CASE REPORT

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Mass spectrometry of the soot left after ethylene oxide explosion answers some questions on the crash of Polish Air Force Flight 101

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Abstract

The Polish TU 154M plane, Polish Air Force Flight 101, had crashed near Smolensk on 10th of April 2010. The crash was investigated by The Interstate Aviation Committee, whose conclusions were questioned by a number of Polish scientists. The cause of the crash still appears to be incompletely documented and requires additional evidence. In this paper, investigations of a solid material eluted from a piece of cloth of one of the victims of the crash are described. High resolution mass spectrometry was applied to analyze the soot left after controlled ethylene oxide (EO) explosions, performed under different conditions. These included electric ignition of EO vapors in a large volume steel container, and explosions of glass tubes filled with liquid EO, stimulated by thermally initiated explosions of pentaerythritol tetranitrate (PETN). One of these explosions was conducted in the vessel used for the electric ignition of EO and the other in a hermetically locked, small volume container. It was shown that the soot comprises a set of C_2H_4O homopolymers and copolymers whose characteristic MS patterns are condition-dependent. The MS spectrum of the postcrash sample referred to above reveals a number of polymers that are also present in the soot obtained in PETN-initiated ethylene oxide explosions. It can be concluded that the piece of cloth was subjected to an EO explosion initiated by an explosion of energetic material, possibly PETN. Similar control experiments with ethylene glycol (EG) showed that the polymers identified in the investigated postcrash sample could not originate from exploding EG.

KEYWORDS
copolymers, EG, EO, ethylene glycol, ethylene oxide, high resolution mass spectrometry, homopolymers, MS, PETN, Polish Air Force Flight 101 crash, postexplosion soot profile

Highlights

- Crash of Polish Air Force Flight 101.
- Examination of cloth of a plane crash victim.
- High resolution mass spectrometry of the slowest TLC fraction from a piece of cloth.
- Ethylene oxide and ethylene glycol postexplosion soot profiles.
- Control ethylene oxide and ethylene glycol explosions initiated with PETN.
- Soot components as long-lasted evidence of explosion.

1 | INTRODUCTION

The Polish TU 154M plane had crashed near Smolensk 10th of April 2010. The reason of the crash was investigated by The Interstate Aviation Committee (IAC), and the results of the investigation were published [1]. It was concluded that the plane had crashed after its collision with trees and the ground. However, many accident circumstances have been left without convincing explanation, including a rather wide distribution of the plane debris and serious disintegration of the bodies of victims. These drawbacks of the official document pushed a number of Polish scientists to open an academic debate on the case. A committee gathering more than 100 specialists of different disciplines was created. The research activity of this body was presented in a series of four yearly meetings in years 2012–2015, held under a common name The Smolensk Conference. A summary of the acquis of these meetings was published in 2015 [2]. Its main conclusion is that an explosion on board of the Polish Tu 154M plane was the most probable cause of the crash. In the last few years, several papers addressing problems connected with the crash were published by the Conference participants in international journals [3–6]. The authors discuss information from the Terrain Awareness and Warning System (TAWS) installed on the crashed plane, the influence of the damage of the aircraft wing on its aerodynamic performance and the forms of damage of the aircraft components in their final state. In all the papers, arguments supporting the above-mentioned conclusion of the Smolensk Conference meetings are reported.

The question of cause of the crash has also been investigated by an official body, namely, The Smolensk Investigation Commission/Subcommittee, created on February 2016 by the Ministry of National Defense, Republic of Poland. That body continues the investigation questioning the IAC conclusions. Also, starting from January 2016, The National Public Prosecutor's Office (NPPO), Republic of Poland, still continues investigation on the matter, formerly carried on by the Chief Military Prosecutor Office. Among the inquiries undertaken by the NPPO, there are re-investigations of the samples collected from the after-crash debris by Polish prosecutors in Smolensk in September 2012. To ultimately resolve the question of the possible occurrence of explosives on the debris, since May 2017 the samples have been investigated in the Forensic Laboratory of the British Police. The results of these investigations have not been disclosed yet. Earlier examination, conducted in the Central Forensic Laboratory of the Polish Police (CFLPP), was concluded with a statement of the absence of traces of explosives on the samples. However, the methodology employed in the latter investigations was questioned by participants of The Smolensk Conference [7].

As a Smolensk Conference participant, I was involved in the physicochemical examination of a fragment of cloth belonging to one of the crash victims. The victim's relative had received the cloth fragment in Moscow on 14th of April 2010 from the hands of a Polish prosecutor present then in the Russian Center of Forensic Medical Expertise in Moscow. In November 2012, it was passed to the researches involved in The Smolensk Conference initiative for investigation. The preliminary but inconclusive results of some physicochemical examinations of

a piece of this material were reported during the 2013 meeting of The Smolensk Conference [7]. Usually, postexplosion analysis is based on the identification of traces of the original explosives [8, 9]. However, we got access to the fragment of the clothes 2 years after the crash, and we did not detect any of energetic compounds using instruments at our disposal at that time [7].

Therefore, we decided instead to trace decomposition products of such compounds. In this paper, we report a list of compounds extracted from the above-mentioned piece of cloth and compare it with the set of compounds identified in the postexplosion soot of ethylene oxide (EO) and ethylene glycol (EG), obtained in control experiments at different conditions. In four of them, the explosion of EO or EG was initiated by thermally stimulated explosion of a small amount of pentaerythritol tetranitrate (PETN). As was revealed in a lecture at the 2014 meeting of The Smolensk Conference, multiple occurrences of the traces of PETN were detected by one of the four chromatographic methods used in the CFLPP in the already mentioned investigations of the Smolensk samples. The speaker exceptionally obtained an official permission of insight into the corresponding report of the CFLPP, which has not been disclosed until now.

2 | MATERIALS AND METHODS

2.1 | The origin of sample A

The Russian Federation investigation services had assigned the victim's body number 88. In the academic investigation, for this person the symbol 5/19 had been used [10], where 5 and 19 are the number of sector in the crash site and number of the body in the sector, respectively. Prior to The Smolensk Conference investigation, the fragment of the victim's cloth, of an irregular shape and the surface of about 600 cm^2, had been stored in dark at room temperature. In its original form, it was clumped with a drop-shaped piece of metal 4 cm long, which underwent melting and caused local damage of the fabric. Using energy-dispersive X-ray spectroscopy (EDS), it was shown earlier that it consists from Zn with ca. 4% of Al [7]. This composition corresponds to the zinc alloy (Zamak), which melts at 385°C. The sample used in the investigations reported presently is a piece of the original cloth fragment of irregular shape with dimensions of ca. 9 × 4 cm (total surface of ca. 46 cm^2) and weight of 1.78 g [7]. The selected piece was not in contact with the metal fragment and did not show deformations, which might have been caused by impact of a high temperature. Prior to its clumping to the cloth, the considered piece of metal must have been positioned far from it, where it could have been exposed to a much higher temperature than that suffered by the cloth.

The procedures of extraction of the above described sample of fabric and thin-layer chromatography (TLC) of the extract were reported previously [7]. Here we analyze the slowest TLC fraction only which will be further referred to as sample A. The fraction was chosen for the analyses since it displayed very rich MS spectrum.

2.2 | Preparation of control samples C1, C2, C3, EG1, EG2, and EG3

2.2.1 | Control sample C1

0.5 ml of liquid ethylene oxide at +3°C was poured on the bottom of a 10 L steel thin-wall container with a steel lid pressed tight with a spring and fitted with an electric detonator (tungsten wire). After waiting 20 s, the electric ignition was applied. A mild explosion took place accompanied with the explosion flush, and most of the gases formed were released through the lid raised by the internal pressure. The walls of the container after cooling were rinsed with 200 ml of MeOH, siphoned, and evaporated to dryness. 25 mg of solids was obtained.

For the preparation of control samples C2 and C3 ca. 0.5 ml of liquid ethylene oxide and ca. 100 mg of pentaerythritol (PETN) was used. Gaseous ethylene oxide was liquefied in a soda lime glass tube sealed from one end, embedded in a cooling medium. After filling, the tube was sealed from its other end (Figure S1 in Supplemental Information). PETN was sealed in a separate glass tube.

2.2.2 | Control sample C2

Tubes containing EO and PETN were placed on the bottom of the 10 L container used previously for obtaining control sample C1, but now the electric detonator was removed. The bottom of the container was heated by a gas burner. The explosion took place after ca. 5 minutes, accompanied with a strong explosion flush. Most of the gases formed were released through the raised cover, and the cover was firmly bent. After cooling, the walls of the container were rinsed with 200 ml of MeOH, siphoned, and evaporated to dryness. 35 mg of solids was obtained.

2.2.3 | Control sample C3

Tubes containing EO and PETN were placed in a thick-walled steel vessel with a thread, and the vessel was screwed up. The volume of the vessel was ca. 50 ml. The vessel was placed inside a laboratory electrical oven and heated up starting from room temperature. After ca. 20 minutes when ca. 280°C was reached on the oven thermometer, a sound of explosion could be heard. The explosion vessel was then cooled down and unscrewed. The soot from the vessel was eluted with methanol at room temperature. The solution was evaporated to dryness, and the obtained solid was used for MS experiments without any additional procedure.

2.2.4 | Control sample EG1

The same vessel was used as for sample C1, now equipped additionally with a small electric heater with 5 ml container placed inside of it. 0.5 to 1.0 ml of ethylene glycol was poured into the container.

Electrical heating was applied for 40 s to allow for a complete evaporation of EG. The amount of EG was selected so that the concentration of its vapors in air inside the 10 L volume vessel was within the explosive limits (3.2%–15.3 %(V)). After 40 s, the electric ignition was applied. A weak explosion occurred, and the resulting gases were released from under a lid raised by internal pressure. The walls of the container after cooling were rinsed with 200 ml of MeOH, siphoned, and evaporated to dryness.

2.2.5 | Control sample EG2

The experiment was conducted like in the case of sample C2. Now the ethylene glycol used was poured to the bottom of the vessel. The explosion was now much softer than in C2 experiment and without flash. The lid, now left undeformed, was only raised and some fumes exuded.

2.2.6 | Control sample EG3

The experiment was carried out like in the case of sample C3. Both, the ethylene glycol and PETN were embedded in glass tubes as in experiment C3. The sound of explosion was now much lower.

2.2.7 | Control samples AP1 and AP2

The samples are liquids used routinely in Warsaw laundries for protective treatment of clothes after chemical washing. They were obtained from two Warsaw laundries selected at random. They were analyzed as they were.

2.3 | MS ESI(+) measurements

Electrospray high resolution mass spectra were acquired using a standard TurboIon Spray ion source. Nitrogen was used as the nebulizing and curtain gas. ESI was carried out in a positive ion mode. Spray tip voltage was kept at 4500 V. The declustering potential was set to 85 V and the focusing potential to 380 V.

All peaks with the relative intensity above 3% of that of the highest peak were analyzed in the spectrum of sample A. In the spectra of control samples C1, C2, C3, AP1, and AP2 the corresponding thresholds were set at 2%, 2%, 4%, ca. 7%, and 2%, respectively. Occasionally, less intense peaks were also analyzed. In the spectra of control samples EG1, EG2, and EG3, this threshold could be set at 0.3% due to the small number of signals present.

The discrimination criterion adopted for the assignments of molecular formulas to the experimental m/z values was the reduced error $\delta = 10^6 \times |[(m/z)_{calc} - (m/z)_{exp}]/(m/z)_{exp}$. For series of N equidistant peaks, the reduced error was calculated according to the formula

$$\delta = [(\delta_1{}^2 + \delta_2{}^2 + ... + \delta_N{}^2)/(N-1)]^{1/2},$$

where δ_k is the reduced error for the k-th peak in the series. For the reported assignments the values of δ do not generally exceed a few ppm. The use of mDa rather than ppm has been suggested [11]. However, in most cases in the series of polymers discussed in this paper, the chain length scatter is relatively small. The discrimination criterion was about 1.0 mDa, and mostly the differences between measured and calculated values were on the order of 0.5 mDa.

2.4 | Equipment and materials

High resolution mass spectra were measured using AutoSpec Premier (Waters) or MaldiSYNAPT G2-S HDMS (Waters) spectrometers, both equipped with an ESI ionization source. MS/MS spectra were measured using LTQ-Orbitrap QExactive mass spectrometer (Thermo Fisher Scientific).

The following solvents and materials were used: methanol 99.8% pure pa (POCH, Gliwice, Poland); CD_3OD, D-99.8%, (Sigma-Aldrich, USA); and $CDCl_3$, D-99.8%, (Sigma-Aldrich, USA); ethylene oxide (SigmaAldrich) and ethylene glycol pure pa (POCH, Gliwice, Poland) were used without purification; PETN was extracted from the popular medicine pills (pentaerythritol tetranitrate) with acetone. Its ^{1}H NMR spectrum confirmed identity with published data [12] and showed no impurities.

The DSC measurement was performed using Mettler-Toledo DSC1 STARe system at a heating rate of 10°C/min under a dry N_2 atmosphere and at a constant flow (50 ml/min) over a range of temperature from 25 to 300 °C. The obtained data were analyzed using the STARe software provided by Mettler Toledo. The total weight of the sample was accurately weighted into a standard 40 µL aluminum crucible using Mettler-Toledo XS105 DualRange balance.

The ^{1}H NMR spectra of PETN and the fabric were measured at 25°C in CD_3OD and $CDCl_3$, respectively, calibrated against the chemical shift of the protonated residuals of methanol, 3.34 ppm, and chloroform, 7.26 ppm, respectively. The UNITY500plus (Varian) three channels spectrometer with a 5 mm 1H{13C/15N} PFG triple probe was used, equipped with a high stability temperature unit.

3 | RESULTS AND DISCUSSION

Since the piece of cloth belonging to victim 5/19 of the crash was not provided with any kind of label certifying its composition, we performed several identification tests for it, as described in the Supplemental Information. The conclusion is that the main component of the fabric is polyethylene terephthalate (PET), with a possible admixture of comonomers [13]. The presence of organic silicon components used in the textile industry as flame retardants was also detected. In the DSC measurements on a thread from the fabric melting occurred at 254.4°C, which is in a perfect agreement with the melting temperature of PET [14] (Figure S3, Supplemental Information). Therefore, the discussed piece of fabric had not been exposed to temperatures in this range, unless in a very short period of time.

The high resolution MS ESI(+) spectra of sample A and six control samples C1, C2, C3, EG1, EG2, and EG3 are shown in Figure S4A and S4B (Supplemental Information).

The MS spectrum of sample A is quite complicated. It contains 960 peaks with the intensity above 3% of that of the highest peak. Only 6 of them could not be assigned. 139 peaks come from contaminations of different types. In the latter assignments, the reported, comprehensive lists of typical contaminants occurring in MS ESI(+) spectra were consulted [15]. The remaining 820 peaks are arranged in regular series, where the interpeak distance expressed in mass units is equal either to the mass of the C_2H_4O group or aliquots of this value. In each series, envelopes of the peak intensities are generally bell-shaped and show more or less pronounced distortions of symmetry around their maxima. The discussed series of signals may therefore come from polymeric/oligomeric species containing chains of C_2H_4O units. In the discussed MS spectrum, 30 series of polymers containing the (C_2H_4O) mers could be identified if three singular peaks containing these mers, A-1, A-3, and A-7, are also included for the sake of nomenclature compactness. Molecular formulas of the polymers are listed in Table S1 (A-1 to A-33, Supplemental Information), and their spectra are displayed as Kendrick plots in Figure 1 and as separated series in Figure S5. Five polymers were identified as homopolymers of ethylene oxide, fifteen polymers as ethylene oxide/oxomethylene copolymers, seven as copolymers of ethylene oxide with the (C_3H_6O) mers, and three as other copolymers of ethylene oxide. The highest peak (A-1) was assigned to a copolymer possibly containing also the (C_2H_2) mers. Two series (A-15 and A-18) were tentatively assigned as ethylene oxide polymers bound with a leftover from the framework of PETN. The assignments were made by considering the collection of nongaseous products of the decomposition of PETN under different conditions, reported in References 9 and 18 to 21. Seven polymers not assigned or not containing the EO mers were also found in this spectrum. They are listed in Table S2 (A-34 to A-40) together with fifteen singular peaks and series assigned to known contaminants, and cationic

FIGURE 1 Kendrick plots [16] of polymers analyzed in this paper using $^{12}C_2{}^1H_4{}^{16}O$ as a base (International Union of Pure and Applied Chemistry [I.U.P.A.C] mass scale). Fractional part of Kendrick mass was calculated using Z = 2, x = 41 and R = 44.026215 [17]. Only polymers containing C_2H_4O units are shown, blue circles – homopolymers of EO; red circles –copolymers of the same formula as present in sample A; pink – copolymers with leftovers from PETN, black – other copolymers containing EO units. The size of circles are proportional to the square roots of intensities of the corresponding peaks, what allows for visualization of very weak series [Color figure can be viewed at wileyonlinelibrary.com]
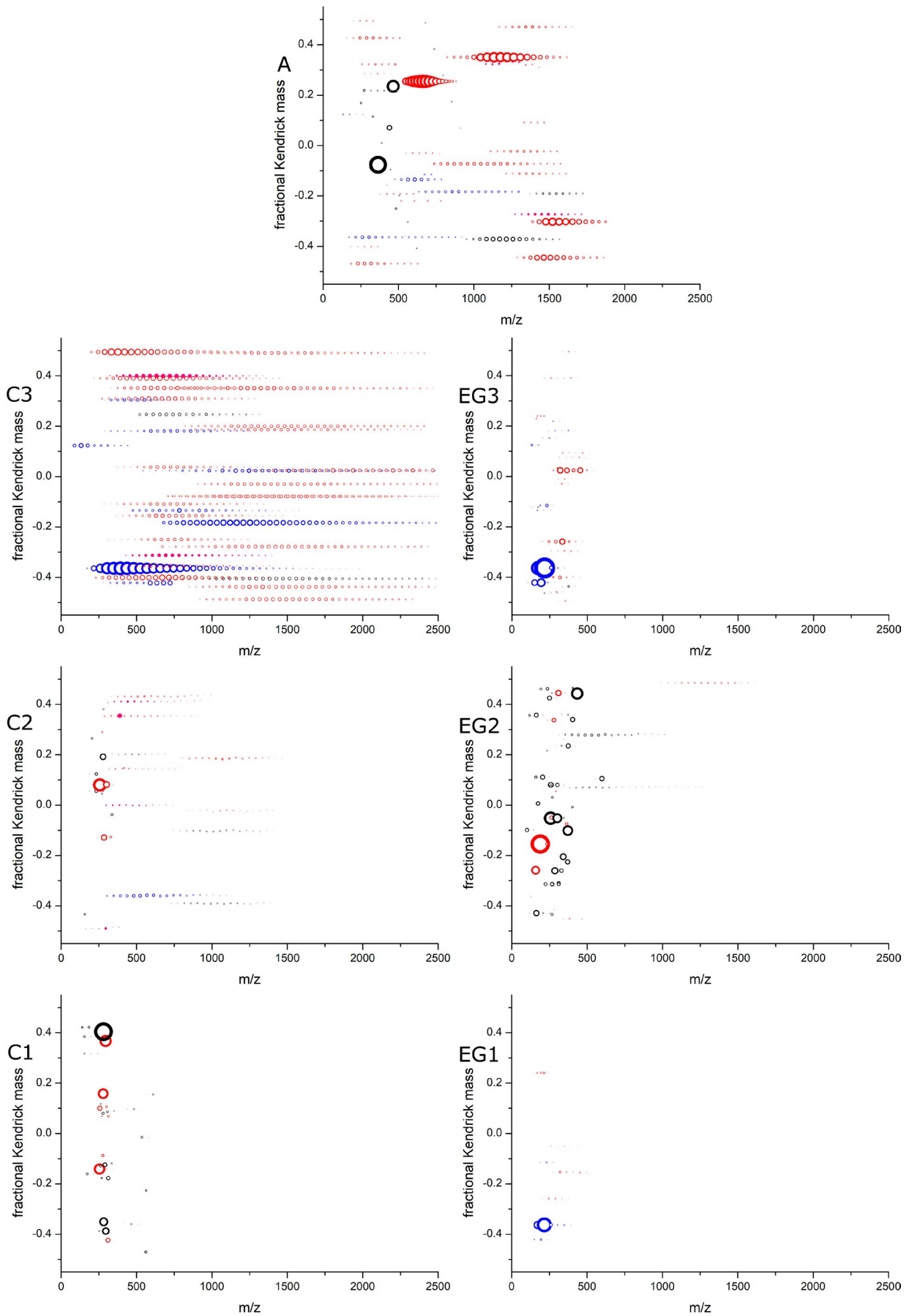
and nonionic antistatic agents used in the industry for chemical finishing of textiles (A-41 – A-55). These peaks are shown together in Figure S6. All peaks in the figures are presented with their relative intensities. Residuals from the MS ESI(+) spectra left after deleting all peaks mentioned above are shown in Figure S7.

In the products of textile industry, there are a lot of substances containing the C_2H_4O units. In the considered case, these are present in the basic component of the fabric, i.e., PET. However, as argued above, the MS spectra of sample A indicate a remarkable occurrence of compounds containing homo–polymeric chains $(C_2H_4O)_n$, where n adopts values from a set of sequential integers. Thus, it is very unlikely that the corresponding MS patterns come from PET or products of its degradation. On the other hand, linear structures $X-(C_2H_4O)_n-Y$ are ubiquitous in the mixtures used for the chemical finishing of textiles [22]. They also occur in the detergents used in professional chemical washing and a postwashing treatment of clothes. To give an illustrative example, we measured MS spectra of two mixtures used for the latter purpose. Samples of the mixtures, to be further denoted by AP1 and AP2, we obtained from two randomly selected Warsaw laundries. The spectrum of sample AP1 is shown in Figure S8 in the Supplemental Information. In it, series of equidistant peaks characteristic for linear compounds of the form $X-(C_2H_4O)_n-H$, with X standing for $C_kH_{2k+1}O$, are predominant (see Table S3). Such compounds are used as nonionic antistatic agents. The MS spectrum of sample AP2 (not shown) is poorer than that of sample AP1. The dominating components of sample AP2 prove to be same as those in sample AP1. We can suspect that the piece of fabric discussed presently comes from the cloth which at least once underwent washing in one of the Warsaw laundries. Actually, series A-48 was assigned as an antistatic agent of the above-mentioned sort. Moreover, two series, A-45 and A-55, were assigned as cationic surfactants used in the chemical washing of clothes [23] (Table S2).

Despite the facts described in the above paragraph, some characteristic features of the MS spectrum of sample A induced us to consider the possible contact of its parent fabric with the deflagration, combustion and/or explosion of ethylene oxide. In what follows, arguments in favor of this hypothesis will be presented.

Another compound that might be suspected to be the source of the features under consideration is ethylene glycol. Its vapor possesses explosive properties. Actually, it was proposed that EG ignition was the cause of the Apollo-Saturn 204 incident [24]. It is known that mixtures of ethylene glycol with water in large quantities (hundreds of kilograms) are used as aircraft de-icing fluids (ADF) [25]. However, in the Tu-154M aircrafts an electrical de-icing system was used [26]. Nevertheless, due to the very close chemical relationship of these compounds, we considered it important to investigate the behavior of ethylene glycol under conditions similar to those used for ethylene oxide.

EO is used as an explosive because during its decomposition mostly gaseous products are formed. In some cases, nongaseous products of explosion were also observed. The soot was found in the postexplosion mixtures, obtained under a variety of experimental conditions [27]. The composition of the soot was not analyzed in

that case, but poly(ethylene-oxide) was identified in the nonvolatile residue formed in deflagration of EO vapor [28].

One of the most striking features of the MS spectrum of sample A is an abundance of signals from copolymers of ethylene oxide with oxomethylene, of the molecular formula $(C_2H_4O)_n(CH_2O)_m$ (see data in rows 9–23 in Table S1). The nature of those copolymers was confirmed with ms/ms experiments carried for chosen peaks of two series (Table S1). The values of m range from 1 to 21, but not all values from this range are represented. In the structure of the relevant spectral patterns, no series with interpeak distances equal to either the mass of CH_2O or an aliquot of it and having a regular envelope can be discerned. The assigned molecular formulas correspond either to cyclic structures of the copolymers or to such structures associated with one water molecule bound to them by hydrogen bonding. In the latter case, one can also consider linear structures with hydroxylic groups at both ends, but in the literature involving MS ESI (+) spectra of polyethers, complexes thereof with water are usually reported (see, for example, Ref. 15). The question which of these two eventualities is realized in practice is not crucial for the issues addressed in this work. Following the literature, in what follows the option with associated water molecule will be adopted.

In the MS spectrum of sample A, apart from those above mentioned, series of signals from homopolymers of EO, $(C_2H_4O)_n$ and $(C_2H_4O)_n(H_2O)_1$, are present, although their overall intensity is rather low (see data in rows 3–7 in Table S1). As is well known [15], such homopolymers are ubiquitous contaminants contributing to the MS ESI spectra, because of a widespread occurrence of chemicals containing polymeric EO in objects of everyday use. The question whether in the considered case these homopolymers are merely contaminants will be addressed later on.

At variance with the homopolymers of EO, the copolymers $(C_2H_4O)_n(CH_2O)_m$ cannot be found on the lists of contaminants polluting the MS ESI(+) spectra. In particular, it is extremely unlikely that, under conditions of the MS ESI (+) experiment, such compounds could have evolved from the assortment of species used in the chemical finishing and washing of textiles. Comprehensive lists of such species are reported in Refs. 22 and 23. In general, the latter contain linear chains of the C_2H_4O units, bearing massive substituents at one end and atom H at the other. For example, the MS spectrum of sample AP1 (Figure S8) reveals the occurrence of substituents of the form $C_kH_{2k+1}O-$ (Table S3). It does not contain peaks coming from compounds containing copolymeric chains (or cycles) of the C_2H_4O and CH_2O mers. It is noteworthy that signals from bare homopolymers of EO could not be detected in it, either. On the other hand, compounds of both these types dominate in the soot left over after controlled explosion of ethylene oxide, performed by us.

The homo- and copolymers of the types mentioned above were obtained in the experiments conducted by us to provide a comparative material to that of sample A. We carried out an electrically induced explosion of ethylene oxide under leaky conditions (control sample C1), and thermally induced explosions of ethylene oxide with addition of pentaerythritol tetranitrate (PETN) under same and

harsh conditions, samples C2 and C3, respectively. In the two latter experiments, both EO and PETN were sealed in separate glass tubes. The harsh conditions were realized by performing the thermally induced explosion in a hermetically locked steel vessel (sample C3). We also conducted three experiments with ethylene glycol, mimicking closely those involving ethylene oxide. We used the same molar amounts of ethylene glycol and similar experimental conditions. The EG counterparts of experiments C1, C2, and C3 are labeled by EG1, EG2, and EG3, respectively. The treatment of the postexplosion soot is described in the Materials and Methods section. One may expect that the explosions in leaky conditions to some extent mimic an explosion in a partially open space.

The experiments C2 and C3, i.e., ones with the addition of PETN, afforded to lower the starting temperature of explosion. Namely, 429°C was reported as the autoignition temperature of EO [29], while 160°C is sufficient to stimulate the explosion of PETN [30]. It was also tempting to check if compounds containing leftovers from the framework of PETN could be detected in the soot.

The high resolution MS ESI(+) spectra of samples C1, C2, and C3 are set together in Figure 1 and Figure S4A (Supplemental Information) along with the spectrum of sample A. At a first glance one can notice significant differences between the spectra of control samples. The spectrum of sample C1 consists predominantly of singular peaks, while the spectrum of sample C2 in addition to singular peaks contains readily discernible series of peaks. Both samples were obtained under relatively low pressure due to a large volume and intentional use of a nonhermetical locking of the reaction vessel. However, the use of PETN created more drastic conditions in the latter case. On the other hand, the spectrum of control sample C3 is dominated by peaks arranged in regular series indicating the occurrence of chains of same mers. This sample was obtained under large pressure, hundreds of times higher than in the case of samples C1 and C2. The choice of conditions for the control experiments is somewhat arbitrary but a precise mimicking of factors featuring the final state of sample A is impossible from obvious reasons.

In the spectrum of control sample C1 twenty-seven polymers containing (C_2H_4O) mers were identified, C1-1 to C1-27, Table S4. Seven of them were copolymers with (CH_2O) and twenty were copolymers with several kinds of mers, namely, (C_2H_2), (C_2H_4), (CO), and (CO_2). The occurrence of such mers might be explained either by the presence thereof among the products of pyrolysis of ethylene oxide [31] or as a result of polymer chain rearrangement [32–36]. In the latter case, it frequently corresponds to the different termination of the polymer chain. As already mentioned, the MS spectrum of this sample does not contain long and regular series of peaks. In it, either singular peaks or at most triples of equidistant peaks are present. In the discussed spectrum, fourteen additional species not containing (C_2H_4O) mers were identified (C1-28 to C1-41), all of them being represented by singular peaks (Table S5 and Figure S6).

The spectrum of control sample C2 is a bit richer. In it, twenty-five polymers containing (C_2H_4O) mers, C2-1 to C2-25, were found (Table S6). One of them is a homopolymer, seven are copolymers

with oxomethylene, and three copolymers contain the (C_3H_6O) mers. Nine copolymers containing the (CH_2O), (C_2H_4), (CO), and (CO_2) mers are also present but in a smaller proportion than in sample C1. Leftovers from the framework of PETN could be tentatively identified in five series of polymers. However, the corresponding assignments are not unique, what will be discussed below. In general, the series present in this spectrum are much longer than those in the spectrum of sample C1. Another six polymers without the EO mers, C2-26 to C2-31, were assigned. They are listed in Table S7. Yet, in this spectrum, we were not able to assign 52 singular peaks listed in the same table, i.e., C2-32 to C2-83. However, it should be noted that they make a relatively small contribution to the spectrum, as can be seen from a comparison of the corresponding parts of Figure S4A and Figure S6.

The MS spectrum of sample C3 contains as much as 1300 peaks (including all identifiable isotopic peaks) of the intensities exceeding 4% of that of the highest peak. All of them were assigned. In the spectrum, 33 series from polymers containing the (C_2H_4O) mers were identified. Eight of them come from homopolymers of ethylene oxide and twenty-three from copolymers of ethylene oxide with oxomethylene (see Table S8, Figure 1, and Figure S9). Also, for this sample, the nature of ethylene oxide/oxomethylene copolymers was confirmed with ms/ms experiments carried for chosen peaks of two series (Table S8). Two series may come from compounds containing leftovers from the framework of PETN, see below. Signals of other types of polymers do not exceed the adopted level of intensity (4%). Below this level, peaks cannot be uniquely separated out. The residual left after deleting from the MS spectrum the 1300 identifiable peaks is shown in the left bottom panel of Figure S7.

All polymers containing the (C_2H_4O) mers, found in samples A and C1 – C3, have been compiled in Table S9. Copolymers of ethylene oxide with oxomethylene were present in all three control samples and in sample A. This appears to be a crucial finding for the conclusions of this work. In each sample, the lengths of the series of these copolymers vary, and their number and the ratio of the (CH_2O) to the (C_2H_4O) mers are different. Homopolymers of ethylene oxide identified in the spectrum of sample A, which in a general context can be suspected to be contaminants, were also present in the spectra of control samples C2 and C3. In the latter samples, they can hardly be qualified as being only contaminants. Their occurrence in postexplosion soot of EO appears to be natural as being expected on chemical grounds. Copolymers of ethylene oxide with the (C_3H_6O) mers present in the spectrum of sample A were found only in the spectrum of control sample C2. The base peak of one series of these compounds (C2-1) is the strongest peak in the spectrum. The comments about copolymers with oxomethylene also apply to other copolymers listed in the bottom section of Table S9. They are present in sample A and the control samples C1 and C2. In sample A two series of copolymers, A-15 and A-18, may contain leftovers from the framework of PETN.

A comparison of the data in the individual columns of Table S10 reveals that sample A contains substances of the same formula as those occurring in the control samples. In particular, out of all

33 polymers present in sample A and containing the (C_2H_4O) mers 2 have their identical counterparts in all three control samples. These are compounds of the general formula $(C_2H_4O)_n(CH_2O)_m$. If the homopolymers of C_2H_4O detected in the spectrum of sample A are included, further 9 polymers containing that mer and present in this sample are also present in two control samples, C2 and C3. One polymer has its counterparts in C1 and C3. Finally, 11 polymers from sample A have their counterparts in only one control sample, of which 6 occur in sample C2 and 5 in sample C3. It means that as much as 23 polymers contained in sample A have their counterparts in at least one of the control samples (see Table S10 and Figure 1). It is to be stressed that polymers having the formula of $(C_2H_4O)_n(CH_2O)_m$ can be regarded as fingerprints left by deflagrated and/or exploded EO.

If the polymer lengths are disregarded, the assortment of EO copolymers in sample A shows greatest similarity to that in control sample C3. Under "similarity of copolymer assortments," we mean here that the samples being compared contain a significant number of EO copolymers having the same general formula. This observation can be inferred from the data in Table S10. It contains the list of 31 polymers identified in the spectrum of control sample C3. Almost each polymer from control sample C3 has its counterpart in sample A. These observations are visualized in Figure 1 with Kendrick plots. As will be shown later on, the distributions of chain lengths of the characteristic copolymers $(C_2H_4O)_n(CH_2O)_m$ in samples A and C3 are substantially different while a striking similarity in this regard is observed for samples A and C2.

Identification of the polymers containing leftovers from the framework of PETN requires additional explanation. Several formulas of products of the PETN decomposition under different conditions were already reported [9, 18–21]. In these compounds the quaternary central carbon atom may be substituted with the following groups: CH_2OH [9]; CHO [18], CH_3 [19], and NO_2 [19]. The use of fully ^2H and ^{15}N labeled PETN allowed for the identification of the CH_2OH, NO_2, OH, CHO, CH_2OCHO groups as the substituents [20]. Also, a polymer of the $(C_3H_4O_2)$ units was found to be a product of the PETN decomposition [21]. Some series of polymers analyzed in this work which match neither the $(C_2H_4O)_n(CH_2O)_m$ and $(C_2H_4O)_n(C_3H_6O)_m$ types nor the known contaminations could be interpreted as polymers bound to various leftovers of PETN. In these assignments, as substituents of the quaternary carbon atom all possible combinations of the seven groups listed above were tried. Only the structures with aldehyde groups were taken into account because only for them a facile binding to the polyoxyethylene(oxymethylene) chain can be expected. Copolymers with the $(C_3H_4O_2)$ mers were considered separately. In most cases isomeric structures can be found due to the multiple possibilities of positioning the CH_2 groups in the leftover and in the polyoxyethylene(oxymethylene) chain. This procedure applied to control samples yielded 3 chemically plausible isomers for series C2-4, 9 for C2-9, 6 for C2-10, and 5 for C2-23, whereas series C2-19 appeared to be copolymers of ethylene oxide with $(C_3H_4O_2)$. For series C3-7 and C3-17, 4 and 6 isomers were obtained, respectively, but both the series may be also assigned to a copolymer of ethylene oxide with the $(C_3H_4O_2)$ mer. For series A-18, four groups of isomers were found containing 4, 4, 12, and 24 (44 in total) possible isomers. Series A-15 was found to be composed from the $(C_3H_4O_2)$ and (C_2H_4O) mers.

Given the relatively large values of the m/z values of the considered series, assignments not involving leftovers of PETN and fitting the data with similarly low reduced errors (δ) might also be possible. Nevertheless, considering the fact that exploding PETN did contribute to the formation of samples C2 and C3, some of the assignments discussed above can with very high probability be correct. Thus, even if not fully persuasive, the above arguments provide a fair substance to the hypothesis that compounds containing leftovers of the framework of PETN combined with polymers of EO do occur not only in control samples C2 and C3 but in sample A as well.

In the cases where many chemically plausible molecular structures correspond to the given molecular formula containing a PETN leftover, for sake of compactness in Tables S1, Tables S6, and S8, only the molecular formula is listed for the series involved.

The numbers of peaks in the MS spectra of the soot obtained in experiments EG1 – EG3 with ethylene glycol are several times smaller than in the respective spectra of samples C1 – C3 (Figure 1 and S4B, Tables S11 to S13). Specifically, in the spectrum of sample EG3 above the 0.3% intensity threshold, only 103 peaks were found while that of C3 contains as many as 1300 peaks about the threshold of 4% (see Materials and Methods section). In the MS spectra of samples EG2 and EG1, the numbers of peaks were 160 and 35, respectively.

All peaks in the spectrum of the EG1 sample were assigned to homo- and copolymers of C_2H_4O with very short chains containing from 3 to 6 EO units. In the spectrum of the EG2 sample, 19 peaks corresponding to 7 polymer series containing 2 to 4 EO units could not be assigned. Most of the assigned peaks (112) in this spectrum correspond to C_2H_4O copolymers containing 1 to 4 EO units. A remarkable exception is series EG2-36 including the characteristic copolymers $(C_2H_4O)_n(CH_2O)_m$, with m = 2 and n ranging from 20 to 34. Other copolymers with relatively long chains are comprised in series EG2-34 and EG2-37 (Table S12). The peaks in these three series have very low intensities. The MS spectrum of the EG3 sample consists of peaks belonging to homo- and copolymers of the EO unit with numbers ranging from 1 to 7. No other polymers were found. In agreement with the published findings [37], to some peaks in the spectra of the EG samples, the C_2H_2O and CH_2O_2 mers could be assigned.

In contrast to the MS spectra of the C and A samples, neither polymers containing the C_3H_6O mers nor leftovers from the framework of PETN were found for the EG samples. As far as the crucial $(C_2H_4O)_n(CH_2O)_m$ copolymers are concerned (which dominate in sample A), ones identified in the three EG samples are analogs of those found in the corresponding three C samples. In the soot obtained in all six (C1 – C3 and EG1 – EG3) control experiments they occur in diverse amounts. However, in the EG1 and EG3 samples (Table S14 and Table S15, they contain much smaller numbers of mers than those occurring in samples A, C2, and C3. This is illustrated in Figures 1 and 2. In Figure 2, shares of the polymer chains

FIGURE 2 Top panel: distributions of lengths, n + m, of the copolymer chains $(C_2H_4O)_n(CH_2O)_m$ in control samples C1 – C3, and A. Bottom panel: same as top panel but for control samples EG1 – EG3, and A. On the y-axis, the sum of peak intensities of the chains having the same number of comonomers is given as a percentage of the total sum of intensities of the polymer peaks concerned, calculated for each sample separately [Color figure can be viewed at wileyonlinelibrary.com]
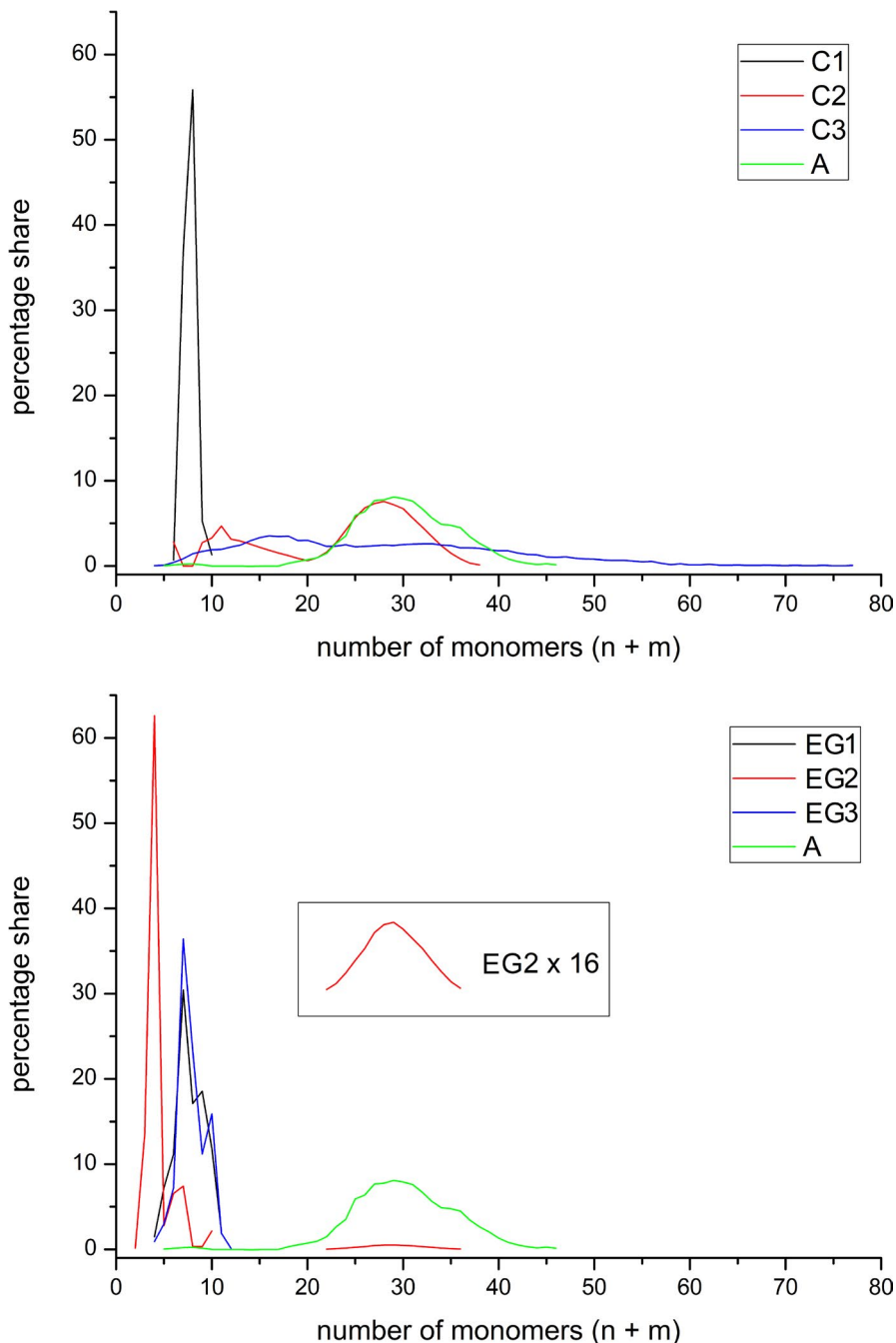
$(C_2H_4O)_n(CH_2O)_m$ against their lengths n + m are plotted. On the y-axis, the sum of peak intensities of the chains having the same number of comonomers is given as a percentage of the total sum of intensities of the polymer peaks concerned. In the top panel, the distributions of the chain lengths in samples C1 – C3 are compared with that in sample A. The bottom panel is same as the top one; however, it involves samples EG1 – EG3. It is seen from the plots that in sample A the distribution of lengths of the considered copolymers has a fairly regular bell shape extending between the values of n + m of 20 and 45, with the maximum located at about 31. In sample C1 the copolymer chains are too short to approach the interesting range. On the other hand, in sample C2 the distribution in the range 23 – 40 almost perfectly matches that of sample A. In sample C3, which was

produced under very high pressure, the distribution is diffuse, with the chain lengths reaching 77. The maximum of the distribution is now shifted down, to about 16, although in the interesting range it shows a plateau, with a remarkable intensity exceeding a half of that in the maximum.

In the case of samples EG (bottom panel in Figure 2), the distributions for EG1 and EG3 show a spectacular similarity. It is surprising because these samples were produced under extremely different conditions. The considered copolymers with longer chain lengths do not occur in them. An exception is sample EG2 which, apart from the abundant copolymers $(C_2H_4O)_2(CH_2O)_m$, with short chains (m = 1, 2, and 3), contains a series of ones $(C_2H_4O)_n(CH_2O)_2$, with n ranging from 20 to 34. They come with low intensities and their distribution

is bell-shaped (see inset in Figure 2). It also fairly fits that in sample A although in the latter the number of the CH_2O mers in the chain is diversified.

In summary, the longer copolymers $(C_2H_4O)_n(CH_2O)_m$ ($n + m > 15$) dominating in sample A were obtained only in control experiments C2, C3, and EG2, where EO was used in the two former and EG in the latter. In all these experiments, the formation of soot was initiated by explosion of PETN.

For all assigned polymers containing the C_2H_4O mer, their length distributions in the control samples and sample A are compared in Figure S10 in the Supplementary Information. Observations similar to those reported above can be inferred from the graphs shown there.

The close similarity of the polymer assortments found in samples A and C3 indicates that sample A resulted from an ethylene oxide explosion initiated by an energetic material. This conclusion is strengthened by the similarity of chain length distributions for the crucial polymers $(C_2H_4O)_n(CH_2O)_m$ in samples A and C2. In a limited form, the latter feature was also observed for samples A and EG2. However, the assortment of polymers created in all our experiments with EG is much poorer than that in sample A. Moreover, with the above described exception, the polymers obtained in these experiments have much shorter chains than those in sample A. We can therefore state that the combustion/deflagration/explosion of ethylene glycol as the origin of sample A is very unlikely.

In spite of large differences in the relative abundances of each type of polymer series the set of the C_2H_4O homo- and copolymers identified in the control samples C1–C3, one may call the postexplosion ethylene oxide soot profile. Thus, the above considerations afford to conclude that the investigated piece of fabric with very high probability was exposed to exploding ethylene oxide. Signals of the homopolymers of C_2H_4O occurring in the spectrum of sample A and generally recognized as unwanted manifestations of contaminants must at least in part come from genuine components of this sample. Finally, there are clues that substances containing leftovers from the framework of PETN are present in it.

Conclusions: It was shown that the soot left after explosion of ethylene oxide may be analyzed with MS spectrometry. Copolymers of C_2H_4O and CH_2O occurring in the soot can be treated as fingerprints of the explosion. In particular, they are not expected to evolve from the mixtures used in chemical finishing and washing of textiles. Our studies showed the usefulness of the soot in seeking the evidence of an explosion of ethylene oxide happened even in a remote past. In particular, we have given convincing arguments that the cloth belonging to a person who died a violent death in the Polish TU 154M plane crash near Smolensk on 10th of April 2010 was in contact with exploding ethylene oxide. The explosion must have been initiated by an energetic material. Among the possible explosives that might have been used for this purpose, pentaerythritol tetranitrate (PETN) may be considered.

Supplemental Information includes (i) details of identification of the fabric belonging to the victim carrying symbol 5/19; (ii) ten figures, S1 to S10; (iii) fifteen tables, S1 to S15; and (iv) 14 references.

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