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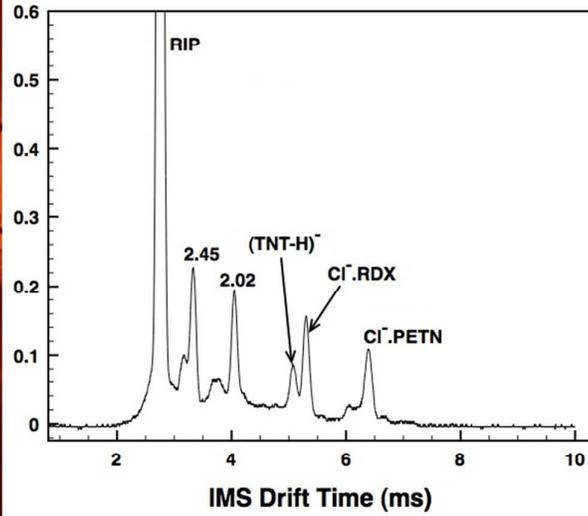
ARTICLE

Laser Desorption with Corona Discharge Ion Mobility Spectrometry for Direct Surface Detection of Explosives

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We present a new high sensitivity technique for detection of the explosives directly from the surface using Laser Desorption - Corona Discharge - Ion Mobility Spectrometry (LD-CD-IMS). We have developed LD based on Laser Diode Modules (LDM) and the technique was tested using three different LDM (445, 532 and 665 nm). The explosives have been detected directly from the surface without any further preparation. We discuss the mechanisms of the LD and the limitations of the technique, such as desorption time, transport time and desorption area. After evaluation of experimental data, we have estimated potential limits of detection of this method to be 0.6 pg for TNT, 2.8 pg for RDX and 8.4 pg for PETN.

Introduction

Due to increasing threats to our society, the detection of explosives becomes an important task to ensure security of the citizens. The atmospheric flow tube mass spectrometry (AFT-MS) recently developed by Ewing et. al.[1,2] is a mass spectrometric (MS) technique able to detect explosives vapours at ambient temperature without pre-concentration in real time. On other hand the desorption electrospray ionization MS (DESI-MS)[3], the direct analysis in real time MS (DART-MS)[4] and the neutral desorption extractive electrospray ionization MS (ND-EESI-MS)[5] techniques were successfully implemented for direct detection of trace amounts of explosives from the surface. In spite of the progress in the miniaturization of MS instruments, MS are still relatively large systems mainly due to vacuum generation units and the energy consumption of such system is relatively high a well.

IMS is ion separation technique based on the interactions of the ions with molecules of the buffer gas in weak homogeneous electric field[6,7]. Due to its ability to operate at atmospheric pressure, high sensitivity, fast response, simple and inexpensive design is IMS a key instrument for explosives and warfare agent detection at airports and homeland security[8]. The most common ionization source used in the IMS instruments is the radioactive ^{63}Ni[6]. There exist several other ionization sources that have been successfully implemented for explosives detection like electrospray ionization (ESI)[9], secondary electrospray ionization (SESI)[10], low temperature plasma ionization (LTPI)[11], distributed plasma ionization (DPI)[12] and dopant assisted photo ionization (DAPI)[13].

The CD ionization source[14,15] has very high potential to replace the radioactive ^{63}Ni ion source. However, the formation of neutral products like O_3 and N_xO_y in CD in air results in formation of very stable negative reactant ions[16-19] $N_2O_2^-$, NO_3^-, CO_3^- and HNO_3^-. Due to high electron affinities of these ions the deployment of CD to IMS is difficult especially for explosives detection[8]. Several solutions have been proposed in order to set up CD as "soft" ionization source with ability to generate reactant ions with significantly lower electron affinities. Hill and Thomas[20] designed pulsed CD able to generate the $O_2^-.(H_2O)_n$ reactant ions. However, this solution requires additional and costly electronic. Tabrizchi and Abedi[21] proposed a curtain gas CD design. In this case, the non-attaching gas (for electrons) like N_2, flows through CD gap resulting in formation of thermal electrons. The requirement of non-attaching gas can complicate the deployment of this technique for hand held instruments; however, due to high sensitivity[22] this method can be optimal for specific applications. Ross and Bell offered the simplest and the most effective solution by their reverse gas flow CD design[23]. In their design the removal of the neutral species from CD gap by the means of reverse flow of gas in CD resulted in ability of this ionization source to generate $O_2^-.(H_2O)_n/O_2^-.CO_2$ reactant ions, required for explosives detection. The implementation of this CD design to IMS required additional gas flow and resulted in significant charge density reduction what may adversely affect the sensitivity.

The implementation of CD to IMS and generation of "soft" reactant ions was also point of the interest in our laboratory[24]. We have observed that not only the removal of reactive species

but also the thermalisation of the energetic electrons plays an important role in CD gap. We have developed single flow IMS with gas outlet located behind the CD. In this design, an additional gas flow is not required and charge density decrease is reduced. This modification has very high potential in the field of explosives detection due to significantly higher charge density in comparison to radioactive [63]Ni[14].

Another important task in the case of detection of low volatile explosives is a efficient sampling technique. The thermal desorption is a reliable technique traditionally used for IMS instruments[25]. In this technique, the investigated sample is transferred to thermal desorption unit where evaporation of the sample occurs. For the surfaces analysis usually wipe pads are used in order to collect the sample from an investigated surface. The Laser Desorption (LD) as an effective sampling technique for IMS instruments was for the first time introduced by Huang et al.[26]. In that study; the sample was applied on the needle tip and transferred to reaction region of IMS where the LD occurred. They achieved a limit of detection (LOD) of 300pg for TNT. Ehlert et al.[27] demonstrated recently the application of LD-IMS technique for direct surface analysis of explosives. They reached LOD ranging from 1ng to 50ng for investigated explosives. In both LD studies they used the pulsed Nd:YAG laser. These lasers are relatively expensive and bulky what can limit wider deployment of this desorption technique.

In present work, we are going to demonstrate the full potential of CD-IMS operated in atmospheric air for direct explosives detection from the surface. In contrast to the former studies, where powerful lasers were used for laser desorption, we present a laser desorption method based on a simple, small and easily available LDM's. We evaluated the desorption efficiencies for LDM's of different wavelengths (445 nm, 532 nm and 635 nm) and discuss the desorption mechanism. Additionally we have estimated the limits of detection of this technique for three explosives (TNT, RDX and PETN) and discuss the limitations of the technique and present the "potential LOD" of the technique.

Experiment

IMS Instrument

A new home built single flow IMS (Figure 1a) was used in the experiment for explosives detection. The IMS was built from twelve stainless steel ring electrodes isolated by Teflon rings. The electrode potentials were supplied from a voltage divider, whereas the last electrode was connected through a resistor to the grounded plate. Spectrometer was equipped with CD ion source in point to plane geometry. The gas outlet was located behind the ion source thus the CD was operated in the reverse flow regime[24]. The distance between the corona tip (diameter 100μm) and the plane electrode was 5mm. The distance between the plane electrode of the CD and Shutter Grid (SG) was 2.8 cm, while the length of the drift region was 12.1 cm. The Bradbury-Nielsen type of SG was located at the third electrode. The SG was manufactured from tungsten wires with

diameter 100 μm separated by 0.5 mm. The opening time of SG was 60 μs in present experiment with repetition rate 60 Hz. Sixteen IMS spectra were averaged resulting in duty cycle of the instrument of 0.272 s. The resolution of the IMS instrument was about 30 FWHM (full width half maximum). In the tests we have achieved the resolution up to 90, however, at expenses of the sensitivity. The ion collector was shielded by aperture grid with transmittance 88%.
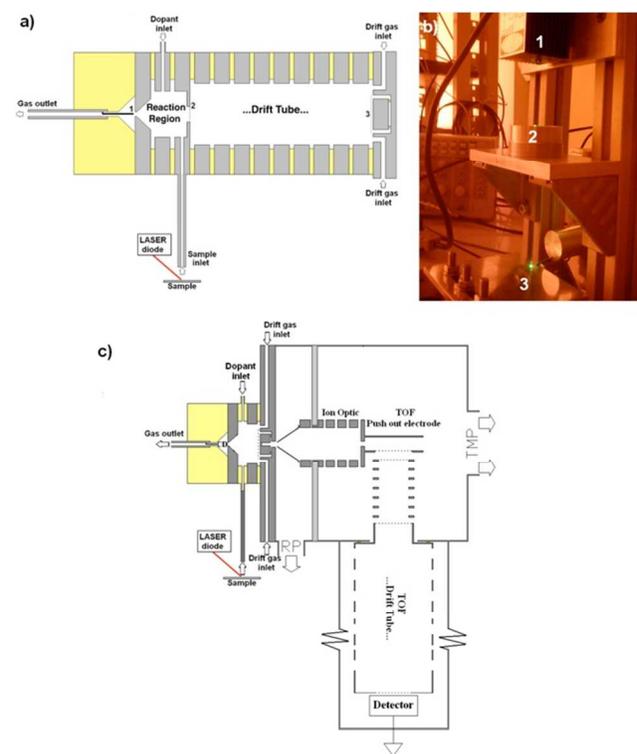

Figure 1. a) The schematic view of CD-IMS instrument, b) photograph with of the LD unit 1-LDM, 2-focusing lens, 3-investigated surface, c) schematic view of APCDI-MS instrument.

The ion current measured at ion collector was amplified using the current to voltage 5×10^8 V/A (FEMTO Messtechnik). We have used digital oscilloscope (Picoscope) to record the IMS spectra. Two high-voltage power supplies (FUG Electronic) were used for corona discharge and for voltage divider of IMS (462 V/cm). The SG was controlled by fast high-voltage transistor switch (Behlke Electronic GMH) and triggered by TTL generator. The operational temperature of IMS was 386 K.

As a drift gas we have used the atmospheric air purified by molecular sieve traps (AgilentMT120-2). The typical drift gas flow in this experiment was 1.2 L/min. The sample air was guided through 5 cm stainless steel capillary of 0.5 mm inner diameter, heated at the 356 K in order to reduce memory effects. The sample gas flow was 0.9 L/min of atmospheric air without any gas purification. The operation parameters of IMS instrument are summarized in Table 1.

Laser diode desorption unit

We have used common LDM's operating at 445, 532, 635 nm with corresponding power of 500, 300 and 300 mW respectively (Power Laser s.r.o.). The laser beam generated by LDM was focused on the surface with a sample in the front of the sampling capillary of IMS instrument as depicted in Figure 1b.

Atmospheric pressure chemical ionization mass spectrometer (APCI-MS)

The APCI-MS instrument was used in this work (Figure 1c.) in order to record mass spectra of the ions formed in CD. The APCI-MS is a modification of IMS-oaTOFMS instrument described in previous paper[28]. In order to compare the results with the current IMS experiment, we have used in APCI-MS system CD of identical design. The CD consists of two electrodes supplied from high voltage power supply (FUG electronic). The distance between the target electrode and the vacuum pinhole was 2.8 cm and the potential applied on this electrode was 1.3 kV. The atmospheric air, of flow 1.2 L/min, additionally purified by molecular sieve traps (Agilent) was used as a drift gas. The sampling system has been made identical with the IMS experiment, including the 5 cm stainless steel capillary of 0.5 mm inner diameter heated at the 356 K and the sample gas flow of 0.9 L/min of atmospheric air without any purification.

Chemicals

The carbon tetrachloride (CCl_4) of purity up to 99% was used as dopant gas. The explosives 2,4,6 trinitrotoluene (TNT), cyclotrimethylene-trinitramine (RDX) and penta-erythritol-tetranitrate (PETN) were obtained from Slovak Department of Defense with purity up to 99%. The surface sample preparation has been made on following way. A specific amount of TNT was diluted in methanol of analytical grade purity. In case of RDX and PETN, the first dilution was made in acetone of analytical grade purity. This solution was in further steps diluted with methanol, until the required concentration of explosive in the solution was reached. The solution was sampled by 1 μL syringe (Hamilton). The volume of the syringe was released on the needle tip. After evaporation of the solvent, on the tip of the needle a defined surface sample of explosive was prepared.

Table 1. Operation parameters of CD-IMS instrument

Drif tube length	12.1 cm
Electric field intensity	462.8 V/cm
SG pulse	60 μs
Drift gas flow	1.1 L/min
Samble gas flow	0.9 L/min
Drift tube temperature	386 K
Used resolution	≈30
CD current	20 μA
445nm LASER diode	500 mW
532nm LASER diode	300 mW
635nm LASED diode	300 mW

Results and discussion

The IMS spectrum of a mixture of investigated explosives (1ng of TNT, 2ng of RDX and 4ng of PETN) we present in the Figure 2a and the corresponding mass spectrum measured under identical conditions in the Figure 2b. The admixture of CCl_4 (dopant) into CD[31] resulted in the formation of reactant ion peak (RIP) with drift time 2.76 ms and reduced ion mobility of $2.96 cm^2.V^{-1}.s^{-1}$. The RIP is composed of $Cl^-.(H_2O)_n$ (n≤8) clusters (Figure 2b). These cluster travel in the drift tube within single IMS peak6. We use APCI technique with dopant gases in order to prepare different the reactant ions and thus to increase the selectivity and the sensitivity of the instruments[31].

The response of the IMS instrument on TNT resulted in the appearance of a peak (5.07 ms drift time and $1.61 cm^2.V^{-1}.s^{-1}$ reduced ion mobility) (Figure 2a). The corresponding MS exhibits ion m/z 226 (Figure 2b) and we assign this ion to $(TNT-H)^-$ formed via proton abstraction reaction8. We associate this MS peak with IMS peak of reduced ion mobility of $1.61 cm^2.V^{-1}.s^{-1}$.

The response of IMS on RDX and PETN resulted in formation of MS peaks at 5.3 ms and reduced ion mobility $1.54 cm^2.V^{-1}.s^{-1}$, respectively 6.39 ms and $1.27 cm^2.V^{-1}.s^{-1}$ (Figure 2a). In the corresponding MS spectra we have detected adduct ions8 $Cl^-.RDX$ (m/z 257) and $Cl^-.PETN$ (m/z 351) (Figure 2b), which we assign to the IMS peaks of $1.54 cm^2.V^{-1}.s^{-1}$, respectively $1.27 cm^2.V^{-1}.s^{-1}$. It has to be point out that the IMS as well as APCI-MS spectra were independent of the wavelength of used LDM.

Besides, above-mentioned peaks, we were able to detect in the Figure 2a IMS peaks at 3.33 ms and 4.05 ms with reduced ion mobilities of $2.45 cm^2.V^{-1}.s^{-1}$ and $2.02 cm^2.V^{-1}.s^{-1}$. These peaks we assign to $Cl^-.(NO)_2$ and $Cl^-.(NO)_3$ clusters[30]. The presence of these NO cluster ions in IMS and MS spectra we relate to CCl_4 admixture to CD ionization source, which is responsible for destruction of O_3. The O_3 plays an important role in NO chemistry converting it into NO_2. Thus, the O_3 inhibition by CCl_4 results in the increase of NO density. In future, we plan to study in more detail the processes responsible for NO cluster formation in CD.

The detection sensitivity of the LD CD-IMS for these explosives was studied by the direct measurements with signal to noise ratio 3:1. The samples were prepared on the tip of the needle as described in experimental section and desorbed by focused laser beam without any scanning across the needle tip area. The desorption area of the laser beam was much smaller than the sample area. The detected signal was related to the mass of the deposited sample, although only a fraction was desorbed. The sensitivity limits determined on this way are listed in the Table 2. The lowest sensitivity was achieved with blue LDM (445 nm) with the highest power 500 mW. As we can see from Table 2 the highest sensitivity for TNT (86 pg) and RDX (305 pg) was achieved with the green LDM (532 nm) and the power 300 mW. Samples of IMS spectra used for determination of the sensitivity of the method for TNT and RDX are presented in the Figures 3a and 3c.

Table 2. Reached sensitivities for explosives using LDM of different wavelength.

|	445 nm (500mW)	532nm (300mW)	635nm (300mW)
LOD TNT	600 pg	**86 pg**	520 pg
LOD RDX	6500 pg	**305 pg**	1315 pg
LOD PETN	5000 pg	1400 pg	**1220 pg**
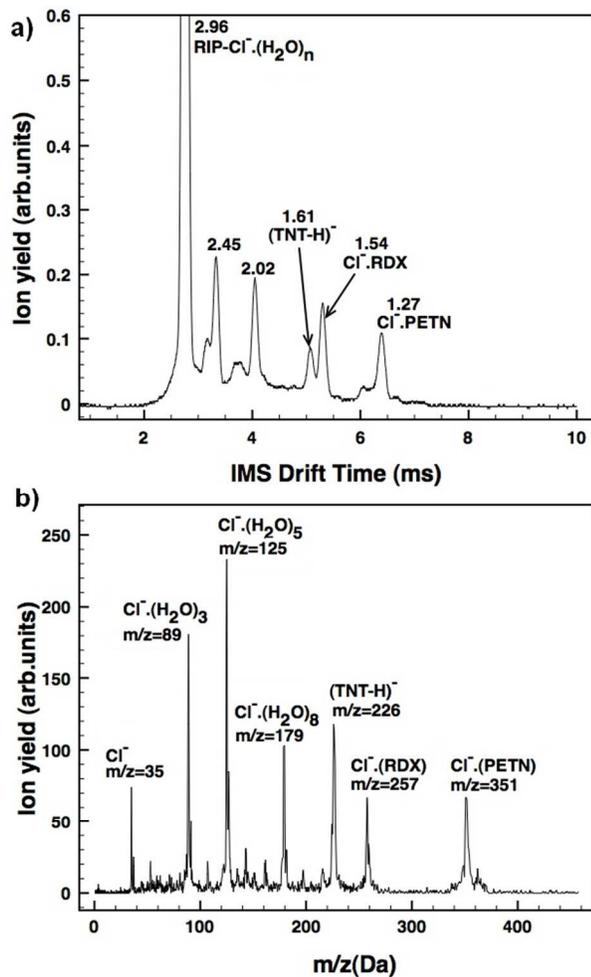
Figure 2 a) IMS and b) MS spectrum of investigated explosives (1ng of TNT, 2ng of RDX and 4ng of PETN)

The investigated linear dynamic range for these explosives is depicted in the Figures 3b and 3d. In the case of PETN the highest sensitivity (1220 pg) was achieved with LDM of 635 nm wavelength and 300mW power. Corresponding IMS spectrum is depicted in Figure 3e and the linear response range of CD-IMS can be seen in the Figure 3f.

Ehlert et al.[27] used 532 nm pulsed Nd:YAG laser for Ambient pressure laser desorption (APLD) and ambient pressure laser induced acoustic desorption (AP-LIAD). They concluded that these methods represent a gentle desorption, compared to classical thermal based desorption, is possible with laser based desorption using very short laser pulses.
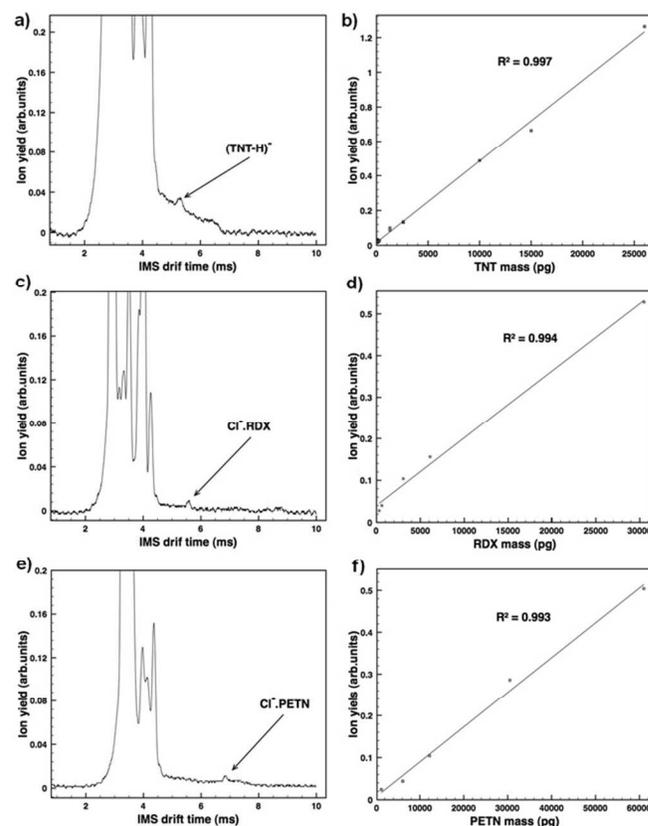

Figure 3 Measured sensitivities for a) 86 pg of TNT, c) 305 pg of RDX, e) 1.22 ng of PETN and investigated linear dynamic range of b) TNT, d) RDX and f) PETN.

The laser desorption mechanismus was discussed by Ehlert et al.[33] and by Shahar et al.[34]. The highest sensitivity for the TNT and RDX was achieved in present experiment for LDM of 532 nm wavelength. In case of PETN the highest sensitivity was obtained with 635 nm LDM. This observation indicates that there exist additional processes, which depend on the wavelength of the laser and play a significant role in the sample desorption from the surface.

We suppose that besides the absorption of the sample holder material (and thus also heating of this material) the absorption of the laser light by the analyte could play as well some role[31,32] in the desorption process. If the wavelength of the laser beam overlaps with an absorption band of the molecule, the light is efficiently absorbed by the sample, and the sample is more efficiently desorbed from the surface. If the wavelength of the laser is outside of an absorption band, the sample is for the laser beam transparent and desorption process is less efficient. In fact, the absorption process offers an additional degree of freedom for selectivity and is and additional advantage of the laser desorption method for IMS technique. By selection of an optimal wavelength, we are able to desorb specific compound from a complex matrix more efficiently. Thus the laser

desorption has potential to bring additional selectivity to IMS technique.

Desorption of the sample by the LD from of the surface takes some time and depends on the power of the laser. In order to evaluate time for desorption of the sample from one point of the needle tip we used APCI-MS instrument. After insertion of the needle tip under focused laser beam we have recorded the mass spectra with 1s resolution. The investigated samples were 6.9 ng and 11.5 ng of TNT, 11 ng and 22 ng of RDX and 12.5 ng and 25 ng of PETN. The studied samples were far above the LOD. Our goal was to determine desorption time profiles by APCI-MS instrument. TNT and RDX were desorbed by the green LDM (532 nm) and PETN by the red LDM (635 nm). The observed desorption time profiles are depicted in the Figure 4. The desorption times for both TNT samples were identical 8 s, in the case of RDX for both samples 6s and for PETN 8 s. Similar desorption time in case of LD was also reported by Ehlert et al.[27] who reported 5 s for desorption for 200 ng of RDX. We are going to evaluate potential LOD of the method. If we take into account the time necessary for total desorption of sample from one spot; the duty cycle of CD-IMS instrument (0.272 s), we are able to calculate the potential LOD of 3 pg for TNT, 42 pg for PETN 42 pg and 14 pg for RDX. This is ~29 times (TNT, RDX), respectively ~22 times (PETN) higher as the values presented in Table 2.

Another important factor in determination of the potential LOD is the area of the needle tip, where the sample is deposited and the desorption area of the laser beam. The laser desorption area is much smaller than the area of needle tip. In the Figure 5a we show a paper irradiated by the focused 635 nm beam (with small hole burned by the laser), next to it is the needle tip used for desorption and determination of LOD. The area of the burn spot is considerably smaller than the tip of the needle (~ 5x). In the case, of desorption from one point, the desorbed amount of the explosives is much smaller than the deposited sample on the needle tip (which was used for determination of LOD in the Table 2). If the needle tip is scanned by the laser beam (needle tip has been slowly moved by hand), we have observed desorption time profile of the sample. The time profile of 25 ng PETN desorbed by 635 nm LDM is shown in the Figure 5b. If we compare the Figure 5b with Figure 4c (beam focused on only one point of the needle tip without scan), we see that time for the removal of whole sample from the needle tip is nearly 40 s (Figure 5b). This is 5 times the time from one point (8 s Figure 4c). Taking into account this factor, we can conclude that the potential LOD of CD-IMS instrument will increase by additional factor 5. We believe, that if we consider the effects of the desorption time profiles and the sample size, the potential LOD of the LD-IMS instrument of 0.6 pg for TNT, 2.8 pg for RDX and 8.4 pg for PETN can be achieved.

The small desorption area in the case of LD-IMS can be very useful for different applications. For example investigation of hard to reach areas like narrow slits and for the applications where the high spatial resolution is required, e.g., imaging IMS, MS or IMS-MS.
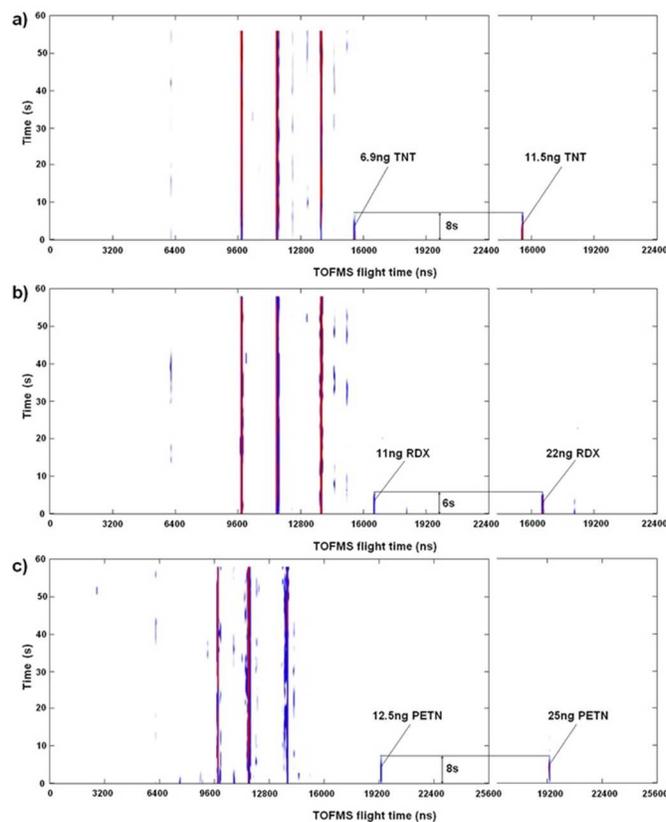

Figure 4 a) The schematic view of CD-IMS instrument, b) photograph with of the LD unit 1-LDM, 2-focusing lens, 3-investigated surface, c) schematic view of APCDI-MS instrument.

On the other hand the restrictions associated with the small desorption area could be mastered by application of multi LDM desorption units or use of surface wipe sampling methods.

The laser radiation can have detrimental effect on the surface, which strongly depends on the type of the material. While in the case of metal materials, transparent plastic materials and glass materials was no degradation observed, in the case of colour plastic and paper materials we observed the strong degradation as we can see from figure 5a. This degradation was caused by the absorption of laser irradiation by the surface. There exist as well possibilities to overcome these problems, by tuning the power of the laser, or by pulsing of the laser beam.

Conclusion

The potential of CD-IMS instrument supported by LD, using blue (445 nm), green (532 nm) and red (635 nm) LDM, for direct surface detection of explosives was studied in this work. The highest sensitivity for TNT and RDX detection was achieved with green LDM while for the PETN with red LDM unit. We have estimated potential LOD's of the method to be 0.6 pg for TNT, 2.8 pg for RDX and 8.4 pg for PETN. We believe that further improvements are possible, mainly related

to higher power LDM units resulting in shorter duration of desorption process have potential to increase response of CD-IMS.

Acknowledgement

Notes and references

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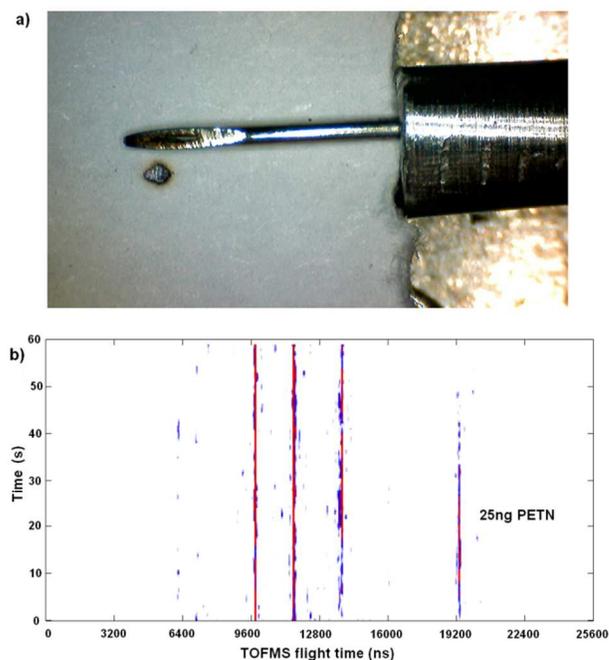
Figure 5 a) comparison of the area desorbed by LDM with needle tip where the sample was deposed and b) desorption profile of 25 ng of PETN reached when the needle tip was continually moving under the focal point of LDM.