Defence Science Journal, Vol. 72, No. 3, May 2022, pp. 353-358, DOI : 10.14429/dsj.72.17676

Obscurant and Radiation Characteristics of Infrared-Screening Smoke Composition Based on Red Phosphorus

Sang Dam Quang, Tinh Nguyen Van, Toan Nguyen Trung*

Le Quy Don Technical University, Hanoi - 100 000, Vietnam
**E-mail: trungtoanktqs@mta.edu.vn*

ABSTRACT

Red phosphorus-based camouflage compositions are often used on naval ships to counter anti-ship missiles. This work focused on investigating the obscurant and infrared radiation characteristics of infrared-screening smoke of pyrotechnic compositions based on red phosphorus, Mg-Al alloy, barium nitrate and Viton A rubber. The results demonstrated that the smoke clouds of the formulation based on red phosphorus and Mg-Al alloy have a high attenuation capability to 1.064 µm laser radiation. Besides, these smokescreens also have a better emission power in the wavelength range of 2.5-5 and 8-14 µm. Therefore, the smoke compositions based on red phosphorus and Mg-Al alloy can be used in camouflage devices on naval ships against infrared and laser-guided missiles.

Keywords: Obscurant; Infrared; Emission; Smoke; Red phosphorus

1. INTRODUCTION

Infrared and laser-guided missiles are among the most dangerous weapon to naval ships because of their maneuverability and high accuracy[1]. One of the most effective and economical ways against such optically guided anti-ship missiles is to establish camouflage smokescreens (obscurant clouds) on the surface of the naval ships[2]. The primary purpose of obscurant clouds is to sacatter and absorb optically guided radiation and thereby interrupt the line of sight between the target and the observer[3,4]. Over the last 70 years, many obscurant smoke compositions have been studied and developed, such as the hexachloroethane (HC) smoke formulations, the phosphorus-based formulations, thermal sublimation smokes, etc.[5-12]. Among the above mixtures, smoke compositions based on red phosphorus (RP) are widely used for military applications. It has an excellent screening performance (i.e., high absorption and scattering capacity) and much fewer toxicity properties than either white phosphorus or HC composition[7,13-17].

The chemistry and mechanism of RP-based smoke have been discussed by many scientists over the world. Most studies suggested that RP-based smoke has a high camouflage ability and a good mass extinction coefficient for laser radiation. L. Klusacek and P. Navratil showed that the screening smoke of the pyrotechnic composition based on RP and epoxy resin has high-efficiency screening infrared radiation (0.82 µm, 3-5 µm, 10.6 µm wavelengths)[13]. Y. Suzuki *et. al* has established that the middle-infrared radiation (MIR) and far-infrared radiation (FIR) screening factor was the absorption of phosphoric acid[18]. Furthermore, the screening smoke based on RP can be a low-temperature infrared decoy for distinct sources of infrared radiation provided by the chimney and the exhaust plume of naval ships with a radiation range of 2.5-5 µm (MIR) and 8-14 µm (FIR). The source of infrared radiation comes from the gaseous and condensed combustion products[19]. S. Cudzilo's research investigated the temperature distribution of the smoke cloud of the mixture based on RP, Mg, and an oxidizer (Teflon/ KNO_3)[20]. The results demonstrated that the smokescreen has strong emission in the wavelengths of 2.5-5 µm. However, there is a small number of published studies on infrared radiation of RP-based screening smoke, and both obscurant and infrared emission characteristics should be studied simultaneously to further evaluate the performance of this composition.

This work aims to investigate the obscurant and the infrared emission characteristics of the screening smoke of RP-based composition. The influence of the chemical formulations on the transmittance, the mass extinction coefficient, the Yield factor and the figure of merit of the screening smokes at 1.064 µm laser radiation (i.e., solid-state laser source widely used in military applications and have many advantages over gas and semiconductor lasers) were determined according to the Lambert-Beer law. The infrared emission characteristics (i.e., the emission distribution and the radiance) were determined using the spectroradiometer (working in the range of 2.5-14 µm).

2. MATERIALS AND METHODS

2.1 Main Materials

RP fine powders (230-325 mesh) and barium nitrate powder (200-230 mesh) were obtained from Xilong Scientific Co., Ltd. The flake-like Mg-Al alloy powder (Mg_4Al_3, 230-325 mesh) was provided by Sichuan Hermus Industry Co., Ltd. An elastomer (trade name Viton A, which is a copolymer of vinylidene fluoride-hexafluoropropene with a fluorine content of 66 %) was obtained from the Dupont company.

Received : 14 November 2021, Revised : 14 April 2022
Accepted : 19 April 2022, Online published : 01 July 2022

2.2 Experiment and Methods

2.2.1 Sample Preparation

Samples were prepared in a sheet form[10]. Viton A rubber was dissolved in acetone (with the rubber/solvent ratio of about 1/15 w/v) for about 12 hours to obtain a homogeneous binder solution. RP powder, Mg_4Al_3 alloy powders, and then barium nitrate powders were mixed into the binder solution for about 30 min with a stirrer at 700 rpm. The final solution was painted onto both sides of 100x100 mm fiberglass fabric to form a sheet and was vacuum-dried at 60 °C for 3 hours to remove the solvents. After the solvent is removed, a thin film of rubber will exist and resist the effects of water vapor on the composition. The formulations of samples (M1-M4) are expressed in Table 1.

Table 1. The formulations of RP-based smoke samples

Materials	Content (wt.%)			
	M1	M2	M3	M4
RP	70	60	50	40
Mg_4Al_3	-	10	20	30
$Ba(NO_3)_2$	15	15	15	15
Viton A	15	15	15	15

2.2.2 Experimental Techniques

The heat of combustion Q was determined using the Parr 6200 calorimeter (Parr Instrument Company, US). The 5.0 g sample (i.e., five 50x50 mm sheets) was prepared for each measurement, and the combustion was ignited by the electrical igniter.

To determine the burning rate of RP-based compositions, the samples were prepared in the form of 100x10 mm - sheets. The high-speed digital camera Fastcam SA 1.1 RV (Photron, Japan) was used to determine the time interval needed for the flame front to travel a known distance on the surface of the sheet (with a recording speed of 500fps), so the burning rate is calculated.

Obscurant characteristics of smokescreen can be evaluated by the transmittance, the mass extinction coefficient, the Yield factor and the figure of merit. These parameters were measured by burning a known amount of RP-based smoke composition in a cubical test chamber (the volume of 1 m^3, with two windows on opposite walls). A continuous-wave laser source (with an output power of 25.0 mW and a beam diameter of 2.0 mm) was passed through the chamber and recorded by a laser power meter. The total path length through the screening smoke was 1000 mm. The experimental setup used to measure the obscurant characteristics of 1.064 µm laser radiation is shown in Fig. 1.

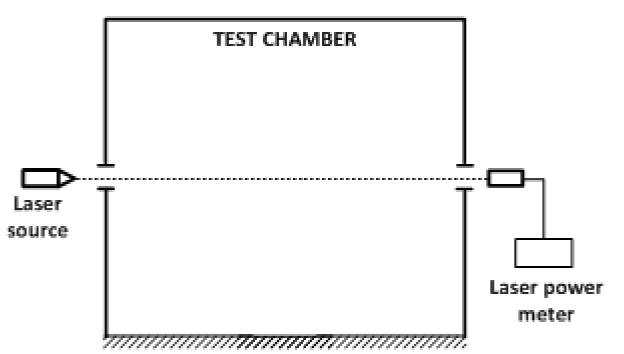

Figure 1. The setup used to determine the transmittance and the mass extinction coefficient.

The transmittance T (e.g., the degree of transmission) was determined by[21]:

$$T = \frac{I_{\min}}{I_0} \quad (1)$$

where I_0 and I_{min} are the initial laser intensity without smoke and the minimum laser intensity after passing through the screening smoke, respectively. Then, the mass extinction coefficient α_λ (m^2.g^{-1}) can be calculated according to the Lambert-Beer Law[3,22,23]:

$$\alpha_\lambda = -\frac{\ln T}{c.L} \quad (2)$$

where c is the concentration of smoke cloud in the test chamber (g.m^{-3}); L is the optical path length through the smoke cloud (m).

The Yield factor Y_f of the obscurant composition is a calculated variable that accounts for the increase in mass of a smoke material that results from its combination with atmospheric constituents. The Yield factor is the ratio of the aerosol mass m_s and the mass of pyrotechnic composition m_p[3,24]:

$$Y_f = \frac{m_s}{m_p} \quad (3)$$

and the mass-based composition figure of merit F_m (i.e., the quality criteria used to ascertain the obscurant performance) was calculated by multiplying the mass extinction coefficient and the Yield factor[3,24]:

$$F_m = \alpha_\lambda . Y_f \quad (4)$$

The infrared radiation characteristics of smoke clouds were measured by the Spectral Master 12-550 Mark III Radiometer (US) with a working wavelength from 2.5-14.0 µm. For each measurement, 10 grams of the sample (i.e., ten 50x50 mm sheets) were burned by an electric prime in a cubical test chamber with a volume of 1 m^3. The lenses of the radiometer were placed facing the smoke cloud through a source window on the wall of the test chamber, and the distance between the lenses and the source window is about 4.0 m. The emission intensity in the wavelength ranges from 2.5 to 14 µm was scanned every 2 seconds (Channel 2) and repeated. The infrared distribution and the radiance were determined by the built-in software. Fig. 2 presents the experimental setup used to measure the infrared emission characteristic [25].

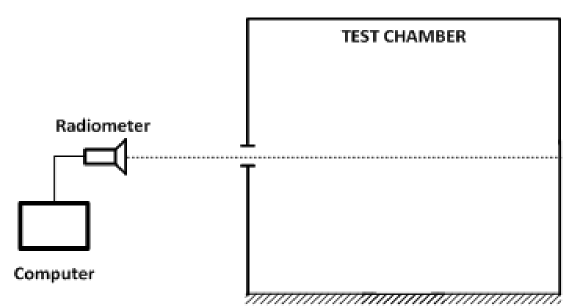

Figure 2. The setup used to measure the infrared emission characteristic.

3. RESULTS AND DISCUSSION

3.1 Combustion Characteristics

The combustion parameters of the smoke composition directly affect the attenuation and infrared emission performance of the smokescreen. Specifically, the component of the gaseous product affects the absorption and scattering of laser radiation. On the other hand, gaseous combustion products emit infrared radiation from well-defined vibrational transitions, condensed phase products release radiance in the form of gray-body emission, and the infrared emission distribution depends only on temperature[19].

Therefore, before the main experiments, the theoretical temperature flame T_F, the heat of combustion Q_v and the combustion product distribution were calculated by the modified REAL thermodynamic code[26,27], which bases on the chemical equilibrium theory and the Gibbs free energy minimized principle. The experimental values of Q_v and the burning rate u were also measured. The T_F, Q_v, u and the combustion products were considered as a function of the RP content. The results are summarized in Table 2.

Table 2. Combustion characteristics of RP-based composition

No.	Main component of combustion products (mol.kg^{-1})	u (mm.s^{-1})	T_F (K)	Q_v (kJ.kg^{-1})	
				Theory	Exp.
M1	H_2 - 1.3, CO - 1.1, PF_3 - 1.2, P_4 - 5.2, C - 3.0, $Ba_3(PO_4)_2$ - 0.2	5.1±0.3	1100	890	810±50
M2	H_2 - 1.7, CO - 0.7, P_4 - 1.4, P_2 - 6.6, C - 3.6, MgF_2 - 1.8, BaF_2 - 0.6	10.5±0.5	2010	1750	1650±80
M3	H_2 - 1.7, CO - 0.2, P_4 - 0.7, P_2 - 6.7, C - 4.1, Mg - 1.9, MgF_2 - 1.5, BaF_2 - 0.5, AlF - 0.6	12.8±0.7	2150	1950	1880±60
M4	H_2 - 1.7, P_4 - 0.5, P_2 - 5.4, C - 2.8, Mg - 3.2, MgO - 1.7, MgF_2 - 1.3, BaF_2 - 0.5	16.5±0.8	2110	1910	1810±80

From Table 2, it can be seen that the theory Q_v values calculated by the REAL program meet an agreement with the experimental data, which confirms the accuracy of the computation. The results from Table 2 also showed that along with the presence of Mg_4Al_3, the adiabatic flame temperature T_f and the heat of combustion Q_v of compositions increase. When the Mg-Al content is more than 30 % (i.e., the presence of Mg in the combustion products confirms that the formulation is fuel-rich), the values of T_f and Q_v tend to decrease.

Besides that, an increase in the content of Mg_4Al_3 alloy results in a higher burning rate. The reason was that the increase in the content of the Mg_4Al_3 alloy increases the thermal conductivity (i.e., the efficient energy feedback) of the mixture from the reaction zone to the pre-reacting zone, resulting in the higher burning rate[25].

3.2 Obscurant Characteristics

For the obscurant clouds based on RP and Mg_4Al_3, soot particles (i.e., Carbon), H_3PO_4 particles (formed by a reaction of P_2, P_4 with atmospheric oxygen and moisture), MgO particles (formed by the reaction of gaseous Mg with atmospheric oxygen) and MgF_2 particles are the main components of the smoke. The obscurant characteristics of the smoke compositions were determined by burning 2.0 g of samples to produce a smoke cloud inside the test chamber. After 10 seconds (to obtain a uniformly dispersed smokescreen in the test chamber), 10-values of laser intensities, which the laser transmitted after passing the smoke cloud, were recorded every 5 seconds[10,21]. The minimum value of laser intensities (I_{min}) was determined and used to calculate the transmittance T according to Eqn. (1), the mass extinction coefficients α_λ and the Yield factors Y_f were calculated according to Eqn. (2) and Eqn. (3), respectively. These results are shown in Table 3.

As can be seen from Table 3, when Mg_4Al_3 alloy is added to the RP-based smoke composition, the concentration of smoke cloud in the test chamber is reduced, which increases the transmittance. This trend is more obvious when the content of Mg_4Al_3 alloy in the mixture is higher. The most interesting result to emerge from the data is that the difference in the mass extinction coefficients of RP-based composition is insignificant (with the values approximately of 1.0 to 1.2 m^2.g^{-1}). This may be due to the relationship between the concentration of the smoke cloud and the transmittance in Eq. (2). It is noteworthy that the values of the mass extinction coefficient of samples in this work are also equivalent to those of the RP/Mg_4Al_3/Teflon mixture (1.4 m^2.g^{-1}) previously reported by S. Cudzilo and W. A. Trzcinski[28]. The calculation results of the transmittance and the mass extinction coefficients (e.g., the screening area per mass of aerosol) also show that the smoke cloud of the RP-based compositions provides good camouflage for 1.064 µm laser radiation.

Table 3. Obscurant characteristics of RP-based screening smoke

Sample	Concentration of smoke c (g.m^{-3})	Transmittance T (%)	Extinction coefficient α_λ (m^2.g^{-1})	The Yield factor Y_f	The figure of merit F_m (m^2.g^{-1})	Relative humidity (%)
M1	4.15	0.8	1.16	2.08	2.4	60
M2	4.07	1.6	1.02	2.04	2.1	
M3	3.70	2.8	0.98	1.85	1.8	
M4	3.19	4.0	1.01	1.60	1.6	

Besides, the Y_f values of the smoke compositions in this study (i.e., Y_f=1.60 to 2.08) are also significantly higher than those of the composition based on Ti/poly-carbon monofluoride or Mg/poly-carbon monofluoride (i.e, Y_f=1.0 to 1.2)[3] and the composition based on RP/Mg/Teflon (i.e, Y_f=0.8)[28]. Therefore, the figure of merit F_m values (e.g., screening area per mass transported) of obscurant composition were calculated and ranges from 1.6 to 2.4 $m^2.g^{-1}$, which is higher than that of the composition based on terephthalic acid[29]. Of these, the composition based on RP/$Ba(NO_3)_2$/Viton A has the greatest F_m value, and along with the decrease in RP content, the value of F_m also decreases.

3.3 Infrared Emission Characteristics

The infrared emission characteristics (i.e., the spectral distribution, the radiation intensity and the radiance) of RP-based composition were measured using the Spectral Master 12-550 Mark III Radiometer and the results are shown in Fig. 3.

As can be seen from Fig. 3, along with the presence of Mg_4Al_3 alloy in the RP-based smoke composition, the infrared emission spectral distribution of smoke clouds changes significantly. In particular, while the smoke cloud of M1 formulation almost only emits infrared radiation in the wavelength of 8-14μm (FIR), the smoke clouds of M2, M3 and M4 formulations (i.e., RP-based composition containing Mg_4Al_3) emit infrared radiation in both the 2.5-5 (MIR) and 8-14 μm (FIR) bands. It should be noted that along with the presence of Mg_4Al_3 alloy in the smoke composition, the combustion characteristics, such as the flame temperature, the heat of combustion and the burning rate, increase, causing infrared radiation in the wavelength of 2.5-5 μm.

To evaluate the effect of the Mg_4Al_3 content on the infrared spectral distribution and the infrared radiance of the smoke clouds, the average values of the infrared radiance of all samples in MIR and FIR bands are summarized in Table 4.

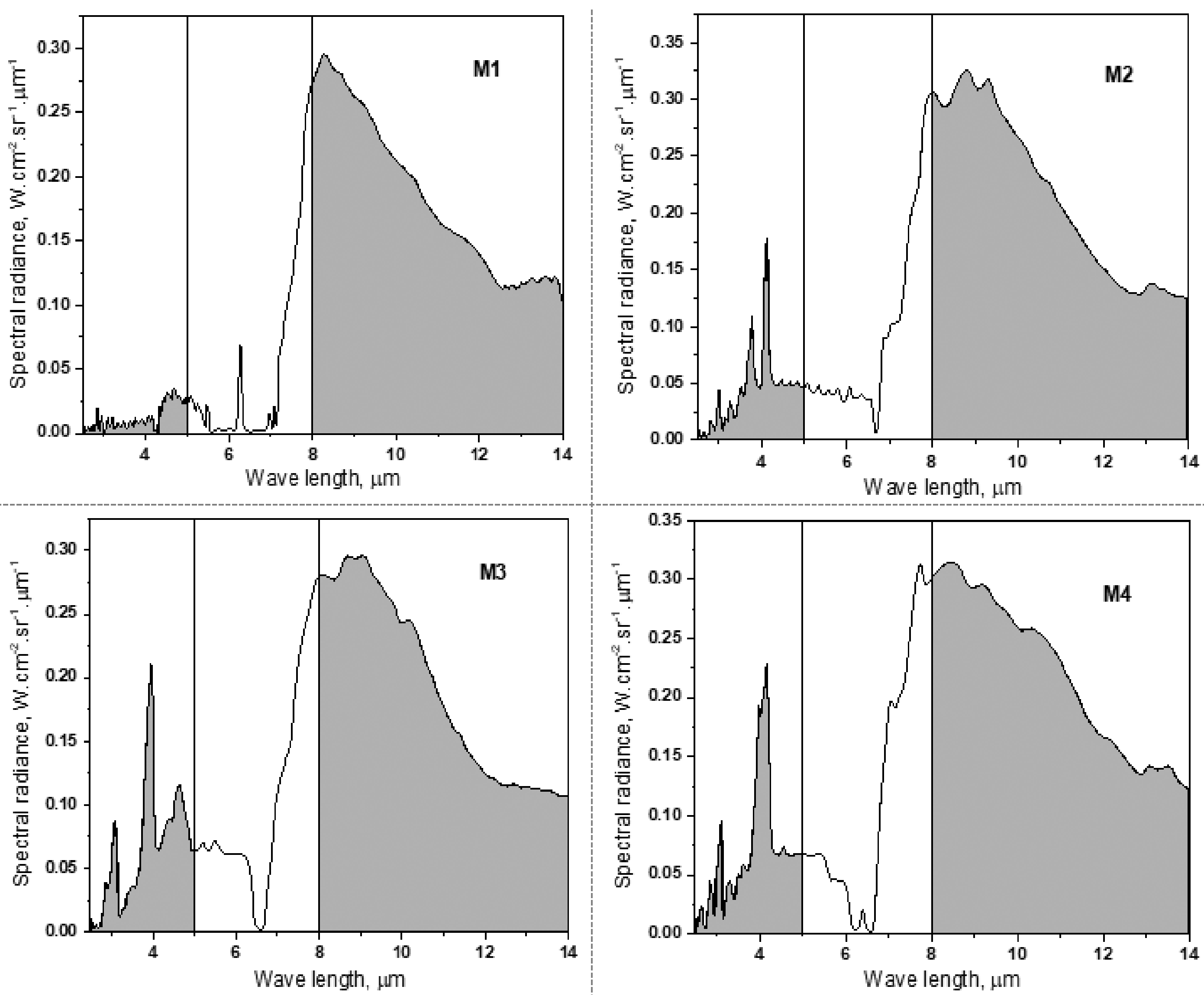

Figure 3. Infrared spectral distribution of RP-based smoke clouds.

Table 4. Infrared radiance of smoke clouds of the RP-based composition

Sample	Infrared radiance (10^{-2} W.cm^{-2}.sr^{-1})		Ratio of radiance in FIR/MIR band
	MIR band	FIR band	
M1	3.1	110.3	35.5
M2	11.3	127.8	11.3
M3	16.7	115.1	6.9
M4	17.4	131.5	7.5

In Table 4, there is a clear trend of increasing the infrared radiance in the MIR band as the content of Mg_4Al_3 alloy increases, along with a decrease in the ratio of the infrared radiance in the FIR band (8-14 µm) to the radiance of the MIR band (2.5-5 µm). The burning rate increases with the Mg_4Al_3 content, resulting in compositions with higher Mg_4Al_3 content having high infrared radiation intensity. However, when the Mg_4Al_3 content increases to 30% (fuel-rich formulation), the flame temperature and the heat of combustion tend to decrease, so the first maximum radiation intensity of about 4.0 µm tends to shift to the longer wavelengths according to Wien's displacement law[30].

4. CONCLUSIONS

The obscurant smoke clouds of RP-based formulation attenuated 1.064 µm laser radiation with high efficiency. The presence of Mg_4Al_3 alloy in the smoke formulations changes the component of combustion products, leading to an increase in the transmittance, but the change in the mass extinction coefficient of RP-based composition is insignificant. On the other hand, along with the increase of RP content in the smoke composition, the Yield factor Y_f and the figure of merit F_m also increase (i.e., the higher screening performance).

While the smoke cloud of the mixture based on RP, $Ba(NO_3)_2$ and Viton performs high infrared emission only in the wavelength of 8-14 µm, the infrared spectral distribution of smoke clouds of the Mg_4Al_3-added mixtures appears in both 2.5-5 and 8-14 µm wavebands. Thus, the mixtures of RP, Mg_4Al_3, $Ba(NO_3)_2$ and Viton proved to promise camouflage devices on naval ships.

Further work needs to be carried out to assess the effect of environmental conditions on the obscurant and emission performance of these RP-based smoke compositions.

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CONTRIBUTORS

Prof. Sang Dam Quang received his PhD from the *Mendeleev University* of Chemical Technology of Russia in 2012. He is currently working as a Scientist in the Department of Energetic Materials of Le Quy Don Technical University, Vietnam. His research interests include the calculation of explosion and combustion processes, preparation of pyrotechnic mixtures and commercial explosives.
Contribution to the current study: He analysed the experiment data and contributed to writing the manuscript.

Dr Tinh Nguyen Van received his PhD from the *Mendeleev University* of Chemical Technology of Russia in 2007. He is Head of the Department of Energetic Materials of Le Quy Don Technical University, Vietnam. His research area is explosive technology.
Contribution to the current study: He carried out the literature review and contributed to prepare the manuscript.

Dr Toan Nguyen Trung received his PhD from the Academy of Military Science and Technology, Vietnam, in 2019. Presently, he is working as a scientist in the Department of Energetic Materials of Le Quy Don Technical University, Vietnam. His research interests include pyrotechnics, the detonation of explosives and the thermal decomposition of energetic materials.
Contribution to the current study: He performed the experiments and guided the entire study.