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Laser Desorption of Traces of Explosives in Ion Mobility Spectrometry

A.E.Akmalov, G.E.Kotkovskii, and A.A.Chistyakov

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, 115409, Russia

Abstract

The efficiency of a YAG:Nd^{3+}laser (λ = 1064 nm) and a diode continuous laser (λ = 440 nm) to initiate laser desorption of traces of trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) is quantitatively compared with use of mass spectrometry. It is shown that a pulsed neodymium laser is more promising for creating a device of contactless sampling for ion mobility spectrometers.

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1. Introduction

To date, apparatus based on ion mobility spectrometry and ion mobility increment spectrometry are widely used for different applications [1-2]. In some cases they are equipped by additional sampling devices to detect traces of explosives with low saturated vapor pressure. Operation of such devices is based on evaporation of explosives from a special napkin under heating after wiping the suspicious surface. The limit of detection for this case is about 10-100 picograms.

There are several problems associated with use of napkins and leading to a decrease in the sensitivity of the method or to the inconvenience of its use: the problem of full transfer of the analyte to a napkin, too prolonged heating (up to 10 seconds), the need for consumables, etc. In this connection, an approach based on the use of laser radiation for non-contact examination of objects by initiating laser desorption seems promising. For example, it was shown that an ultraviolet laser beam of nanosecond duration effectively evaporates (desorbs) the explosive substances from a wide class of surfaces, and the duration of the temporal profile of concentration of evaporated molecules does not exceed one second [3-4].

The purpose of this paper is to compare the simplest and cheapest sources of laser radiation to assess the effectiveness of desorption of traces of explosives by mass of a desorbed substance, and to investigate the possibility of creating a contactless sampling device, taking into account the results obtained.

2. Theory

Various mechanisms for initiating laser desorption are known. Resonance absorption of a quantum by an adsorbed molecule can cause a direct photo desorption of the molecule [5-6]. Another possible process is a non-thermal desorption associated with the transfer of electronic excitation energy to the adsorbed molecule of a solid upon absorption of radiation. A possible mechanism of thermal desorption under laser action is also a local heating. In this case, when the energy of laser excitation relaxes into the energy of thermal vibrations of a substrate, the adsorbed molecule can be considered as a point source of the thermal wave with rather high temperature of a surface around it.

In practice, the process of thermal desorption is realized most often. In this case the thermal action of light results in the heating of a surface sufficient to initiate the desorption process. The value of attainable temperature is determined by the parameters of laser radiation (intensity, duration, energy of a quantum), as well as the properties of the material being irradiated (absorption coefficient, thermal conductivity, heat capacity).

At present, YAG:Nd^{3+}, CO_2-, and N_2 - lasers are the most often used sources to initiate desorption of trace amounts of low-volatile nitro compounds from surfaces of various objects. A CO_2 -laser is especially effective, according to opinions of some authors, but its mass and dimensions made the practical use of this laser source at scenes of incidents almost impossible. The creation of a non-contact laser-based sampling system for ion mobility spectrometers needs compact and cheap laser sources also effective for desorption of explosives.

3. Experiment

A YAG: Nd^{3+} -based laser: λ = 1064 nm, pulse duration 16 ns, pulse energy up to 100 mJ, and a semiconductor laser with diode pumping: λ = 440 nm, continuous generation mode, average power 700 mW were chosen in this study.

To quantitatively determine the mass of desorbed substances a calibrated Shimadzu GCMS-GP2010 quadrupole mass spectrometer was used. It is equipped with a thermos-programmable module of a direct injection of a sample and ionization by an electron impact.

To carry out the research, the laser-vacuum direct injection module was developed (Fig. 1). It consists of a special gateway and a laser-vacuum rod. It makes possible to hit the sample by a laser beam near the ion source of mass spectrometer.
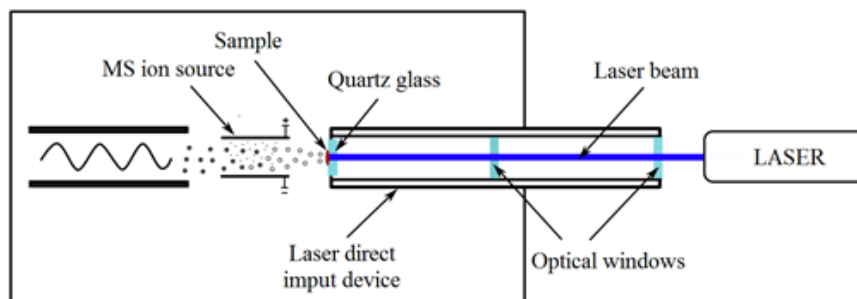

Figure 1: Laser-vacuum direct injection module.

The experiment was made in the following way. A prepared sample is placed at the end of the laser-vacuum rod, after that the rod is installed through a gateway in the mass-spectrometer. A laser beam passes through the optical windows inside the rod and hits the sample through a transparent substrate. The desorption products enter the ion source and are analyzed by mass spectrometer. The amount of desorbed material is determined by a pre-calibrated curve obtained before in the programmable thermal desorption mode.

The following nitro compounds were investigated: trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX).

Samples were prepared as follows. Solutions of the investigated substances in acetonitrile of 10^{-5} g / μL concentration with a volume of V = 1 μL were placed on a clean quartz substrate at a spot of S = 0.06 cm^2 . After that samples were dried for 3 minutes. All the samples were optically thin layers for the wavelengths used.

4. Results and discussion

4.1. Desorption by λ=1064 nm radiation

The prepared samples practically have no intrinsic absorption of radiation of λ = 1064 nm. Nevertheless, action even by a single pulse leads to desorption of the samples from quartz probably due to absorption by impurities. The obtained dependences of the desorbed quantities of TNT and RDX on laser intensity at a single pulse mode of irradiation is shown in Fig.2.
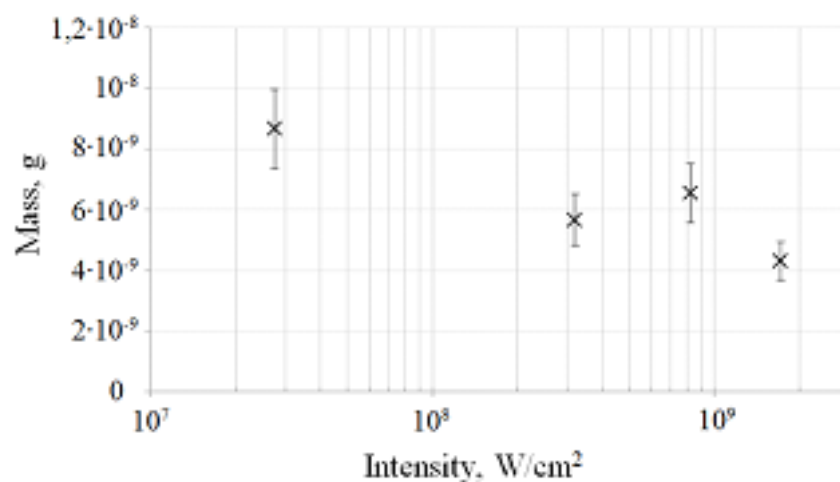
a)
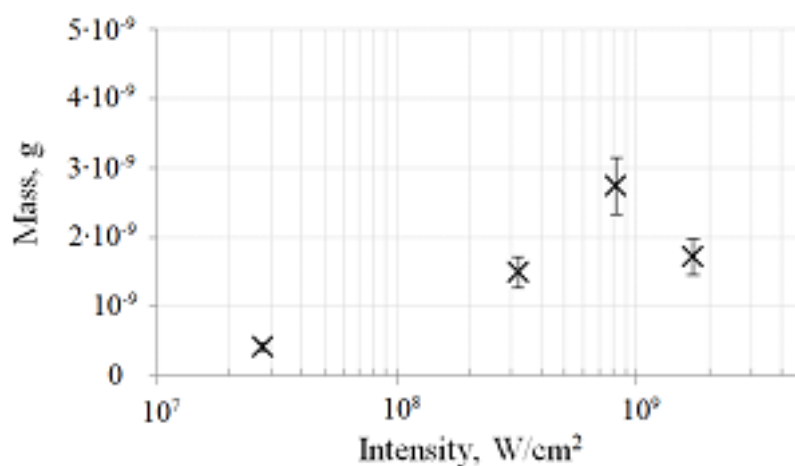
b)

Figure 2: Desorbed quantity as depend on intensity of a single laser pulse (λ=1064 нм, 14 mJ/pulse): a) TNT; b) RDX.

It is important to note that the ratio of the amplitudes of the mass-peak NO to the main fragmentation peak m/z = 210 in the obtained results exceeds the fragmentation ratio by a factor of two for TNT (nitro aromatic compound) and does not exceed it for nitro ether-RDX (Fig. 3). This allows us to state that most of the desorbed substance is present at an un-dissociated state, which ensures their reliable detection by ion mobility spectrometers.

Table 1 presents the summary of quantitative results of desorption under single pulse irradiation at λ = 1064 nm.
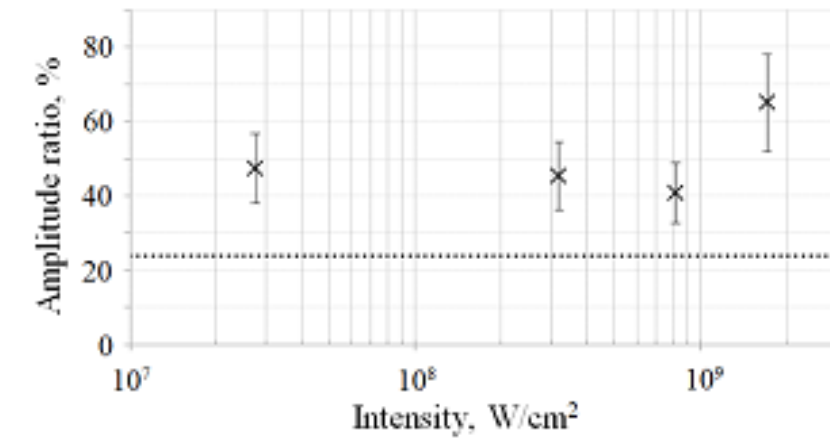
a)
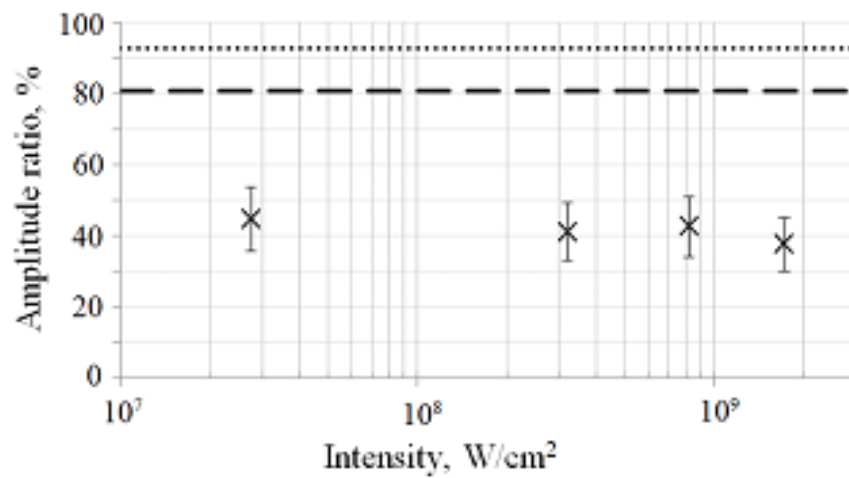
b)

Figure 3: Dependence of the ratio of the amplitude of NO peak to the amplitude of m/z = 210 peak for TNT desorption by a single laser pulse (λ=1064 nm, 14 mJ/pulse) - a); dependence of the ratio of the amplitude of NO peak to the amplitude of m/z = 46 peak for RDX desorption -b). Dotted and dashed lines correspond to fragmentational and thermo-desorption case.

Table 1

Sample	Desorbed mass M at $q=2{,}75\times10^7\,W/cm^2$ per a pulse	Desorbed mass M at $q=3{,}20\times10^8\,W/cm^2$ per a pulse	Desorbed mass M at $q=1{,}72\times10^9\,W/cm^2$ per a pulse	Desorbed mass M at $q=8{,}22\times10^9\,W/cm^2$ per a pulse
TNT	7,5 ng	5,5 ng	6,7 ng	4,2 ng
RDX	0,4 ng	1,5 ng	2,7 ng	1,7 ng

It is seen that the optimal radiation intensity seems to be $q = 1.72 \times 10^9 W / cm^2$. The amount of desorbed substance is changed approximately between 2 and 7 ng per 1 pulse.

4.2. Desorption by λ=440 nm radiation

Preliminary studies have shown that action of λ=440 nm radiation on RDX samples within 1-30 seconds does not lead to any consequences: desorption of the explosive is completely absent. Therefore to obtain the desorption effect, it was decided not to limit the time of radiation exposure but to fix the influence of radiation parameters on the desorption rate and on the total desorbed mass.

The graphical mass spectrometric data obtained under laser (λ = 440 nm) exposure of TNT samples is shown in Fig.4. The dependence of ion current on time for the main TNT fragmentation peak (m / z = 210) turns out to be substantially shifted to short times if compared with the dependence of ion current upon evaporation of TNT in vacuum without laser action.
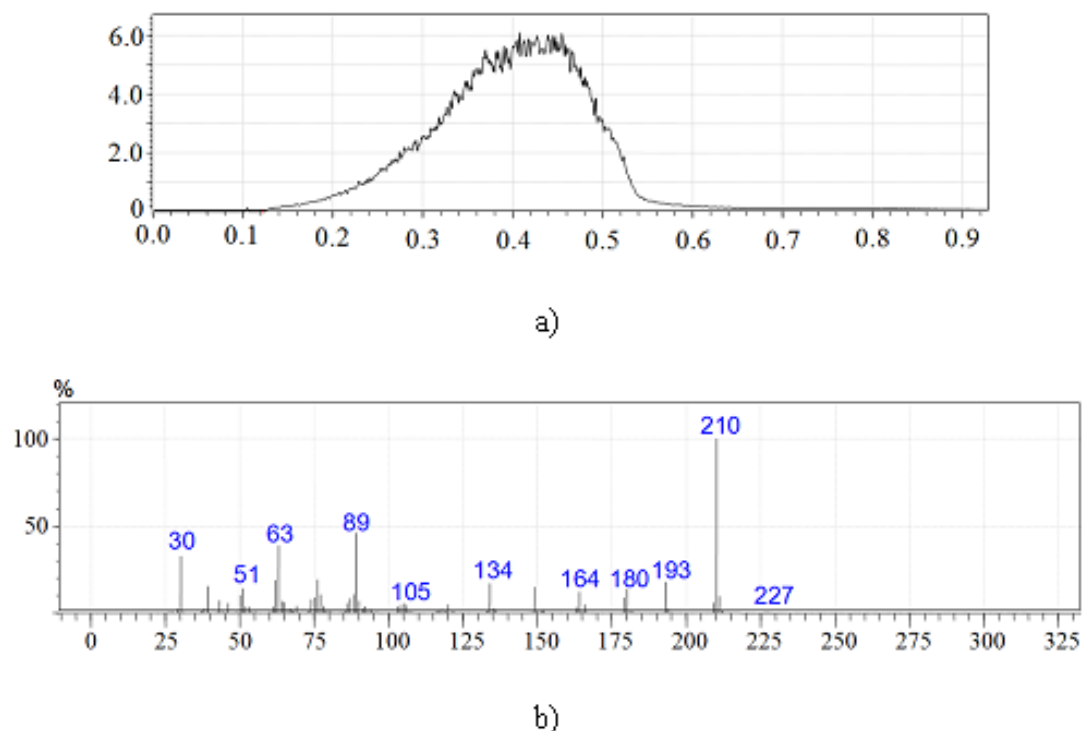

Figure 4: Results of irradiation (λ = 440 nm) with intensity of 13 W / cm² of TNT samples: a) a fragment of the ion current curve for ions with m / z = 210; b) the typical mass-spectrum at the amplitude of ion current.

Calculation of the desorbed mass results in a value of 1800 ng for TNT. The time dependence corresponding to the maximum of the dynamics of entry of the desorbed substance into the ion source versus the radiation intensity is shown in Fig. 5.
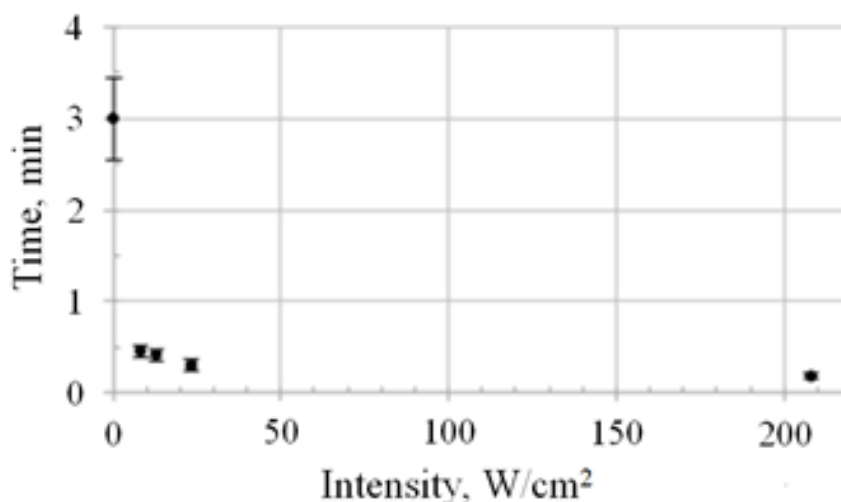

Figure 5: Desorption time of TNT samples as depend on laser intensity (λ=440 нм, P=500 mW).

It is interesting to compare the effectiveness of a pulsed laser source (λ = 1064) nm and a continuous laser (λ = 440 nm) at comparable time intervals. According to Table 1 the desorbed TNT mass is 6.7 ng per pulse for the chosen radiation intensity. Then, within 0.4 minutes (Figure 5), one can assume the desorbed quantity as 6.7 ng * 0.4 min * 60sec * 10 Hz = 1608 ng. It is clear that areas of the spots under irradiation by the laser sources used are significantly different, and desorption by continuous radiation comes from a much larger surface area of the sample.

Nevertheless, the efficiencies of pulsed and continuous sources when initiating TNT desorption process at irradiation times of 25 seconds or more are comparable (1608 and 1800 ng correspondingly). At shorter exposure times, an advantage is provided by a pulsed (λ=1064 nm) source.

Figure 6 shows the mass spectrometry data obtained under exposure of RDX samples under radiation of λ = 440 nm. The dependence of the ion current on time for the main fragmentation peak of RDX with $m/z = 46$ turns out to be substantially shifted - from 5 minutes to 1 minute - if compared with the dependence of the ion current upon evaporation of RDX into vacuum without laser action.

The calculation of the desorbed mass for RDX results in a value of 70 ng. The dependence of the time corresponding to the maximum of the dynamics of the intake to the ion source of the desorbed substance on the radiation intensity is shown in Fig. 7
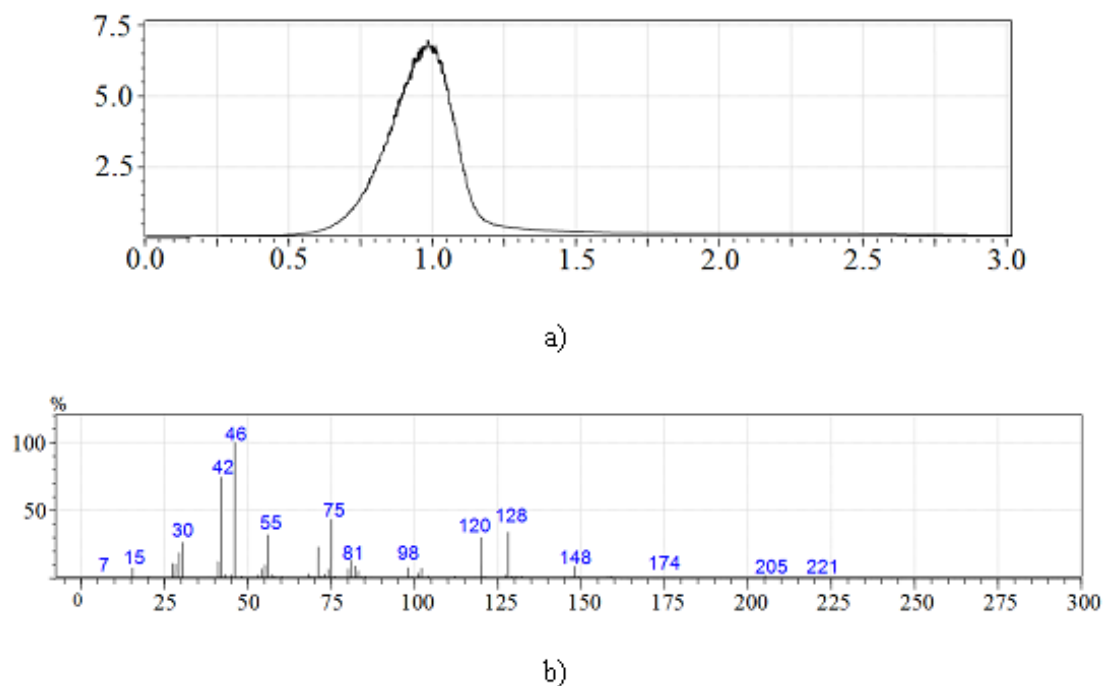
a)

b)

Figure 6: The results of action of radiation $\lambda = 440$ nm of intensity 13 W / cm^2 for RDX sample: a) the fragment of the ion current curve for ions with m / z = 46; b) the mass-spectrum at the amplitude of ion current.
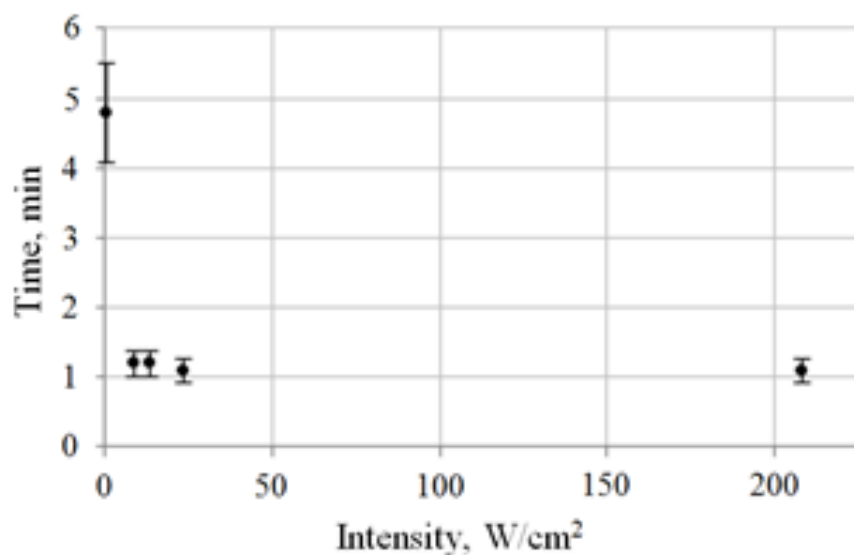

Figure 7: Desorption time of RDX samples as depend on laser intensity (λ=440 нм, P=500 mW). The desorbed mass equals $7*10^{-8}$ g.

A comparison of the efficiency of a pulsed laser source with $\lambda = 1064$ nm and a continuous laser source ($\lambda = 440$ nm) at comparable time intervals for RDX can also be performed using Table 1. For RDX, the maximum desorbed mass for pulsed laser is 2.7 ng per one impulse. Then, for a time of 1.1 minutes (Fig. 7), one can assume the desorbed mass as 2.7 ng * 1.1min * 60sec * 10 Hz = 1782 ng. Thus, the difference

reaches more than 20 times in favor of a pulsed source if it processes the spot area equal to the area of the continuous source spot during the measurement.

The presence of a little yield of nitric oxide when exposed to non-resonant radiation from a pulsed source on TNT at intensities up to 10^9 W / $cm^2$and its absence for RDX is not an obstacle for detection of desorbed compounds by ion mobility spectrometry. The low cost and dimensions of a neodymium laser operating at the fundamental harmonic (λ=1064 nm) makes promising its use in the development of a contactless sampling device combined with ion mobility spectrometers.

5. Conclusion

The quantitate investigations of the efficiency of pulsed and continuous laser sources and research of the possibility of creating a contactless sampling device for an ion mobility spectrometer were carried out. The most inexpensive and simple lasers were used. TNT and RDX explosives under mass spectrometric analysis showed that a YAG: Nd^{3+} laser with a wavelength λ = 1064 nm is more effective for desorption than a continuous laser with a wavelength λ = 440 nm.

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