

Laser desorption of traces of low volatile explosives

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Abstract. Comparison of desorption effectiveness of two laser sources: continuous diode laser ($\lambda = 440$ nm, $P = 0.5$ W) and laser based on YAG: Nd³⁺ ($\lambda = 266$ nm, $\tau_{\text{pulse}} = 6$ ns, $E_{\text{pulse}} = 1.0$ mJ, $f = 10$ Hz, $I_{\text{pulse}} = 10^8$ W/cm²) was carried out for the explosive cyclotrimethylenetrinitramine (RDX). The results of mass spectrometric studies of RDX laser desorption from a quartz substrate are discussed. It is shown that a continuous diode laser ($\lambda = 440$ nm) effectively desorbs the analyte without accompanying dissociation. The typical desorbed mass is 70 ng for RDX at 1.1 minutes exposure. However a laser based on YAG: Nd³⁺ seems to be more efficient for the same time exposure.

1. Introduction

A problem of detecting explosives is particularly acute due to the worldwide growth of terrorist acts. There are various devices based on principle of ion mobility spectrometry (IMS) and field asymmetric ion mobility spectrometry (FAIMS) that can solve the problem. However a lot of explosives have an extremely low pressure of saturated vapor ($\sim 10^{-14}$ g/cm³ for RDX, $< 10^{-16}$ g/cm³ for 1,3,5,7-tetranitro-1,3,5,7 tetraazacyclooctane (HMX)), which greatly complicates the searching for such devices. A pre-concentration method based on processing of a surface with a special tissue, followed by heating of the tissue in a thermal desorption unit of IMS (FAIMS)-based detectors, is widely used to increase the sensitivity of gas phase analyzers. It should be noted that the “tissue” method may be dangerous because of the contact with a suspicious object. The difficulties arising from a handling of rough and relief surfaces could be also observed.

The method of laser desorption of explosives is elaborated [1] for solving these problems. The ultraviolet (UV) YAG: Nd³⁺ laser is one of the most effective sources for laser desorption having an opportunity of portable implementation [2-3]. Although the current progress allows construct such laser sources sufficiently miniature, the weight of them exceeds usually 1.5 kg. Therefore, a much more lightweight and compact (0,3 kg with power supply) continuous diode laser with wavelength of $\lambda = 440$ nm and laser power of 0.5 W has been used in this work to initiate desorption. The purpose of this study is to compare the desorption efficiency of pulsed and continuous laser sources operating in UV and visible ranges.



2. Theoretical basis

The initiation of laser desorption may occur through various mechanisms, such as direct photo desorption, non-thermal desorption, desorption at a local heating of a surface. Direct photo desorption is observed in the course of resonance absorption of a quantum in a spectral range of excitation of adsorbed molecules [4]. Non-thermal desorption is similar to the direct photo desorption but is realized after electron excitation of a solid in the course of energy transmittance to an adsorbed molecule [4]. Local heating mechanism is a point localization of heat energy that provides desorption of molecules at low thermal conductivity of a substrate.

The most common process is thermal desorption - heating of a surface due to thermal relaxation of the excited states after absorption of a quantum of light [4-6].

3. Experimental setup and technique

A semiconductor laser diode operating at $\lambda=440$ nm and power of 0.5 W was used in this work as a source of radiation. The desorption efficiency of this source was compared with the same one demonstrated by YAG: Nd³⁺ ($\lambda = 266$ nm, $\tau_{\text{pulse}} = 6$ ns, $E_{\text{pulse}} = 1.0$ mJ, $f = 10$ Hz, $I_{\text{pulse}} = 10^8$ W/cm²) - [2,3].

The desorbed mass was determined by the quadrupole calibrated mass spectrometer Shimadzu GCMS-GP2010 with electron impact ionization and the ability of quick direct introduction of a sample into vacuum for immediate analysis.

The laser-vacuum module providing an ability of laser desorption near the ion source of the mass spectrometer was specially designed and used for this research (Figure 1).

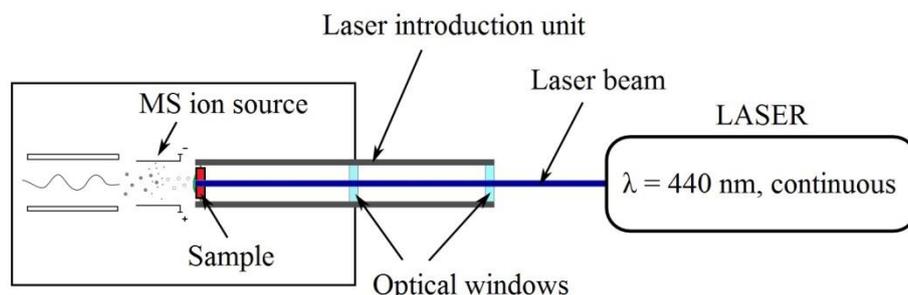


Figure 1. Experimental setup.

The sample was a quartz glass substrate covered by a solution of 10^{-5} g RDX in acetonitrile. After acetonitrile drying within 3 minutes the RDX molecules formed on the surface an optically thin layer for the wavelength used. Then the sample was fixed on the laser-vacuum rod after that within 2 seconds was entered into the mass spectrometer for analysis.

4. Results and discussion

Figure 2 shows the ion current time dependence characterizing desorption of sample molecules under both evaporation into vacuum and heating by an ion source of the mass spectrometer.

This dependence is a smooth curve with a maximum corresponding 5 minutes delay from a placement of the sample into mass spectrometer. In the case of laser exposure (Figure 2b) the time of maximum of the dependence is significantly less: one minute instead of five.

Mass spectra (Figure 3) in both cases correspond to RDX with an accuracy of 90% compared with the NIST database.

The dependence of RDX desorption time from a quartz substrate on the laser intensity was obtained (Figure 4).

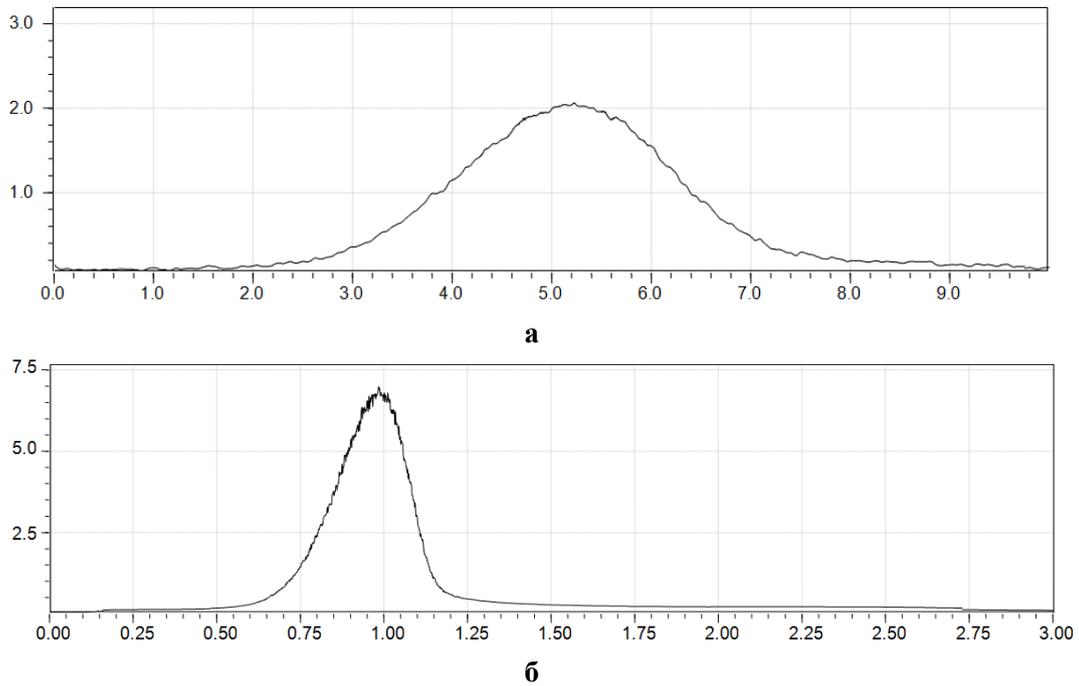


Figure 2. Ion current time dependence: a) without laser exposure; b) under laser irradiation ($\lambda=440$ nm, $W=0.5$ W, $q=24$ W/cm²).

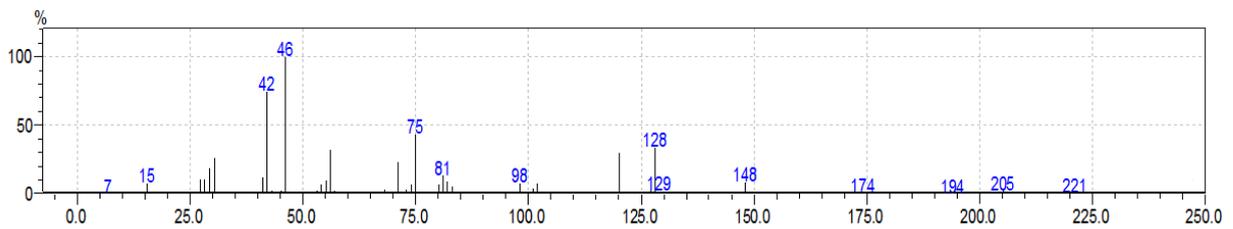


Figure 3. Mass spectrum of RDX under desorption of a sample without laser exposure. Coincides with the mass spectrum at laser exposure.

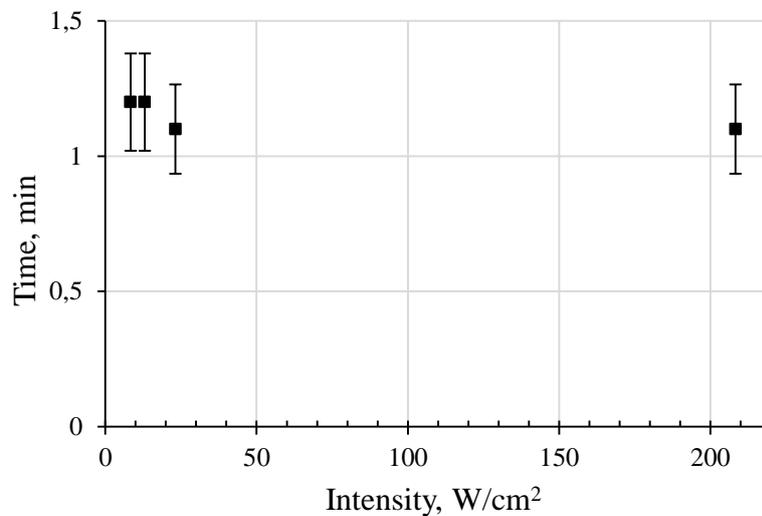


Figure 4. The dependence of RDX desorption time on laser intensity from a quartz substrate under laser exposure ($\lambda=440$ nm, $P=0,5$ W). The desorbed mass is $7.0 \cdot 10^{-8}$ g).

The intensity was varied by changing area of radiation spot on a sample surface. The radiation power was the same for all intensities. The time corresponding to desorption of about 90% total mass registered was chosen as desorption time. As seen in Figure 4, the amount of the desorbed substance ($7.0 \cdot 10^{-8}$ g) and the laser exposure time required for desorption are almost independent on the radiation intensity. It presumably means that the spreading of heat over the surface and in depth from irradiated region of the sample is rapid for all intensities used. So, desorption of RDX is possible for this laser source only through heating of bulk of quartz (and, of course, metal) substrate which exclude possibility of rather effective local heating.

We compared the efficiency of a nanosecond UV laser source with wavelength of $\lambda = 266$ nm, and the continuous laser source used in this research at comparable time intervals. The maximal quantity of desorbed RDX under $\lambda=266$ nm laser radiation was 2 ng per pulse [2,3]. So, the desorbed quantity can be estimated as $2\text{ng} \cdot 66\text{sek} \cdot 10\text{ Hz} = 1320$ ng for 1.1 minutes irradiation when operating in frequency mode at 10 Hz. Thus, the difference in desorbed quantities with continuous laser reaches 20 times in favor of the pulsed source (the spot area while processing the surface by the pulsed laser must be equal to the continuous source spot area). It should be noted that exposure of nitro molecules under UV nanosecond laser radiation should carry out with the pulse intensity no more than 10^9 W / cm² to reduce the probability of photo dissociation of these molecules with forming of NO and NO₂ fragments.

Thus, it can be concluded that initiating desorption process of RDX traces from a surface using a nanosecond pulsed UV source is preferable than using the continuous laser diode ($\lambda = 440$ nm), that expressed in the less time of registration and (or) bigger amount of the substance desorbed.

5. Conclusion

The objective of this work is to compare the efficiency of laser desorption of RDX molecules from a quartz glass substrate for two laser sources: continuous diode laser with wavelength of $\lambda = 440$ nm and laser power of 0.5 W and laser based on YAG: Nd³⁺ ($\lambda = 266$ nm, $\tau_{\text{pulse}} = 6$ ns, $E_{\text{pulse}} = 1.0$ mJ, $f = 10$ Hz, $I_{\text{pulse}} = 10^8$ W/cm²). It is shown that a pulse laser is approximately 20 times more effective than the investigated continuous laser source. However, due to the small size and weight of the continuous laser it is also suitable to create the non-contact portable sampling device.

6. References

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