REMOTE DETECTION OF NARCOTICS AND EXPLOSIVES BY FLUORESCENCE LIDAR

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ABSTRACT
The capability to quickly diagnose the presence of forbidden for distribution materials such as explosives or narcotics is crucial for maintaining home land security. Fluorescence lidars show promise for meeting this objective, but more research is required to establish the degree to which spectra of these substances can be identified. In our report we present the measured fluorescence spectra of numerous narcotic and explosive materials induced by UV pulses of tripled Nd:YAG laser. Principal component analysis is applied to these spectra to estimate the potential of the method for discrimination among particular substances. The exploratory prototype of fluorescence lidar is designed to study the possibility of remote identification of narcotics and explosives deposited on the different kinds of substrates, such as wool, cotton, skin, hairs. Measurements performed at 150 m distance allow to estimate the minimum concentrations of substances which can be identified.

1. INTRODUCTION
The capability to detect remotely the presence of hazardous materials such as explosives or narcotics is crucial for maintaining the security. The methods of optical spectroscopy offer the potential for accomplishing this goal. This problem can be solved if substance possesses the characteristic spectrum, i.e. the spectrum contains individual band that always manifests itself when a particular agent is present. For detection of different hazardous materials numerous techniques were suggested, such as Raman spectroscopy and the spectroscopy of laser-induced breakdown1-2. Unfortunately none of these techniques allows to perform monitoring of contamination at distance of 100 m order, because corresponding scattering cross sections are too low.

Laser-induced fluorescence is efficient enough to perform remote measurements, but fluorescence spectra usually have no characteristic individual bands and the information is distributed over a wide spectral interval, which complicates the identification. The fluorescence lidars have proved their potential for remote detection of chemical and biological agents3, so it is logically to study their potential for detection of narcotics and explosives. The fluorescence lidars allow long-range identification of the biological particles dispersed in the air, but in the case of explosives, the micro amount of substance is usually deposited on the different kinds of underlying surfaces (substrates). The problem of identification in this situation becomes more severe, because the fluorescence of substrate can mask the spectrum of interest. To explore the potential of the fluorescence technique for detection of narcotics and explosives we have performed the measurements of their fluorescence spectra in a wide spectral range. The principle component analysis is used to clarify the possibility to discriminate between the individual spectra.

2. EXPERIMENTAL SETUP
The prototype of fluorescence lidar was built to explore the possibility of narcotics and explosives identification. The system exploits a tripled Nd:YAG laser emitting 60 mJ per pulse at 355 nm wavelength with 25 Hz repetition rate. The laser is mounted on the receiving telescope of 300 mm aperture. The UV laser beam is collimated and made coaxial with the collecting optical axis using two adjustable 45 deg. folding mirrors. The combined emitter and receiver are mounted on a base allowing to make scans in vertical and horizontal planes for pointing the beam to the target. The fluorescence signal collected by the receiver passes through the optical fiber to the imaging spectrometer (SpectraPro-500). The UV highpass filter at the entrance blocks the elastic scattered radiation. The specially designed objective is used to project the fiber output to the entrance slit of the spectrometer. The 600-line/mm grating of this spectrometer in combination with a 20 µm wide entrance slit ensures the measurements in the 380-700 nm spectral range with resolution of 2.5 nm. An ICCD camera of 1024×768 pixels (Princeton Instr. PI-MAX) detects the dispersed radiation at the exit window of the spectrometer. The intensifier gate is synchronized with each fired laser pulse. In one typical measurement 1000 laser pulses are integrated. The spectral range 380-700 nm is too large to be covered with a single measurement. To obtain the full spectrum three
measurements inside this range are glued, so this complete spectrum consists of 3000 points.

Table 1. Relative intensities of the maxima of fluorescence spectra

<table>
<thead>
<tr>
<th>Narcotics</th>
<th>( I_{\text{max}} )</th>
<th>Explosives</th>
<th>( I_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocaine</td>
<td>1</td>
<td>Plastic</td>
<td>0.25</td>
</tr>
<tr>
<td>Heroin</td>
<td>0.2</td>
<td>Hexogen</td>
<td>0.01</td>
</tr>
<tr>
<td>Ecstasy</td>
<td>0.1</td>
<td>HMTD</td>
<td>0.008</td>
</tr>
<tr>
<td>Amphetamine</td>
<td>0.09</td>
<td>Octogen</td>
<td>0.003</td>
</tr>
<tr>
<td>Morphine</td>
<td>0.06</td>
<td>Ammonium</td>
<td>0.0022</td>
</tr>
<tr>
<td>Codeine</td>
<td>0.02</td>
<td>nitrate</td>
<td></td>
</tr>
<tr>
<td>Marijuana</td>
<td>0.015</td>
<td>TEN</td>
<td>0.001</td>
</tr>
<tr>
<td>Opium</td>
<td>0.015</td>
<td>Trotyl</td>
<td>0.001</td>
</tr>
<tr>
<td>Ephedrine</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the first stage of our research we performed the measurement of individual fluorescence spectrums of different substances to create the corresponding spectral data base. Three main groups of materials are considered: explosives (hexogen, octogen, trotyl, TEN, plastic, ammonium nitrate, HMTD), narcotics (heroin, cocaine, opium, marijuana, amphetamine, ecstasy, codeine, morphine), and different types of substrates, e.g. clothes (wool, cotton), skin, hair and others. The samples of ~10 mm size are deposited on the quartz substrate and laser beam is focused on the sample in the spot of 2 mm diameter. Thus obtained results allow to compare the fluorescence efficiency of studied materials. Laser energy was kept below 1 mJ to avoid the substances modification.

Identification methods generally involve comparing an unknown spectrum with one or more reference spectra, thus the spectra can be identified if these are linear independent. As a measure of liner independency the eigenvalue of their covariance matrix can be taken. For linear independency of the spectra \( F_{\lambda}(\lambda) \) measured with error \( \delta \) the condition \( l_{\text{min}}>\delta^2 \) has to be fulfilled, here \( l_{\text{min}} \) is the minimum eigenvalue of covariance matrix

\[
c_{ij} = \frac{\sum_{\lambda} F_{i}(\lambda)F_{j}(\lambda)d\lambda}{\sum_{\lambda} F_{i}(\lambda)^2d\lambda}
\]

The minimum eigenvalues calculated for different pairs of narcotics are shown in Fig.2. Dotted line at this picture corresponds the measurement accuracy of 10%. In the absence of substrate fluorescence and \( \delta=10\% \), practically all narcotics (except for opium – marijuana pair) can be identified.

![Fig.2. Possibility to distinguish among some narcotics by their spectra.](image)

More representative consideration can be performed with the use of the principal component analysis (PCA) technique. Such approach was successively applied recently to the analysis of fluorescence spectra of bacteria\(^5\). PCA remaps the spectral data into a new coordinate system to search for embedded patterns that may not have been evident in the original data. The detailed description of this method is given in Ref.5. In our computations 3000 spectral points are grouped in 500 bins (resolution element) and these bins are processed into the principal components. The intensity in each of the bins is treated as a separate variable. For each pair of variables the covariance is calculated and eigenvectors and eigenvalues of the corresponding covariance matrix are found. The first two largest eigenvectors have the largest eigenvalues and capture the largest amount of variation. In the space of eigenvectors each spectrum is represented by a single point.

Fig.3 presents the spectra of narcotics plotted in the space of first two eigenvectors. At the same plot the spectra of several substrates (black wool material, skin of palm, hair) are shown. The more is the distance
between the points, the easier discrimination among spectra. Fig.2 helps to establish the correspondence between spectra linear independency and the point’s separation in Fig.3. As it follows from Fig.2, for δ=10% the pair amphetamine – morphine is close to the discrimination limit. The separation between these points in Fig.3 can be considered as discrimination scale \( r_{\text{disc}} \), and the circle of radius \( r_{\text{disc}} \) centered at the chosen spectrum gives an estimate if this spectrum can be discriminated between neighbor spectra. For example, the spectrum of ecstasy can’t be identified if narcotic is deposited on the palm. The same time narcotics deposited on the wool material can in principle be detected. The easiest for identification is cocaine, because the maximum of it’s fluorescence is shifted to short wavelengths (~420 nm).

![Fluorescence spectra of narcotics remapped in the space of first two eigenvectors.](image)

The results of PCA analysis for explosives are shown in Fig.4. As we see such important explosives as hexogen or tetryl can be reliably identified. Tetryl, as it follows from the Table 1, has low fluorescence cross section, but its spectrum has secondary maximum near 600 nm, which simplifies the identification. The plastic is characterized by the highest among explosives fluorescence cross section, because it contains the oil. We should mention that different sorts of plastic had significantly different spectra. The results shown in Fig.3,4 demonstrate that identification of studied samples with fluorescence is possible in controlled settings, but this technique may have difficulties in discriminating the weak optical intensities expected remotely.

Retrieval of the mixture composition from the results of spectral measurements is an ill pose problem which can be solved, for example, by using Tikhonov method (inversion with regularization)\(^6\). In our inversion algorithm based on regularization approach we consider only the simplest situation when only one narcotic (explosive) is deposited on the substrate. The substrate is unknown a priori, but its spectrum is contained in data bank.

![Example of detection of cocaine deposited on a black wool material.](image)

To verify the potential of fluorescence technique for remote detection, a set of experiments was performed in day time from the window of the laboratory. The target consisting of substrate and deposited sample was located at 150 m distance. In these measurements only cocaine and hexogen were used as the samples. The typical example of detection of cocaine deposited on the black wool material is shown in Fig.5. At such distance we are able to identify about 10 mg of cocaine deposited on wool material. For the hexogen this value is about 1 order larger.
4. CONCLUSION

The analysis of the measured fluorescence spectra of numerous narcotics and explosives demonstrates that fluorescence lidar has potential for their remote identification on the underlying surfaces. The same time, the obtained results should be considered as preliminary. In our measurements we tested a limited set of underlying surfaces, the corresponding list will be extended in the future. Only pure narcotics were exploited in the study, while in reality these can contain a lot of additions. Moreover, there are a lot of modifications of narcotics (for a example of ecstasy) and their spectra can vary significantly. All this is true also for explosives. Thus the problem of remote identification of these substances is extremely challenging and further studies in this field are demanded We expect significant improvement of technique by exploiting several UV wavelengths for excitation.

REFERENCES