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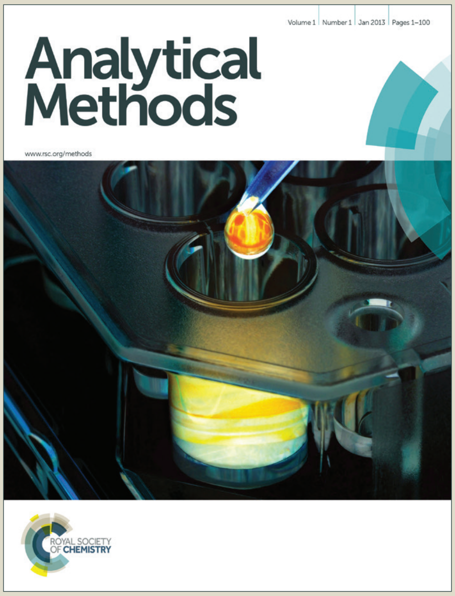

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PAPER

Rapid, On-site Detection of Residual Explosives Based on a Lab-in-a-capillary and UV Fiber Sensor

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An integrated portable system based on a lab-in-a-capillary and a UV (190-400 nm) reflected fiber sensor was demonstrated for on-site detection of trace amounts of explosives in a micro-nanoliter droplet. The filtration and measurement of the residual explosive sample were integrated in a compact device. The micro-droplet (1 nL to 1 μL) was loaded onto the capillary-end by the equilibrium between gravity and negative air pressure for UV spectral analysis. Also, a new mixed spectrum decomposition algorithm (MSDA) was used to calculate the concentration of multiple explosives in the soil of the explosion site. This system for real-time explosive analysis features a short sample preparation and analysis time (< 5 s), low sample consumption (10 nL), wide detection range (1-250 ng/μL), low detection limit (< 10 pg), and is easy to disassemble and clean, which fulfills the requirements for on-site explosive detection.

Introduction

Terrorist attacks have become a worldwide threat, and bombings are the major cause of casualties. For instance, bombings on Bali Island in 2002 kill 202 dead and injured at least 330, bombings in Mumbai in 2003 killed 52 dead and injured 167, bombings in the subway stations of London in 2005 killed 90 dead and injured > 1000, and bombings during the 2013 Boston Marathon killed 3 and injured 183. The identification of the on-site residual explosives is a necessary part in the investigation that follows. Trinitrotoluene (TNT), dinitrotoluene (DNT), picric acid (PA), cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX) are the five most common explosives. Numerous detection methods for residual explosives have been proposed or are already in service due to the crucial significance of explosive detection. There are many classic trace amount detection techniques for residual explosives, such as dropping reaction methods, mass spectrometry (MS),[1,2] gas chromatography (GC),[3] high performance liquid chromatography (HPLC),[4] and infrared absorption spectroscopy (IRAS). However, these traditional techniques have the disadvantages of complexity, being time consuming (> 1 h), requiring large amounts of sample (10 μL to 10 mL) and not being cost efficient. Moreover, most of these traditional detection methods cannot be performed on site. Also, novel explosive detection methods using conjugated organic polymer film as fluorescent chemosensor were reported.[5-9] Other techniques like surface-enhanced Raman scattering (SERS),[10,11] colorimetric probe[12] and fluorescent gold cluster incorporated single nanofiber[13] were also reported that can be used to detect the nitro aromatic explosives and these methods showed great potential in field application. But, all these techniques were only applied to a few specific single explosives like TNT or DNT and none of them were used to detect explosive mixture. Consequently, an easy-to-operate, rapid, low sample consuming, inexpensive, and portable integrated device for the qualitative and quantitative analysis of different kinds of residual explosives or explosive mixture is urgently needed.

This paper proposes a novel portable device that integrates sample filtration, purification, and fiber sensor-based UV spectral analysis. It was capable of quantitatively detecting and

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analysing mixed residual explosives in soil. A new mixed spectrum decomposition algorithm (MSDA) was also developed to robustly identify the composition of the explosives. The feasibility and performance of this system were proven using real soil samples containing a single explosive (TNT) and mixed explosives (“Comp B”).

Materials and methods

Materials

Post-blast debris samples and pure explosives dissolved in acetone were directly obtained from the Institute of Forensic Science, Ministry of Public Security, People’s Republic of China (Beijing, China). The working solutions of each sample ranged from 0.1-500 ng/μL and were prepared by appropriate dilution of the stock solutions using acetonitrile. Chromatographically pure (> 99.9%) acetonitrile was purchased from Siyou Fine Chemicals Co. Ltd. (Tianjin, China). PTFE membranes for sample filtration was obtained from Millipore (Billerica, MA, USA).

New portable device

A new portable device was designed as shown in the schematic cutaway view in Figure 1 that included a lab-in-a-capillary and a UV reflected fiber sensor. The lab-in-a-capillary consisted mainly of a double-layer filtration valve and a capillary flow passageway. The capillary flow passageway had a diameter of 200 μm. The double-layer filtration valve was set on the capillary flow passageway, each of the filtration valves consisted of one layer of PTFE membrane with the aperture of the microvoid measuring 3-5 μm (as shown in Fig. 1) and could filter out almost all suspended particles in the sample solution.

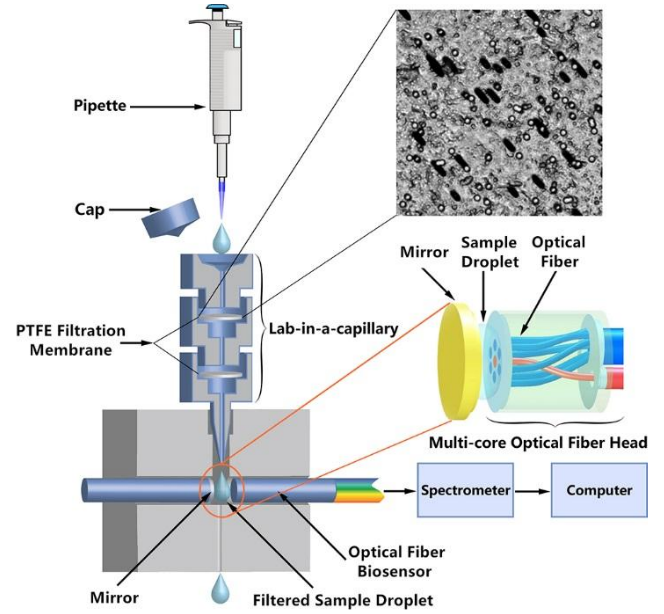

Fig. 1 Schematic cutaway view of the lab-in-a-capillary and UV reflected fiber optical sensor.

The UV reflected fiber sensor consisted of a mirror and a multi-core optical fiber head. The fiber head, comprised of one central fiber and six outgoing fibers, was set under the lab-in-a-capillary for spectra analysis. The core diameter of the fiber was 100 μm, and the effective detection area of the multi-core optical fiber head was ~ 0.07 mm^2.

A soil suspension was added to the lab-in-a-capillary via a pipette, which then flowed through the double-layer filter valve by gravity. Only clear soil solutions could reach the bottom of the lab-in-a-capillary and form a micro-droplet with a diameter of 250-300 μm. A cap was placed on the lab-in-a-capillary so that the droplet was held on top of the fiber between the mirror and the multi-core optical fiber head by surface tension. By adjusting the distance between the mirror and the multi-core optical fiber head, the micro-droplet could be pressed into a thin liquid film with a thickness of 100 μm for UV spectra analysis as in Fig. 2(a), which enabled a trace analysis in a volume of 10 nL (corresponding to a 0.07-mm^2 effective detection area of the UV reflected fiber sensor and a 100-μm thick micro-droplet). To extend the absorbed optical path and improve the sensitivity of the UV spectral analysis, the micro-droplet could also be drawn back by a thickness of 0.5-2.0 mm by adjusting the distance between the mirror and the multi-core optical fiber head, as shown in Fig. 2(b).

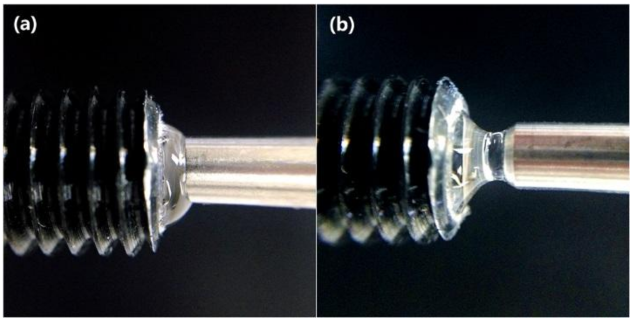

Fig. 2 Droplet shape control. (a) A thin liquid film formed and held between the fiber head and mirror. (b) The light path was extended by adjusting the distance between the mirror and the multi-core optical fiber head.

The portable system was set as shown in Fig. 3, which integrated the lab-in-a-capillary for sample preparation and the UV reflected fiber optical sensor for spectral analysis. The UV reflected fiber optical sensor was manufactured by Xingyuan Corporation (Beijing, China). A micro deuterium-halogen lamp (DT-Mini-2-GS, Ocean Optics) was used as the UV light source, with a wavelength range from 190-2000 nm. The spectral collector used a micro-spectrometer (Maya2000pro, Ocean Optics, Dunedin, FL) with a wide wavelength range (175-1100 nm). The spectral signal was collected by the Maya2000pro spectrometer and was analysed by a microcomputer, as shown in Fig. 3. When the soil suspension to be measured was injected from the inlet of the lab-in-a-capillary by the pipette, it automatically flowed through the double-layer filter valve by gravity. All soil grains and other solid particles that cannot be dissolved were blocked by the double-layer filter valve, so only a clear soil solution could reach the detection site and be captured by the reflected optical fiber sensor by surface tension. The incident light from the micro deuterium-halogen lamp travels through the incoming central fiber and is successively transmitted through the micro-droplet of soil solution. The light is then reflected by the mirror and passes back through the micro-droplet once more. The reflected light is finally collected by the six outgoing fibers in the multi-core fiber head into the spectrometer for spectral analysis. The spectrum data from the spectrometer were stored in the micro-computer using Spectrasuite 2.0 software (Ocean Optics) and analysed with a novel MSDA. The entire processing procedure could be finished within 5 s.

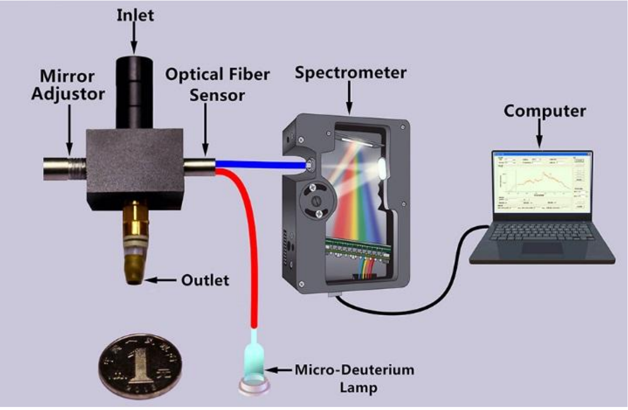

Fig. 3 Layout of the portable device.

Absorbance calculation

Lambert-Beer's law states that the absorbance *A* of a solution is proportional to the solute concentration and the light path length through that solution,[14] written as:

$$A=\varepsilon\cdot L\cdot c \tag{1}$$

where ε is the absorption coefficient of the solute, *L* is the light path length, and *c* is the solute concentration.

The solution absorbance *A* at a specific wavelength is defined as:

$$A=-\lg\frac{I_t}{I_i} \tag{2}$$

where I_t is the transmitted light, and I_i is the incident light intensity.

However, when the fluctuation of the light source is not neglected and the stray light and the dark noise of a CCD are taken into account, the corrected absorbance A of the solution is calculated by the following equation:

$$A=\lg\left(\frac{I_{solvent}-I_b}{I_{solution}-I_b}\right) \tag{3}$$

where $I_{solvent}$ is the transmitted light intensity of solvent, $I_{solution}$ is the transmitted light intensity of the solution, and I_b is the background intensity.

MSDA

In general, high-explosives, which has stronger destructive power, are always mixture of different single explosives, so the determination of the explosive mixture is necessary. According to Lambert-Beer's Law, the mixed spectrum equals the sum of each single spectrum.

First, we measured the UV (190-400nm) absorption spectra of every pure explosive at a concentration of 100 ng/μL, calling these explosive fingerprints, and then we analysed a soil blank at the scene as the "base" series $\boldsymbol{V}_1(\lambda)$, $\boldsymbol{V}_2(\lambda)$, $\boldsymbol{V}_3(\lambda)$, ... Theoretically, the absorption spectra of a mixed explosive sample $\boldsymbol{S}(\lambda)$ is:

$$\boldsymbol{S}(\lambda)=a_1\boldsymbol{V}_1(\lambda)+a_2\boldsymbol{V}_2(\lambda)+a_3\boldsymbol{V}_3(\lambda)\cdots+a_k\boldsymbol{V}_k(\lambda) \tag{4}$$

Where $\boldsymbol{V}_1(\lambda)$, $\boldsymbol{V}_2(\lambda)$, $\boldsymbol{V}_3(\lambda)$, ... are vectors stand for different explosive and soil blank absorption spectra and $\boldsymbol{S}(\lambda)$ is a vector stands for the absorption spectra of the mixed explosive sample. For a specific wavelength λ_p,

$$S(\lambda_p)=a_1V_1(\lambda_p)+a_2V_2(\lambda_p)+a_3V_3(\lambda_p)\cdots+a_kV_k(\lambda_p) \tag{5}$$

Where $V_1(\lambda_p)$, $V_2(\lambda_p)$, $V_3(\lambda_p)$, ... stand for the absorbance value of different explosive and soil blank at the wavelength of λ_p and $S(\lambda_p)$ is the absorbance value of the mixed explosive sample at the same wavelength.

According to the principle of the least square methods, we introduce matrixes:

$$\boldsymbol{V}=\begin{bmatrix}1 & V_1(\lambda_1) & V_2(\lambda_1) & \cdots & V_k(\lambda_1)\\ 1 & V_1(\lambda_2) & V_2(\lambda_2) & \cdots & V_k(\lambda_2)\\ \vdots & \vdots & \vdots & & \vdots\\ 1 & V_1(\lambda_n) & V_2(\lambda_n) & \cdots & V_k(\lambda_n)\end{bmatrix},\boldsymbol{S}=\begin{bmatrix}S(\lambda_1)\\ S(\lambda_2)\\ \vdots\\ S(\lambda_n)\end{bmatrix},\boldsymbol{A}=\begin{bmatrix}e\\ a_1\\ \vdots\\ a_k\end{bmatrix} \tag{6}$$

Then, we can estimate the value $\boldsymbol{A}$ of using the least square methods:

$$\hat{\boldsymbol{A}}=\begin{bmatrix}\hat{e}\\ \hat{a}_1\\ \vdots\\ \hat{a}_k\end{bmatrix}=(\boldsymbol{V}'\boldsymbol{V})^{-1}\boldsymbol{V}'\boldsymbol{S} \tag{7}$$

Finally, we can obtain the calculated expression of the mixed explosives spectra:

$$\boldsymbol{S}(\lambda)=\hat{e}+\hat{a}_1\boldsymbol{V}_1(\lambda)+\hat{a}_2\boldsymbol{V}_2(\lambda)+\hat{a}_3\boldsymbol{V}_3(\lambda)+\cdots+\hat{a}_k\boldsymbol{V}_k(\lambda) \tag{8}$$

where $\hat{e}$ is the error (its theoretical value equals zero), and the $\hat{a}_1,\hat{a}_2,\cdots,\hat{a}_k$ coefficients represent the concentrations of different explosives in the sample.

The most common composite explosives consist of two or three types of explosive mixtures. In the above methods, to detect an unknown sample, we established a combination of one to three different kinds of explosive fingerprints (***Group 1***: TNT, DNT, PA, HMX, RDX; ***Group 2***: TNT&DNT, TNT&PA, TNT&HMX, …, HMX&RDX; ***Group 3***: TNT&DNT&PA; TNT&DNT&PA; …; PA&HMX&RDX) and blank soil spectra as the "base" series to obtain three groups of different results (25 results in total). Then, we used the least calculated absolute value of $\hat{e}$, which is significantly smaller than the other values in the same group, as the final result (the least $|\hat{e}|$ value must be at least one order of magnitude lower than the second lowest).

Results and discussion

Concentration gradient experiments for to determine the effective wavelength band of explosive fingerprints

According to Lambert-Beer's law, the absorbance at a certain wavelength band is proportional to the solute concentration. A series of experiments were conducted on different pure explosive solutions with gradient concentrations to verify this in our system. Using TNT as an example, the absorption spectrum of a series of working solutions of TNT diluted in acetonitrile (ranging from 0.5-100 ng/μL) was measured as shown in Fig. 4. The maximum absorbance ratio of the TNT solute concentration at wavelength = 223.7 nm had a high linearity of 0.99997 and a detection limit of ~7 pg.

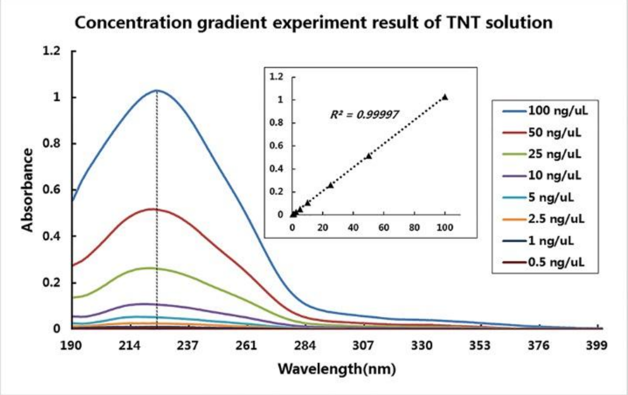

Fig. 4 The absorption spectrum of a series of working solutions of TNT diluted in acetonitrile (ranging from 0.5-100 ng/μL) and the linearity at maximum absorbance wavelength(223.7 nm).

The linearity between absorbance and solute concentrations in the spectrum of five pure explosives was measured to determine the effective wavelength band of the MSDA, in which each explosive had a high linearity between the absorbance and solute concentration. These result are shown in Fig.5 as a 'Linearity-Wavelength' graph of the five explosives. The range of the ordinate was set as 0.999-1, and the effective wavelength band ranging from 203-265 nm in which all explosive solutions had a high linearity (> 0.999) was then determined. Then, the absorbance spectra in this high linearity band were chosen as the region of interest (ROI) for our algorithm.

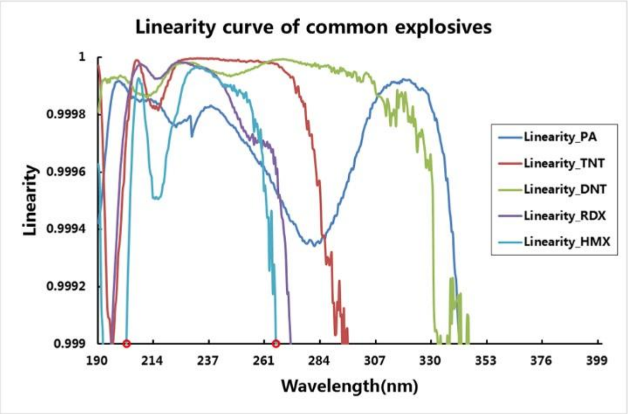

Fig. 5 The curve of linearity between the absorbance and solute concentration of common explosives was drawn to determine the effective wavelength band of the explosive fingerprints where all explosive absorbance ratios had a high linearity (> 0.999). The effective wavelength band ranging from 203-265 nm (marked with red circles) was selected as the ROI.

Evaluation of the portable device

The portable system had a brief analysis time of < 5 s, while traditional spectral analysis requires ⩾ 60 min. A clear and transparent sample droplet with almost no suspended particles was formed after filtration in the lab-in-a-capillary with the double-layer membranes. The absorption spectra of pure soil at the effective wavelength band was tested six times using our system (shown as No. 1-6 in Fig. 6) and once using a standard spectrophotometer (shown as 'Standard' in Fig. 6) to evaluate the stability and reliability of our system. All spectra are shown in Fig.6. The relative standard deviation (RSD) was 0.2-3%, indicating that the six spectra matched the standard spectrophotometer spectrum well. These results proved that the portable system, with its integrated filtration, purification, and spectra analysis, is stable and reliable.

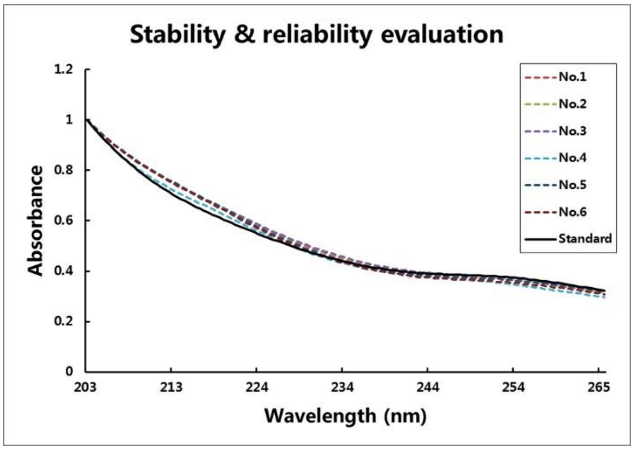

Fig. 6 Absorption spectra of pure soil at the effective wavelength band (normalized at the wavelength of 203 nm). No. 1-6 refer to the six parallel tests performed on our device. "Standard" refers to the test performed using a standard spectrophotometer.

Analysis of on-site debris containing a single explosive

In our UV spectrophotometry for explosives detection, fulvic acid (FA) and humic acid (HA) are two major interference in the post-blast soil, which was validated on the Center for Environmental Quality Test, Tsinghua University for FA and HA content determination. The test procedure was as follows: dissolving the soil sample in solution mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ to extract the FA and HA fractions, this step didn't require decalcification.[15] The total organic carbon (TOC) of the extracted FA and HA solution was determined by the potassium dichromate oxidation titration method.[16] Then by acidifying the FA and HA solution mixture with 0.5 M H_2SO_4, FA was fractionated from HA. The TOC of the HA solution was determined using the same method. The TOC of the soil sample was 7.26 $g{\cdot}kg^{-1}$, which was covered by the humic content range (0-10%) in natural soil.[17] The carbon contents of FA and HA were 4.48 $g{\cdot}kg^{-1}$ and 2.78 $g{\cdot}kg^{-1}$ respectively. These results are in the same level compared with most of the soil samples in other places.[18, 19] Therefore the soil samples used in our study are of universality. In filed investigations, the absorption spectra of blank soil on-site from the deeper soil layer under the explosion site was acquired to compensate the interference of filed soil in MSDA as an interference contrast.

The post-blast debris samples containing a single explosive (TNT) were directly obtained from the Institute of Forensic Science, Ministry of Public Security, People's Republic of China (Beijing, China). The sample extraction procedure was as follows: 0.5 g of the post-blast debris sample was slowly added to 1 mL acetonitrile and gently shaken for 3 s. Then, the turbid solution was transferred and directly injected into the lab-in-a-capillary of the device as shown in Fig.3, and in ~3 s, the absorbance spectrum of the filtered sample solution was recorded by the Spectrasuite 2.0 software. The absorbance spectrum of the sample droplet and all relative explosive "fingerprints" at the effective wavelength band were recorded for further analysis using the MSDA. The $\left|\hat{e}\right|$ values of the sample spectrum in ***Groups 1***, ***2***, and ***3*** were calculated using the MSDA introduced above and are shown in Fig.7. It can easily be seen from Fig.7 (a) that the $\left|\hat{e}\right|$ value calculated using the TNT fingerprint and blank soil as the "base" series is one order of magnitude less than that of DNT. However, we did not find any $\left|\hat{e}\right|$ values that satisfied the conditions in either ***Group 2*** or ***Group 3***. Thus, we determined that the sample contained TNT alone. The expression of the sample absorbance spectrum was calculated to be:

$$S = 0.0049 + 0.1058 * TNT + 1.0159 * Soil\,,$$

from which we determined that the concentration of TNT in the filtered droplet was 10.58 ng/μL. Also, the explosive content in the soil was calculated to be 21.16 μg/g.

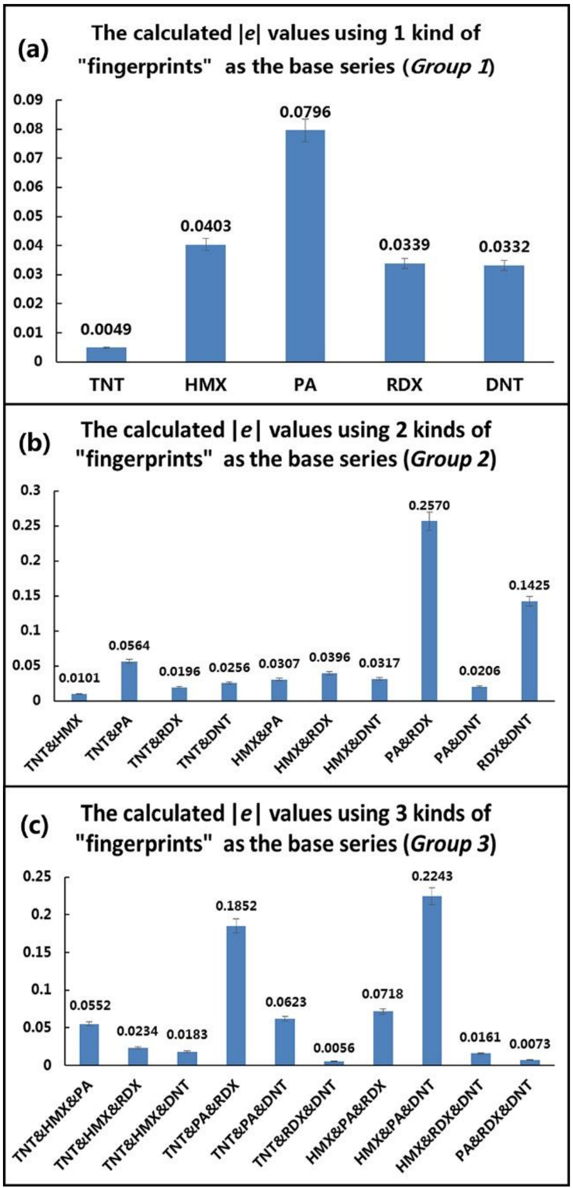

Fig. 7 $\left|\hat{e}\right|$ values of the sample spectrum in ***Groups 1-3*** calculated using the MSDA algorithm. (a) The $\left|\hat{e}\right|$ value in ***Group 1*** calculated using the TNT fingerprint and blank soil as the base series is one order of magnitude lower than that of DNT. (b) and (c), The $\left|\hat{e}\right|$ values in ***Group 2*** and ***Group 3*** do not satisfy the identification conditions. Thus, we determined that the sample only contained TNT.

Analysis of samples containing multiple explosives

Composition B (Comp B) is an explosive consisting of mixtures of RDX and TNT. It is used as the main explosive filling in artillery projectiles, rockets, land mines, hand grenades, sticky bombs, and various other munitions. Thus, it is common at the scene of explosions. Samples containing Comp B were simulated by doping multiple explosives into the blank soil. The sample extraction procedure was the same as that described above. In our experiments, we doped 10 μg TNT and 25 μg RDX into 0.5 g blank soil. After the absorbance spectra of the simulated sample droplet at the effective wavelength band were recorded, the $\left|\hat{e}\right|$ values of the spectra in ***Groups 1- 3*** were calculated using the MSDA (Fig. 8).

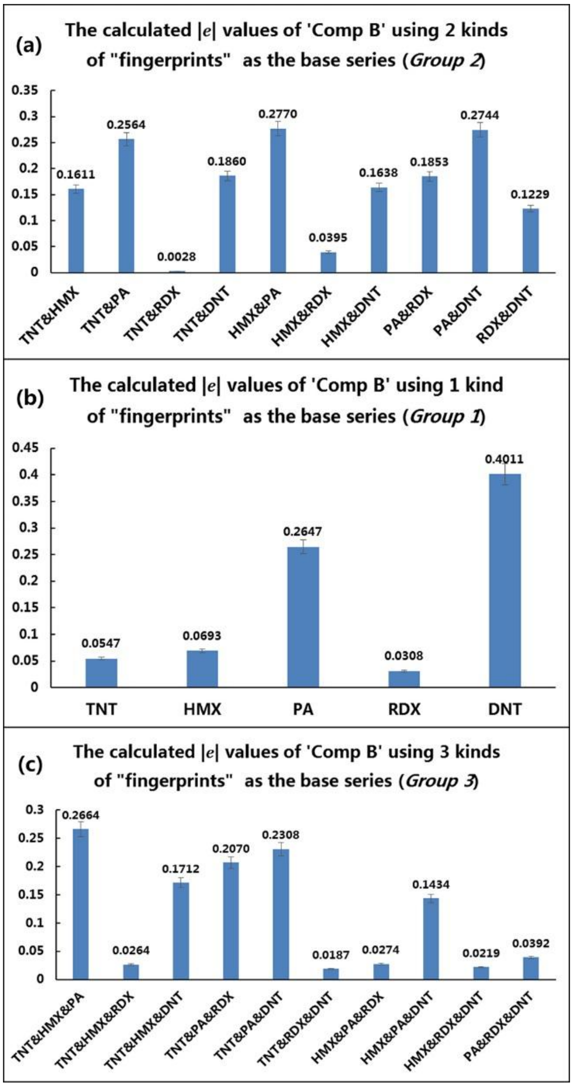

Fig. 8 $|\hat{e}|$ values of the simulated sample spectra in ***Groups 1-Group 3*** calculated using the MSDA. (a) The $|\hat{e}|$ values in Group 2 calculated using the fingerprint of TNT and RDX and blank soil as the base series is one order of magnitude lower than that of HMX & RDX. (b) and (c), The $|\hat{e}|$ values in ***Groups 1 and 3*** did not satisfy the identification conditions. Thus, we concluded that the sample contained Comp B (TNT & RDX).

According to the same principle as above, we found that the $|\hat{e}|$ value in ***Group 2*** calculated using the fingerprint of TNT and RDX, as well as blank soil (TNT & RDX) as the base series, is one order of magnitude lower than that of HMX & RDX. Further, no $|\hat{e}|$ values satisfied the analysis criteria in ***Groups 1 and 3***. Thus, we easily determined that the soil contained Comp B (i.e., mixtures of RDX and TNT). From the calculated expression of the spectrum:

$$S = -0.0028 + 0.1035 * TNT + 0.2583 * RDX + 1.0038 * Soil ,$$

we calculated the explosive content of the simulated soil sample as 10.35 μg TNT and 25.83 μg RDX, which closely matches the 10 μg TNT and 25 μg RDX added to the sample.

Conclusions

In this paper, a portable device was developed to detect and quantitatively analyse the residual explosives in soil. It combines the lab-in-a-capillary technique and a reflected optical fiber sensor to perform UV spectral analysis for micro-nanoliter droplets of sample. The double-layer filter valve in the lab-in-a-capillary filtered out suspended particles of sample solution fast and effectively, and the micro-droplets with a volume in the micro-nanoliter range could be controlled by the equilibrium between gravity and the negative air pressure of the capillary flow passageway. A MSDA was proposed to analyse the spectra of the soil samples to identify the explosive component(s) of the mixtures based on the explosive fingerprints and calculating the explosive content of the samples. Using this portable device, the total time from sample preparation to spectrum analysis was < 5 s, the sample consumption could be < 10 nL, the detection limit reached <10 pg, and the detection range covered 1-250 pg/nL. The experiments detecting TNT and Comp B in soil proved that the portable device is stable and reliable, and it is a promising technique for on-site analysis of trace amounts of explosives from post-blast debris, food safety, and clinical medicine, etc.

Acknowledgements

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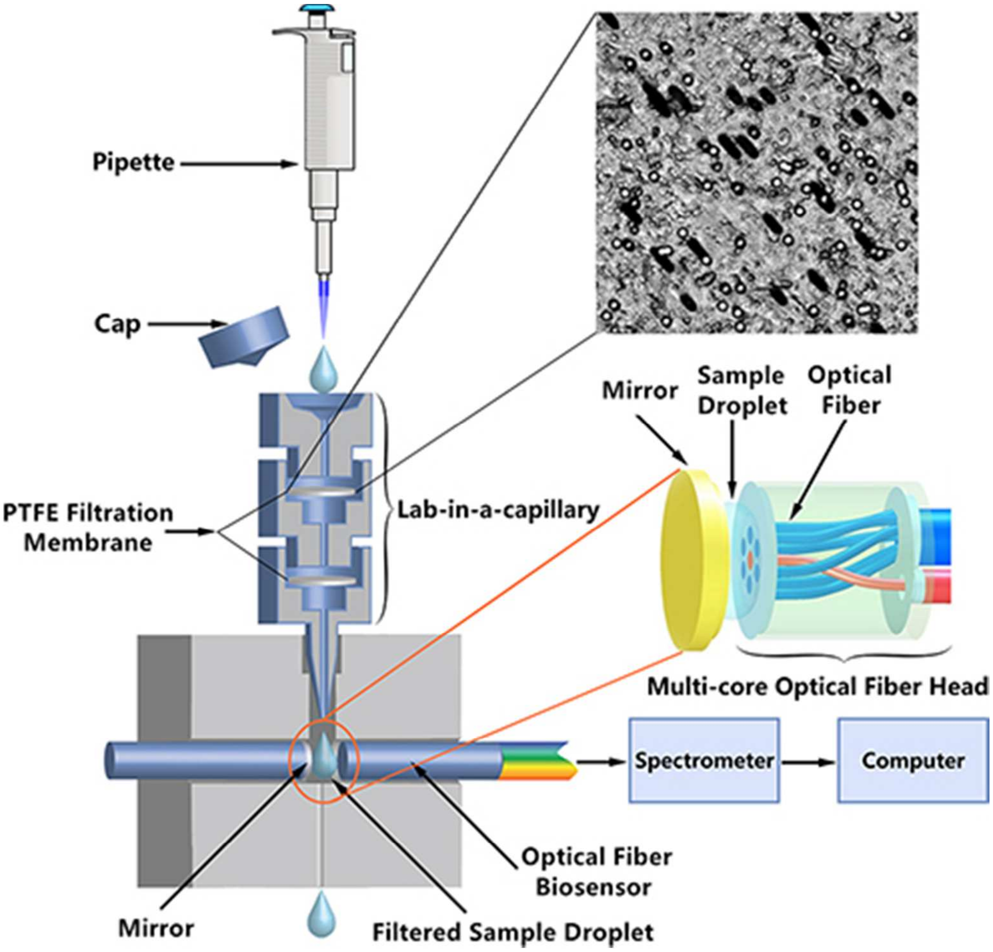

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