Thermal decomposition studies of riot control agent ω-chloroacetophenone (CN) by pyrolysis-gas chromatography–mass spectrometry

Anil K. Nigam, M.V.S. Suryanarayana*, P.K. Gutch, Shiv P. Sharma, L.N.S. Tomar, R. Vijayaraghavan

Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, India

ABSTRACT

Pyrolysis-GC/MS system with on-line micro-furnace was used to make rapid evaluation of ω-chloroacetophenone (CN) decomposition under inert thermal atmospheres. The volatile products evolved during pyrolysis were analyzed by thermal gravimetric analysis (TGA) and Py-GC/MS to obtain specific thermogram and pyrogram. Thermal gravimetric analysis results showed that CN undergoes sublimation at 167 °C prior to its decomposition at 229 °C. Totally 45 degradation products were identified based on mass spectral library matching with the aid of correlation of the values of boiling point (bp) and retention time. A large number of mono-aromatics and polycyclic aromatic hydrocarbons were observed beyond 600 °C. In addition to the aromatic hydrocarbons, oxygenated compounds were also observed during the pyrolysis process. The pyrolysis mechanism was proposed based on the determined pyrolysates and their relative abundance with temperature. The investigation results can provide significant information for understanding the thermal behavior of CN and evaluation of the potential influence of the pyrolysates to living being and the environment.

1. Introduction

ω-Chloroacetophenone (CN) was invented by a German chemist, Carl Graebe, in 1869 [1]. It is a riot control agent, harassing agent, lachrymatory agent, nonlethal or less than lethal agent and supplied to paramilitary and police forces in a small pressurized aerosol can known as "Mace" or tear gas [2–9]. It causes temporary incapacitation of the individual through intense irritation of tissues and the creation of a strong sensation of discomfort, including difficulty in breathing and pain, without causing long-term disability or death [10–23]. The incapacitating nature of this chemical has led to the development of dispersal devices to use it, either individually or in solutions combining several agents as an alternative to brutal force for individual protection, crowd control during civil disturbances, or rescuing hostages and to a lesser extent as chemical weapon on the battlefield [24,25]. It is also regularly used by the military for mask confidence training and by police departments for individual protection. It can be dispersed as fine powder or in solvents as jets or streams from spray cans, tanks or larger weapons, hand grenades, or mortar artillery munitions, and also as aerosols or smoke by pyrotechnic generators [26]. CN is generally dispersed into the environment by firing the shells filled with them. The fir-

ing of the shells and their subsequent explosion often leads to toxic degradation products due to its decomposition, especially at higher temperatures. People exposed to CN will also be exposed to many of the volatile degradation products, which may be hazardous in nature. Apart from the immediate exposure, some of the transformation products may stay for longer durations in the environment and cause fatal effects [27–36]. For evaluation of potential influence on the living being and the environment by the pyrolysates of CN, it is imperative to investigate its pyrolysis behavior so that danger of its degradation can be avoided. At the same time, it is also desirable to know about the possible routes of its fragments so that the nature of the transformation products of CN formed under thermal stress can be predicted to understand the toxicity due to the exposure. This helps in selecting optimum dispersal temperature for designing suitable pyrotechnic generator to avoid toxicity due to the formation of toxic products. Generally, the pyrolysis products of organic compounds is a complex mixture, which may include different homologues series [37,38]. For separation and determination of the complex pyrolysate, the commonly used method is the high resolution gas chromatography (HRGC) in conjunction with other detection methods, such as mass spectrometry (MS), infrared spectrometry (IR), nuclear magnetic resonance (NMR), etc. CN has been studied quite extensively using gas chromatography–mass spectrometry (GC/MS), selected ion flow tube mass spectrometry and thermal desorption gas chromatography–mass spectrometry (TD-GC/MS) [39–45]. The information on the pyrolysis of CN

* Corresponding author. Tel.: +91 7512231921; fax: +91 7512341148.
  E-mail address: sai_kirtana@rediffmail.com (M.V.S. Suryanarayana).

Table 1
Identification and quantification of the pyrolysis products.

No.	t_R (min)[a]	Compound	CAS No.[b]	bp (°C)[c]	Area (%)		
					600 °C	700 °C	800 °C
1	2.478	Benzene	71-43-2	80.24	0.242	0.754	3.638
2	3.308	Toluene	108-88-3	110.78	–[d]	0.081	0.631
3	4.28	Chlorobenzene	108-90-7	131.87	0.058	0.108	0.0364
5	4.48	Ethyl benzene	100-41-4	136.35	–	–	0.548
6	4.69	Styrene	100-42-5	145.31	–	0.666	1.549
7	4.916	Benzocyclobutene	694-87-1	150.15	–	0.156	1.556
8	5.848	Benzaldehyde	100-52-7	178.9	2.993	12.094	20.338
9	6.313	Phenol[e]	108-95-2	182.0	0.606	2.187	2.481
10	6.422	Benzocyclobutenone[e]	3469-06-5	215.03	–	0.502	0.424
11	6.59	Benzofuran[e]	271-89-6	174.15	–	0.175	–
12	6.91	Benzyl chloride	100-44-7	179.55	–	0.757	0.385
13	7.984	Acetophenone	98-86-2	202.15	24.497	22.174	16.711
14	8.058	α,α-Dihydroacetophenone	1075-06-5	210.6	–	3.693	0.948
15	8.905	β-Chlorostyrene[e]	622-25-3	189.0	–	0.191	0.331
16	9.274	Dichloromethyl benzene	98-87-3	214.0	0.056	1.117	1.524
17	9.672	Benzoic acid[e]	65-85-0	249.0	0.568	0.752	–
18	10.124	Naphthalene[e]	91-20-3	218.14	–	0.309	2.18
19	11.866	Chloroacetophenone	532-27-4	247.15	67.617	51.72	18.507
20	13.002	Dichloroacetophenone	2648-61-5	249.15	1.362	0.756	0.256
21	13.489	Biphenyl	92-52-4	255.15	–	0.402	1.358
22	14.031	Acenaphthylene[e]	83-32-9	277.54	–	1.059	0.994
23	14.358	Diphenylmethane[e]	101-81-5	264.42	–	–	0.352
24	14.675	Biphenylene	259-79-0	280.15	–	–	1.959
25	15.650	1,1-Diphenylethylene[e]	530-48-3	277.25	–	0.047	0.212
26	15.704	Dibenzofuran[e]	132-64-9	284.86	–	0.34	1.065
27	15.732	Bibenzyl	103-29-7	280.65	–	0.187	–
28	15.777	Z-stilbene[e]	645-49-8	262.0	–	0.294	0.706
29	16.710	9H-Fluorene	86-73-7	297.44	–	0.068	0.489
30	17.357	Benzophenone	119-61-9	306.24	–	0.260	0.499
31	17.758	Diphenylethyne[e]	501-65-5	300.0	–	0.230	1.568
32	18.278	9,10-Dihydrophenanthrene	776-35-2	306.2	–	0.035	0.098
33	18.457	E-stilbene	103-30-0	306.65	0.187	2.221	4.705
34	18.763	Phenanthrene	85-01-8	340.45	–	0.105	0.426
35	18.919	Fluorenone	486-25-9	341.65	–	0.080	0.435
36	19.491	Anthracene	120-12-7	342.18	–	0.084	0.507
37	19.577	3-Phenanthrol	605-55-0	344.0	–	0.086	0.204
38	19.869	Benzil	134-81-6	347.15	0.187	0.373	0.164
39	20.182	Trans-α-chlorostilbene[e]	948-98-1	322.15	–	0.373	–
40	21.132	Isomer of 39	20426-47-5		–	0.121	–
41	21.579	β-Phenylpropiolophenone	7338-94-5	340.6	–	0.126	0.171
42	22.121	Chalcone[e]	94-41-7	345–348	0.114	0.580	1.052
43	22.609	2,5-Diphenyl furan[e]	955-83-9	344.15	–	0.091	0.0349
44	22.973	Unidentified			3.250	4.195	1.702
45	23.056	2-Propene-1-one-1-(2-chlorophenyl)-3-phenyl[e]	20426-47-5	379.1	0.487	0.862	0.544

[a] Retention time.
[b] Chemical Abstract Service Registry Number.
[c] Boiling point obtained from book Thermophysical Properties of Chemicals and Hydrocarbons. By Carl L. Yaws, Elsevier Publication.
[d] Not detected.
[e] Compound used as a reference material.

has been not available so far. The present study aims to obtain more detailed information on pyrolysis products from CN with on-line pyrolysis (pyr) gas chromatography–mass spectrometry (Py-GC/MS) technique. The pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) technique employed in the present study provides unique advantage for identification of the pyrolyzates formed during decomposition of CN at various temperatures. In Py-GC/MS, pyrolysis components are identified by matching the measured mass spectrum against standard mass spectra library. The commonly used method is the probability-based match (PBM) algorithm [46,47]. For complex mixtures, PBM results can be determined with the aid of correlation of retention behavior [48,49] and boiling point (bp) [50]. The objective is to simulate CN pyrolysis behavior with the deficiency of oxidants to determine thermal decomposition products produced during pyrolysis process and their contribution to understand the decomposition pathway. The investigation results are useful for understanding of thermo-chemical properties of CN and evalua-

tion of the potential influence of pyrolysates to living being and environment.

2. Experimental

2.1. Materials

ω-Chloroacetophenone was synthesized in house as per the reported method [51]. Purity of chemical was checked by the GC/MS, IR and NMR methods. A stock solution containing 50 mg amount of CN in 2 ml of acetone (99%, Merck) was prepared and used in pyrolysis experiments.

2.2. Analytical standards

Analytical standards phenol (99%), benzocyclobutenone (98%), benzofuran (98%), β-chlorostyrene (99%), acetophenone (99%), benzoic acid (98%), naphthalene (99%), acenaphthylene (97%),

diphenylmethane (98%), 1,1-diphenylethylene (98%), dibenzofuran (99%), Z-stilbene (98%), diphenylethyne (98%), trans-α-chlorostilbene (98%), dichloroacetophenone (99%), biphenyl (99%), calcone (99%), bibenzyl (99%), diphenylmethane (99%), trans-α-chloro-stilbene (99%), 3-phenylfurane (99%), chlorochalcone (99%), and 2,5-diphenylfuran (99%) were purchased from Aldrich. The retention times of these reference materials were used for validation of the identification results.

2.3. Instrumentation

2.3.1. Thermogravimetric analysis

Thermogravimetric analysis was performed on a Perkin Elmer Pyris 1 TGA at a heating rate of 20 °C/min from ambient to 600 °C. Experiment was carried out on approximately 12.953 mg sample heated in a flow of nitrogen (60 ml/min furnace, 40 ml/min balance). Temperatures where $\partial mass/\partial t$ was maximum (T_{max}) were measured from the DTGA curves. Kinetic analysis of the weight loss of the sample was carried out using thermo-kinetic software.

2.3.2. Py-GC/MS analysis

Pyrolysis-GC/MS analysis was run on a Frontier Laboratories model PY-2020iD double-shot pyrolyser. The samples were pyrolyzed for 0.5 min at different temperatures ranging from 100 to 800 °C with a step of 100 °C increment. The pyrolyser was directly coupled to the inlet port of a Agilent 6890N gas chromatograph interfaced to a Agilent 5973 inert mass selective detector. The pyrolysis gases from CN were introduced directly into the GC/MS analysis system. The pyrolyser is based on a technique in which a small deactivated stainless steel cup loaded with a sample is dropped into a small sized vertical micro-furnace by gravitational free-fall with push button mechanism. This system provides precise temperature control and minimal condensation of pyrolysates in the system. A sample of 1 µl of CN stock solution was placed in the small stainless steel cup and solvent was allowed to evaporate prior to heating. Sample cup is attached to the pyrolyser. After the GC conditions were established and pyrolyser furnace temperature reached to the desired experimental temperature, the sample cup was dropped into the pyrolysis furnace by manually pressing the "sample drop button" and introduced the sample cup to reach instantly to set pyrolysis temperature; the run was then immediately started. Once the system started to run, the sample controller stopped sampling after 0.5 min and the pyrolysis gases from CN sample were introduced directly into GC/MS analysis system. All pyrolysis tests were repeated three times at each pyrolysis temperature to ensure reproducibility. An F-Lab UA-5 metal capillary column (30 m × 0.25 mm × 0.25 µm) was employed for the study with cross-bonded diphenyl-5% and dimethyl polysiloxane-95% as a stationary phase. The oven was programmed to hold at 50 °C for 2 min and ramped at 8 °C/min to 280 °C after which it was held at this temperature for 5 min. The GC injector temperature was kept at 250 °C with the injector split ratio set to 100:1. Helium was used as a carrier gas with a constant flow rate of 0.7 ml/min. The separated pyrolyzates from the GC were transferred to mass spectrometer (MS) via a heated interface maintained at 280 °C temperature. The ion source and quadrupole mass analyzer temperatures were kept at 230 °C and 150 °C, respectively. Mass spectrometer was tuned at 70 eV in EI mode with the mass range of 50–550 amu. Post-experimental data analysis (peak integration) was done by the Chemstation software (Agilent Technologies).
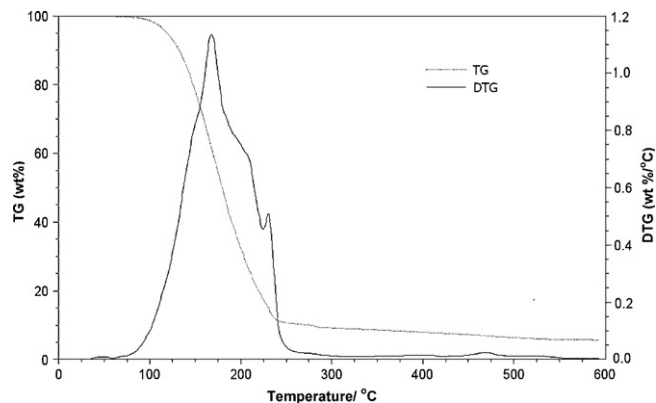

Fig. 1. TG/DTG curve of CN.

2.4. Data process

The qualitative and semi quantitative analysis were done in following steps.

2.4.1. Matching the detected mass spectra against standard mass spectra library

The PBM algorithm [46,47], which uses a reverse search to verify that peaks in the reference spectrum were present in the unknown spectrum, was used to match the detected mass spectra. The spectral similarity was measured by reverse match factor (R.Match). Generally, there are several tentative components in the matching list at a specific peak, and only one of them was selected as the identified component.

2.4.2. Confirmation of the tentative components

For the tentative components with very similar mass spectra, the correlation of boiling point (bp's) and retention behavior of organic compound [48,49] can provide useful information for the identification, i.e., the higher is the bp of a compound in the homologous series; the later is the component elution from the column. For the chemical substances on non-polar column, the bp's of organic homologous are linear with their retention times [48].

2.4.3. Quantification of the identified components

In order to simplify the quantification procedure and conveniently compare the variation of the pyrolysates versus temperature, the identified components were quantified by normalization of their integration peak areas. Thus, the area percentage used in Table 1 was considered as the relative concentration of the pyrolysates at different temperatures.

3. Results and discussion

3.1. TG data analysis

Thermo-gravimetric (TG) and derivative thermo-gravimetric (DTG) profile for CN residue as a function of temperature is shown in Fig. 1. TG analysis shows that initial weight loss at 100 °C temperature and final weight loss at 230 °C temperature. Moreover, the DTG curve clearly indicates multiple peaks in which the weight loss is attributed to various phenomena. For the sake of convenience, the pyrolysis process is subdivided into three stages based on the DTG profile. The first stage is a weight loss for drying the sample (below 100 °C). The weight loss on the lower temperature is ascribed to the loss of inherent moisture. The second stage showing rapid weight loss between 100 and 230 °C is ascribed to the sublimation and trace thermal decomposition of CN residue. Most of the weight
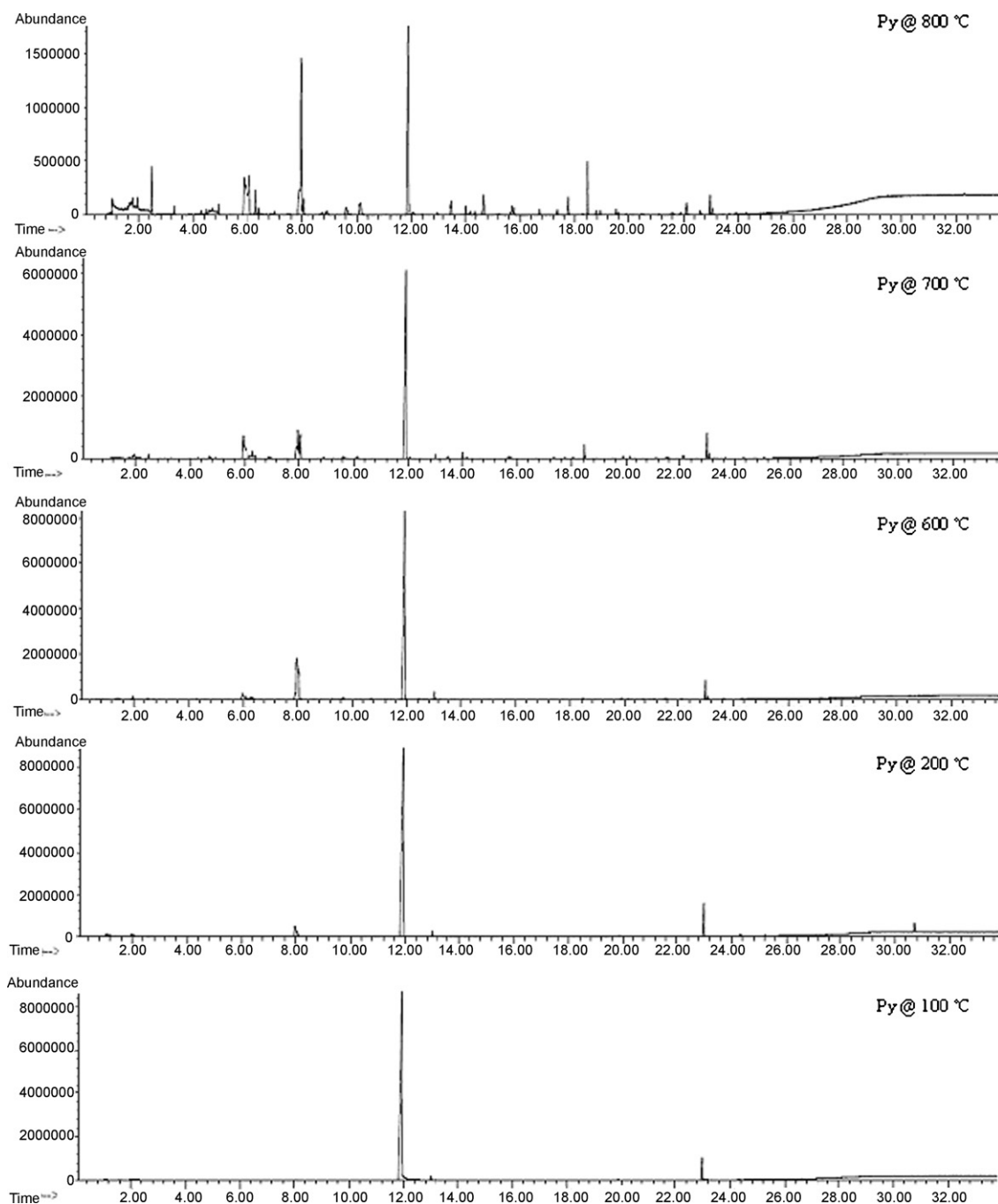
Fig. 2. TIC of the pyrolysis products at different temperatures.

loss (about 70 wt.%) exhibits in this range. Two peaks centered at 167 and 229 °C are observed in DTG curve (weight loss rate) in this stage; sublimation is the major cause for mass loss at 167 °C while secondary peak at 229 °C is attributed to trace thermal degradation. Therefore, based on the DTG curve it appears that at lower temperature sublimation is predominant over decomposition. The last stage in the weight loss is attributed to further cracking process of CN residues in a wide temperature range from 230 to 600 °C. About 6 wt.% of the total weight loss at lower rate in this stage and a total weight loss of 94.33 wt.% was observed at 600 °C during TG/DTG experiment. These results are inline with the work reported earlier for tear gas thermal decomposition studies [52].

The TGA data analysis though provides thermal stability of CN, it does not provide complete and real time profile of thermal decom-

position products at that pyrolysis temperatures. This is due to CN sublimation prior to decomposition and hence removes the thermo-balance parameters thereby showing mass loss. Thus thermal gravimetric analysis is not an ideal technique for quantitative decomposition studies of CN. In order to understand decomposition temperature and mechanism, a comprehensive study with on-line Py-GC/MS analysis has been carried out.

3.2. Py-GC/MS analysis

In order to get an insight on qualitative as well as quantitative information and thermal degradation mechanisms of CN, on-line thermal analyses were performed with flash Py-GC/MS at temperatures from 100 to 800 °C. The total ion chromatograms (TIC)
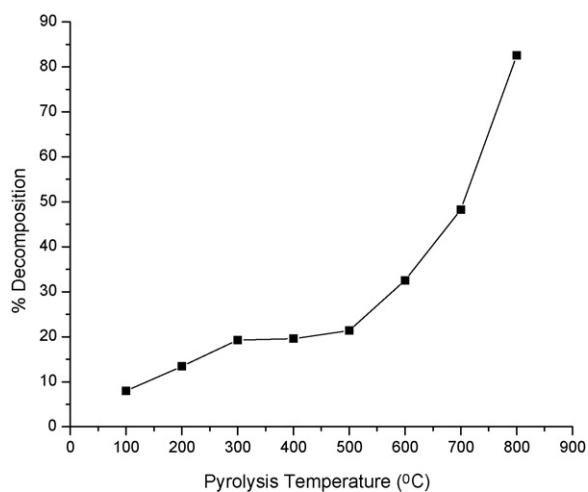
Fig. 3. Decomposition of CN vs. pyrolysis temperature.

obtained at various pyrolysis temperatures are shown in Fig. 2. The typical pyrogram of pure CN in acetone at 100 °C exhibited only one peak corresponding to the parent compound which revealed that CN is quite stable up to this temperature. However, further increase in the pyrolysis temperature results in decomposition at 200 °C with the appearance of two additional peaks of lower intensity. This is due to the formation of trace amounts of acetophenone
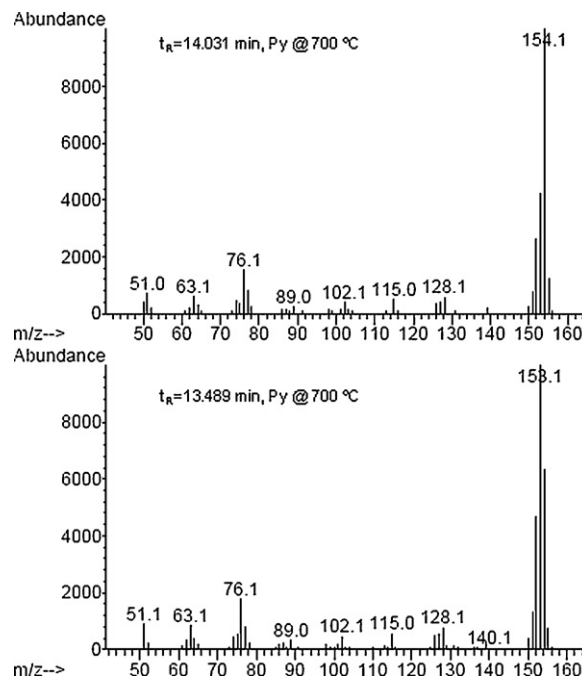

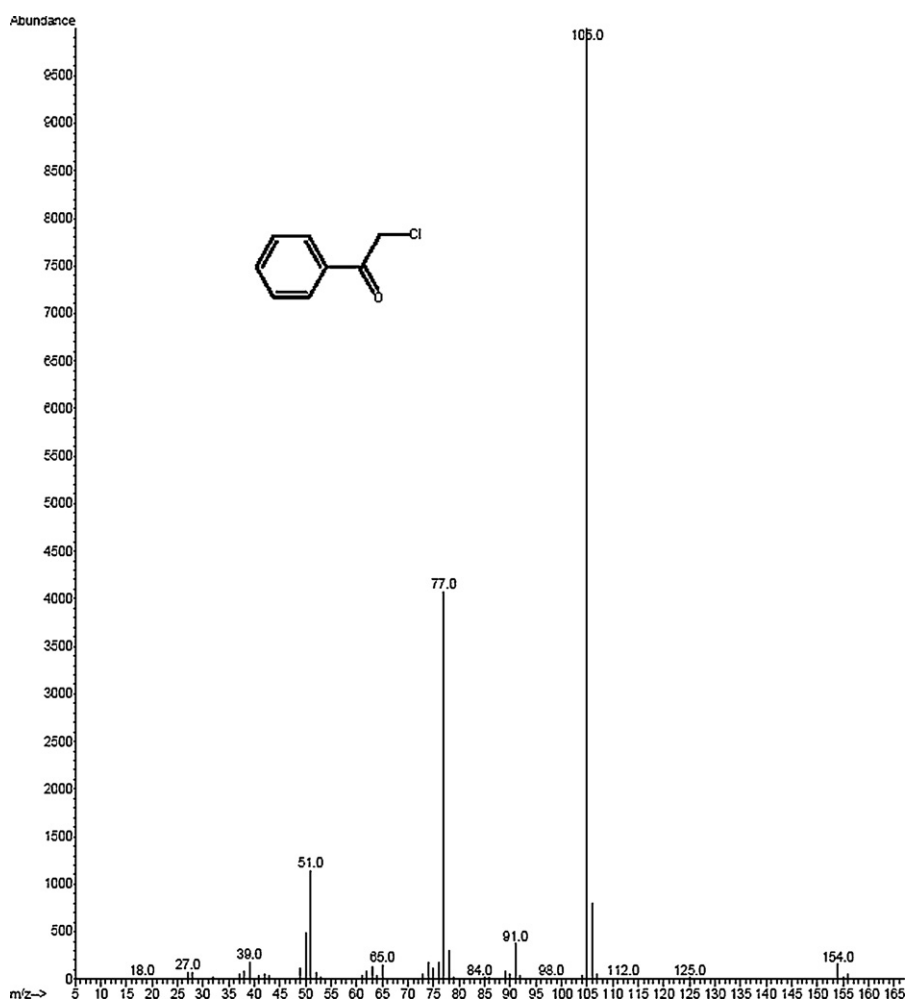**Fig. 5.** Measured mass spectra of the pyrolysates at 14.032 and 13.5 min (pyrolysis at 700 °C).

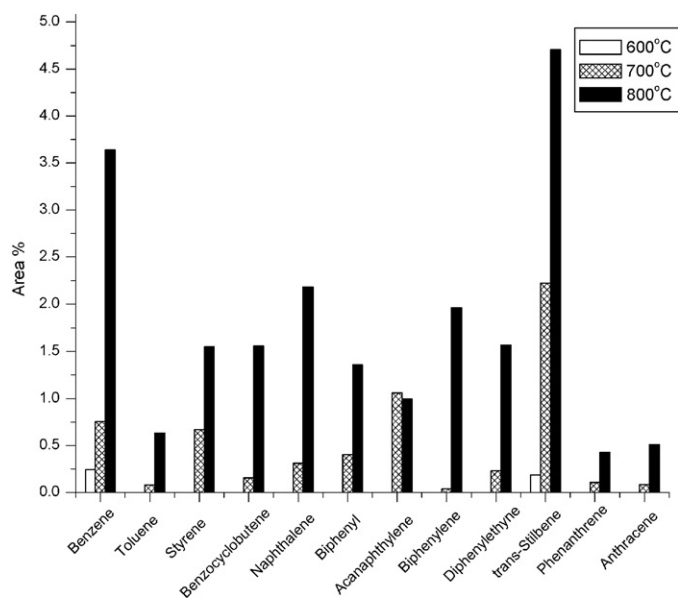**Fig. 4.** Plot of chemical structure and standard mass spectrum of CN.

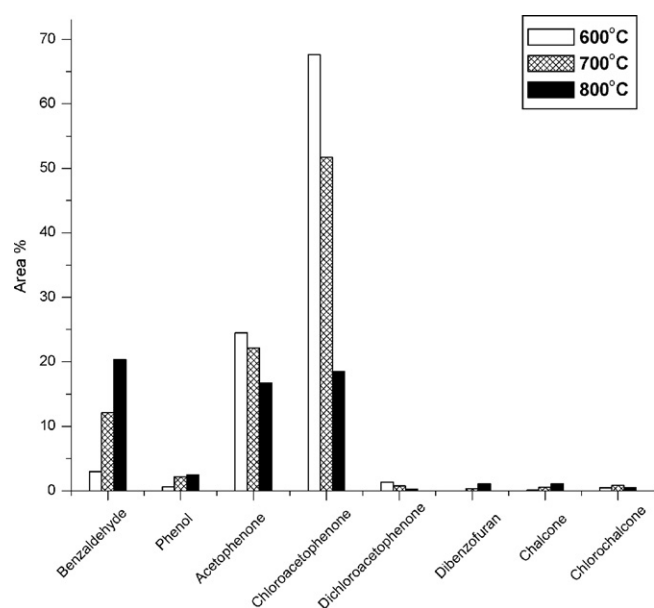**Fig. 6.** Content variation of some representative mono and PAHs vs. the pyrolysis temperature.

Fig. 7. Content variation of some oxygenated compounds vs. the pyrolysis temperature.

and dichloroacetophenone. Total ion chromatogram at 300–600 °C shows similar trends with varied concentration of acetophenone and dichloroacetophenone. Thus, CN pyrograms at 100–600 °C document incomplete degradation. However, trace amount of other product is also observed at retention time 22.973 min, which could not be identified in the present study, though it existed throughout the analysis. The mass spectral data obtained from Py-GC/MS analysis suggests the formation of many simple aromatic compounds during pyrolysis above 600 °C. Further increase in the pyrolysis temperature results in extensive degradation of the parent compound leading to the appearance of number of peaks in the pyrogram. Pyrolytic decomposition of CN usually generates a large amount of gaseous organics such as CO, CO_2, HCl, CH_4, C_2H_2, C_2H_6 and mono-aromatic & polycyclic aromatic hydrocarbons. At this point, it is quite reasonable to consider the pyrolytic products formed at this temperature as a result of thermal degradation of parent CN as well as that of primary and secondary pyrolytic products. Based on calculation of peak area in the pyrogram, the percentage decomposition at different temperatures ranging from 100 to 800 °C is shown in Fig. 3. CN shows approximately 8% decomposition at 100 °C and further increase in pyrolysis temperature to 300 °C results in increase in decomposition up to 20%. Rate of decomposition is marginal at pyrolysis temperature ranging from 300 to 500 °C and 22% decomposition is observed at 500 °C. It is interesting to observe that CN decomposition sharply increases with further increase in the temperature beyond 500 °C and maximum decomposition (82%) is observed at 800 °C. The high thermal stability of CN may be accounted for delocalization of π electrons derived out of aromaticity. In addition to this mesomeric effects of carbonyl group and negative inductive effect of Cl atom also contribute to its inherent stability. Besides this, its sublimation at 167 °C (as observed in TGA/DTG studies) may also be a contributing factor for its thermal stability due to low heat conduction between the vapour phase molecules.

3.3. Identification and quantification of the pyrolysis products

Chemical structure and standard mass spectrum of CN is shown in Fig. 4. It can be seen that relative abundance at the molecular ion peak (m/z 154) is weak and this makes the identification of CN in a complex mixture more difficult. The chemical structure of CN is not very complicated; however, its pyrolysate is very complex as evident from the TICs shown in Fig. 2. Similarity in mass spectra at two different retention times of a complex total ion chromatogram results in confusion. For example; two almost similar mass spectra of acenaphthylene and biphenyl at the retention times 14.031 and 13.489 min of the pyrolysates at 700 °C depicted in Fig. 5, leading to ambiguity in identification based on PBM procedure. In the PBM procedure as discussed in Section 2.4, the R.Match for acenaphthylene and biphenyl are larger than 90%, which appears to be a very good match. It shows that for the GC/MS analysis of the complex homologous series, the similarity of the detected mass spectra at different peaks makes it difficult to identify the components only by the R.Match. If the boiling points (bp) of acenaphthylene and biphenyl are known, the correlation of bp and retention time [48] can resolve the ambiguity in identification. The bp's of acenaphthylene and biphenyl are 277.54 and 255 °C, respectively. According to the correlation of bp and retention time, the retention time of biphenyl should be less than that of acenaphthylene. Therefore, the peaks at 13.489 and 14.031 min are corresponding to biphenyl and acenaphthylene, respectively. The identification of acenaphthylene could also be confirmed by the retention time (14.031 min) of acenaphthylene reference material. The above identification results show that the data processing procedure, i.e., PBM search in conjunction with the correlation of bp and retention time, used in this study is reliable. The various pyrolysates obtained at different temperatures were identified using similar procedure. The identification results are listed in Table 1. The identified components were classified into two subgroups for convenient comparison: (1) the hydrocarbons or
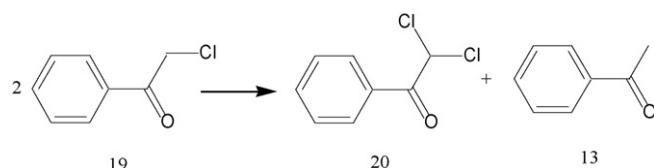

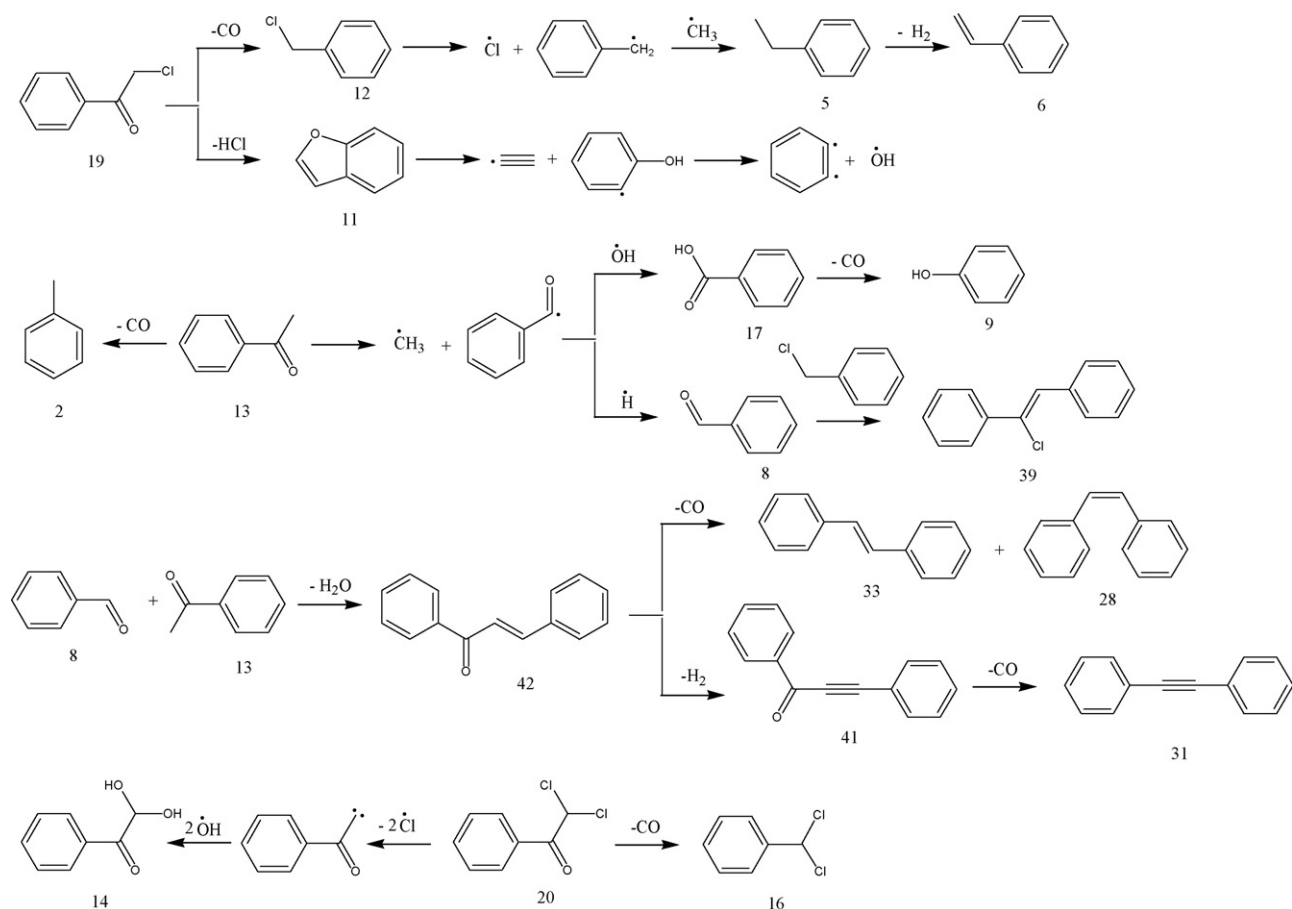**Fig. 8.** Primary pyrolysis of CN at low temperature.

Fig. 9. Secondary pyrolysis of CN and the radicals or components produced during the primary pyrolysis at higher temperature.

aromatic hydrocarbons; (2) the oxygenated compounds. The contents of the identified pyrolysis components are calculated and listed in Table 1. The contents of the 45 identified compounds varied from 0.03% to 24.5%. It can be seen that dominant species are oxygenated compounds when the temperature is less than 700 °C and hydrocarbons or aromatic hydrocarbons are dominant when the temperature is higher than 700 °C. It can also be seen that all the produced PAHs, such as anthracene, phenanthrene, 9H-flourene, etc., are priority toxic substances.

3.4. Semi-quantitative analysis of pyrolysis components

It can be seen that an amount of 32% of CN is obviously decomposed at 600 °C which further increased to 82% at 800 °C. The main decomposition compounds are highly carcinogenic aromatic compounds like benzene, phenol, biphenylene, diphenylethyne benzaldehyde, acetophenone, and trans-stilbene. These compounds would have been further pyrolyzed with an increase in temperature. Fig. 6 shows the percentage decomposition of several representative mono-aromatics and PAHs as function of temperature. It can be seen that most of these aromatic hydrocarbons are produced at higher temperature (>700 °C) in this study. The contents of these compounds increased obviously with an increase in temperature and had a tendency to decrease with the ring's number increased at a specific temperature. Besides the decomposition compounds, like mono-aromatics and PAHs, there are other oxygenated compounds that could be seen from Table 1. Fig. 7 shows the contents variation of CN and several oxygenated compounds with pyrolysis temperature. It can be seen that content of these

oxygenated compounds vary significantly with the change of temperature.

3.5. Health concerns

A potential health threat exists regarding the formation of mono-and polycyclic aromatic hydrocarbon [27–36]. Py-GC/MS data reveals that these are formed at higher pyrolysis temperature by free radical mechanism. The mass spectra of CN derived compounds observed at temperatures 300–500 °C do not show peaks for most of mono- and poly-cyclic aromatic hydrocarbon except for chloroacetophenone, dichloroacetophenone and acetophenone. This provides evidence that these compounds though to possess free radical intermediates are not formed under the condition present in the system at low pyrolysis temperatures. These results lead us to assume that thermal dispersion of CN at a reduced temperature may be less likely to produce these degradation products.

3.6. Pyrolysis mechanism of ω-chloroacetophenone

Based on the contents variation of the pyrolysis components as a function of temperature, a most probable mechanism involving radicals and reactions of intermediate radicals, is proposed in following steps.

3.6.1. Primary pyrolysis of CN at lower temperature

CN is first decomposed into intermediate radicals and transformed as molecule into acetophenone and dichloroacetophenone (Fig. 8).
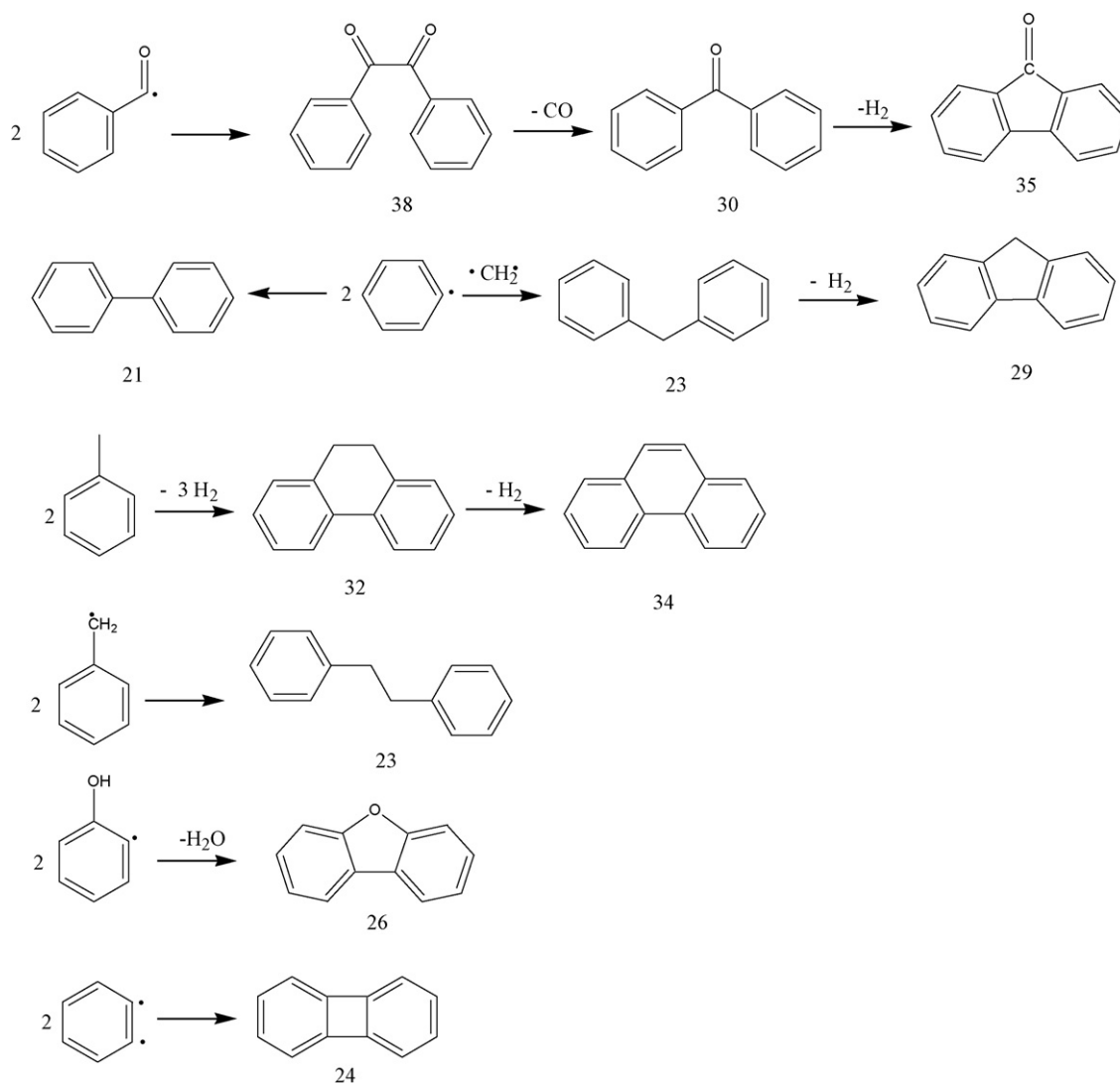
Fig. 10. Polymerization of the radicals produced during the primary or secondary pyrolysis.

3.6.2. Secondary pyrolysis of CN and its radicals or components produced during the primary pyrolysis at higher temperature

CN and compounds that produced during the primary pyrolysis may be further pyrolyzed (Fig. 9). At higher pyrolysis temperatures CN may first decompose into benzyl chloride and benzofuran by the elimination of one molecule of CO and HCl molecule, respectively. Benzyl chloride and benzofuran may further decompose and transform as decomposition compounds or other radicals. Some of the mono- and di-aromatics can be produced by the interaction of these radicals. The oxygenated compounds that produced at 600 °C are benzaldehyde, phenol, etc. The occurrence of benzaldehyde is due to homolytic cleavage of methyl carbonyl carbon–carbon bond occurred at this temperature. These reactions can account for increase or decrease in the contents of the pyrolysis component with variation of temperature as shown in Figs. 6 and 7.

3.6.3. Polymerization of the radicals produced during the primary or secondary pyrolysis

It is interesting to note that despite the presence of only one aromatic ring in the chemical structure of CN, a number of PAHs are identified as shown in Table 1. This can be attributed to the fact that the genesis of the PAHs should be by the polymerization of the radicals or fragments that are produced during the primary and secondary pyrolysis. Fig. 10 shows that some of the radicals can be interacted and transformed as new molecules or radicals. The PAHs, the mono-aromatics, and their oxygenated derivatives can be produced in this pathway. It can also account for decrease in the contents of the PAHs with increase in the ring's number and lower contents of the oxygenated compounds.

4. Conclusions

The pyrolysis behavior of CN was investigated by TGA and on-line Py-GC/MS analysis. The TG/DTG curves showed a slight weight loss at temperature range of 50–100 °C followed by a main decomposition at temperature range of 167–229 °C. Sublimation was major cause for mass loss at 167 °C while secondary peak at 229 °C attributed to trace CN thermal degradation. Results from pyrolysis-GC/MS suggested that slight weight loss at the temperature range of 100–500 °C resulted from bond cleavage between carbon and chlorine atoms. A maximum decomposition beyond 600 °C temperatures was attributed to decomposition of parent CN as well as its degradation compounds produced by the primary and secondary pyrolysis reactions, such as mono-aromatics, PAHs and oxygenated compounds. The contents of the pyrolysis components varied within a wide range with change in temperature. The sep-

arated pyrolysis components were identified using PBM algorithm with the aid of correlation of boiling points and retention time. Based on thermal studies of CN, its pyrolysis mechanism was proposed. These investigation results provide useful information for evaluation of CN thermal behavior and its potential influence to living thing.

Acknowledgement

References

[1] F.R. Sidell, Riot control agent, in: Textbook of Military Medicine, Medical Aspects of Chemical and Biological Warfare, Office of the Surgeon General, US Army, TMM Publications, Washington, DC, 1997, pp. 307–324.

[2] US Department of Health and Human Services, Hazardous Substances Data Bank (HSDB online database), 2-Chloroacetophenone, 2010, http://toxnet.nlm.nih.gov/cgi-bin/sis/search.

[3] O'Neil, et al., The Merck Index—An Encyclopedia of Chemicals, Drugs and Biologicals, 14th ed., Merck & Co., Inc, Whitehouse Station, NJ, 2010.

[4] Material Safety Data Sheet, 2-chloroacetophenone, 2004, http://www.chemicon.com/webfiles/MSDS/ECM508MSDS.pdf.

[5] United States Environmental Protection Agency (US EPA), Integrated Risk Information System (IRIS) on 2-Chloroacetophenone, 2000, http://www.epa.gov/ttn/atw/hlthef/chlo-phe.html.

[6] R.P. Pohanish, M. Sittig, Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens, vol. 2, 5th ed., William Andrew Publishing, Norwich, NY, 2008.

[7] C.R. Warden, Respiratory agents: irritant gases, riot control agents, incapacitants and caustics, Crit. Care Clin. 21–4 (2005) 719–737.

[8] H. Salem, B. Ballantyne, S.A. Katz, Inhalation toxicology of riot control agents, in: Inhalation Toxicology, 2nd ed., CRC, New York, NY, 2005.

[9] K. Blaho-Owens, Chemical crowd control agents, in: R. Byard, J. Payne-James, T. Corey, C. Henderson (Eds.), Encyclopedia of Forensic and Legal Medicine, Elsevier Academic Press, 2005, pp. 319–325.

[10] P. Holland, R.G. White, The cutaneous reactions produced by o-chlorobenzylidenemalononitrile and chloroacetophenone when applied directly to the skin of human subjects, Br. J. Dermatol. 86 (1972) 150–154.

[11] N.S. Penneys, R.M. Israel, S.M. Indgin, Contact dermatitis due to 1-chloroacetophenone and chemical mace, N. Engl. J. Med. 281 (1969) 413–415.

[12] P.G. Blain, Human incapacitants, in: M.R. Dobbs (Ed.), Clinical Neurotoxicology, 1st ed., Saunder Elsevier Publication, Philadelphia, USA, 2005, pp. 660–673.

[13] K.M. Thorburn, Injuries after use of the lachrimatory agent chloroacetophenone in a confined space, Arch. Environ. Health 37 (1982) 182–186.

[14] R. Treudler, B. Tebbe, U. Blume-Peytavi, K. Krasagakis, C.E. Orfanos, Occupational contact dermatitis due to omega-chloracetophenone tear gas, Br. J. Dermatol. 140 (3) (1999) 531–534.

[15] E.J. Olajos, H. Salem, Riot control agents: pharmacology, toxicology, biochemistry and chemistry, J. Appl. Toxicol. 21 (2001) 355–391.

[16] E.J. Olajos, W. Stopford, Riot Control Agents: Issues in Toxicology, Safety and Health, CRC Press, Boca Raton, FL, 2004.

[17] Directorate of Medical Research, The Toxicology of CN, CS, and DM (Edgewood Arsenal Special Summary Report), Department of the Army 47, Edgewood Arsenal, MD, 1965.

[18] B. Ballantyne, The comparative acute mammalian toxicity of 2-chloroacetopphenone (CN) and 2-Chlorobenzylidene Malononitrile (CS), Arch. Toxicol. 40 (1978) 75–95.

[19] B.P. McNamara, E.J. Owens, J.T. Weimar, T.A. Ballard, F.J. Vocci, Toxicology of Riot Control Chemicals—CS, CN and DM (Edgewood Arsenal Technical Report, EATR 4309), Department of the Army, Edgewood Arsenal, MD, 1969.

[20] P.G. Blain, Tear gases and irritant incapacitants; 2-chloroacetophenone, 2-chlorobenzylidene malononitrile and dibenz[b,f]-1,4-oxazepine, Toxicol. Rev. 22 (2) (2003) 103–110.

[21] C.J. Hilmas, M.J. Poole, A.M. Katos, P.T. Williams, Riot control agents, in: R. Gupta (Ed.), Handbook of Toxicology of Chemical Warfare Agents, Elsevier Academic Press, 2009, pp. 153–175.

[22] G.M. Recer, T.B. Johnson, A.K. Gleason, An evaluation of the relative potential public health concern for the self-defense spray active ingredients oleoresin capsicum, o-chlorobenzylidene malononitrile, and 2-chloroacetophenone, Regul. Toxicol. Pharmacol. 39–1 (2002) 1–11.

[23] M.D. Philip Buttaravoli, Irritant incapacitant exposure (lacrimators, riot control agents tear gas) Minor Emergencies, vol. 2, 2007, pp. 249–251.

[24] H. Salem, E.J. Olajos, S.A. Katz, Riot control agents, in: S.M. Somani, J.A. Romano (Eds.), Chemical Warfare Agents: Toxicity at Low Levels, CRC Press, Boca Raton, FL, 2001, pp. 331–360.

[25] S.M. Somani, Chemical Warfare Agents, Elsevier Academic Press, New York, 1992.

[26] United States Army, FM 3-11/MCRP 3-3.7.2, Flame, Riot Control Agent and Herbicide Operations, United States Army, Washington DC, 1996.

[27] US Public Health Service, Toxicological Profile for Polycyclic Aromatic Hydrocarbons, Agency for Toxic Substances and Disease Registry, Public Health Service, US Department of Health and Human Services, Atlanta, GA, 1990.

[28] C.P. Kaushik, A.K. Haritash, Polycyclic aromatic hydrocarbons (PAHs) and environmental health, Our Earth 3 (3) (2006) 1–7.

[29] United States Environmental Protection Agency, Polycyclic Aromatic Hydrocarbons (PAHs), 2008, http://www.epa.gov/osw/hazard/wastemin/priority.htm.

[30] R.G. Harvey, Mechanisms of carcinogenesis of polycyclic aromatic hydrocarbons, Polycycl. Aromat. Comp. 9 (1996) 1–23.

[31] A. Luch, The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons, Imperial College, London, 2005, ISBN 1-86094-417-5.

[32] P. Boffeta, N. Jourenkova, P. Gustavsson, Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons, Cancer Causes Contr. 8 (1997) 444–472.

[33] CEC, Working Document on Sludge (3rd Draft), Commission of the European Communities Directorate-General Environment, ENV.E.3/LM, Brussels, 27 April, 2000.

[34] P. Henner, M. Schiavon, J.L. Morel, E. Lichtfouse, Polycyclic aromatic hydrocarbon (PAH) occurrence and remediation methods, Analysis 25 (9–10) (1997) M56–M59.

[35] C.E. Boström, P. Gerde, A. Hanberg, B. Jernstrom, C. Johansson, T. Kyrklund, A. Rannug, M. Törnqvist, K. Victorin, R. Westerholm, Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air, Environ. Health Perspect. 110 (Suppl. 3) (2002) 451–488.

[36] S.K. Samanta, O.V. Singh, R.K. Jain, Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation, Trends Biotechnol. 20 (2002) 243–248.

[37] R.R. Baker, L.J. Bishop, The pyrolysis of tobacco ingredients, J. Anal. Appl. Pyrol. 71 (2004) 223–311.

[38] H.P. Wang, S.H. Liao, K.S. Lin, Y.J. Huang, H.C. Wang, Pyrolysis of PU/CFCs wastes, J. Hazard. Mater. 58 (1998) 221–226.

[39] W.A. Carrick, D.B. Cooper, B. Muir, Retrospective identification of chemical warfare agents by high-temperature automatic thermal desorption–gas chromatography–mass spectrometry, J. Chromatogr. A 925 (2001) 241–249.

[40] G.J. Francis, D.B. Milligan, M.J. McEwan, Detection and quantification of chemical warfare agent precursors and surrogates by selected ion flow tube mass spectrometry, Anal. Chem. 81 (21) (2009) 8892–8899.

[41] P.A. D'Agostino, L.R. Provost, Analysis of irritants by capillary column gas chromatography–tandem mass spectrometry, J. Chromatogr. A 695 (1995) 65–73.

[42] E.R.J. Wils, A.G. Hulst, Gas chromatographic-mass spectrometric identification of tear-gases in dilute solutions using large injection volumes, J. Chromatogr. 330 (1985) 379–382.

[43] M. Pacentl, S. Dugheri, R. Gagliano-Candela, G. Strisciullo, E. Franchi, F.D. Esposti, N. Perchiazzi, P. Boccalon, G. Arcangeli, V. Cupelli, Analysis of 2-chloroacetophenone in air by multi-fiber solid-phase microextraction and fast gas chromatography–mass spectrometry, Acta Chromatogr. 21 (3) (2009) 379–397.

[44] D.N. Tripathi, R.C. Malhotra, A. Bhattacharya, Gas chromatographic–mass spectrometric identification of chloroacetophenone, o-chlorobenzylidenemalononitrile and dibenz[b,f]-1:4-oxazepine, J. Chromatogr. 315 (1984) 417–420.

[45] B.R. Gandhe, R.C. Malhotra, P.K. Gutch, Gas chromatographic retention indices of tear gases on capillary columns, J. Chromatogr. 479 (1989) 165–169.

[46] F.W. McLafferty, M.Y. Zhang, D.B. Stauffer, S.Y. Loh, Comparison of algorithms and databases for matching unknown mass spectra, J. Am. Soc. Mass Spectrosc. 9 (1998) 92–95.

[47] S.Y. Loh, F.W. Mclafferty, Exact-mass probability based matching of high-resolution unknown mass-spectra, Anal. Chem. 63 (1991) 546–550.

[48] X.G. Shao, G.Q. Wang, Quantitative prediction of the normal boiling points for organic compounds using gas chromatographic retention times on two columns with different polarity, Chromatographia 59 (2004) 615–620.

[49] J.M. Santiuste, J.M. Takacs, Relationships between retention data of benzene and chlorobenzenes with their physico-chemical properties and topological indices, Chromatographia 58 (2003) 87–96.

[50] C.L. Yaws, Thermophysical Properties of Chemicals and Hydrocarbons, William Andrew Inc., Norwich, NY, 2008.

[51] J. Ledgard, Chapter 4: Preparation of lacrymator, disabling and irritant substances A Laboratory History of Chemical Warfare Agents, vol. 2, Lulu.com, 2006, pp. 67–68.

[52] P.K. Gutch, S.K. Raza, R.C. Malhotra, Studies on thermal degradation of benzylidene malononitriles, J. Therm. Anal. Calorim. 71 (2003) 593–599.