Hazard assessment of substances produced from the accidental heating of chemical compounds

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Abstract

Accidental events concerning process industries can affect not only the staff working in, but also the environment and people living next to the factory. For this reason a regulation is imposed by the European Community to prevent accidents that could represent a risk for the population and the environment. In particular, Directive 96/82/CE, the so-called 'Seveso II directive', requests a risk analysis involving also the hazardous materials generated in accidental events.

Therefore, it is necessary to develop simple and economic procedure to foresee the hazardous materials that can be produced in the case of major accidents, among which the accidental heating of a chemical due to a fire or a runaway reaction is one of the most frequent. The procedure proposed in this work is based on evolved gas analysis methodology that consists in coupling two instruments: a thermogravimetric analyzer or a flash pyrolyzer, that are employed to simulate accident conditions, and a FTIR spectrometer that can be used to detect the evolved gas composition.

More than 40 materials have been examined in various accident scenarios and the obtained data have been statistically analyzed in order to identify meaningful correlations between the presence of a chemical group in the molecule of a chemical and the presence of a given hazardous species in the fume produced.
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1. Introduction

The release of hazardous substances is an important topic in industrial risk assessment since its consequences could involve not only the industrial production area but also the community living in the surroundings.

In order to preserve people and environment from those hazardous events, the commission of the European Community approved the Directive 82/501/EEC [1]. This is the first European regulation on the control of major accident hazards: it defined the hazardous industrial activities on the basis of the substances involved in the chemical process, i.e. raw materials and products, without considering the accidental productions of toxic by-products. Fourteen years later, new EC Directive 96/82/EC [2] extended the application field of the previous Directive defining a dangerous substance as a "... mixture or preparation listed [. . .] and present as a raw material, product, by-product, residue intermediate, including those substances which it reasonable to suppose generated in the event of accident". Consequently, this directive introduces the need to develop new low-cost methodologies to foresee the substances that may be produced in accidental scenarios.

Various major accidents can result in the emission of toxic substances. Among the most frequent scenarios there are [3]:

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unwanted reactions caused by accidental contact of reactive substances, runaway reactions due to loss of control of chemical processes and fires. All these scenarios have been recently investigated at a laboratory scale. In particular, some criteria have been proposed for identifying hazardous by-products with respect to 'unwanted reactions' accidents [4] as well as for thermal runaway in industrial nitration processes [5]. However, the risk assessment is usually focused on fire hazard since it represents the most frequent scenario of industrial accidents [3]. One of the major fire effects is the release of toxic by-products whose characteristics depend on the fire conditions, i.e. the degree of ventilation where the fire occurs and the temperature reached during the accident. As a consequence, it is widely accepted that real-scale fire tests should be the best method to identify the by-products generated in a fire, but it is also obvious that real-scale tests are not practicable owing to the large cost and the large amounts of toxic substances produced. Therefore, a few works recently tried to identify scale-up procedures from small-scale tests [6–13]. However, no final conclusions have been drawn from these works and there are no widely accepted procedures to foresee which by-products can be reasonably produced in a real fire. A somewhat different approach from looking for scale-up rules is to identify the precursor of dangerous substances formed in accidental events, considering influence of scenario characteristics and yields of toxic by-products [14]. To improve this method, a suitable laboratory procedure is proposed to identify, in some well-controlled conditions, which species can be reasonably expected from a given chemical involved in a real fire (whose conditions, i.e. temperature and ventilation rate, cannot be predicted).

In this frame, the main goal of this work has been to develop a simple and inexpensive experimental methodology able to identify the toxic by-products that may be produced as a consequence of accidental heating of chemicals. Moreover, the data measured for a large set of chemicals have been statistically analyzed looking for some meaningful correlations among the chemical raw formula of the chemical and the toxic by-products. Such correlations represent a first attempt to develop a simple screening tool to decide whether a compound has to be experimentally characterized or not.

2. Materials and methods

As previously mentioned, the main aim of the present work has been to investigate the composition of the by-products generated by fires in chemical warehouse. The methodology of analysis used was the evolved gas analysis (EGA). This technique allows to determine the nature and amount of gaseous species evolved during the thermal degradation of a material, i.e. combustion or pyrolysis, as a function of temperature. One of the most effective approaches to EGA consists in an on-line analysis during thermal degradation to obtain qualitative and semi-quantitative information [15]. This can be done by coupling two different instruments by

an interface, namely an oven able to heat the sample with a giving heating rate and an analytical device able to identify the gaseous species produced during the heating. Therefore, a real time analysis is possible using only one sample and following the time evolution of the gaseous production during the sample heating. One of the systems satisfying these characteristics can be realized by coupling thermogravimetry and IR-spectrometry. The advantages of coupling thermogravimetric analyzer (TG) and Fourier transform infra red spectrometer (FTIR) are the relative small time required to obtain the results, the identification of several functional groups of the evolved gas on the basis of the vibrational spectra and the low detection limit (approximately 10 ppm). Actually, the TG-FTIR is widely used to investigate thermal polymers degradation [16,17]. Moreover, FTIR is cheaper than other instruments (for instance mass spectrometry (MS)) and consequently the coupled TG-FTIR can be used also by small and medium enterprises (SMEs), which are the main target of the Directive 96/82/EC since they often use or storage hazardous materials without having the possibility of using methods requiring high economical investment. This is the reason why in the last decade the use of FTIR technique increases compared to other devices [18].

On the other side, detection limits of EGA measurements are influenced by several factors: among the others, acquisition parameters of the FTIR, dilution by purge gas flow and extinction coefficients of the investigated chemicals. Since all the instrumental parameters are the same for the experiments reported in this paper, the detection limits of different gases depend basically on the extinction coefficients, which are characteristic of each species and wavelength considered. This can result, when very different extinction coefficients are present and the quantities of product formed are limited, in a misidentification of compounds formed in the same quantities. The influence of different detection limits of the species considered on the overall results of this work has been mitigated using a progressive spectra subtraction to solve the measured cumulative spectra of the gas mixture. This method requires to identify the compounds giving the higher contribution to the detected spectra and to subtract their spectra (available in digital libraries) from the cumulative spectra. Therefore, the remaining spectra are re-analyzed to detect other species.

Therefore, TG-FTIR has been extensively used in this work. However, TGA is intrinsically limited by a relatively low maximum heating rate (about 2.5 °C/s). This does not allow to investigate pyrolisis of low-boiling materials since they evaporate before decomposing. Therefore, a flash pyrolyzer (PY) characterized by a very high heating rate value (about 10^3–10^4 °C/s) has been also coupled with FTIR to allow identifying thermal decomposition products also for the most volatile compounds.

The employed apparatus, sketched in Fig. 1, is based on a heated gas line connecting thermogravimetric analyzer (TGA 850 Mettler Toledo) or flash pyrolyzer (CDS 100 Pyrobrobe) with FTIR spectrometer (Nicolet Nexus). The gas line has
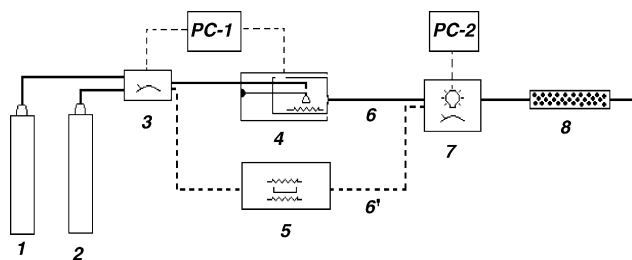
Fig. 1. Experimental apparatus: (1) nitrogen cylinder; (2) air cylinder; (3) mass flow rate controllers; (4) TG; (5) PY; (6) and (6′) hot transfer line; (7) FTIR; (8) VOC trap; PC-1 and PC-2 are personal computers used for apparatus control and data acquisition.

been heated to 200 °C to prevent condensation of the combustion gases [19]. The gaseous products generated from sample decomposition or oxidation should be transported from TG/PY to FTIR as fast as possible to avoid further decomposition and/or reactions. In other words, the residence time in the connection line must be much smaller than the characteristic time of decomposition [20]. Using a carrier gas whose flow-rate strongly reduces the residence time in the transfer line can fulfill this condition. Nitrogen and oxygen mixtures are usually used since these molecules without permanent dipole moment do not affect FTIR analysis. Moreover, these gases are also needed to simulate a proper combustion atmosphere ranging from pyrolysis (with pure nitrogen) up to a fully ventilated fire (with 21% of oxygen). Mixture composition is defined by a control system that regulates the mass flow-rates from two cylinders of nitrogen and air, respectively. In particular, the reactive gas (air or nitrogen) flow-rate has been chosen from 50 to 100 ml/min depending on the scenario. Moreover, also 50 ml/min of nitrogen have been required as a purge gas except for the experiment with 21% of oxygen in which only an air flow has been used.

As previously mentioned, TG can reproduce any heating curve set by user and carry out a thermal analysis measuring the loss of sample mass caused by gas evolution as a function of time and temperature. The maximum heating rate is about 2.5 °C/s and the maximum temperature (about 1100 °C) could be hold indefinitely. The use of flash pyrolyzer allows to reach high temperatures (about 1000 °C) rapidly thus simulating pyrolysis decomposition, which could occur in a real fire. It is characterized by a very fast heating rate (10^3–10^4 °C/s) but the maximum temperature could be hold only for approximately 20 s.

The FTIR apparatus represents the detector system of the gases generated, giving real time spectra of these gases. FTIR measurement gas cell is made of borosilicate glass (Pyrex) with a volume of 100 ml and a pathlength of 10 cm. The cell temperature is from ambient to 200 °C at atmospheric pressure. In the standard test conditions the average residence time of evolved gas in this cell is about 45 s depending on the gas flow rate, which can vary from 100 to 150 ml/min. The identification of the species present in the evolved gases has been done by searching the best match with the spectra avail-

able in digital libraries. In this work several libraries with a total amount of about 20,000 spectra have been used with the aforementioned progressive spectra subtraction procedure.

3. Test methodology

The complex phenomena of a real fire are classified for testing purposes by ISO/IEC TR 9122-4 [21] in three categories, as summarized in Table 1. Non-flaming (or decomposition) fires present an initial phase before the real ignition, from which developing fire starts and reaches the flashover point when the combustion involves all the materials. After flashover there is a fully developed fire that could occur in low ventilation (1–5% O_2) or high ventilation (5–10% O_2) conditions. To simulate these scenarios in terms of average environmental temperature versus time, various so-called 'fire curve' equations have been proposed. In particular, non-flaming fires can be approximated by a 'slow heating curve' (SHC) (Eq. (1)) for the first 21 min:

$$T = 154t^{0.25} + 20 \tag{1}$$

where temperature, T, is in °C and time, t, is in min.

When ignition is reached and a developing fire occurs, a fire curve equation named 'standard curve' (SC) can be used to simulate both developing and developed fires:

$$T = 20 + 345 \log_{10}(8t + 1) \tag{2}$$

In this work both heating curve equations have been employed to simulate different fire scenarios by setting TG to follow a certain heating curve in the proper atmosphere conditions. In particular, five different fires have been simulated:

(1) non-flaming conditions followed by a developing fire using firstly Eq. (1) to set-up TG heating curve for 21 min with an air flow (21% O_2), followed by a TG heating curve defined by Eq. (2) with a 15% O_2 carrier gas up to 800 °C;
(2) developing fires simulated by implementing Eq. (2) with a 15% O_2 carrier gas in the TG heating curve up to 800 °C;

Table 1
ISO/IEC TR 9122-4 classification of fire phases [21]

Fire phase	Oxygen concentration (%)	Temperature (°C)
1: Decomposition		
a: Smoldering (self-sustained)	21	<100
b: Non-flaming (oxidative)	5–21	<500
c: Non-flaming (pyrolytic)	<21	<1000
2: Developing fire (flaming)	10–15	400–600
3: Fully developed fire (flaming)		
a: Relatively low ventilation	1–5	600–900
b: Relatively high ventilation	5–10	600–1200

Values reported refer to average environmental conditions within the fire compartment.

(3) developed fires with high ventilation controlled conditions. In this case the heating curve is set-up through the same Eq. (2) till 1000 °C with a 8% O_2 carrier gas to simulate an high ventilation;

(4) developed fires with low ventilation condition are as for case 3), but the temperature reaches 800 °C in an environment of 100% N_2;

(5) fires characterized by fast heating rate in a poor O_2 atmosphere have been simulated using PY in inert carrier conditions (100% N_2).

All of these scenarios have been carried out to analyze the different behavior of the substances examined. The investigation has been focused on the most hazardous situations, i.e. when the complete combustion of the fuel does not occur, leading to decomposition reactions (further oxidation processes that can occur if the decomposition products reach the flame region of the fire are consequently neglected). This situation can be simulated by slow heating in a poor oxygen environment or by pyrolysis. Consequently, the compounds have been mainly tested in low ventilated developed fire and pyrolysis. Only few materials (one for each class considered) have been examined in all the fire scenarios previously indicated as summarized in Table 2.

The analyzed materials show a decomposition temperature close to the values typically reached in a fire. The classes of homologous substances shown in Table 2 have been defined gathering the chemical compounds with the same functional groups. The aim of this grouping was to evidence correlations between the substances and the typology of the products generated.

4. Results and discussion

From each TG-FTIR experiment several results have been obtained. In particular, TG curve that represents the loss of mass occurred during the experiment has been measured. The derivative of this curve (DTG) is more effective to evidence the time related to the pick of material loss. Obviously, the higher rate of material loss from the sample corresponds to the higher rate of production of gaseous byproducts. FTIR analysis gives the spectra of these evolved gases in real time determining a spectra waterfall related to the evolved gas composition as a function of time (and consequently as a function of temperature). An elaboration of the spectra waterfall is the Gram–Schmidt curve that is calculated by integration of the spectral intensity as a function of time. It provides the pattern of the gas evolution, which is approximately the same as that deduced from the DTG curve. These measurements allow to identify the temperature at which the largest amount of gases is emitted from the sample, as well as their qualitative composition. Similar results are obtained from PY-FTIR experiments, apart from the DTG curve, which is not available from these experiments. In fact sample heating can be roughly considered as

instantaneous in PY-FTIR experiments and consequently the sample reaches the maximum temperature almost instantaneously.

It should be noted that a very small amount of sample (about 10–50 mg) is required for these experiments, which are completed in a few minutes. As previously discussed, these are very cheap and fast experiments.

An example of this procedure is shown for 4-Cl-3-nitrobenzyl alcohol tested in a simulated fully developed fire in the absence of oxygen in Fig. 2, where TG and DTG curves are reported. We can see that these curves indicate only one pick of mass loss. This mean that there is only one emission of gaseous species, which happens at about 250 °C. Comparing the spectra of the gaseous products with a proper digital library, it is found that almost only the same substance is detected in the gas release. This means that this compound under simulated fully developed fire conditions evaporates but not decomposes due to its high volatility. Decomposition products of 4-Cl-3-nitrobenzyl alcohol can be detected by PY-FTIR test since it avoids evaporation occurred before decomposition. In fact, the results of the PY-FTIR test showed the presence of chlorobenzene, CO, HCN and NO in the evolved gases.

A somewhat different example is shown in Fig. 3 that reports TG-curves for tetracyanoethene in a simulated fully developed fire with low ventilation (100% N_2). While the TG analysis lasts at about 45 min, Fig. 3 shows a zoom of the first 18 min to evidence the most significant mass losses. Actually, the overall weight loss in the last part of the thermogravimetric test is about 14% of the initial sample mass. In this case DTG-curve shows at least five picks of mass loss identified as NH_3 and HCN emissions in accordance with FTIR spectral results. The overall Gram–Schmidt curve reported in Fig. 4 follows the DTG evolution showing the picks of mass loss approximately at the same time (and consequently at the same temperature) obtained by thermogravimetric analysis. Moreover, following the pick height curves as function of time at wave number equal to 966 and 715 cm^{-1} (related to the NH3 and HCN maximum pick, respectively) we can see that NH_3 is released starting from about 200 °C, while HCN from about 350 °C. At higher temperature other species are released. In particular, HCNO has been detected although its FTIR spectra are weaker than that of NH_3 and HCN and have not been shown in Fig. 4.

This kind of analysis have been carried out for all the substances and the results are summarized in Table 2, where the species identified in the evolved gases related to a certain scenario are indicated. We can see from these results that different fire scenario can lead to quite different results in terms of evolved gaseous species. No clear trend can be identified from these results in terms of worse case scenario. This means that a full characterization is required to completely identify the species that can be produced during a real fire. In other words, a complete set of five experiments is required for a reliable hazard assessment, which can be carried out rapidly and at low cost.

Table 2
Synoptic of the main experimental results

Functional group	Name	CAS	Fire scenario				
			1	2	3	4	5
Ar, NO$_2$, Cl, OH	4-Cl-3-nitrobenzyl alcohol	55912-20-4	A-B-C	A-B-C-I	A-B-C	A-C	B-D-F-I
	4-Cl-2-nitrobenzyl alcohol	55996-18-5				A-C	B-D-F-I
	2-Cl-5-nitrobenzyl alcohol	80866-80-4				A-C	B-F-G
	5-Cl-2-nitrobenzyl alcohol	73033-58-6				A-B-C-F	B-F-I
Ar, NO$_2$, Cl, CHO	2-Cl-6-nitrobenzaldehyde	6361-22-4				A-B-C-F	B-C-D-F-I
	2-Cl-5-nitrobenzaldehyde	6361-21-3	A-B	A-B-C-D	A-B-C-D	A	A-B-C-D-F-I
	5-Cl-2-nitrobenzaldehyde	6628-86-0				A-B-C	A-B-D-C-F-I
	4-Cl-3-nitrobenzaldehyde	16588-34-4				A-B-C	A-B-C-D-F-I
Ar, NO$_2$, OH	3-Nitrobenzyl alcohol	619-25-0					A-B-D-H-L
	4-Nitrobenzyl alcohol	619-73-8	A-L	A-B	A-L	A-B-L	A-B-D-F-H
	2-Nitrobenzyl alcohol	612-25-9				A	A-B-D-F-H
	3,5-Dinitrobenzyl alcohol	71022-43-0	A-B	B-D-F	A-B-D-F	A-B-D-F-L	B-D-F
	3,4-Dinitrobenzyl alcohol	79544-31-3				A-B-D-F–L	B-D-F
Ar, NO$_2$, CHO	4-Nitrobenzaldehyde	555-16-8	A-B	A-B	A-B	A-B	B-D-F-H
	2-Nitrobenzaldehyde	552-89-6				A	A-B-D-F-H
Ar, NO$_2$, OH, CHO	4-Hydroxy-3-nitrobenzaldehyde	3011-34-5	A-B	A-B-D-F	A	A-B-F	A-B-F
	5-Hydroxy-2-nitrobenzaldehyde	42454-06-8				A-B-F	B-F
	3-Hydroxy-4-nitrobenzaldehyde	704-13-2				A-B-F	A-B-D-F
	3-Hydroxymethyl-2-nitrobenzaldehyde	53055-05-3				A-B-G	A-B-D-F-G
CN	Tetracyanoethene	670-54-2	D-E-F	B-D-E	B-D-E	E-F	B-E-F-G
Ar, CN	1,2,4,5-Tetracyanobenzene	712-74-3				B-E-F	B-E-F-G
CH$_3$	3,5-Dimethyl isoxazole	300-87-8					A-B-G
NH$_2$, CH$_3$	3-Amino-5-methyl isoxazole	1072-67-9	A-G	A	A	A	A-B-F-G
	Propylamina	107-10-8					A-E-G
NH$_2$	3-Amino isoxazole	36216-80-5					B-E-F-G
	4-Amino-3-isooxazolidinone	68-41-7				E-F-G	B-E-F-G
	Ammonium formate	540-69-2		E		E	B-E
Ar	3-Phenyl-5-isooxazolidinone	1076-59-1				B-E	B-E
Ar, NH$_2$	Diphenylamina	122-39-4	A	A	A	A	A-B-F-G-H
OH	2-Hidroxypyridine-N-oxide	13161-30-3	B-D	A	A	A	B-E-F-G
Ar, NO$_2$	3-Nitro-1,8-naphthalic anhydride	3027-38-1	B	A-B	A-B	A	B-D
	2,4,7-Trinitro-9-fluorenone	129-79-3				A	B-D-F
	3-Nitrophthalic anhydride	641-70-3	B	A	A-B-D	A	B-D-F
Ar, Cl	1,4-Dichlorobenzene	106-46-7	A	A	A	A	A
NH$_2$, OH	Adenosine	58-61-7				E-F-G	B-E-F-G
	Cytidine	65-46-3	B-D-E	E-F-G	B-D-E-F-G	E-F-G	B-E-F-G
NH$_2$, OH, CH$_3$	2′,3′-O-Isopropylideneuridine	362-43-6				A-F	A-B-E-F-G
NH, OH	Glyphosate	1071-83-6		B-E-G		A-B-E-F-G	B-E-F-G
Ar, Cl	Tetraconazole	112281-77-3				C-F-M	B-F
Cl, NH, CH$_3$	Atrazine	1912-24-9		A-B-C-F		A-B-C-F	A-C-F
	Terbutylazine	5915-41-3		A-C		A-C	C-F-G
	Simazine	122-34-9		A-B-C-E-F-G		A-B-C-E-F-G	F-G
Ar, NO$_2$, CH$_3$	Trifluralin	1582-09-8		A			A-B-F-G
	Benefin	1861-40-1					A-B-D-G
	Ethalfluralin	55283-68-6		A-B		A-B-E-F-G-M	B-D-F-G-M
Ar, Cl, NH$_2$	Chloridazon	1698-60-8		B-C-E-F		B-C-E-F	B-E-F
Ar, Cl, NH, CH$_3$	Linuron	330-55-2		G			A-B-C-F-G
Ar, NO$_2$, NH, CH$_3$	Pendimethalin	40487-42-1		A		A-D-E-F-G	A-B-D-F-G
NH, CH$_3$	Prometryn	7287-19-6		A		A	A-F-G

For each chemical the main species identified with EGA are reported: (A) same chemical, (B) CO, (C) HCl, (D) NO$_x$, (E) NH$_3$, (F) HCN/HCNO, (G) *n*-alkane/*n*-alkene, (H) benzene/benzaldehyde, (I) Cl-benzene/Cl-benzaldehyde, (L) nitrobenzene/dinitrobenzene/nitrobenzaldehyde, (M) HF.
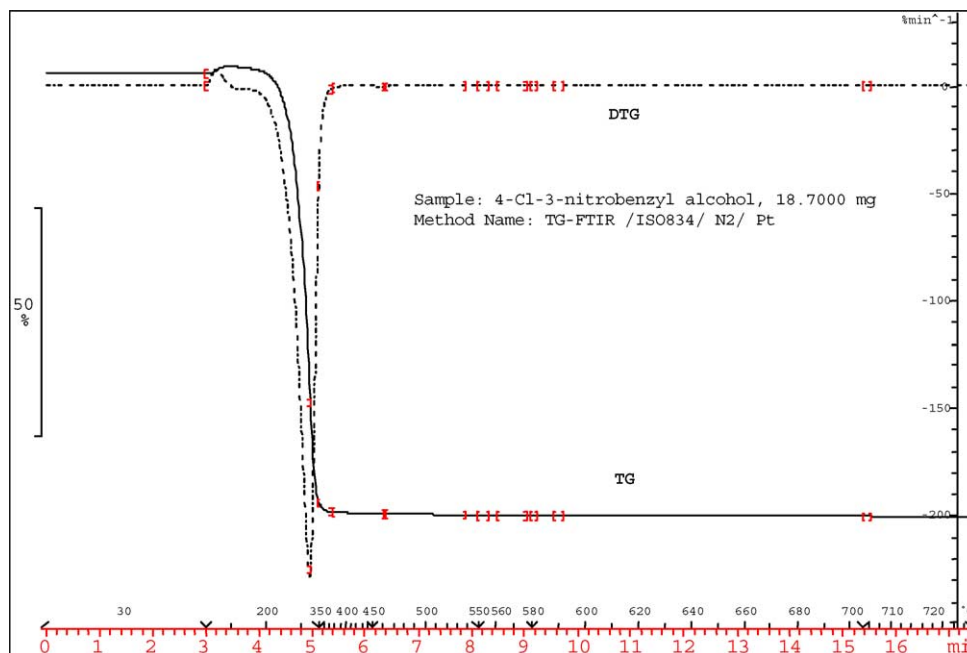
Fig. 2. TG and DTG curves of 4-Cl-3-nitrobenzyl alcohol in TG-FTIR test with simulated fully developed fire conditions and 100% N_2 as carrier gas.

5. Statistical analysis

Since the number of products deriving from the chemical industry is very high, it is practically impossible to perform an experimental analysis of the decomposition products for all the existing chemicals. Consequently, a screening tool able to indicate the likelihood that a given chemical can produce toxic by-products when involved in an accident would be very useful. A practical way to develop such a tool could be to collect a large number of experimental data concerning different chemicals and looking for some common behaviors.

The set of data collected in this work involves a relatively large number of different chemical species, which contain various functional groups as summarized in Table 3. This allows for a first analysis of the by-products found by EGA in terms of correlation between the presence of a given functional group in the molecule of the chemical and the production of a given by-product when chemical is accidentally heated.
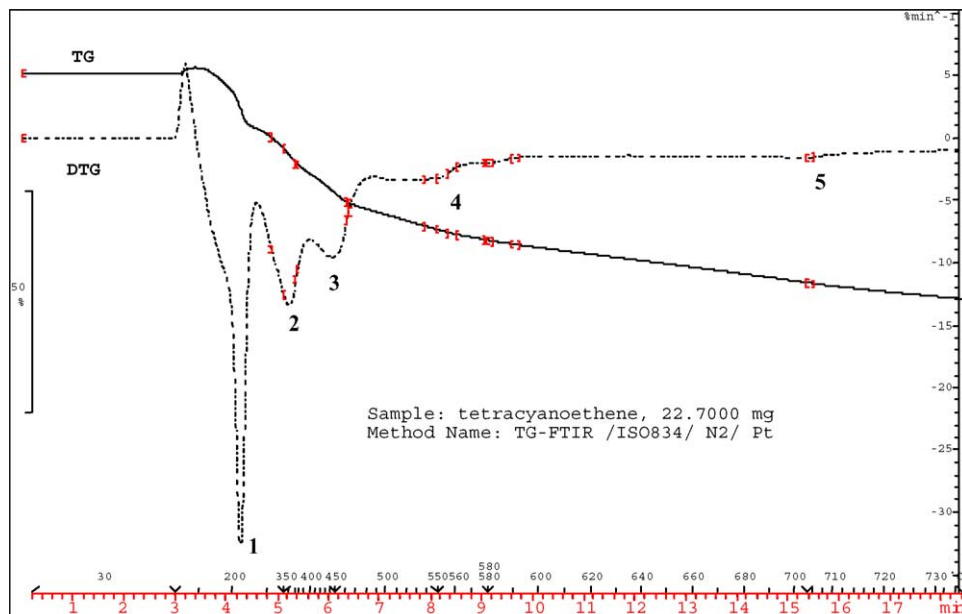

Fig. 3. TG and DTG curves of tetracyanoethene in TG-FTIR test with simulated fully developed fire conditions and 100% N_2 as carrier gas. Five picks of mass loss have been evidenced and labeled from 1 to 5.
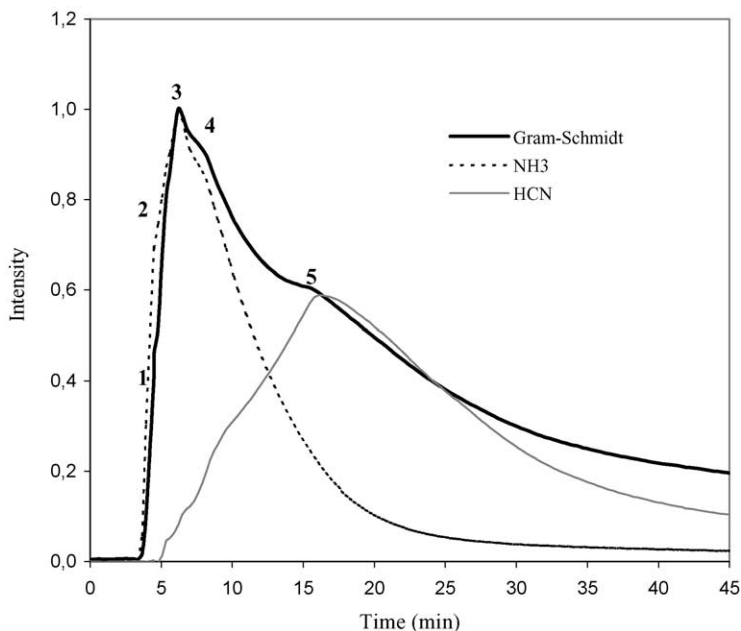
Fig. 4. Gram–Schmidt curves of the tetracyanoethene in TG-FTIR test with simulated fully developed fire conditions and 100% N_2 as carrier gas. Five picks, corresponding to the main picks of mass loss obtained in DTG and shown in Fig. 3 have been labeled from 1 to 5.

Apart from CO_2 and H_2O, which can be obviously always present when some oxygen is available since we are considering organic compounds, the first by-product identified in this work has been CO. As expected, CO has been detected at least in some conditions, from almost all the examined chemicals as the result of a partial oxidation. The only exceptions are 1,4-dichlorobenzene (which simply evaporates in all the conditions without reacting), propylamina, terbutylazine and prometryn. These latter chemicals do not react with oxygen in the conditions investigated leading only to non-oxidized (that is, decomposition) by-products. However, these seem to be exceptions to a general rule-of-thumb stating that CO formation cannot be ruled out "a priori" for any chemical.

A somewhat similar conclusion hold true for HCl emission. We can see from Table 3 that almost all the fires chemicals with Cl in their molecule emit HCl when heated. Apart from 1,4-dichlorobenzene that does not react, these results respect a generally valid rule-of-thumb stating that all the chlorinated chemicals can emit HCl in some conditions when accidentally heated.

Different conclusions can be drawn for NO_x emissions. Almost all the chemicals considered in this work contain some nitrogen atoms in the molecule. However, not all the chemicals emit NO_x in the evolved gases. This is true not only for chemicals containing nitrogen in different group (that is, NO_2, NH_i, CN, ...) but also for similar species.

This makes difficult analyzing the correlation between the presence of a given functional group in the molecule and the formation of NO_x. Consequently, the data collected in this work have been statistically analyzed to verify the existence of any correlation between the chemical structure of the compounds, and their decomposition products.

In particular, statistical inference has been employed since allows to verify whether a sample is representative of a population or not. In this case the statistical sample is constituted by the results obtained in the present work, whereas the population corresponds to all existing substances. Considering the data reported in Table 3, an hypothesis involving a correlation between the presence of a functional group and the production of a certain by-product (H_1: alternative hypothesis) can be defined: this is compared to another hypothesis (H_0: null hypothesis) stating that the experimental data occur randomly. To evaluate which hypothesis is more probable, the 'two way test' with the χ^2 distribution has been used [22]: it compares the χ^2 value calculated by the experimental results to the value from a normal distribution that simulates random data. If the first term is greater than the second one, the alternative hypothesis will be true, otherwise the null hypothesis is accepted. As usual, a confidence interval about this statement should be defined by a proper significance level (α), which represents the probability to refuse the null hypothesis when it is true. Therefore, the χ^2 value about a normal distribution is calculated by the chosen confidence interval ($1 - \alpha$) and by the degree of freedom of the sample in order to define the most representative normal distribution of the experimental data. If the observed χ^2 value is greater than normal distribution χ^2 with a certain significance level (α), the discrepancy is significant:

the null hypothesis is refused with an uncertainty equal to α.

This test has been applied to the data summarized in Table 3 to look for a correlation between the presence of a functional group (β_i) in the molecule of the chemical tested and the generation of a by-product (B_k).

It is known that the χ^2 validity decreases when the sample becomes smaller since the random variations increase their relative influence. Therefore, for samples from 30 to 200 elements an expression containing Yates correction has to be used to calculate the χ^2_{ik} value related to a set of experimental data involving species containing a given functional group β_i

Table 3
Synoptic of the results for all the experimental conditions investigated, compared to hazardous decomposition products as indicated in Material Safety Data Sheet (MSDS)

Ar	NO$_2$	Cl	OH	CHO	CH$_3$	NH$_i$	CN	F	Name	Result	MSDS
x	x	x	x						4-Cl-3-nitrobenzyl alcohol	A-B-C-D-F-I	B-C-D
x	x	x	x						4-Cl-2-nitrobenzyl alcohol	A-B-C-D-F-I	B-C-D
x	x	x	x						2-Cl-5-nitrobenzyl alcohol	A-B-C-F-G	B-C-D
x	x	x	x						5-Cl-2-nitrobenzyl alcohol	A-B-C-F-I	B-C-D
x	x	x		x					2-Cl-6-nitrobenzaldehyde	A-B-C-D-F-I	B-C-D
x	x	x		x					2-Cl-5-nitrobenzaldehyde	A-B-C-D-F-I	B-C-D
x	x	x		x					5-Cl-2-nitrobenzaldehyde	A-B-C-D-F-I	B-C-D
x	x	x		x					4-Cl-3-nitrobenzaldehyde	A-B-C-D-F-I	B-C-D
x	x		x						3-Nitrobenzyl alcohol	A-B-D-H-L	B-D
x	x		x						4-Nitrobenzyl alcohol	A-B-D-F-H-L	B-D
x	x		x						2-Nitrobenzyl alcohol	A-B-D-F-H	B-D
x	x		x						3,5-Dinitrobenzyl alcohol	A-B-D-F-L	B-D
x	x		x						3,4-Dinitrobenzyl alcohol	A-B-D-F-L	B-D
x	x			x					4-Nitrobenzaldehyde	A-B-D-F-H	B-D
x	x			x					2-Nitrobenzaldehyde	A-B-D-F-H	B-D
x	x		x	x					4-Hydroxy-3-nitrobenzaldehyde	A-B-D-F	B-D
x	x		x	x					5-Hydroxy-2-nitrobenzaldehyde	A-B-F	B-D
x	x		x	x					3-Hydroxy-4-nitrobenzaldehyde	A-B-D-F	B-D
x	x		x	x					3-Hydroxymethyl-2-nitrobenzaldehyde	A-B-D-F-G	B-D
							x		Tetracyanoethene	B-D-E-F-G	B-D-F
x							x		1,2,4,5-Tetracyanobenzene	B-E-F-G	B-D
					x				3,5-Dimethyl isoxazole	A-B-G	B-D
						x			3-Amino isoxazole	B-E-F-G	B-D
					x	x			3-Amino-5-methyl isoxazole	A-B-F-G	B-D
					x	x			Propylamina	A-E-G	B-D
						x			4-Amino-3-isooxazolidinone	B-E-F-G	B-D
						x			Ammonium formate	B-E	B-D
x									3-Phenyl-5-isooxazolidinone	B-E	B-D
x						x			Diphenylamine	A-B-F-G-H	B-D
			x						2-Hydroxypyridine-N-oxide	B-D-E-F-G	B-D
x	x								3-Nitro-1,8-naphthalic anhydride	A-B-D	B-D
x	x								2,4,7-Trinitro-9-fluorenone	A-B-D-F	B-D
x	x								3-Nitrophthalic anhydride	A-B-D-F	B-D
x		x							1,4-Dichlorobenzene	A	B-C
			x			x			Adenosine	B-E-F-G	B-D
			x			x			Cytidine	B-D-E-F-G	B-D
			x		x	x			2′,3′-O-Isopropylideneuridine	A-B-E-F-G	B-D
			x			x			Glyphosate	A-B-E-F-G	B-D
x		x						x	Tetraconazole	B-C-F-M	C-F-M
		x			x	x			Atrazine	A-B-C-F	C-D
		x			x	x			Terbutylazine	A-C-F-G	B-C-D
		x			x	x			Simazine	A-B-C-E-F-G	B-C-D
x	x				x			x	Trifluralin	A-B-F-G	D-M
x	x				x			x	Benefin	A-B-D-G	B-D-M
x	x				x			x	Ethalfluralin	A-B-D-E-F-G-M	B-D-M
x		x				x			Chloridazon	B-C-E-F	B
x		x			x	x			Linuron	A-B-C-F-G	B-C-D
x	x				x	x			Pendimethalin	A-B-D-E-F-G	B-D
					x	x			Prometryn	A-F-G	B-D

For each chemical the main species identified with EGA are reported: (A) same chemical, (B) CO, (C) HCl, (D) NO$_x$, (E) NH$_3$, (F) HCN/HCNO, (G) n-alkane/n-alkene, (H) benzene/benzaldehyde, (I) Cl-benzene/Cl-benzaldehyde, (L) nitrobenzene/dinitrobenzene/nitrobenzaldehyde, (M) HF.

and the production of the by-product B_k:

$$\chi_{ik}^2 = \frac{[|a_{ik1,1}a_{ik2,2} - a_{ik1,2}a_{ik2,1}| - (1/2N)]^2 N}{R_{ik1}R_{ik2}C_{ik1}C_{ik2}} \qquad (3)$$

where $a_{ik1,1}$: number of substances that contain the functional group β_i and which release the by-product B_k; $a_{ik1,2}$: number of substances that contain the functional group β_i and which do not release the by-product B_k; $a_{ik2,1}$: number of substances that do not contain the functional group β_i and which release the by-product B_k; $a_{ik2,2}$: number of substances that do not contain the functional group β_i and which do not release the by-product B_k; R_{ik1}: number of substances that contain the functional group β_i; R_{ik2}: number of substances that do not contain the functional group β_i; C_{ik1}: number of substances that release the by-product B_k; C_{ik2}: number of substances that do not release the by-product B_k; N: total number of analyzed substances.

χ_{ik}^2 term is compared to the $\chi_{(1)0.95}^2$ related to a normal distribution with a confidence interval equal to 0.95 and one degree of freedom since if one of the four measured frequencies ($a_{ik1,1}$, $a_{ik1,2}$, $a_{ik2,1}$ and $a_{ik2,2}$) varies, the other ones are defined in accordance with the constant values of subtotal (R_{ik1}, R_{ik2}, C_{ik1} and C_{ik2}).

Moreover, the χ^2 test is limited also by the minimum expected frequency that must be at least equal to 5. If this requirement is not fulfilled, "Fisher test" has to be employed. This method considers that frequencies ($a_{ik1,1}$, $a_{ik1,2}$, $a_{ik2,1}$ and $a_{ik2,2}$) can randomly change, fixing subtotals (R_{ik1}, R_{ik2}, C_{ik1} and C_{ik2}) as constant values. The probability to obtain one of these random combinations can be calculated by Eq. (4)

$$P_{ik} = \frac{C_{ik1}!C_{ik2}!R_{ik1}!R_{ik2}!}{a_{ik1,1}!a_{ik1,2}!a_{ik2,1}!a_{ik2,2}!N!} \qquad (4)$$

where P_{ik} is related to an investigated correlation between a given species β_i and by-product B_k. To decide whether the alternative hypothesis is true or not, the significance level (α) has to be compared to the total probability. This term is calculated by the summation of P_{ik} values related to the observed data and those combinations obtained decreasing for one unit the smallest of the observed frequencies until it is equal to zero. Such combinations represent more extreme situations than measured data, since they are closer to the extreme case, which verifies the statement of the alternative hypothesis. If the total probability is less then selected significance (α), it means that the observed data and more extreme combinations randomly occur with a small probability, accepting the alternative hypothesis. Vice versa, this hypothesis is refused when the total probability cannot be neglected, concluding that the experimental data combination is randomly obtained.

This method has been used to identify which by-products are expected (or not expected) to be formed from a given chemical involving certain functional group. For each compound, by-products identified experimentally from five sim-

ulated scenarios have been gathered together as previously discussed.

This kind of statistical analysis has been used to define whether the presence of the NO_2 functional group in the molecule of the heated species is related to the emission of NO_x. In this case the null hypothesis says a random composition of gas released, whereas the alternative hypothesis assumes a correlation between the presence of $Ar + NO_2$ group in the examined compounds and the NO_x production. The observed data are summarized in Table 4: the χ_{Ar+NO_2,NO_x}^2 value is equal to 22.23, while the $\chi_{(1)0.95}^2$ related to a normal distribution is equal to 3.84. Consequently, the null hypothesis is refused: a statistically meaningful correlation between NO_x production and the presence of $Ar + NO_2$ groups is found. It follows that emission of NO_x is probably connected with the presence of $Ar + NO_2$ group in chemicals. In other words, when the groups $Ar + NO_2$ are present in the molecule of a given chemical we expect with high confidence the emission of NO_x as a consequence of an accidental heating of such a chemical.

A completely different result is obtained when the same statistical analysis is performed for $\beta_i = NH_i$ and $B_k = NO_x$. In this case it has been found that the presence of NH_i in the molecule statistically inhibits the formation of NO_x.

Similar considerations are true for the emission of NH_3. However, in this case the results of the statistical analysis show that the emission of NH_3 can be statistically related to the presence of NH_i functional groups in the molecule, while the presence of $Ar + NO_2$ groups statistically inhibits the formation of NH_3.

This means that when $Ar + NO_2$ groups are present in a given molecule we can expect with high confidence the emission of NO_x and not the emission of NH_3 when the chemical is involved in an accidental heating, while the opposite is true when the chemical molecule contains NH_i groups. In this case NH_3 emission is expected with high confidence, while NO_x emission is not expected.

These conclusions agree with some experimental results previously reported in the literature, showing that NO_x emission are expected for species involving $Ar + NO_2$ group not investigated in this work [23]. Moreover, other works showed that chemicals not investigated in this work and containing NH_i groups emit NH_3 instead of NO_x [16,24].

These works also report HCN emissions from such chemicals, although no correlation with NO_2 or NH_i groups can

Table 4
Contingency table for the correlation between $Ar + NO_2$ groups and NO_x by-products

$Ar + NO_2$ groups	NO_x by-products		Total
	Yes	No	
Yes	22	4	26
No	3	20	23
Total	25	24	49

be evidenced. Similar conclusions arise from the analysis of the data reported in Table 3. Almost all the chemicals contain N atoms in the molecule and almost all emit HCN and/or HCNO. The statistical analysis previously discussed in this case is not able to evidence any statistically meaningful correlation between the presence of NH_i or NO_2 functional group and the emission (or not emission) of HCN/HCNO.

For what concerns the simultaneous presence of $Ar + NO_2$ and NH_i in the molecule, only very few data are available and no final conclusions can be drawn from such data.

The analysis concerning the emission of R (that is, non aromatic hydrocarbons) is less straightforward. No clear correlations between the presence of a given functional group in the molecule and the emission of R as by-product are evident from the data summarized in Table 3. Almost all the species containing CH_3 group in the molecule emit R as by-product in the evolved gases. However, also some chemicals without CH_3 group in the molecule emit non-aromatic hydrocarbons.

Also in this case a statistical analysis is required to discriminate what correlations are statistically meaningful. The results clearly showed that the emission of non-aromatic hydrocarbons is statistically related to the presence of CH_3 functional group in the molecule of the heated species. On the contrary, no correlations statistically meaningful arose from the analysis of benzene/benzaldehyde by product emissions.

Chlorinated aromatic species can represent a severe hazard. From the data reported in Table 3 we can see that only the species containing $Ar + Cl + O$ in the molecule emit Cl-benzene or Cl-benzaldehyde. However, not all these chemicals lead to the formation of such by-products, and no clear correlations between the kinds of oxygenated group are evident.

Statistical analysis showed the existence of a correlation between the presence of $Ar + Cl + O$ groups in the molecule and the by-products formation, while no differences have been evidences from various oxygenated groups. Again, Ar-Cl emissions are expected with high confidence when $Ar + Cl + O$ functional groups are present in the molecule of the considered chemical. Also in this case this conclusion agrees with the results of previous investigations concerning chemicals not considered in this work [25].

Nitro-aromatic species have been found in the gases emitted from very few chemicals, as summarized in Table 3. We can see that similarly to the Ar-Cl emission, also in this case all the species emitting Ar-N by products contain $Ar + NO_2 + OH$ in the molecule, but not all the species containing such groups emit Ar-N by-product. However, it has been found a correlation statistically meaningful between the presence of $Ar + NO_2 + OH$ groups in the molecule and the emission of Ar-N by-products.

Also HF emission has been detected in the evolved gases but no meaningful correlation between the presence of F atom in chemicals and this by-product has been evidenced, since very few data are available.

Finally, it should be noted that in almost all the gases emitted from the chemicals investigated the same chemical species has been found. This means that also for relatively low-volatile chemicals, their presence in the fumes must be considered.

6. Conclusions

A simple and inexpensive experimental procedure, particularly suitable for SMEs, is proposed to identify the main hazardous by-products that can be generated from accidental heating of chemicals. Such a procedure, based on the EGA, requires to couple a TG or a PY with a FTIR and to perform a series of five tests characterized by different heating rate and oxygen content in the carrier gas as discussed in Section 3. In particular, PY-FTIR is suggested to investigate by-products of low-boiling substances that cannot be analyzed with TG apparatus.

The results of these runs, in terms of evolved hazardous species, have to be gathered together leading to a set of by-products that can be emitted in case of accidental heating.

Obviously, only a few of them will be emitted in a real accident, depending on the real conditions (e.g., temperature and oxygen availability). Gathering together the emissions from different possible scenario should provide a reasonable "worst case".

In spite of the proposed methodology is quite simple and economic, the huge amount of chemicals handled in the process industry makes the experimental characterization of all the products cumbersome. As a consequence, screening criteria able to foresee the by-products most likely emitted in case of accident would be useful.

Using the results presented in this work, some conservative rules-of-thumb have been deduced for the emission of hazardous substances as the result of an accidental heating:

1. for any organic compound, fumes containing the same chemical, water, carbon monoxide and dioxide are expected;
2. chlorinated organic compounds will produce HCl;
3. aromatic compounds with NO_2 functional group will produce NO_x;
4. organic compounds with NH_i functional group will produce NH_3;
5. organic compounds with N atoms in the molecule will produce HCN and/or HCNO;
6. organic compounds with CH_3 functional group will produce light non aromatic hydrocarbons;
7. chloride aromatic hydrocarbons with O atoms in the molecule will produce light chlorinated aromatics;
8. aromatic compounds with NO_2 and OH functional groups with molecule will produce light nitro-aromatic species.

It should be stressed that these are only positive rules-of-thumb, since they are conservative. Negative rules-of-thumb that could be also deduced from the aforementioned statistical

analysis (such as, "aromatic compounds with NH_i functional group will not produce NO_x") would be not conservative and might be dangerous. This is evident from the results summarized in Table 2 showing that, for instance, NO_x is formed from cytidine (with NH_i group).

Clearly, the reliability of these rules-of-thumb is limited by the number and kind of chemicals considered in this work. However, they are in agreement with experimental findings previously reported in the literature and can be considered as a first step towards the development of a reliable and generally accepted screening tool. This obviously requires a continuous up dating of these rules-of-thumb through a comparison with new experimental data.

Finally, it should be noted that these rules-of-thumb not always agree with the hazardous decomposition products reported in the Material Safety Data Sheets (MSDS), as can be easily seen from Table 3. Firstly, it is evident that the analysis proposed gives more specific information than MSDS about by-products from heating chemicals. In particular, the CO emission from almost all chemicals are expected also by this data, as well as HCl by-product from chlorinated compounds, with an only exception concerning chloridazon. The major discrepancies emerge for the chemicals containing N atoms. In MSDS such chemicals always produce NO_x, without distinguishing the different effects of NH_i or NO_2 functional groups statistically analyzed in this work. Moreover, data reported in MSDS never expect the NH_3 emission and rarely foresee the HCN/HCNO decomposition products from chemicals with N atoms. In MSDS it also follows that fluorinated organic chemicals always emit HF while this aspect is not evidenced by our experimental results. Finally, new rules-of-thumb (concerning $Ar + Cl$, $Ar + NO_2 + OH$ and CH_3), which are not considered in MSDS, have been evinced in this work. Consequently, this analysis reveals innovative aspects comparing to the methodology and the information already available in literature on the prediction of the by-products from heating chemicals.

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