been made in the local analysis of chemical compounds by photoacoustic spectroscopy (PAS). In particular, there are several commercial photoacoustic spectrometers, designed for simultaneous detection of several materials at the level of few ppb in multicomponent media [92]. The latest data on local detection of trace amounts of substances in the gas phase by PAS were reported in [93–98].

One of the first studies on the possibility of applying laser photoacoustic spectroscopy for standoff detection of trace explosive residues on the object surface was carried out by Miklos et al. [99]. They attempted to detect the material under study on the surface of a distant target by direct detection of the acoustic waves excited in atmosphere as a result of absorption of laser radiation by the object studied. The emphasis was on the use of a high-power laser and on the increase in the efficiency of acoustic energy collection using a parabolic mirror with a sensitive microphone in the focus. In our opinion, despite some positive effect of these measures, the influence of external factors (in particular, atmospheric turbulence) makes this approach inefficient.

A more promising approach was demonstrated in [32], where a peculiar PAS version was applied. A schematic of the experiment is shown in Fig. 6. A sample (target) with a chemical compound under study on the surface was exposed to laser radiation with a wavelength tunable within the characteristic absorption band of this compound. The relation between the laser energies absorbed and scattered by the target changes with a variation in the laser wavelength. For example, an increase in absorption in the target leads to a decrease in the scattered light intensity on the surface of piezoelectric sensor (quartz resonator in the form of a tuning fork). Acoustic waves are excited in quartz due to the acousto-optic effect upon absorption of scattered laser radiation on the sensor surface. When the repetition frequency of laser pulses coincides with the resonant

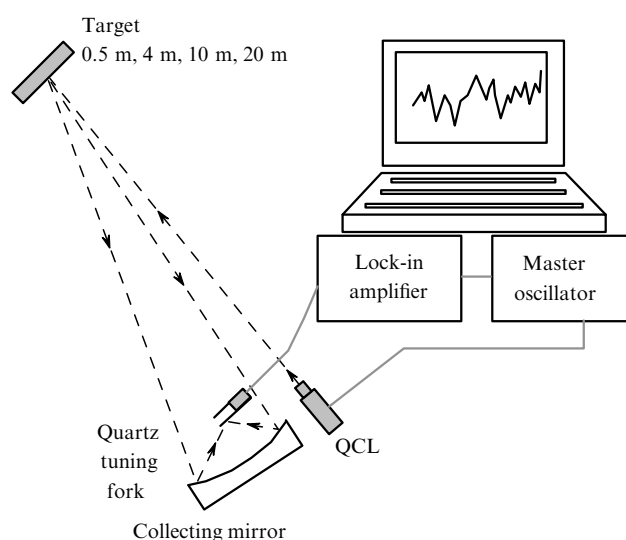


Figure 6. Schematic of the experimental setup for photoacoustic standoff detection of trace explosive residues on the object surface [32].

frequency of the tuning fork, its vibration amplitude reaches a maximum, which is proportional to the light intensity scattered by the target. In turn, the piezoelectric effect generates a voltage signal, which also depends linearly on the laser intensity scattered by the target. A QCL with a radiation wavelength tunable in the range of $9.25\text{--}9.80 \mu\text{m}$ ($1081.08\text{--}1020.41 \text{ cm}^{-1}$) with a step of 0.01 nm was used as a radiation source in [32]. The laser power was 100 mW with a pulse duty factor of 5% .

The experiment was performed as follows. The target surface was covered by a thin layer of a material studied (RDX, TNT, or PETN) of known mass. Under target irradiation by a tunable QCL the tuning fork vibration amplitude was recorded as a function of laser wavelength. The photoacoustic spectrum of RDX, recorded as the ratio of recorded signals in the presence and absence of explosive residues on the target surface, is shown as an example in Fig. 7 (on the right). A fragment of the IR transmission spectrum of RDX, obtained by van Neste et al. [32] using conventional absorption spectroscopy, is shown for comparison on the left. The part of the spectrum corresponding to the QCL tuning range is selected for convenience. There is good agreement between the photoacoustic and trans-

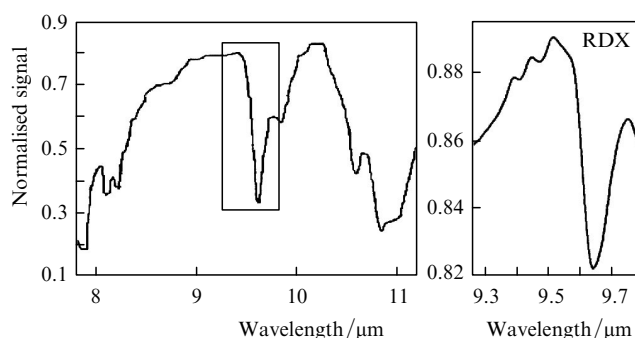


Figure 7. RDX photoacoustic spectrum, recorded at a distance of 20 m (on the right), and the conventionally obtained IR transmission spectrum (on the left), with the QCL tuning range selected [32].

mission (inverted absorption) spectra. It was stated in [32] that reproducible photoacoustic spectra were recorded up to RDX surface concentrations of $\sim 100 \text{ ng cm}^{-2}$. Taking into account that the signal arrived at the detector from an area of size comparable with the laser spot diameter (25 mm), the detection limit obtained in [32] can be estimated as $\sim 500 \text{ ng}$.

The possibilities of a method similar to the above-described one but with a simultaneous use of two QCLs were demonstrated in [34] by the same research team. The tuning range of the second laser was $7.38\text{--}8.0 \mu\text{m}$ ($1355.01\text{--}1250 \text{ cm}^{-1}$). Thus, the tuning ranges of the lasers used overlapped the absorption lines characteristic of most well-known explosives. The pulse-repetition rates of the two lasers were somewhat different (by 143 Hz). An individual detector was chosen for each laser, with a resonant frequency coinciding with the laser pulse-repetition rate. It was convincingly shown by this example in [34] that, applying some tunable QCL with a narrow lasing line, one can always overlap the part of the mid-IR range that is necessary for identifying most known explosives (Fig. 8). This is especially important for detecting explosives in real media in the presence of overlap of vibrational–rotational spectra of the substance analysed and interfering chemical compounds.

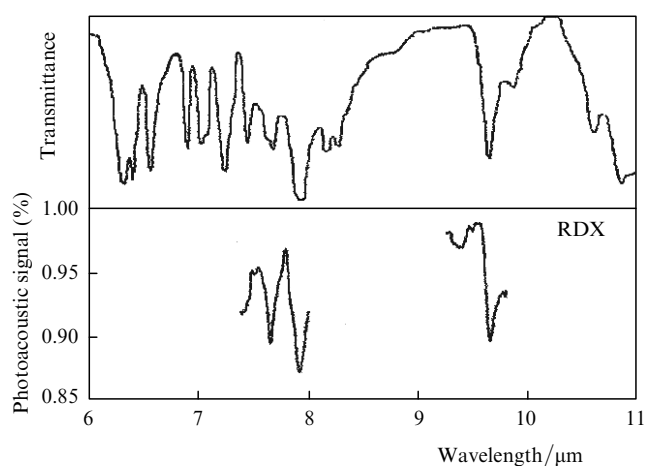


Figure 8. RDX spectra: (top) the transmission spectrum of a bulk sample, recorded using absorption IR spectroscopy, and (bottom) the wavelength dependences of the photoacoustic signal, recorded in the corresponding tuning ranges of two QCLs [34].

The authors of [34] believe that the distance to the object under study can be increased to 100 m by optimising the measurement scheme and applying higher power lasers. Indeed, it was noted above that the Q factor of a quartz cavity in vacuum exceeds the corresponding value at atmospheric pressure by at least an order of magnitude. Therefore, placing the sensor in a closed evacuated cell with an input window transparent in the necessary spectral range, one can increase the detection range distance to 100 m.

In addition, we should note that the sensitivity of this method should depend on both the target material and the state of its surface (for example, roughness, which eventually determines the character of the scattered radiation directional pattern). Unfortunately, this information is absent in the studies under consideration. Moreover, to implement

this method in practice, one has to solve a purely technical problem: scan the object under study by a laser beam. This problem is caused not only by the necessity of monitoring large areas but also by the following circumstance. The spectra of laser radiation scattered from surfaces of different materials in the absence of explosives form some background, characteristic of each object. Therefore, elimination of its effect on the spectrum of recorded signal during examination is a necessary condition for identifying explosives. Since trace explosive residues are present on object surfaces in the form of individual particles rather than a continuous coating, this problem can be solved under real conditions by scanning the laser beam over the surface of the object under examination.

Nevertheless, despite the number of problems that are still to be solved, the prospects of the above-described approach for standoff detection of explosives will apparently be determined to a large extent by the increase in the QCL radiation power and design of an optical system of acceptable sizes for effective collection of scattered laser radiation.

7.2 Standoff laser deflection spectroscopy

The essence of deflection spectroscopy in the conventional version is as follows [27, 29]. The surface of the sample under study is heated by intensity-modulated radiation. Due to the heat transfer the surface layer of the medium that is in contact with the sample becomes periodically heated. The formation of a temperature gradient in the medium near the surface and the related change in its refractive index are revealed by deviation of the probe beam oriented parallel to the sample surface (mirage effect). Due to the high sensitivity of this method, it is especially promising for measuring low ($\sim 10^{-7} \text{ cm}^{-1}$) optical absorption in materials [29, 100–102].

Photothermal deflection spectroscopy in a modified form was also applied to local detection of trace explosive residues in the gas phase [103–108]. A distinctive feature of this technique is the use of a microcantilever as a sensitive element [80–85], on the surface of which molecules of the material analysed are adsorbed. IR radiation from a source tunable in the necessary wavelength range interacts with the adsorbate and, being absorbed by it, heats the two-component microcantilever. This leads to a change in the microcantilever temperature and its additional bending. Since the bending is proportional to the absorbed energy, its dependence on the incident radiation wavelength corresponds to the IR absorption spectrum of the adsorbate. The sensitivity of photothermal spectroscopy using a microcantilever is directly related to the thermal sensitivity of the two-component sensor. Thus, the microcantilever plays the role of an uncooled high-sensitivity IR detector. In the simplest case the signal from this detector is read using a probe laser beam, which reflects off from the microcantilever working surface and is incident on the input area of position-sensitive photodetector (see Fig. 5).

The possibility of using photothermal deflection spectroscopy for local analysis with a microcantilever as a sensitive element was demonstrated for the first time in [80]. The extremely high sensitivity of two-component microcantilever to variations in temperature ($\sim 10^{-5} \text{ K}$), corresponding to an absorbed energy $\sim 20 \text{ fJ}$, was obtained in [83]. In turn, a research team from the Oak Ridge National Laboratory also demonstrated the high sensitivity

and selectivity of deflection spectroscopy, which make it possible to locally detect ~ 400 pg of TNT, RDX, or PETN adsorbed from the gas phase on the microcantilever surface [82]. To regenerate the sensor, it was proposed to use the strong temperature dependence of desorption, for example, by heating the sensor with the IR radiation used.

The application of standoff deflection spectroscopy for detecting trace explosive residues was demonstrated for the first time in [34]. A schematic of the experimental setup is shown in Fig. 9. One can see that the deflection methods for detecting in the standoff and point modes are radically different. A standard IR monochromator was used to select monochromatic radiation with a wavelength varied in the range of 2.5–14.5 μm in standoff detection. In the method under consideration, as well as in photoacoustic standoff spectroscopy, the photothermal spectrum of laser radiation scattered by the target was recorded. However, the sensitive element was a microcantilever, which was bent as a result of heating by the incident radiation, and this bending was recorded optically. A commercial silicon microcantilever with a length of 350 μm , width of 35 μm , and thickness of 1 μm (MicroMasch, Oregon) was used. At a distance of 1 m from the target the sensitivity to the TNT, RDX, and PETN traces present on the target surface was ~ 100 ng cm^{-2} (Fig. 10). This sensitivity is generally sufficient for detecting trace explosive residues that are generally present on the surface of explosive devices, masking shells, and on the clothes and other things of persons dealing with explosive devices [34]. The distance from the object is believed to significantly increase by optimising the microcantilever parameters and applying a tunable QCL as a radiation source. The latter is beyond doubt, because the power of the radiation source used in [34] was apparently below 0.1 mW.

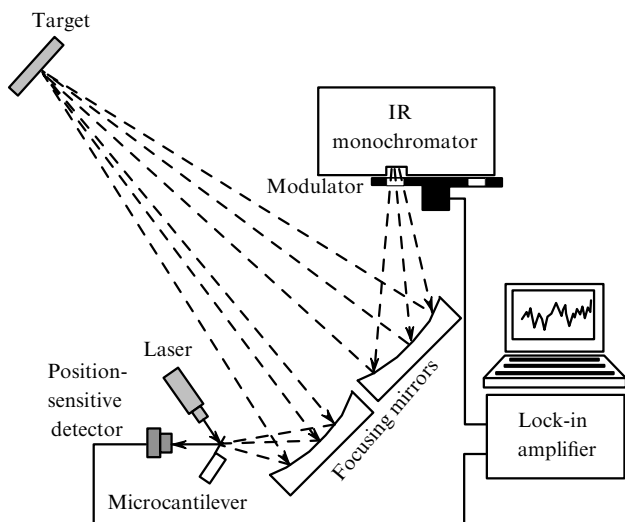


Figure 9. Schematic of the experimental setup for standoff detection of trace explosive residues on the object surface by deflection spectroscopy [33].

We should also mention bending spectroscopy, a method independently developed in [109–111] for measuring low absorption in thin films of microcrystalline silicon, in particular, in the mid-IR range (~ 5 μm). As evidenced by the measurement scheme reported in these studies, this technique does not radically differ from the deflection spectroscopy discussed above. However, the sensitivity of

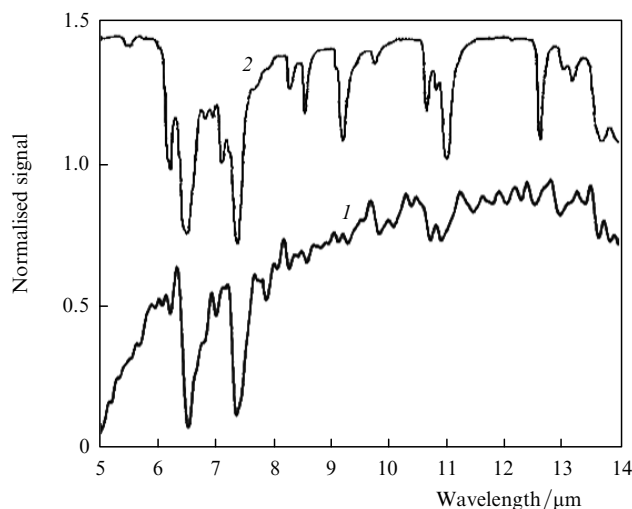


Figure 10. (1) TNT photothermal spectrum, recorded by deflection spectroscopy at a distance of 1 m and (2) the transmission spectrum, obtained by conventional IR spectroscopy [33].

bending spectroscopy was much higher (at least by an order of magnitude) due to the optimised design and the use of resonant properties of microcantilever, which was placed in an evacuated volume [110]. It is important that the effect of external conditions on the microcantilever noise characteristics [84] is simultaneously suppressed in this case.

7.3 IR photothermal imaging under resonant irradiation

This method is based on laser photothermal IR radiometry and active IR imaging [39–47]. The fundamental difference of these two methods from their passive analogues [112, 113] is that they are based on recording the derivative of thermal radiation flux with respect to temperature rather than the flux itself [45–47]. This allows one, in particular, to suppress the effect of constant background component from foreign sources, whose temperature may exceed that of the object under study.

The possibility of using active IR imaging for standoff detection of TNT and RDX traces was demonstrated for the first time in [35–37]. In this method a material under study is exposed to laser radiation with a wavelength lying in the absorption range of this material. Due to the resonant absorption the material is selectively heated, and the temperature of the surface covered by this material exceeds that of the free surface. As a result, a temperature contrast arises between individual details of the pattern observed with a thermal detector. To exclude the constant background, which hinders the explosive identification, the differential image of the object (obtained by subtracting the image obtained in the absence of laser irradiation from the image under irradiation) was analysed in all cases. The differential signal was normalised to the laser power.

The experiment (Fig. 11) was performed using a commercial QCL (Daylight Solutions), continuously tunable in the range of 6.1–6.4 μm . In the cw regime the laser power was up to 30 mW at a lasing linewidth of ~ 1 cm^{-1} . The radiation wavelength was chosen so as to fall in the narrow window in which wet air is relatively transparent; this is necessary for detecting trace explosive residues at significant distances under real conditions. The explosives under study exhibit significant absorption in this spectral range (due to

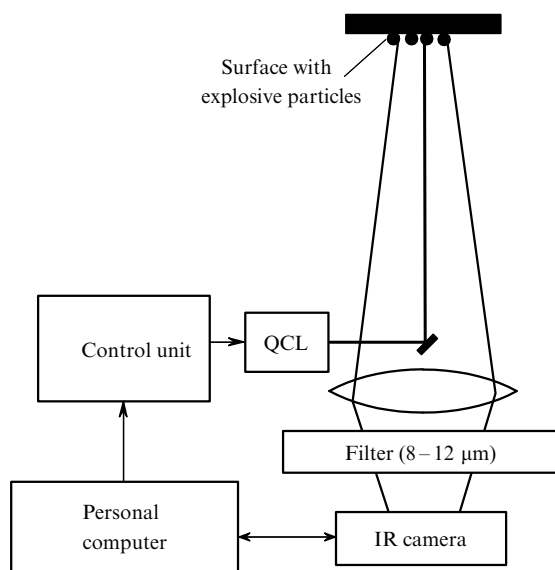


Figure 11. Schematic of the experimental setup for standoff detection of trace explosive residues on the object surface by IR photothermal imaging of object exposed to resonant radiation [36].

the N–O bonding). In addition, the above-mentioned laser wavelengths are beyond the detection range of most IR

detectors with filters, which are generally tuned to the short-wavelength part of the mid-IR range (3–5 μm) or to the long-wavelength part (8–12 μm). The photothermal signal was collected using a lens with the focal length $f = 100$ mm onto an array of uncooled microbolometers with vanadium oxide sensitive elements (FLIR, Inc.; 320×240 pixels, pixel size 38 μm , NETD = 85 mK, 30 frames per second). A filter was placed between the lens and array to ensure detection of photothermal signal in the spectral range of 8–12 μm .

To demonstrate the selectivity of this method to different types of explosives, the materials under study were deposited on a transparent polypropylene film. They were subjected to both nonselective (without a laser) and laser heating; in the latter case the QCL radiation was tuned to the resonance characteristic of the chemical compound analysed. The thus obtained differential images are shown in Fig. 12. The sequence of images demonstrates the selectivity of multi-spectral approach even for different types of explosives. According to the estimates [35–37], the TNT detection sensitivity obtained in laboratory conditions at a distance of 4 m from the target was ~ 100 ng. Depending on the wavelength, the lasing power changed in the range of 3–18 mW. The size of the irradiated area was 10 mm in all cases (it is limited by dotted circles in Fig. 12).

It follows from the aforesaid that resonant IR imaging photothermal spectroscopy (apparently, this name better characterises the essence of the method) makes it possible to

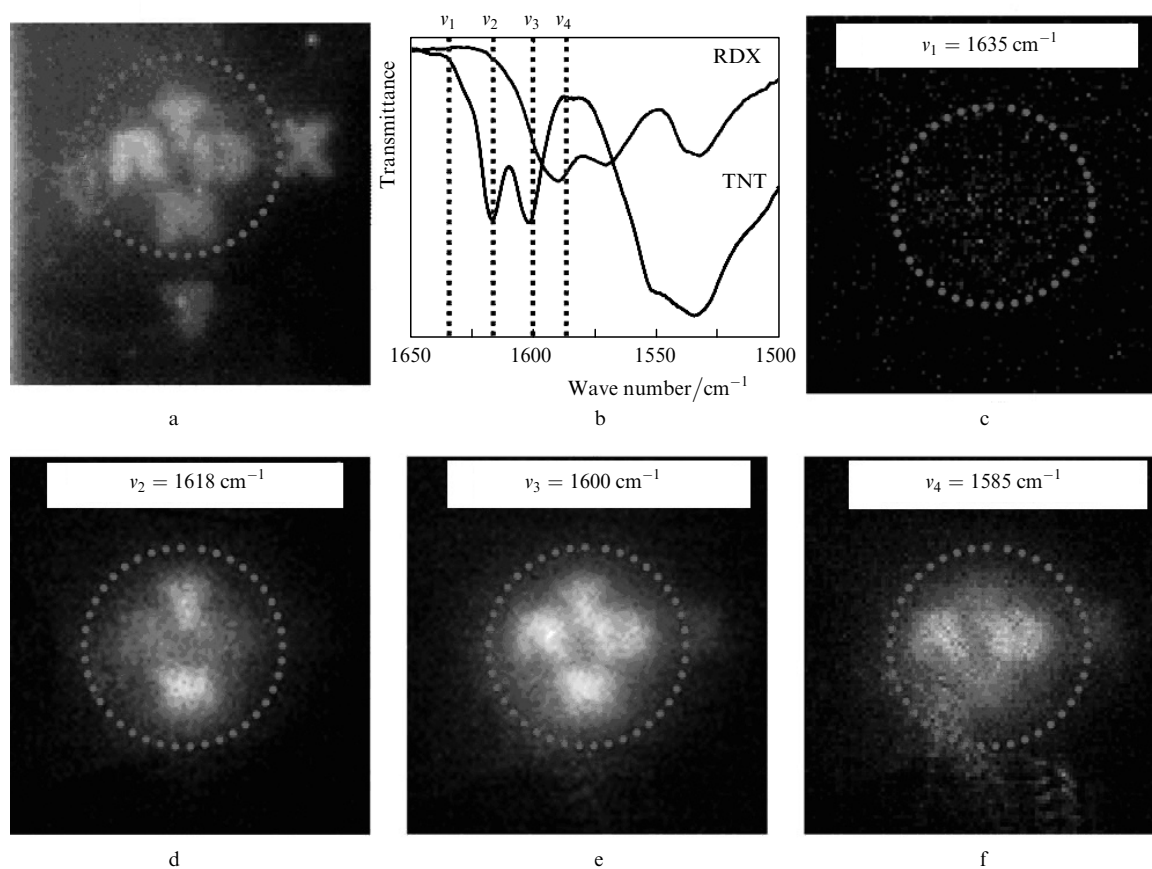


Figure 12. IR photothermal imaging of a target exposed to resonant radiation (RDX and TNT microparticles are deposited on a propylene film in the form of letter designations of explosives studied) [36]: (a) the result of nonselective film heating in the wavelength range of 7–14 μm , (b) the features of the RDX and TNT absorption spectra in the wavelength range under study, (c) the nonresonant heating of target by laser radiation ($\nu_1 = 1635$ cm^{-1}), (d) the resonant heating of only TNT molecules ($\nu_2 = 1618$ cm^{-1}), (e) the resonant heating of both RDX and TNT molecules ($\nu_3 = 1600$ cm^{-1}), and (f) resonant heating of only RDX molecules ($\nu_4 = 1585$ cm^{-1}).

perform hidden detection and identification of trace explosive residues in the form of particles on surfaces of different materials under conditions that are safe for human eye and skin (the power density in the IR range should not exceed 100 mW cm^{-2}).

The method of differential absorption, which applies several radiation wavelengths, both in on- and off-resonance with the absorption line of the material, allows one to successfully distinguish the contributions of different materials to the total absorption. The differential multispectral approach makes it possible to significantly reduce the probability of positive false alarm (PFA) even in the presence of such interfering factors as foreign particles of black materials (broadband absorbers) on the surface.

It was noted in the above-mentioned studies that the development of this measurement technique is directly related to the progress in QCL parameters, primarily, increase in the radiation power, expansion of lasing range in the mid-IR region, and expansion of the tuning range. The sensitivity of IR detectors and collection efficiency of the IR radiation from the object are also important factors. In addition, image processing methods should be developed to improve this detection technique. It is believed that application of high-speed detectors will make it possible to record the heating (cooling) kinetics of materials on different substrates, due to which a more effective algorithm for recognising explosives could be developed. Studies in this field are urgent because the aforementioned processes are related to the thermodynamic parameters of materials, as well as to the particle density and sizes, which are different for different explosives [47].

This suggestion is confirmed by the results of independent studies on detection and identification of defects on the surface of optical coatings, obtained by Pearson et al. [114]. To gain information on defects, they also used the method of differential absorption under irradiation by a tunable pulsed CO_2 laser. The thermal signal was recorded by a single-element detector, applying pulsed photothermal

radiometry (PPTR) [46, 47, 115]. As was shown in [114], an object can be identified due to the correlation between its absorption coefficient $\alpha(\lambda)$ (considered as known) and the characteristic decay time of the photothermal signal.

An impressive result on standoff detection of trace explosive residues using a similar method demonstrated another research team [116], who in fact implemented the above-formulated suggestions on the development of this method, specifically: significantly increased the collection efficiency of thermal radiation and applied an IR detector with a sensitivity higher by a factor of 3. As a result, they showed standoff detection of TNT traces at a distance up to 150 m [116]. It is important that this result was obtained under field conditions at fairly strong wind gusts, reaching 35 knots. At the same time, this progress was made at the expense of significant increase in the size of the experimental setup and its complication.

During these studies an experimental facility ROSE (Remote Optothermal Sensor) for standoff detection of trace explosive residues on the object surface was developed. It was located in a van (Fig. 13) and included the following main elements: a tunable cw CO_2 laser, mirror optics for collimating laser radiation (Cassegrain telescope with an aperture of $\sim 30 \text{ cm}$), Ritchey–Chrétien telescope (aperture $\sim 61 \text{ cm}$) for collecting thermal radiation from object, and IR chamber with a cooled focal-plane array HgCdTe detector with $\text{NETD} = 20 \text{ mK}$ and pixel size of $30 \times 30 \mu\text{m}$ (Focal Plane Array, FPA). A schematic diagram of ROSE is shown in Fig. 14.

During the measurements the laser spot area on the target surface was $\sim 1 \text{ cm}^2$. The thermal signal from this area was focused on one pixel of the detector array. Under exposure to resonant laser radiation with a wavelength corresponding to the absorption peak maximum ($10.653 \mu\text{m}$, 10P26 line), the temperature increased only in the TNT-containing areas. If the laser wavelength ($10.591 \mu\text{m}$, 10P20 line) fell in the weak-absorption range, the object temperature increased only slightly (Fig. 15).

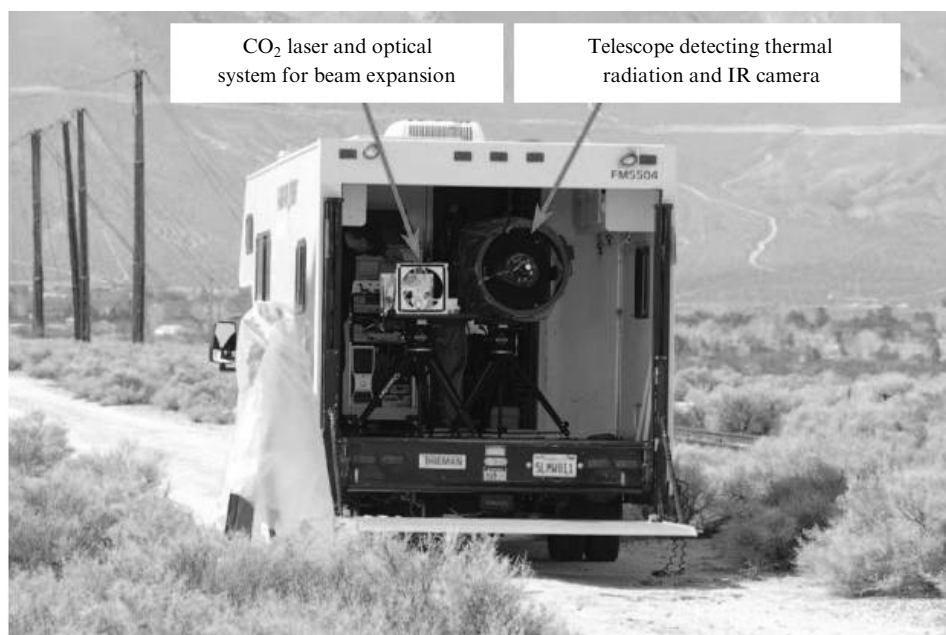


Figure 13. Photograph of the experimental remote optothermal sensor ROSE for standoff detection of explosives [116].

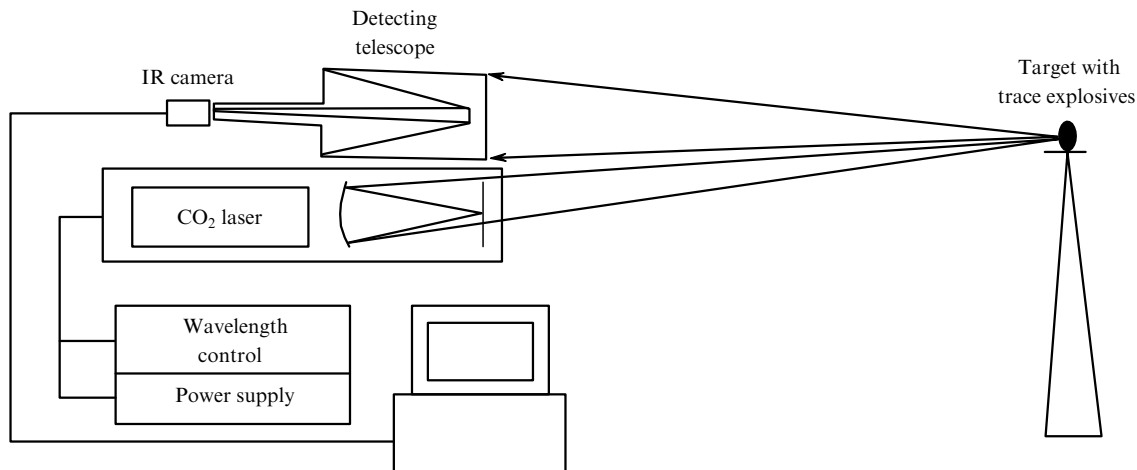


Figure 14. Schematic diagram of ROSE.

Thus, the spatial distribution of the change in temperature reveals the location of the recorded object on the target and makes it possible to identify a specific chemical compound, even in the presence of other absorbing materials. Specific features of active thermography with a laser scanner were considered in [115].

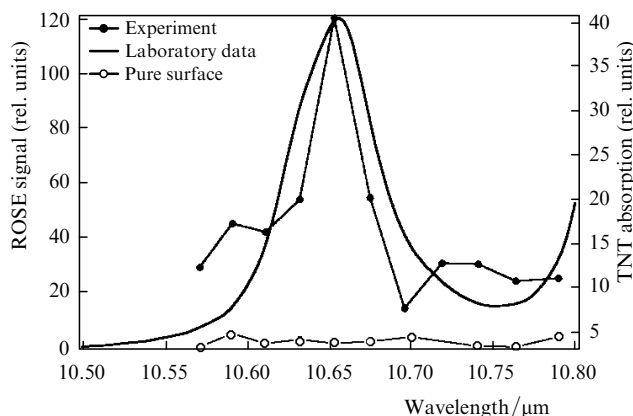


Figure 15. Dependences of the detected signal on the laser wavelength for samples with TNT traces, located at a distance of 150 m [116].

Mukherjee et al. [116] noted the high sensitivity of this method (with a PFA many orders of magnitude lower than in most methods that are currently used to detect trace explosive residues): it was estimated to be $\sim 2 \mu\text{g cm}^{-2}$ at a distance from the object of 150 m and signal-to-noise ratio $\text{SNR} = 1$. The authors suggested application of tunable QCLs with a power above 1 W (without loss of sensitivity) to be promising for the system developed. Concerning the detection range distance, it was stated that ROSE, with further optimisation of the thermal radiation detection system and data processing algorithm, can be used for standoff detection of trace explosive residues at distances up to 1 km. The optimisation primarily concerns the application of adaptive optics, because under real conditions atmospheric turbulence manifests itself at large distances.

In addition, Mukherjee et al. [116] believed this method to be also promising for detecting and identifying trace explosive residues on the people's clothes and things at small

distances (for example, in airports). At the same time, they did not restrict the technique under consideration to only detection of trace explosive residues. Other very important applications are search for drugs and contactless monitoring of pharmaceutical, chemical, and biological products.

8. Conclusions

Based on the analysis of the data in the literature on the use of different methods of highly sensitive standoff detection of trace explosive residues on the object surface using laser photothermal spectroscopy, we can draw the following conclusions.

The results on the detection of explosive particles on the object surface by laser photothermal spectroscopy are urgent and promising for developing new methods of standoff detection of trace explosive residues, because these methods satisfy most above-considered requirements for standoff detectors of trace explosive residues.

The progress in the new methods based on the photothermal effect is primarily related to the application of new promising devices: QCLs (tunable in the mid-IR range) and sensitive detectors based on microcantilevers and acoustic quartz resonators. There is good reason to believe that the development of these devices, new schemes of multispectral approach, and more efficient algorithms for recognising explosives will play a key role in the improvement of photothermal standoff methods for detecting trace explosive residues (10–100 ng) on the object surface at distances of ~ 100 m and more.

Note that the development of this direction is only in the initial stage. As follows from the analysis performed, there are some technical problems to solve in order to significantly improve the parameters of standoff sensors based on the photothermal effect. However, the design of an explosive sensor with a high sensitivity and selectivity is only a part of the problem. The other (maybe, most difficult) part is the practical implementation of the results of laboratory experiments in a working device; to this end, numerous experiments with different materials under real conditions must be performed.

Note also some prospects of combined mobile systems for standoff analysis, which are based on different physical principles. For example, one would expect combination of

Table 1. Comparison of the methods of standoff detection of trace explosive residues in the form of particles on the object surface.

Detection method	Laser radiation power (energy)	Detection threshold	Distance from object/m	Selectivity	Measurement time/s	Eye safety	References
LIBS	350 mJ	10–100 ng	45	intermediate	~1	dangerous	[21]
Raman Spectroscopy	2.5 W	10 µg	30	high	~10	– “ –	[16]
PF–LIF	0.5 mJ	20 ng (estimate)	10	– “ –	~1	safe	[19]
Active IR Imaging	< 40 mW	20 µg	5	intermediate	~1	– “ –	[26]
Passive Hyperspectral IR Imaging	–	40 µg cm ⁻²	50	– “ –	~1	– “ –	[112]
PAS	100 mW	~500 ng	20	high	~1	– “ –	[32, 34]
PDS	< 0.1 mW	100 ng cm ⁻²	1	– “ –	~1	– “ –	[33]
Resonant IR PT Imaging	20 mW	< 100 ng	4	– “ –	~1	– “ –	[35, 36]
Resonant IR PT Imaging	–	2 µg (estimate)	150	– “ –	~1	dangerous	[116]

PAS with laser-induced breakdown spectroscopy to increase the analysis selectivity in the presence of interfering components, whose absorption spectra are overlapped with the absorption spectrum of the detected analyte.

As was noted above, along with the methods based on the photothermal effect, there are some other applications of laser spectroscopy for standoff detection of trace explosive residues on the object surface. The comparative characteristics of the main methods of standoff detection of trace explosive residues and the photothermal spectroscopy methods considered here are listed in Table 1. A comparison of the most important characteristics of the methods presented in Table 1 is in favour of the standoff techniques based on the photothermal effect.

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