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CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED M83-PE SMOKE GRENADES

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To reduce the possibility of flaming, the smoke formulation for the M83 smoke grenade has been modified by the addition of a burn retardant, pentaerythritol (PE). These M83-PE grenades were chemically characterized to qualitatively and quantitatively determine the combustion products produced with the addition of PE. Data was needed prior to material release and for incorporation into the item's Life Cycle Environmental Assessment (LCEA). Similar to other terephthalic acid (TA) based smokes, benzene, formaldehyde, and carbon monoxide were the principal compounds observed of toxicological concern. A comparison is made between the M83-PE and the M83 smoke grenades, which shows that benzene appears to be lower in the PE grenades; but, formaldehyde appears to be higher. All concentrations exceed the currently accepted American Conference of Government Industrial Hygienists (ACGIH) Threshold Limit Values (TLV'S). Carbon monoxide and carbon dioxide levels decreased between the M83 grenades and M83-PE grenades, whereas concentrations for sulfur oxides and nitrogen oxides appeared to be unaffected. Analysis of the particle size data between the M83-PE and M83 grenades show that they both have MMAD's < 3μm. A majority of the particles are therefore respirable and can be deposited deep into the lung.

14. SUBJECT TERMS

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PREFACE

The work described in this report was authorized under Project No. 622622. This work was started in September 2001 and completed in December 2001. All experimental data are contained in notebook 01-0122. All safety requirements were followed for detonation of the smoke grenades as described in SOP CR8-5NP001. Testing was performed at the pyrotechnic chamber located in Building E3266. Raw data and the final report from this study are stored in the Toxicology Archives, Building E3150, Aberdeen Proving Ground, MD 21010.

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Acknowledgments

The authors would like to thank Joe Domanico and Gene Tracy, Engineering Directorate, for their help in receipt and storage of the grenades. Additionally, the authors recognize their expertise and pyrotechnic knowledge concerning the use of pentaerythritol in the smoke formulation.

QUALITY ASSURANCE

The report of this study, titled "Chemical characterization of the pyrotechnically disseminated M83-PE smoke grenades", was examined for compliance with Good Laboratory Practices as published by the U. S. Environmental Protection Agency in 40 CFR Part 792 (effective 17 Aug 1989). The dates of all inspections and the dates the results of those inspections were reported to the Study Director and management were as follows:

Phase Inspected	Date	Date Reported
Dissemination and sampling	25 Sep 01	25 Sep 01
Data and Final Report	31 Oct 02	31 Oct 02

To the best of my knowledge, the methods described were the methods followed during the study. The report was determined to be an accurate reflection of the raw data obtained.

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Toxicology, Aerosol Sciences and
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CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED M83-PE SMOKE GRENADES

1. INTRODUCTION

Historically, the use of smokes and obscurants has been important to the military in both combat and training situations. Hexachloroethane (HC) grenades and smoke pots were once used for training purposes due to their excellent obscurant qualities. However, they were later observed to produce hazardous combustion products of toxicological concern[1]. Terephthalic acid (TA) emerged as the new fill component for smoke grenades and pots due to its less toxic nature as compared against the current American Conference of Government Industrial Hygienists (ACGIH) recommended limits[2,3]. Threshold Limit Values (TLV's) are listed for known hazardous substances and represent the concentrations that workers may be exposed to daily without experiencing health effects. The three subcategories of TLV's listed are Threshold Limit Value-Time Weighted Average (TLV-TWA), Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) and Threshold Limit Value-Ceiling (TLC-C)[4]. These represent the various exposure conditions and durations that may occur. The M83 smoke grenade and M8 smoke pot are two hardware configurations that utilize terepthalic acid formulations. Chemical characterizations have been performed for these items with analyses showing benzene and formaldehyde concentrations to be at or above their respective TLV's[3]. Still, these formulations are considered to be the least toxic smoke grenades available to the military for training purposes.

With a continued thrust to reduce potential hazards associated with the M83 grenades, a research effort has been initiated to address the high temperature flaming occurrences which sometimes appear among these hardware items, particularly in the M8 smoke pots. Modification of the smoke formulation was performed to create a slower burn, and therefore greatly reduce the possibility of a burn hazard. Experiments confirmed that when pentaerythritol (PE) was added to the TA smoke formulation, it served as a burn rate retardant[5]. Although retardants normally reduce the smoke yield, the performance of the M83-PE grenades was not compromised because the PE is a smoke-producing component itself.

On addition of a new component to the existing formulation, a new Health Hazard Assessment (HHA) must be performed before Material Release of the item may be granted. Paramount to this is a chemical characterization to determine what effect the modified formulation and burn rate have on the combustion products produced. Comparisons may therefore be made to determine whether increased risks occur through higher concentrations of toxic substances.

2. MATERIALS AND METHODS

2.1 Materials – M83-PE Grenades

The M83-PE grenades (Lot # PB1057-2) were transported from Picatinny Arsenal, NJ to the Edgewood Chemical and Biological Center's (ECBC) Engineering Directorate for storage. On days of testing, the grenades were delivered to the 20,000-liter pyrotechnic chamber. The hardware design of the grenade is the same as the M83 grenades, but the starting smoke formulation is different. The composition of the M83-PE and M83 smoke mix are provided in Table 1. Within the mix, 33% of the TA from the original M83 smoke formulation has been replaced with PE (Figure 1). The weight of the smoke mix batch was 499 kg and was prepared by Pine Bluff Arsenal (PBA) on February 26, 2001. The total weight of the grenades was nearly 500 g with the fill weight comprising 300 g. No discernible differences were present between the starter mixes of the two grenades

2.2 Chamber Exposure System

The grenade was clamped in a vise on a metal table such that the spring-loaded handle was clear of the vise jaws. Placed in the middle of the 20,000-liter chamber, a steel lanyard was hooked to the pull ring via a quick-connect fastener. The lanyard line was fed through the chamber, and the door was secured. The grenade was activated by taking the slack up on the line and pulling the lanyard. Confirmation of dissemination was performed by visually observing the smoke through a chamber portal window. The fan was activated in the chamber to provide uniform dispersion and the smoke was diverted through a 4-inch diameter pipe to a smaller 300-liter sampling chamber (Figure 2).

During the run, the bleeder valve between the two chambers was reduced to allow in less dilution air and more of the disseminated smoke to be diverted from the 20,000-liter chamber. Smoke dilution was conducted to maintain a stable aerosol concentration for sampling the combustion products. Initially at t_0, the bleeder valve was fully open (90°) to allow a sufficient quantity of dilution air to avoid overloading the sampling equipment. At t_{10} minutes, the bleeder valve was reduced to 40° to allow less dilution air and at t_{20} minutes, the bleeder valve was completely closed so as to not allow in any dilution air. Thirty minutes has been shown to be the limit for maintaining a concentration with these grenades in the described dynamic system. Chamber environmental parameters monitored during all of the tests were temperature, relative humidity, and airflow.

2.3 Chamber Concentration

To monitor chamber concentration, 25 mm A/E glass fiber filter pads (Gelman Scientific) were used to collect particulate samples for total aerosol concentration at t_5, t_{15} and t_{25} minutes during a 30-minute test. Two liters of air (1 minute @ 2 liters/min) were

drawn from the 300- liter chamber onto the pads using a calibrated vacuum pump (Sierra Instruments). Additionally, one filter pad sample was taken from the 20,000-liter chamber at t_7 minutes (1 minute @ 1 liter/min) to ascertain whether an equivalent quantity of smoke material was disseminated between testing days. Gravimetric analysis was performed on the resulting pads using a Cahn microbalance to determine concentrations from the 20,000-liter chamber and 300-liter sampling chamber.

2.4 Particle Size Analysis

A 10-stage cascade impactor (Sierra Instruments) was used to monitor particle size distribution. For each grenade, air was drawn from the 300-liter chamber through the impactor at t_{15} minutes for 0.75 minutes @7 liters/minute. All stages were weighed on a Cahn microbalance for subsequent analysis. To avoid overloading the impactor, or clogging the slits in the stages, the total weight collected among all the pads was kept under 10 mg.

2.5 Chemical Characterization

2.5.1 Volatile Organic Combustion Products (VOC's)

At t_5, t_{15} and t_{25} minutes, VOC's of the combusted smoke were collected from two separate ports of the 300-liter chamber onto solid sorbent 20:35 mesh tenax TA tubes (Dynatherm Inc. Part Number MX0621112035). Prior to dissemination, samples were collected from the ports for background determination. Samples were collected for two minutes @20ml/min with a Sierra vacuum pump, refrigerated, and subsequently analyzed by thermal desorption gas chromatography mass spectrometry (GC/MS). Flow rates were set with valves and rotameters and checked against an external flow measuring device (Drycal).

Quantitative analysis was performed on compounds of toxicological concern. Gastight syringes (Hamilton) were used to draw predetermined gas volumes from aerosol cans (Scott Specialty Gas) containing a known concentration of analyte in air. The analyte was injected onto a tenax tube and swept onto the sorbent with a low flow of nitrogen (<50 ml/min). A minimum of four standards were injected with a correlation coefficient (r^2) > 0.99. All sampling and analysis procedures described were in accordance with the NIOSH approved screening method[6]. The thermal desorption GC/MS conditions are shown in Appendix A.

2.5.2 Formaldehyde Analysis

Air samples were drawn from a separate port of the 300-liter chamber at t_5, t_{15}, and t_{25} minutes for 2 minutes @1 liter/min. 2,4 dinitrophenylhydrazine cartridges (LpDNPH) from Supelco Inc (Cat no. 21014) were used to trap formaldehyde onto a high purity silica absorbent. Using gravity feed, the cartridges were eluted with approximately 5 ml of acetonitrile and prepared for gas chromatography flame ionization (GC-FID)

analysis (Appendix B for instrument conditions). This method has proven reliable in the analysis of formaldehyde and other longer chain carbonyl compounds[7].

2.5.3 Inorganic Analysis

The solid "fallout" material from the grenades was not collected or analyzed during this study. The non-hazardous nature of the metals contained in the starting composition should not have any environmental impact. Some samples were collected from earlier experiments in which the percentage of added pentaerythritol was varied in order to find the optimal smoke formulation. These samples are archived and may be analyzed if any later environmental concerns arise.

Using a 2 liter gastight syringe (Hamilton), gas samples were pulled from the chamber at t_5, t_{15}, and t_{25} minutes through a short length of ¼" Tygon tubing. The samples were transferred to a 4.5-liter Teflon gas-sampling bag (Alltech) for determination of carbon monoxide, carbon dioxide, sulfur oxide, and nitrogen oxide concentrations. These are typical inorganic gases that have been observed in terephalic acid smokes.

According to the air volumes predetermined by the manufacturer, samples were pulled from the bag onto a compound specific detector tube using a Matheson portable gas sampling pump (Model 400). Concentrations were recorded by monitoring the colorimetric change observed on the sorbent material.

3. RESULTS

3.1 Statistical Analysis

Ten grenades were disseminated to obtain a sufficient amount of data to perform statistical analyses. A Two Way Analysis of Variance (ANOVA) was performed to determine if there were differences between sampling intervals (t_5, t_{15}, t_{25} minutes) and sampling days. If the ANOVA determined that there were differences, a multiple comparison test was used to compare all possible combinations of sampling intervals and days. If the data were normally distributed with equal variance, the Bonferroni Test was used. If normality and equal variance could not be met by transforming the data, the Tukey multicomparison test was used. All statistical analyses were performed using the Jandel computer software package Sigma Stat 2.03 for Windows[8].

3.2 M83-PE Disseminated Grenades

Each grenade was weighed before and after dissemination to determine the quantity of material burned from the grenade. There were no significant differences in the amount of M83-PE material burned among the ten grenades (Figure 3). The mean was 177.8 ± 2.8 g., and the coefficient of variation (C.V.) was 1.6%. Figure 3 also shows that with decreasing quantities of PE added to the smoke mixture, the grenade burns

hotter and therefore disseminates a greater amount of material[5]. During the study, several grenades were disseminated with either 20% PE added or 30% PE added to illustrate this trend. Disseminated weights from M83 grenades with no PE added were taken from previous work and possessed the highest weight loss.

3.2.1 20,000-Liter Chamber Concentrations

As shown in Figure 4, the chamber concentrations observed at t_7 minutes for grenades 2-10 was 2598 ± 260 mg/m^3. It was observed that with increased percentages of PE added to the TA mix, the total aerosol concentration in the large chamber decreased. Filter pad samples taken at t_7 minutes from the large chamber collected the highest amounts of aerosol during a 30-minute test. Grenade 1 produced an erroneously low filter pad weight that was excluded in the mean calculation through use of the extreme studentized deviate (ESD) method or Grubb's test. The test is used to identify values that deviate from the mean by ± 2 standard deviations (SD). Presumably the bleeder valve was left closed instead of 90° open, causing an exaggerated concentration of smoke material to exit the 20,000 liter chamber through the 4"pipe.

3.2.2 300-Liter Sampling Chamber

In Figure 5, a plot of individual aerosol concentrations at t_5, t_{15}, and t_{25} minutes are shown with the corresponding mean and standard deviation given at each time. As with the 20,000-liter chamber, concentrations for the first grenade were excluded because the bleeder valve was presumably left closed instead of 90° open. With no dilution air entering the 300-liter chamber, the amount of total aerosol collected on the filter pads overloaded the pads causing weight measurements to be much higher than the t_5, t_{15}, and t_{25} minute means (> 2 S.D.). The higher weights corresponded with the lower filter pad weight observed from the 20,000-liter chamber for the first grenade. The t_5 minute sample during run number 8 dropped 24 % below the average aerosol concentration at t_5 minutes (due to improper valve positioning). This data point did not meet the outlier criteria (mean ± 2 S.D.) and was included in statistical calculations. On grenade 10, the t_5 minute sample was not collected due to sampling error. There were no significant differences between the sampling intervals or days at $p \leq 0.05$. The mean at t_5 was 1490 ± 178 mg/m^3 (C.V 11.9%), the mean at t_{15} minutes was 1416 ± 108 mg/m^3 (C.V = 7.6%), and the mean at t_{25} minutes was 1463 ± 128 mg/m^3 (C.V = 8.7%). For chemical characterization, the total averaged concentration for all grenades over the 30-minute runs was 1455 ± 143 mg/m^3 (C.V = 9.8%).

3.3 Particle Size Analysis

Particle size was calculated from seven of the ten grenades. Along with exclusion of the first grenade, the particle size calculated for the seventh grenade deviated from the mean by ± 2SD and was therefore excluded by the ESD method. Data collection during the tenth grenade underwent a sampling error. With the loss of two additional grenades (numbers 7 and 10), the total aerosol concentration at which particle size was recorded also changed. The mean concentration at which particle size was recorded was 1445 ±

140 mg/m^3 (C.V = 9.7%) and the mean concentration for the 300-liter chamber was 1455 ± 143 mg/m^3 (C.V = 9.8%). The mass median aerodynamic diameter (MMAD), geometric standard deviation (σ_g), and respirable mass percentage are all presented in Table 2.

3.4 Chemical Characterization

As previously discussed, data acquired from grenade 1 was not incorporated in the chemical characterization analysis because the bleeder valve was not opened, but grenades 7 and 10 were included.

3.4.1 Volatile Organic Combustion Products (VOC's)

At t_5, t_{15}, and t_{25} minutes, volatile organic combustion products were collected and analyzed. Benzene was the only compound trapped that exhibited any significant concentration levels. Figure 6 depicts the individual concentrations observed from the two ports. For each grenade, the concentrations were not significantly different between the two ports, making it possible to presume that concentrations were uniform in the 300-liter chamber. Therefore, the concentration values for t_5, t_{15} and t_{25} minutes were averaged between the ports and are shown in Figure 7. All values exceed the Threshold Limit Value (TLV) established by the ACGIH (Table 3)[4]. The current TLV-TWA for benzene is 0.5 ppm and the TLV-STEL is 2.5 ppm. The mean concentrations for all grenades at t_5, t_{15}, and t_{25} minutes were 12.6 ± 5.4 ppm, 13.8 ± 4.2 ppm and 17.2 ± 6.1 ppm. The general trend among the grenades is that benzene concentrations increase over time. The mean concentration at t_{25} minutes was significantly higher as compared to the concentrations at t_5, and t_{15} (at $p \leq 0.05$), while the t_5 and t_{15} means were not significantly different (at $p \leq 0.05$) from each other. Figure 8 shows the benzene concentrations that one would be exposed to on average over thirty minutes. In combining all data, the concentration of benzene produced by dissemination of these grenades is 14.5 ± 5.4 ppm.

At t_5, t_{15}, and t_{25} minutes the benzene concentrations from grenades 5, 6 and 7 had spiked concentrations as compared to the respective concentrations for the other grenades, but their individual values were not significantly different (at $p \leq 0.05$) from the overall t_5, t_{15}, and t_{25} means. The spikes may not be attributed to improper flow adjustments into the sampling chamber because there were no spikes seen while monitoring the total smoke concentrations of the 300-liter sampling chamber (see figure 5). The tenax tubes from grenades 5, 6 and 7 were refrigerated for an extended period of time due to equipment breakdown. It was thought that the benzene concentrations might differ, but that any differences would be lower due to losing some of the volatile combustion products from the sorbent. At this time, the spike anomaly cannot be explained.

3.4.2 Formaldehyde Analysis

For each grenade, Table 3 lists the formaldehyde concentrations (GC analyses) that one would be exposed to on average over thirty minutes. In combining all data, the

concentration of formaldehyde produced by dissemination of these grenades is 24.2 ± 4.2 ppm. This concentration greatly exceeds the TLV-C of 0.3 ppm[8]. A Two Way ANOVA has shown that there was no difference between sampling time intervals at $p \leq 0.05$, but there were significant differences between run numbers (Table 4). Grenades 2 and 4 showed the most differences due to a slight decline in formaldehyde. Additional data is presented in Table 5, where formaldehyde detector tubes were also collected and compared to the concentrations obtained through GC analysis. For many of the table values, the > symbol infers that the maximum quantity of formaldehyde was exceeded on the tube. The mean formaldehyde concentration obtained over all the grenades was >28 ± 6 ppm for the tubes.

3.4.3 Inorganic Analysis

Table 5 lists the inorganic gas concentrations observed for each grenade. The values are the average of three readings taken at t_5, t_{15} and t_{25} minutes. The mean concentrations for all nine runs are also presented with their corresponding standard deviations. TLV-TWA values for each of the inorganic gases analyzed are also shown.

4. DISCUSSION

When the smoke composition is altered for an existing type-classified formulation, it is important to perform a new chemical characterization of the combustion products. Data are necessary to perform a new HHA before material release of the item. In this case, the hardware design and method of dissemination remained the same as in the M83 smoke grenades, but the smoke formulation was changed to remove some of the terephathalic acid and replace it with pentaerythritol, a burn retardant. The purpose for this was to make the M83 training grenades safer items through eliminating the possibility of a burn or flame hazard. The formulation shown in Table 1 was determined to be the optimal mixture of TA and PE without sacrificing obscuration yield.

Comparisons may be made between the chemical characterization performed on the M83-PE grenades with previous work performed by Muse, et.al. on the M83 grenades[3]. Changing trends may be identified on the addition of the burn retardant, but there are several reasons why quantitation of differences is not possible. First, Muse conducted an inhalation toxicology study where chemical characterization was performed as an aside, whereas the present study was designed with chemical characterization as the primary study endpoint. Secondly, analytical methodology for determining benzene and formaldehyde concentrations has improved from the earlier study. Stricter confidence limits associated with these concentrations are now observed. Finally, combustion product concentrations can fluctuate as the concentration of total aerosol in the 300-liter sampling chamber fluctuates.

Table 6 shows some of the trends in combustion product differences between the two grenades. Benzene concentrations decrease nearly 50% from the M83 to the M83-PE grenades. Both concentration values represent those associated with a 30-minute

exposure; however, t_5, t_{15}, and t_{25} minute samples were taken from only 3 grenades for Muse, et al. Confidence limits are therefore wider.

Formaldehyde concentrations increase about 40% from the M83 to the M83-PE grenades. Preliminary work performed on varying percentages of PE also confirm this trend. Five grenades were disseminated with 20% TA replacement with PE. At a mean aerosol concentration of 2190 ± 387 mg/m^3, formaldehyde concentrations were calculated to be 20 ± 5 ppm. The total aerosol concentration for the M83 grenades is higher than the M83-PE replacement grenades, implying that the formaldehyde concentrations of 20 ± 5 ppm is also elevated. If equivalent aerosol concentrations were used, and if the formaldehyde concentration was 17-18 ppm, the concentrations calculated for the 20% TA replacement with PE would still fall between the M83 grenades (no PE) and the M83-PE grenades (32% PE).

The increased levels of PE could be explained from how it is produced. Pentaerythritol is formed through an aldol condensation reaction between acetaldehyde and formaldehyde, followed by a Cannizzaro reaction[9]. In PE combustion, the possibility could exist where a reverse aldol reaction occurs and releases additional formaldehyde as compared to the M83 grenades without PE. Higher concentrations of formaldehyde could cause lower total concentrations of other combustion products, namely benzene.

The MSDS for pentaerythritol states that hazardous decomposition products are toxic fumes of carbon monoxide and carbon dioxide[10], but increased levels of these compounds were not seen in the M83-PE grenades. Carbon monoxide and carbon dioxide levels were actually observed to decrease between the M83 grenades and M83-PE grenades. Concentrations for sulfur oxides and nitrogen oxides appeared to be unaffected.

Analysis of the particle size data between the M83-PE and M83 grenades illustrate similar results. Both have MMAD's less than 3μm, indicating that a majority of the particles are respirable and can be deposited deep into the lung. Typically, all particles less than 5 μm will follow this deposition pattern[11].

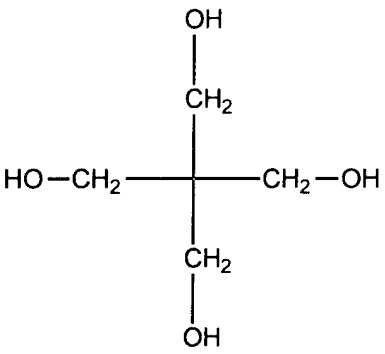
5. CONCLUSIONS

Pentaerythritol was introduced to the M83 TA based training grenades to act as a burn retardant and reduce some of the flaming hazards associated with them. With the PE added, there was less total aerosol produced by the grenades as compared to grenades without PE. Many of the same combustion products were seen, but some of their concentrations levels had changed. This could be caused by the differing burning temperatures or by less total aerosol produced.

Statistical analysis was performed on data collected from pyrotechnically disseminated M83-PE grenades. Benzene, formaldehyde, and carbon monoxide were all present in concentrations above their respective TLV-TWA's. In comparison to the M8

grenades, benzene concentrations decreased by nearly 50%, formaldehyde concentrations increased by nearly 40%, and carbon monoxide levels remained about the same. No discernible differences were seen in other measured inorganic gases, including carbon dioxide, sulfur oxides, and nitrogen oxides. Particle size distribution revealed the presence of small particles with MMAD's of 1-2 μm.

The TA based formulations still appear to produce the least toxic smokes for military use. Although some combustion product concentrations have been changed, there were no additional products seen and no dramatic increases or decreases observed. None of the grenades exhibited a flaming incident, supporting the assertion that PE reduces the flaming hazard introduced by M83 grenades without PE.



$C_5H_{12}O_4$

CAS Number: 115-77-5

MW: 136 g mol^{-1}

Figure 1. Structure of pentaerythritol.

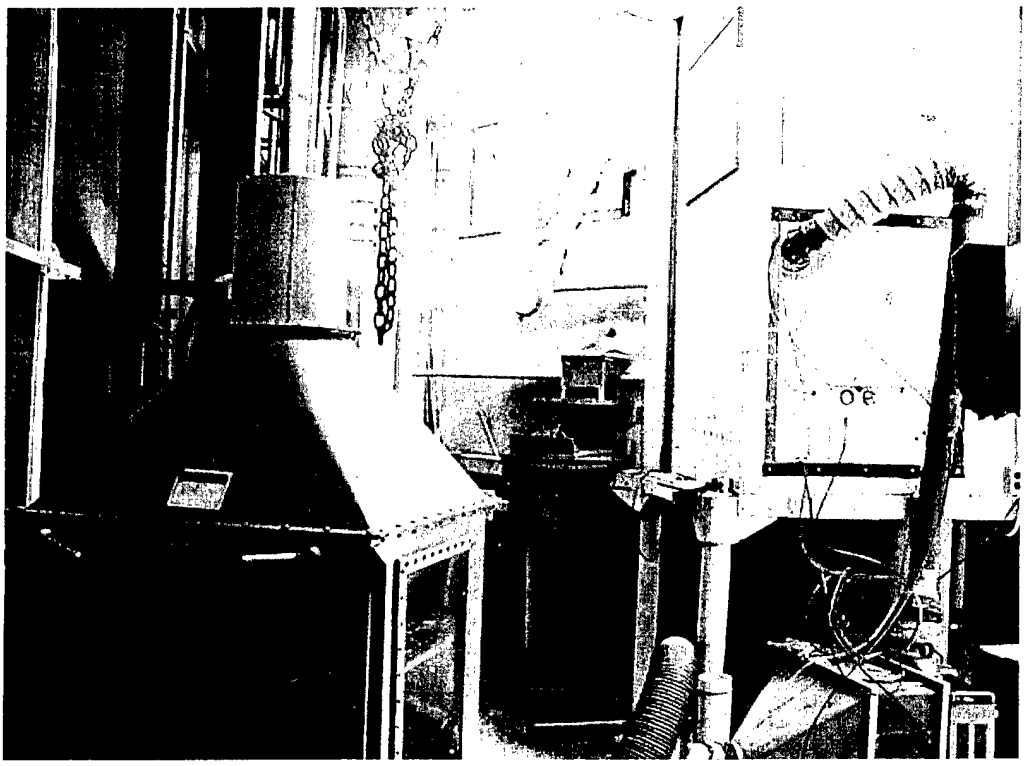


Figure 2. 20,000-liter chamber diverted to 300-liter sampling chamber.

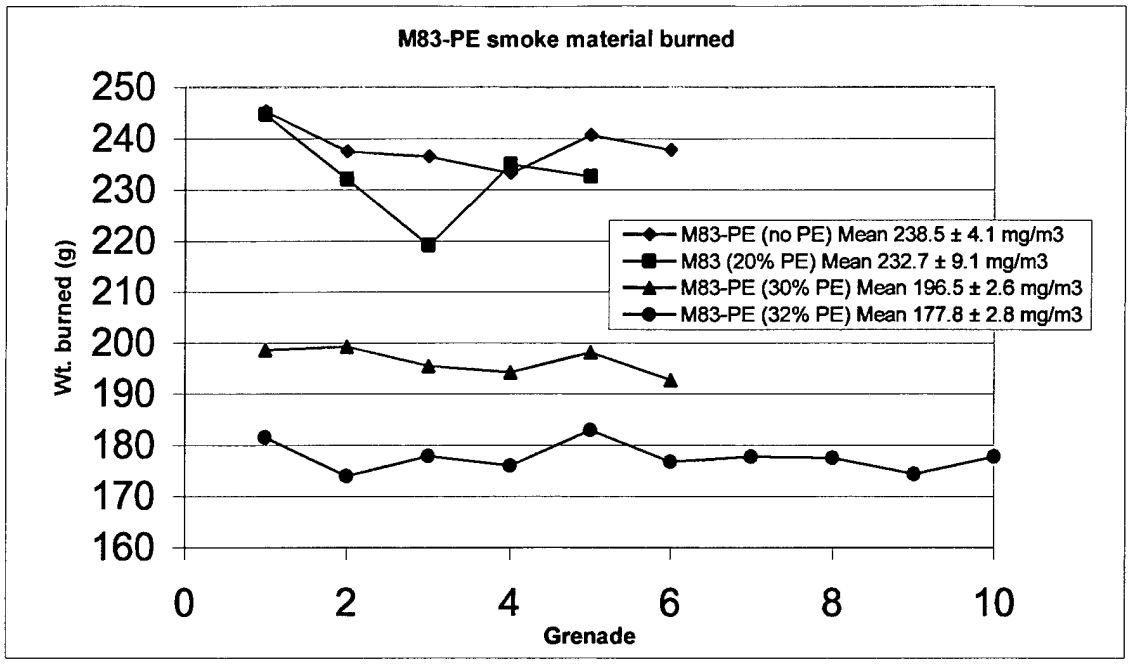


Figure 3. Weight (g) of smoke material burned from M83-PE grenades.

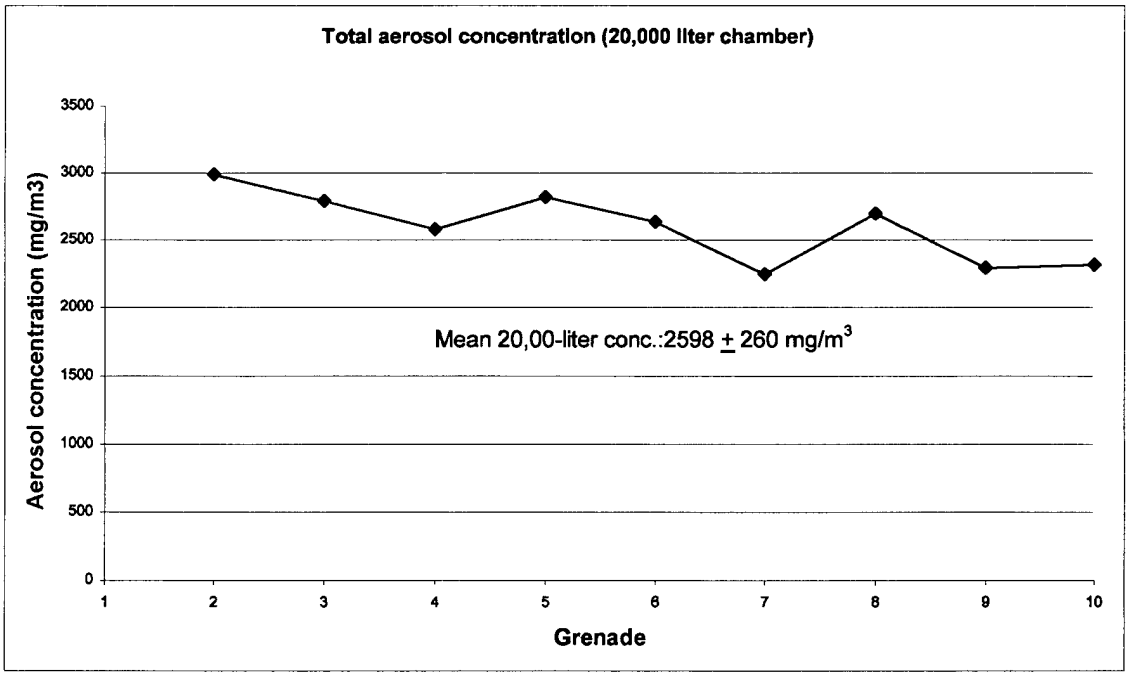


Figure 4. 20,000-liter chamber concentrations (mg/m^3) taken at t_7 minutes.

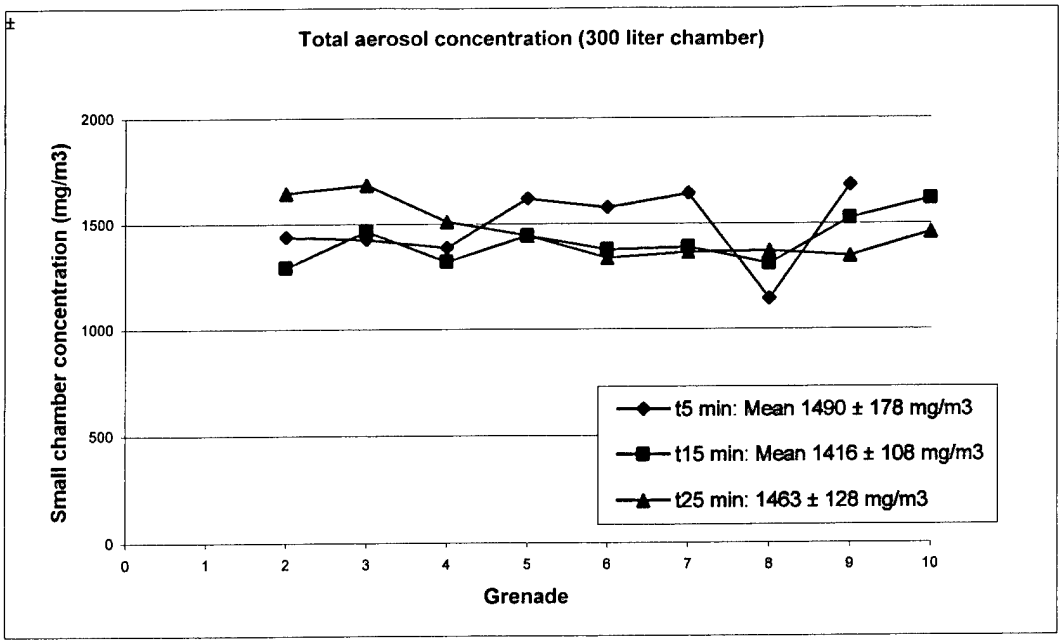


Figure 5. 300-liter chamber concentrations (mg/m^3) taken at t_5, t_{15}, and t_{25} minutes.

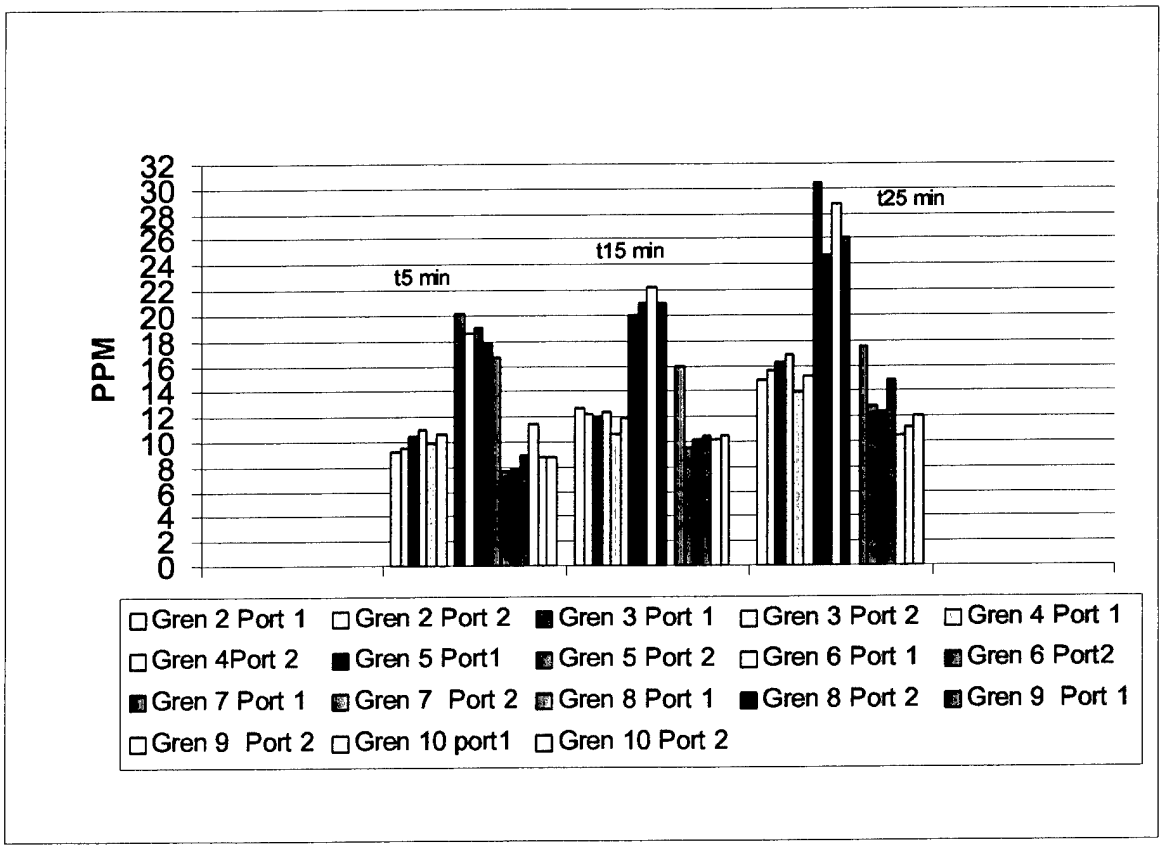


Figure 6. Benzene concentrations from 300-liter chamber.

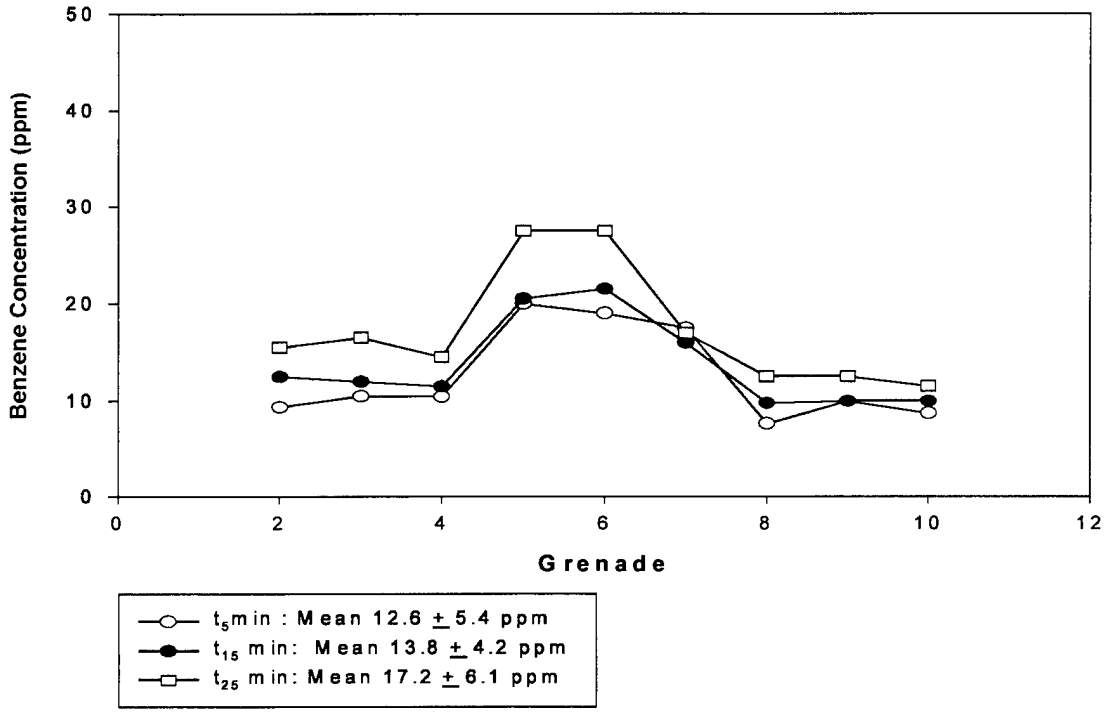


Figure 7. Benzene concentrations vs. grenade at t_5, t_{15}, and t_{25} minutes.

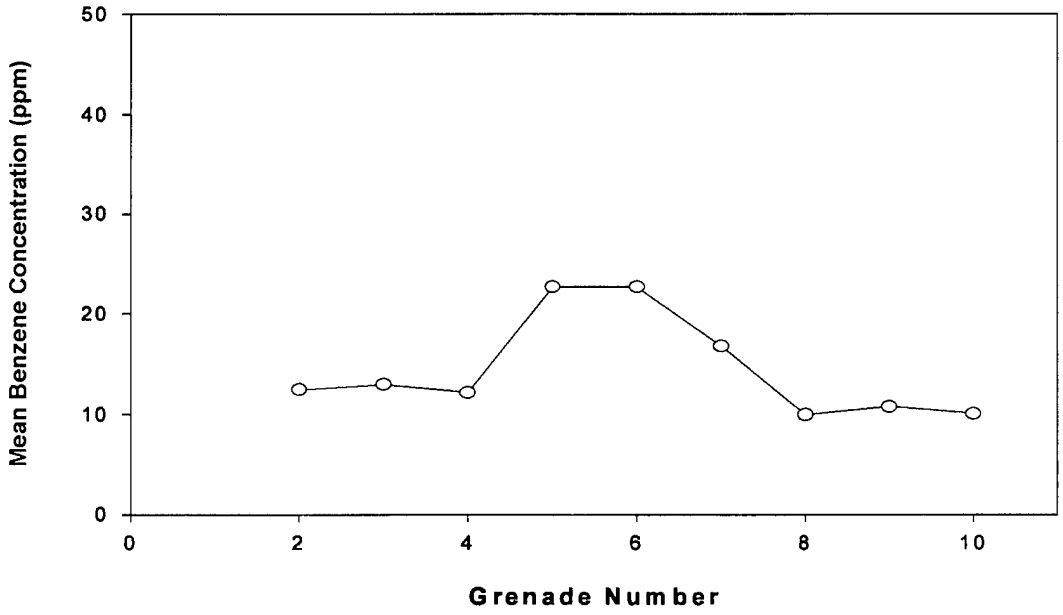


Figure 8. Mean benzene concentrations (ppm) vs. grenade number.

Table 1. M83-PE and M83 smoke formulations.

Material	*M83-PE	*M83
Terephthalic acid	36.26	56.4
Pentaerythritol	17.91	0
Sugar	13.64	13.9
Magnesium carbonate	7.55	3.0
Sodium bicarbonate	1.18	0
Potassium chlorate	22.36	22.8
Stearic acid	1.00	3
Binder	0.75	1

*98% of the total fill weight

Table 2. *Particle Size Analysis.

MMAD (μm)	1.8 ± 0.1
σ_g	1.5 ± 0.05
Respirable Mass (%)	87.0 ± 1.6

*Data presented as the average of grenades 2-6,8,9

Table 3. Concentrations of VOC's measured in M83-PE grenades.

Grenade	[b]Benzene		[c]Formaldehyde	
	[a]Conc. (ppm)	St. Dev.	[a]Conc.(ppm)	St. Dev.
2	**12.5**	3.1	**16.9**	0.7
3	**13.0**	3.1	**23.2**	0.7
4	**12.2**	2.1	**18.3**	1.7
5	**22.6**	4.1	**24.9**	1.8
6	**22.6**	4.4	**24.0**	0.8
7	**16.8**	0.8	**27.2**	2.7
8	**10.0**	2.4	**27.0**	0.2
9	**10.8**	1.4	**27.7**	2.2
10	**10.0**	1.4	**28.9**	0.5
Average 2-10	**14.5**	5.4	**24.2**	4.2

[a]values are the mean of 5, 15 and 25 minute readings for each grenade.
[b] TLV-TWA for benzene is 0.5 ppm and the TLV-STEL is 2.5 ppm as established by the ACGIH 2002.
[c] TLV-C for formaldehyde is 0.3 ppm as established by the ACGIH 2002, GC analysis
Values above their TLV (TWA) are in bold

Table 4. Bonferroni Multiple Comparison Test results using formaldehyde concentrations from sampling intervals 5, 15 and 25 minutes.

Grenade	2	3	4	5	6	7	8	9	10
2		Yes	No	Yes	Yes	Yes	Yes	Yes	Yes
3			Yes	No	No	No	No	No	Yes
4				Yes	Yes	Yes	Yes	Yes	Yes
5					No	No	No	No	No
6						No	No	No	Yes
7							No	No	No
8								No	No
9									No

Yes = significant difference between sampling days
No = no significant difference between sampling days

Table 5. Inorganic gas combustion products measured using Matheson gas detector tubes

Grenade	[b]CO [a]Conc.(ppm)	[c]CO_2 [a]Conc.(ppm)	[d]NO_x [a]Conc.(ppm)	[e]SO_x [a]Conc.(ppm)	Formaldehyde [a]Conc.(ppm)
2	**125**	667	1.5	0.5	**28**
3	**116**	633	1.1	.5	**>27**
4	**116**	633	1.1	**2.7**	**27**
5	**125**	633	1.0	**8.0**	**>32**
6	**141**	767	1.6	**7.7**	**>35**
7	**125**	Not run	1.8	**6.3**	**>28**
8	**103**	Not run	1.3	**7.7**	**>33**
9	**158**	467	1.1	**8.7**	**>35**
10	**166**	800	1.7	**9.7**	**27**
Avg 2-10	**131 ± 31**	657 ± 121	1.4 ± 0.4	**5.7 ± 3.1**	**>28 ± 6**

Values are the mean of 5, 15 and 25 minute readings.
[b] TLV-TWA for carbon monoxide is 25 ppm as established by the ACGIH 2002.
[c] TLV-TWA for carbon dioxide is 5000 ppm as established by the ACGIH 2002.
[d] TLV-TWA for nitrogen dioxide is 3 ppm as established by the ACGIH 2002.
[e] TLV-TWA for sulfur dioxide is 2 ppm as established by the ACGIH 2002.
Values above their TLV -TWA are in bold

Table 6. Benzene and Formaldehyde comparisons between the M83-PE and M83 grenades

	M83-PE grenade	*M83 grenade
Total aerosol conc. (mg/m^3)	1455 ± 143	1710 ± 387
[Benzene conc. (ppm)]	14.5 ± 5.4	34 ± 9
Total aerosol conc. (mg/m^3)	1455 ± 143	1854 ± 329
[Formaldehyde conc. (ppm)]	24.2 ± 4.2	15 ± 9

* Data from Muse et al (1997)

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APPENDIX A

THERMAL DESORPTION GC/MS CONDITIONS

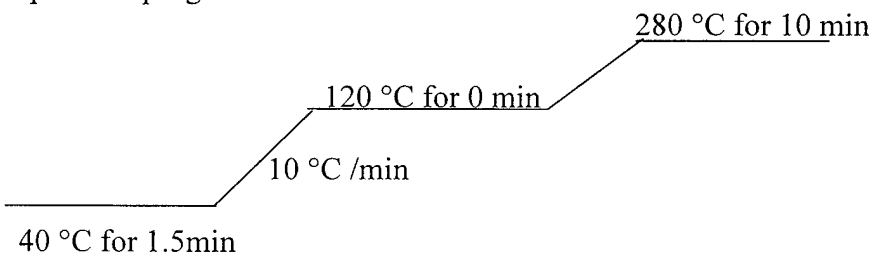
Thermal Desorption Conditions

Instrument:	Dynatherm ACEM900 Thermal Desorption Unit		
Valve temp:	150 °C	Dry time:	1 min
Tube temp:	250 °C	Tube heat:	3 min
Transfer line temp:	200 °C	Tube cool:	1 min
Trap temp:	250 °C	Trap heat:	3 min

GC conditions

Instrument:	HP 6890 Gas Chromatograph
Column:	HP-5MS 30m x 0.25mm x 0.25 μm
Column Flow(He):	1.0 mL/min (velocity 36 mL/min, head pres 7.06 psi)

Temperature program



Detector conditions

Detector:	HP5973 mass selective detector
MS quad temp:	150 °C
MS source temp:	230 °C
Scan parameters:	30-550 amu ; threshold 150

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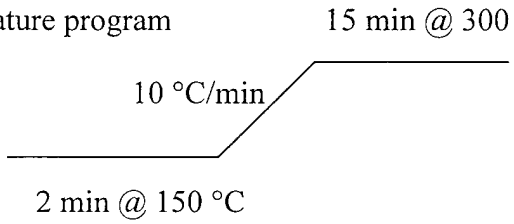
APPENDIX B

GC/FID CONDITIONS

Instrument:	HP 5890 Gas Chromatograph
Column:	J+W Scientific DB-5 30 m x 0.53 mm x 1.5 μm
Liner:	Single Taper (HP part number 5181-3316)
Injection volume:	2 μL splitless
Column flow(He):	1.0 mL/min (velocity 36 mL/min ,head press = 8.5 psi
Inlet purge:	Off time: 0 min; On time: 0.5min
Injector temp:	220 °C

Temperature program



Detector conditions

Detector:	Flame ionization detector
Detector temp:	300 °C
Detector flow:	400 mL/min (air); 30 mL/min (hydrogen)