Propylene Glycol Dinitrate (PGDN) as an Explosive Taggant

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Abstract: Propylene Glycol Dinitrate (PGDN) is a liquid nitrate ester explosive which has been used as a gelatinating agent in some energetic formulations. The aim of the present work was to assess whether PGDN could be used as a detection taggant. The PGDN was synthesized in the laboratory using laboratory grade propylene glycol (PG). The purity of the synthesized PGDN was assessed using gas chromatography-mass spectrometry (GC/MS) and Fourier transform infrared spectroscopy (FTIR).

A study of the thermal decomposition of PGDN was carried out using both DSC and thermogravimetry-mass spectrometry analysis (TG/MS) methods. The gases produced during thermal decomposition were identified by mass spectrometry and the influence of the heating rate was investigated. The duality of DSC-TGA was highlighted by studying the complementarity between these two methods.

Vapour pressure and enthalpy of vaporisation of PGDN were considered as the foremost taggant characteristics, and were estimated using TGA and taking benzoic acid as the reference. The vapour pressure of PGDN at ambient temperature is 2.54 Pa, therefore the PGDN could be a good candidate as a detection taggant compared to other explosive taggants (Nitroglycerin, EGDN, DMNB and PDCB).

Keywords: PGDN, taggant, thermal decomposition, vapour pressure, DSC-TGMS

1 Introduction

Propylene glycol dinitrate (PGDN), shown in Figure 1, belongs to the category of nitrate ester high explosives [1]. It can be used as a liquid explosive or as a liquid propellant, for instance in torpedoes, Otto Fuel II, by the US navy [2].

The pre-blast forensic detection of explosives is based essentially upon techniques which use the vapour pressure in order to detect either a taggant agent or a parent explosive molecule.
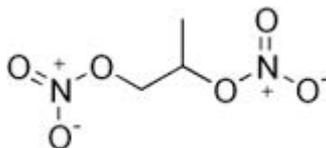

Figure 1. PGDN.

Explosive taggants are divided into two categories, pre-blast (detection) taggants and post-blast (detonation) taggants. Figure 2 shows the kinds of taggants used and their nature (chemical, ceramic, magnetic *etc.*). Each kind of taggant is characterized by some physicochemical property allowing access to the necessary forensic information related to both the manufacture (in the case of detonation) and detection (in the case of pre-blast) of explosives. Chemical taggants are the principal and foremost detection taggants used. The aim of their presence in explosives is for the identification of commercial and military explosives by instrumental detection at airports, entrances to public buildings and other appropriate sites [3]. 2,3-Dimethyl-2,3-dinitrobutane (DMNB) is the most suitable detection agent, being chemically and energetically inert, it does not affect the explosive's properties [4].
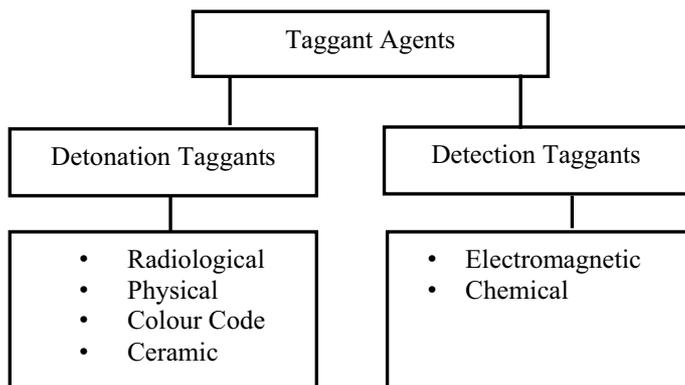

Figure 2. Different kinds of explosive taggants.

The concept of explosive taggants was introduced earlier in the USA by the antiterrorism act of 1979. Section 303 of the legislation mandated the use of identification and detection taggants in explosive materials. After the Oklahoma

City bombing, in April 1995, the President signed Public Law 104.132 and the National Research Council (NRC) evaluated several options for taggants.

Unfortunately, improvised explosives could not be identified by taggants. Nevertheless, the precursors used in the synthesis of improvised explosives could contain some specific additives which would allow their forensic detection, for instance, 2-ethylhexanoic acid in the case of the synthesis of improvised EGDN from coolant, and nicotine in the case of the improvised synthesis of NG and PGDN from E-smoking cigarettes [5, 6].

The present work investigated the possibility of using a nitrate ester energetic agent (PGDN) as an explosive chemical taggant in the forensic field by exploring its thermal properties (vapour pressure and thermal decomposition). PGDN was synthesized in the laboratory and characterized by using both gas chromatography-mass spectrometry (GC/MS) and Fourier transform infra-red (FTIR) techniques. The thermal proprieties of PGDN were highlighted by using the methods of differential scanning calorimetry (DSC) and thermal gravimetry-mass spectrometry (TG/MS). Generally, the technique used to assess the vapour pressure depends on the volatility of the target compound; a few studies have tried to estimate the vapour pressure of some explosives using several techniques [7-9] (chromatography, dynamic thermal analysis *etc*.). In our case, TGA could be a good candidate for the estimation of the vapour pressure of PGDN. The rearranged Langmuir and Clausius-Clapeyron equations have been used to estimate the enthalpy of vaporization and the results are compared to the vapour pressures of some common explosives. The activation energy and the heat of decomposition have been measured by DSC. The thermal decomposition gases of PGDN were identified by TG/MS.

2   Experimental

2.1 Synthesis
PGDN was synthesized using laboratory grade propylene glycol (PG). The nitration of PG was performed by the action of the nitronium ion generated by mixing nitric and sulfuric acid. During the synthesis, the physical parameters were controlled appropriately, and similar to those cited in [6]. After the synthesis, a brief wash with distilled water was carried out. The products were then further washed with aqueous sodium carbonate solution to neutralize the residual acids. This operation was followed by washing with distilled water until neutral pH. The yield was between 63-65%.

2.2 Analytical methods

GC/MS

An Agilent 6890 series gas chromatograph (GC) connected to an Agilent 5973 network mass spectrometer (MS) was used. The column DB5 had dimensions 30 m × 0.32 mm, and the carrier gas helium flowed at 1 mL·min^{-1}.

Prior to GC/MS analysis, a volume (0.5 µL) of each sample was dissolved in dichloromethane (2 mL) and an aliquot (1 µL) of the solution obtained was introduced using the splitless mode. The injection port temperature was 180 °C. The oven temperature was initially at 35 °C for 3 min, was then heated at a linear rate of 20 °C/min until 250 °C and finally kept for 5 min at this temperature.

The MS quadrupole temperature was set at 150 °C and the MS source temperature at 230 °C. The solvent delay time was 2.2 min. The MS was operated in the scan mode (30-300, amu).

FTIR

Fourier Transform Infrared Spectra were recorded with a Mettler Toledo FTIR by averaging 60 scans, in the spectral range 4000-400 cm^{-1} with a resolution of 1 cm^{-1}. A volume (1 µL) of each sample was analyzed in the ATR mode.

DSC

Samples were tested under a nitrogen flow in cylindrical high pressure crucibles using a DSC822 Mettler Toledo system which had been previously calibrated with indium and zinc. The samples were heated from 50 °C to 280 °C at four different heating rates (β = 1, 3, 5 and 8 °C/min). The onset temperature was determined by the intersection point of the base line and the first profile segment corresponding to decomposition.

TG/MS

The thermogravimetry-mass spectrometry analysis (TG/MS) was performed using a TGA/SDTA 851 microbalance under argon flow (100 mL/min) with less than 10 mg of PGDN. Each sample was heated from 50 °C to 300 °C at four different heating rates (β = 1, 3, 5 and 8 °C/min). Prior to these measurements a blank was obtained by analyzing an empty cell to ensure the stability of the signal and to quantify the residual amount of each compound in the argon flow. Benzoic acid was used as the reference in order to estimate the calibration constant by isothermal TGA analysis at four temperatures (298.15, 323.15, 333.15, 343.15 K).

The amounts of H_2O/CH_4 (m/e = 18), CO/N_2 (m/e = 28), NO (m/e = 30), O_2 (m/e = 32), C_3H_8 (m/e = 44), NO_2 (m/e = 46), and NO_3 (m/e = 62) were

determined using a Omnistar™/ThermoStar™ mass spectrometer, which was directly coupled to the microbalance.

3   Results and Discussion

3.1 GC/MS analysis

The GC/MS analysis showed that the retention time (5.13 min) and main fragments in the mass spectra (m/z: 30, 46, 76) of synthesized PGDN (Figures 3a and 3b) were the same as observed in Figures 4a and 4b for standard PGDN. The second observation was that, additionally, from the chromatogram of the synthesized PGDN, the purification process had been successful.
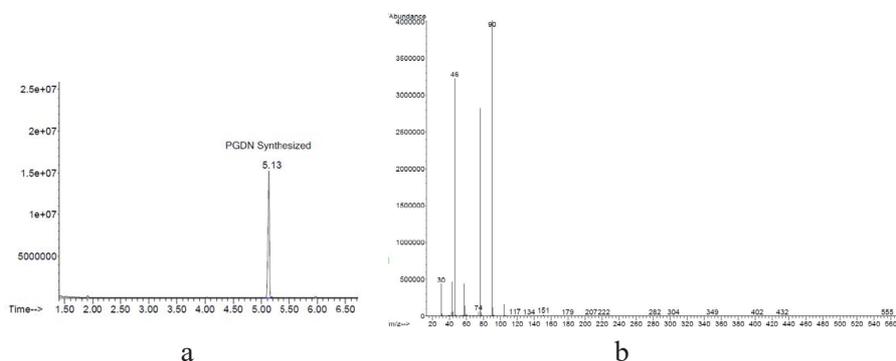

Figure 3.   Chromatogram and mass spectrum of synthesized PGDN: (a) chromatogram, (b) mass spectrum.

3.2 FTIR analysis

In order to focus on the absorption bands of PGDN, the IR spectra of both propylene glycol (PG) and PGDN were superimposed (Figure 5). The PG spectrum shows a broad absorption band at 3000-3600 cm^{-1} with a maximum at about 3370 cm^{-1}, which is attributed to the O–H stretching of the hydroxyl groups and probably some water; this band is completely absent in the case of PGDN. This is accompanied by the appearance of two new bands at 1635 and 1270 cm^{-1}, related to the NO_2 groups, indicating the successful PGDN synthesis [10].
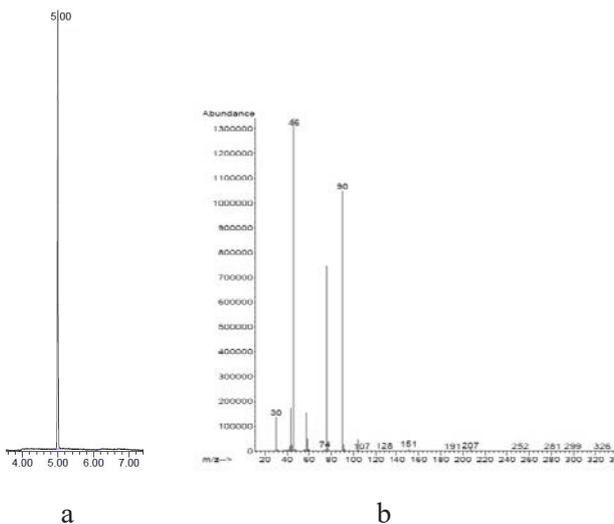
a   b

Figure 4. Chromatogram and mass spectrum of standard PGDN: (a) chromatogram, (b) mass spectrum.
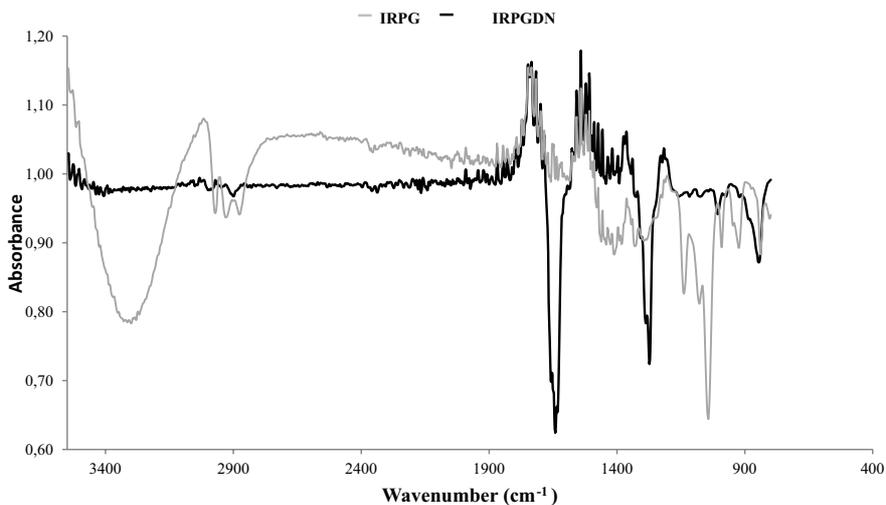

Figure 5. Infra-red spectra of PG and PGDN.

The bands around 2943 and 2923 cm^{-1} are due to the stretching vibrations of C–H and the absorption band at 1460 is related to the C–H bending vibration. Three peaks at 1215, 1084, and 1037 cm^{-1} correspond to the C–O bond of the alcohol and other bonds.

3.3 Thermal decomposition

3.3.1 DSC analysis

According to the DSC thermograms in Figure 6, PGDN decomposition occurs between 170-230 °C. The heating rate affects the temperature of decomposition, allowing calculation of the Arrhenius parameters; Table 1 reports the onset decomposition temperatures and the heat of decomposition, which is averaged at 4011 J·g⁻¹
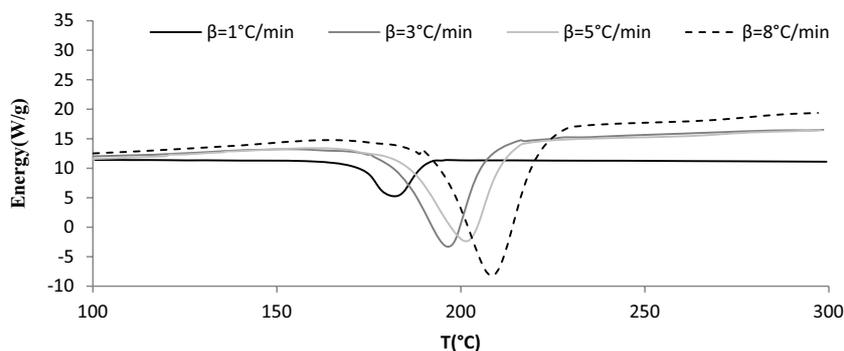

Figure 6. DSC thermograms of PGDN at different heating rates.

Table 1. PGDN DSC parameters

β [°C·min⁻¹]	T_{onset} [°C]	T_{max} [°C]	ΔH [J·g⁻¹]
1	172.83	182.19	4121.91
3	180.50	196.67	4134.39
5	182.00	203.00	4003.21
8	192.68	208.48	3788.00
Average			**4011.87**

The activation energy was estimated using two models, Ozawa and Kissinger [5, 11], and the results are presented in Table 2. Both models gave practically the same value and were lower than the literature value [12]; this is probably due to the process of PGDN synthesis (the source of the nitronium ion affects the purity of the final product). Additionally, the model for calculation of the activation energy was not given in the literature.

Table 2.   Activation energy of PGDN estimated with the Kissinger and Ozawa models

Explosive	Ozawa		Kissinger		E_a from literature [12] $[kJ \cdot mol^{-1}]$
	Correlation factor (R^2)	E_a $[kJ \cdot mol^{-1}]$	Correlation factor (R^2)	E_a $[kJ \cdot mol^{-1}]$	
PGDN	0.9982	133.07	0.9980	134.78	168.45

3.3.2 TG/MS Analysis

The results of TGA concerning the thermal decomposition of PGDN are related to those obtained by DSC analysis. In fact, the decomposition temperature of PGDN increases with increasing heating rate (Figure 7). However, the values obtained (between 120 and 165 °C) are different from those in Table 1. This may be due to differences in the operating principles of the two techniques (DSC and TGA).
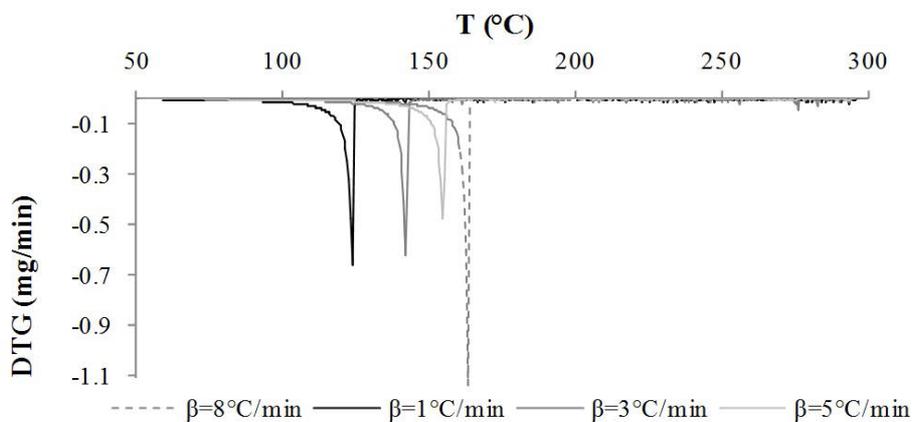
Figure 7.   DTG curves of PGDN.

The temperature of decomposition determined by TGA, using a heating rate 8 °C·min^{-1} corresponds to the temperature of decomposition found by DSC using 1 °C·min^{-1}. The rationale behind this discrepancy is the following: the TGA experiment is carried out in an open system (open crucible), which allows simultaneous evaporation/vaporization and thermal decomposition phenomena, thus the decomposition temperature is observable at a lower temperature [13, 14].

The thermal decomposition of PGDN was followed by mass spectrometry. The appearance of neither H_2O, CH_4, and O_2, nor N_2, CO, and NO_3 was observed in the decomposition products. Nevertheless, peaks at m/e = 30, 44 and 46 are

observed (Figure 8); they can be respectively related to NO, C_3H_8, and NO_2. This result is found at all heating rate.
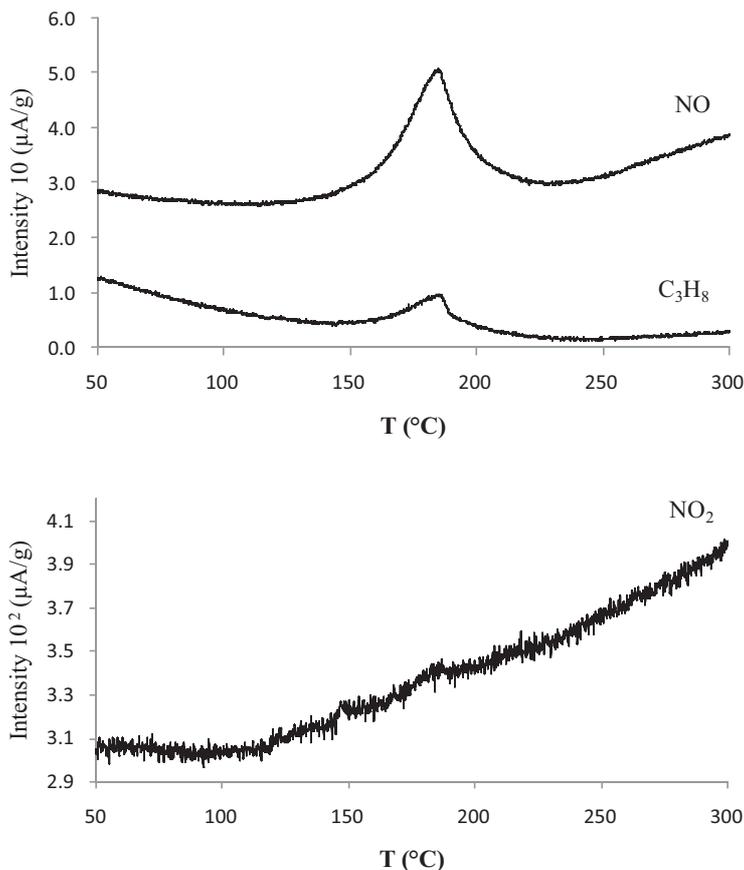

Figure 8. NO, C_3H_8 and NO_2 TPD profiles obtained by mass spectrometry at a heating rate of 3 °C/min.

3.4 Vapour pressure

3.4.1 The post processing

The vapour pressure and enthalpy of vaporization of PGDN were measured using TGA methods by exploiting the Langmuir and Clapeyron equations, which are expressed by the following equations [15]:

$$P = k\nu \tag{1}$$

$$\ln(P) \; = \; B - \frac{\Delta H_V}{RT} \tag{2}$$

where P is the vapour pressure (Pa), k is a constant including the vaporization coefficient and v is related to the constant mass loss rate $(dm/dt)(T/M)^{1/2}$, where T is the temperature and M is the molecular mass. The value for k was obtained from the known vapour pressure of benzoic acid in the temperature interval (298.15-343.15 K) using isothermal TGA.

ΔH_v (kJ·mol^{-1}) enthalpy of vaporization, T is the absolute temperature (K). The constants R and B are the ideal gas constant (J·mol^{-1}·K^{-1}) and a constant specific to a given instrument, respectively.

3.4.2 Constant of calibration

The Table 3 shows the mass loss rate of the benzoic acid in the temperature interval (298.15-343.15 K); these values were used to calculate υ.

Table 3. Mass loss rate values of benzoic acid at different temperatures using isothermal TGA

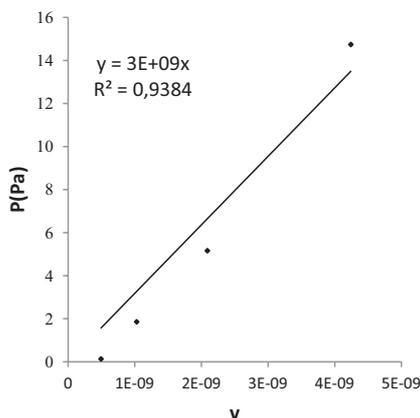| Temperature [K]	Mass loss rate [kg·s^{-1}]	Vapour pressure [Pa] [6, 11]	υ [kg$^{1/2}$K$^{1/2}$mol$^{1/2}$s^{-1}]
298.15	−1.00E-11	0.130	4.94E-10
323.15	−2.00E-11	1.855	1.0288E-09
333.15	−4.00E-11	5.159	2.0892E-09
343.15	−8.00E-11	14.740	4.2407E-09

Figure 9. Determination of the calibration constant by the benzoic acid parameter curve.

The calibration constant k = 3E + 09 was determined using the graph represented in Figure 9; this parameter was exploited to calculate the vapour pressures of PGDN.

3.4.3 Vapour pressure of PGDN

Table 4 shows the vapour pressures of PGDN in the temperature range 298.15-343.15 K. At ambient temperature, the vapour pressure of PGDN was 2.54 Pa, rather low compared to the rare literature value related to the estimation of the vapour pressure of PGDN (11.59 Pa, Gaworski *et al.* [16]). Nevertheless, the new work related to some explosives which are presented in Table 5 [7], shows that the value of the vapour pressure of PGDN determined by TGA sounds reasonable when compared to EGDN which is more volatile than PGDN.

Table 4. Vapour pressure and TGA parameters of PGDN

Temperature [K]	Mass loss rate [kg·s^{-1}]	υ [kg$^{1/2}$K$^{1/2}$mol$^{1/2}$s^{-1}]	Vapour Pressure [Pa]
298.15	−2.00E-11	−8.48E-10	2.54
323.15	−3.00E-10	−1.32E-08	39.7
333.15	−5.00E-10	−0.24E-08	67.2
343.15	−1.00E-09	−4.55E-08	136

Table 5. Vapour pressure of some common explosives [7]

Explosive	Reference	Temperature range [°C]	Vapour pressure at 25°C [Pa]
Nitromethane	McCullough	55-101	4980
TATP	Oxley 2009	15–50	8.66
EGDN	St. John	25	3.7
PGDN	**This work**	**25-70**	**2.54**
NG	St. John	25	0.031
PETN	St. John	25	0.0007
TNT	Dionne	25	0.00077
Picric acid	Cundall	40.9-132.9	9.7E-5
RDX	St. John	25	8E-5
DATB	Cundall	92.8-176.8	5.44E-6

The same table shows that, compared to some common explosives, PGDN has a considerable vapour pressure value at ambient temperature, and it seems that it could be very useful as a chemical taggant in explosive detection.

3.4.4 Enthalpy of vaporization of PGDN

Figure 10 shows the Clausius-Clapeyron plots ln(v) *vs.* 1/T of PGDN. According to Equation 2, the enthalpy of vaporization is obtained from the slope of the linear regression which had a value of 32.92 kJ·mol^{-1}. Compared with the same category compounds (EGDN and NG) presented in Table 6, the enthalpy of vaporization of PGDN is the lowest, probably due to the fact that in the case of PGDN the decomposition starts below its boiling point, and thus does not need a lot of heat for the vaporization transition.

Table 6.   Enthalpy of vaporization of some liquid nitrate ester explosives

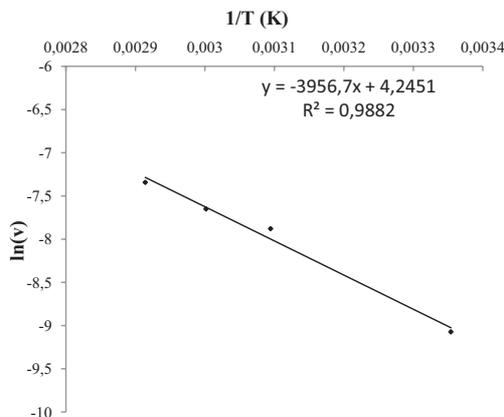| Explosive	Reference	Temperature range [°C]	Enthalpy of vaporization [kJ·mol^{-1}]
PGDN	[16]	-	42.49
PGDN	**This work**	**25-70**	**32.93**
EGDN	[17]	25	55.2
NG	[17]	68-192	104.5

Figure 10. Determination of the enthalpy of vaporization of PGDN by the rearranged Clausius-Clapeyron curve.

4   Conclusions

The synthesis of PGDN was successfully achieved and the yield was acceptable. Physicochemical characterization has allowed conclusions regarding the purity of the product.

The thermal decomposition of PGDN produces different gases which

were identified by TG/MS analysis, and are not the same as those in the case of detonation.

The thermal decomposition of PGDN has shown that the temperature of decomposition depends on both the method and heating rate used. The technique used for its determination should be stated.

TGA can be used for the estimation of the vapour pressure of PGDN, and the results have shown that PGDN is a good candidate as a chemical explosive taggant for forensic detection. It possesses several advantages which would allow it to be used in both commercial and military explosives. In addition, in contrast to an inert chemical taggant (DMNB), the detonic properties of PGDN allow for perfect energetic compatibility with explosives.

The use of propylene glycol, which is not considered a toxic compound and presents no environmental hazards, in the synthesis of PGDN, consolidates the use of PGDN among the liquid nitrate ester list (EGDN, NG *etc*.).

The forensic pre-blast detection of explosives requires that the taggant used must be easy to detect, and possess energetic characteristics. The synthetic process and the precursor used in the synthesis of PGDN, and its high vapour pressure make it a suitable liquid nitrate ester taggant.

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