

**NISTIR 6191**

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**Demonstration Of Biodegradable, Environmentally  
Safe, Non-Toxic Fire Suppression Liquids**

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**Daniel Madrzykowski  
David W. Stroup, Editors**

**July 1998**



**U.S. Department of Commerce  
Technology Administration  
National Institute of Standards and Technology  
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**CHAPTER 4**  
**SMOKE CHARACTERIZATION**

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# SMOKE CHARACTERIZATION

## 4.1 Introduction

The impact of fire suppression agents on the quantity and composition of smoke generated during extinguishment has been investigated in two series of crib fires. Both series examined the physical and chemical properties of smoke from crib fires before, during and after extinguishment. Fire fighters have observed that a cloud of very bright “white smoke” is often generated as they extinguish a fire using a fire suppression agent (Figure 1). This “white smoke” is not usually observed when they use water to extinguish fires. Questions have arisen concerning what causes the generation of “white smoke” and whether or not it represents a significant new hazard for fire fighters.

In the first series of crib fires, seventeen identical wood cribs were ignited, one per test. Each crib fire was allowed to develop fully before being extinguished using water alone or water with a fire suppression agent. During the crib fires, smoke samples were collected before and after extinguishment for chemical analysis. This allowed determination of the concentration of polycyclic aromatic hydrocarbons, the ratio of elemental to organic carbon for pre-extinguishment (free burn) and post-extinguishment smoke. The inorganic and organic components of “white smoke” particulates were compared to smoke particulates collected from water extinguished fires in an attempt to identify a chemical “marker” which could be used to distinguish whether water or an agent solution was used to extinguish the fire.

The second series examined the physical and chemical properties of the smoke, both the particulate and gas phases. The concentrations of carbon monoxide, carbon dioxide, oxygen, nitrogen oxides, hydrogen chloride, and hydrogen cyanide, as well as the mass concentration and size distribution of soot particulates were measured before and after extinguishment with water alone and with agent solutions.

The objective of this effort was to characterize how fire suppression agents impact the physical and chemical properties of smoke. Specifically, the production of “white smoke” as a physical or chemical phenomenon was examined. Using this information, the hazard of the smoke exposure for fire fighters from the use of fire suppression agents of this type could be assessed.

## 4.2 Fabrication of the Cribs

Cribs for the first series were assembled completely out of Southern pine lumber, while for the second series, acrylonitrile butadiene styrene (ABS) and polyvinyl chloride (PVC) plastic sticks were included in each crib. Each square base crib consisted of 10 layers, with each square layer containing seven 55.9 cm (1.8 ft) long sticks of 3.8 cm (1.5 in) x 3.8 cm (1.5 in) cross section and each successive layer laid crosswise to the previous layer (Figure 2). These cribs are similar in design to the cribs burned by Gross [1], Block [2], and Bryner et al. [3]. Southern pine was selected to represent the framing lumber found in typical residential structures. For the second series, six pine sticks per crib were replaced with three ABS and three PVC sticks. The ABS sticks were selected

to represent the asphaltic roofing, carpeting, and polyurethane furnishings while the PVC sticks were added to simulate the vinyl tile and PVC plumbing components within a house. All the cribs were assembled approximately one month before the first scheduled fire test. This allowed all the cribs to reach about the same moisture content before the first crib was burned. The moisture content of each crib ranged from 6 to 8% as measured using both Delm Horst and Lignomat moisture meters\*. For the series of burns, the crib weights ranged from 24 to 27 kg (52.8 to 59.4 lb). For the second series of cribs with the additional mass of ABS and PVC sticks, each crib weighed between 29 and 34 kg (63.8 and 74.8 lb) of which approximately 3.2 kg (7 lb) was PVC and 2.6 kg (5.8 lb) was ABS.

### **4.3 Furniture Calorimeter Test Facility**

After allowing the cribs to dry, the cribs were burned under a 2.4 x 2.4 m (7.9 x 7.9 ft) collection hood (Figure 3) with an exhaust rate of about 2 m<sup>3</sup>/s (70.6 ft<sup>3</sup>/s). Each crib was ignited using 500 mL (0.13 gal) of heptane poured into a round steel pan (40.6 cm (16 in) diameter and 2.54 cm (1 in) deep) which was positioned 3.8 cm (1.5 in) below the bottom layer of the crib. The heptane averaged about 1.5% of the initial mass of the crib. The instrumentation associated with this facility measured the mass loss rate of the crib, the heat release rate, and gas concentrations of carbon monoxide, carbon dioxide and oxygen. The mass loss rate of the burning crib was monitored with a water-cooled load cell with a sensitivity of about 3 g. The heat release rate was determined via oxygen consumption calorimetry [4,5], which involves measuring the oxygen concentrations, the flow velocity, and the temperature in the exhaust duct. After drying the sample gases via a cold trap to remove water, the concentrations of carbon monoxide and carbon dioxide were measured using non-dispersive infrared gas analyzers. The oxygen concentration was monitored via paramagnetic analyzer.

### **4.4 Sample Collection and Analysis - First Series of Cribs**

In the first series of crib burns, after the heptane burned out (typically 2.5 to 3 minutes after ignition) the fire was allowed to grow, involve the entire crib, and burn in a steady fashion before being extinguished 8 minutes after ignition. The mass burning rate of the cribs during the steady phase was approximately 30 g/s (0.07 lb/s) which resulted in a peak heat release rate of approximately 400 kW (378 Btu/s). Each crib was extinguished using either water, a solution of water and agent, or foamed water/agent solution. A single agent solution was applied without air as a liquid spray and with air injection as a compressed air foam. Above the collection hood, smoke was withdrawn from the exhaust duct via a heated, glass sample probe. The sample smoke was immediately diluted using dry nitrogen and then pulled through a filter manifold which held four 47 mm diameter filters. Prior to each crib burn, each of the four filter holders attached to the manifold was loaded with either a quartz fiber filter, a Nucleopore filter with 0.8 mm (0.03 in) diameter pores, or an Anapore (Al<sub>2</sub>O<sub>3</sub>) ceramic filter, each filter had been weighed prior to the test. Each filter holder was connected to a separate mass flow controller and vacuum pump to allow samples to be collected

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\* Certain equipment or materials are identified in this report. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology or the U.S. Fire Administration, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

serially or simultaneously. Each filter could be used to sample during the free burn stage, prior to extinguishment, or after the extinguishing agent had been applied to the crib. Sample flow rates and collection times were monitored for each filter. After each fire, the filters were weighed and placed in a desiccator for 24 hours. After reaching a constant weight, each sample was placed in a Petri dish lined with baked-out aluminum, sealed with Teflon tape and then stored in a refrigerator ( $< 2\text{ }^{\circ}\text{C}$ ).

The Nucleopore and Anapore filters were examined in an attempt to identify inorganic particles unique to either agent solution or water extinguishment. Samples of the Nucleopore filters, approximately  $1\text{ cm}^2$  each, were cut from the filters. These samples were then carbon coated with approximately 10 nanometers of carbon for conductivity. Individual particles from the samples were analyzed using conventional and environmental scanning electron microscopes and energy dispersive x-ray analysis.

Quartz fiber filters were cut in half and one half was analyzed for polycyclic aromatic hydrocarbons (PAHs) [6]. Most of the filter samples were sufficiently loaded with emissions to allow for the measurements of PAHs from 3.7 mm diameter circles punched from the original 47 mm filters. Filter samples were examined using on-line Supercritical Fluid Extraction - Gas Chromatography/Mass Spectrometry [7,8,9] in an attempt to identify polycyclic aromatic hydrocarbons unique to either water or foam extinguishment. The other half of the quartz fiber filters was analyzed for the ratio of elemental carbon to organic carbon using optical-thermal decomposition analysis [10].

#### **4.5 Sample Collection and Analysis - Second Series of Cribs**

In the second series of crib burns, after the heptane burned out (typically 2.5 to 3 minutes after ignition) the fire was allowed to grow, involve the entire crib, and burn in a steady fashion before being extinguished at 8 minutes after ignition. The mass burning rate of the cribs during the steady phase was approximately 30 g/s (0.07 lb/s) which resulted in a peak heat release rate of approximately 400 kW (378 Btu/s). Each crib was extinguished using either water or an agent solution. Four different agents were utilized and are referred to as Agents A, B, C, and D. The extinguishing agent, whether it was foam solution or water, was applied from a specific number of nozzles, at a specific flow rate and delivery pressure. The specific location of the nozzles, flow rates and delivery pressures are described in section 6.1 of this report.

Above the collection hood, smoke was withdrawn from the exhaust duct via a tapered, heated, glass sample probe. Attached to the end of the sample probe were two 47 mm filters, an Anderson Cascade Impactor, two gas impingers, and a chemiluminescent nitrogen oxides analyzer. Prior to each crib burn, each of the two filter holders was loaded with a quartz fiber filter, which had been pre-weighed. Each filter holder was connected to a separate mass flow controller and vacuum pump to allow samples to be collected in a serial or parallel fashion. Each filter could be used to sample during the free burn stage, prior to extinguishment, or after the extinguishing agent had been applied to the crib. Sample flow rates and collection times were monitored for each filter. After each fire, the filters were reweighed and placed in a desiccator for 24 hours. After obtaining a constant weight, each sample was placed in a Petri dish and stored in a desiccator. Each of the eight stages in the cascade impactor contained a sample collection substrate, which was also pre-weighed before each burn. The impactor had its own dedicated pump and regulator to pull 28.32 L/min of sample through

the impactor. After each run the collection substrates were reweighed, desiccated for 24 hours and rechecked.

The hydrogen chloride and hydrogen cyanide were collected in preweighed 250 mL glass impinger bottles containing approximately 100 mL of 10 or 15 millimolar solutions of potassium hydroxide. To maximize the collection efficiency, two impingers were used in series, separated by a 45 mm diameter polytetrafluoroethylene filter to collect the sample from the exhaust stream. The second impinger served to trap any gases that might break through the first impinger. Each sample was analyzed for hydrogen chloride or hydrogen cyanide via ion chromatography. A commercially available ion chromatograph equipped with a total conductivity detector was used to analyze for  $\text{Cl}^-$  and  $\text{CN}^-$ . An anion column preceded by a precolumn module was used. All chemicals were of reagent grade quality. The water used was conditioned to 18.3  $\text{M}\Omega\text{-cm}$  and passed through a 0.45 mm nominal porosity filter. The eluent for the ion chromatograph was 5 mM KOH. Stock solutions of  $\text{Cl}^-$  and  $\text{CN}^-$ , nominally 1000 ppm, were prepared by dissolving 0.2100 g of dried KCl and 0.2511 g of dried KCN, respectively, in 100 mL of 18.3  $\text{M}\Omega\text{-cm}$  water. Calibration solutions of 2.0 ppm  $\text{Cl}^-$  and 1.0 ppm  $\text{CN}^-$  were prepared by dilution of the stock solutions with the eluent. The eluent flow rate through the system was 1.2 mL/min. The sample loop had a volume of 100 mL. Unknowns were diluted 1:10 with eluent. Standards and unknowns were loaded into the loop using a 1 mL syringe and a 0.45 mm syringe filter. The sample loop was rinsed with approximately 1 mL of the analyte solution before the sample was injected onto the column.

A portion of the sample gas was dried and then pulled through the chemiluminescent nitrogen oxide analyzer. This analyzer also had its own dedicated vacuum pump. Before each series of crib tests, the analyzer was calibrated with span gas of a known concentration and zeroed with nitrogen. During the pre-test check for the fourteenth crib burn, the ozone generator malfunctioned and caused the reaction chamber to implode. The analyzer was not utilized for the last six crib burns.

## **4.6 Results**

### **4.6.1 First Series of Crib Burns**

The analysis of Nucleopore and Anopore filters demonstrate that although the filters were lightly loaded, large numbers of small particles aggregates were present (Figure 4). The size and structure of these aggregates are consistent with carbon containing particles originating from areas of incomplete combustion. These particles are found in samples from fires extinguished by water only and by the fire suppression agent solution. This analysis also demonstrated a second group of particles (Figures 5 and 6) which appear to be residual from liquid evaporation. Qualitatively, the particles from both water and water/agent contain major amounts of calcium with minor trace amounts of manganese, chlorine, and magnesium (Figures 7 and 8). The particles from the water/agent extinguishment also contain minor to trace amounts of phosphorous, sulfur, copper, and sodium (Figure 9).

The polycyclic aromatic hydrocarbon analysis demonstrates some differences between the free-burn and extinguished samples (Figures 10-13). The PAH profiles of the surfactant-extinguished samples demonstrate that although the relative levels of the different peaks may be similar, the overall

magnitudes of the responses can vary significantly from sample to sample. Most notably, the emissions from the foam as well as the solution spray-extinguished fires were depleted in the PAHs with molecular weights greater than 228, compared to the water-extinguished burn, which showed relatively high levels of the range of PAHs measured. The suppression of the formation of higher molecular weight PAHs by the foam and surfactant during extinguishing of the crib fires may be due to the greater efficiency of the cooling by the two extinguishing agents compared with water. By their nature, the agent solution and foam might better coat or penetrate, and possibly cool, the combusting surfaces of the burning cribs.

One additional observation is that there was a general lack of the two softwood combustion species, retene and methyldehydroabietate, in the emission from all of the pre-extinguishment samples. The rate of combustion during all the free burns was quite high, suggesting that the two softwood-related species are not formed or do not survive the rapid (oxygen-rich) combustion phase of a fire, but are present in the smoldering, fuel-rich combustion of the extinguishing fire, regardless of the extinguishing agent.

#### **4.6.2 Second Series of Crib Burns**

For each of the extinguishment configurations, oxygen concentration, carbon dioxide concentration, carbon monoxide concentration, nitrogen oxides concentration, and heat release rate are plotted as a function of time (Figures 14-27). For all three configurations, the oxygen concentration (Figures 14-16) for water as well as the four agents all decrease to about 19.3% just before extinguishing agent is applied. In the two higher flow rate configurations, the oxygen concentrations return quickly to pre-ignition values. There does not appear to be significant differences between the four agents and water. For the lowest flow rate, 2 nozzles and 0.09 l/s (1.4 gpm), the oxygen values do not return as uniformly to pre-ignition concentrations. The lower flow rate may be less efficient at extinguishing the fire and slight differences in how the crib was burning or how the extinguishing agent is applied could be expected to have greater impact than in the higher flow rate cases where there may be excess extinguishing agent.

The ability of the higher flow rate configurations to extinguish the crib more completely than the lower flow rate is also demonstrated in the carbon dioxide (Figures 17-19) and carbon monoxide plots (Figures 20-22). The carbon dioxide concentrations increase to about 2.5 % just before the extinguishing agent is applied. CO<sub>2</sub> and CO concentrations obtained for the lowest flow rate configurations do not decrease as quickly as the higher flow rate configurations.

The impact of the higher flow rate configurations is also seen in the nitrogen oxides concentration plots (Figures 23 and 24). The higher flow rate configuration plots are much more uniform across the different agents than the lower flow rate configuration. The production of nitrogen oxides requires high temperatures, and three of the five fires (A, B, and C) (Figure 24) demonstrate different delays until the nitrogen oxides begin to appear. The range of delays observed are not well understood. Differences in fire development could account for the spread in the time before the appearance of nitrogen oxides. As the fire grows, the concentration of nitrogen oxides continues to increase until extinguishment. All the fires appear to have about the same slope after the appearance of the oxides. However, the similarity in slope after nitrogen oxides begin to appear suggests that if the crib fires had been allowed to burn for some additional time period, all of the crib fires would

have been generating between 5 and 6 ppm of nitrogen oxides. It is interesting that this delay only appears in the pre-extinguishment generation of the nitrogen oxides. After extinguishment, the concentrations of nitrogen oxides drop uniformly to less than 0.5 ppm without any observable delay. These delays in generation were only observed in concentrations of nitrogen oxides, not the oxygen, carbon monoxide, or carbon dioxide.

Heat release rate versus time for three configurations demonstrates the reproducibility of the crib fires (Figures 25-27). Peak heat release rates ranged from 300 to 400 kW. Total heat released from the cribs ranged from 90 to 120 MJ.

Size distributions of aerodynamic mass mean diameters for all smoke samples are tabulated in tables 1, 2 and 3. Each table contains the series of cribs, which was extinguished using a specific set of nozzles, flow rate and pressure. As compared to the free burn or pre-extinguishment sample, the mean diameter either remains unchanged or decreases slightly for cribs extinguished with water. The diameter decreases more significantly with each of the extinguishing agents. Since the impactor which was used to collect this data was designed to simulate the human respiratory system, the smaller mass mean diameter particles from the foam extinguished fires would penetrate further into the respiratory system (see Figure 28) [11,12].

The concentrations of hydrogen chloride for all smoke samples are summarized in tables 4, 5 and 6. Pre-extinguishment values range from 270 to 550 mg/m<sup>3</sup>. With the application of extinguishing agent, the concentration of hydrogen chloride decreases at least 30% and sometimes as much as 80%. The Occupational Safety and Health Administration (OSHA) sets the prolonged exposure limit (PEL) at 5 ppm (approximately 5 mg/m<sup>3</sup>) [14]. The foam agents do not appear to be more or less efficient than water in decreasing the hydrogen chloride concentration.

Tables 7, 8, and 9 show the concentrations of hydrogen cyanide for all smoke samples. Pre-extinguishment values range from 6 to 31 mg/m<sup>3</sup>. Application of extinguishing agent rapidly reduced the values to near zero in all but two fires. OSHA sets the prolonged exposure limit at 10 ppm TWA (time weighted average) (approximately 10 mg/m<sup>3</sup>) [15]. The agents do not appear to be more or less efficient than water in decreasing the hydrogen cyanide concentrations.

While the impactor data provides insight into the size distribution, the gravimetric filter samples demonstrate the overall mass concentration of smoke particulates, before and after extinguishment (tables 10, 11, and 12). During the free-burn portion of the crib fire, the mass concentrations range between 650 and 950 mg/m<sup>3</sup>. With the application of extinguishing agent the mass concentrations drop to a range between 100 and 260 mg/m<sup>3</sup>. While the water extinguishment values are the lowest for each configuration, the difference may not be great enough to be significant when compared to the other agents. All the extinguishing agents reduce the mass concentration by 60 to 90%. As the fire is extinguished, fewer smoke particulates are generated. The lowest flow configuration is the least efficient at extinguishing the fire and this is reflected in a 60 - 80% reduction in mass concentrations. The agents do not appear to be more or less efficient than water in decreasing smoke mass concentrations.

## 4.7 Discussion

These two series of crib burns help to characterize how extinguishment affects the chemical and physical properties of smoke. Extinguishment by any of the fire suppressant combinations, water alone, agent solution, agent solution foam, caused the smoke to undergo significant changes in chemical composition and physical attributes. These changes were observed with all the agents and were not specific to any one agent or agent/water combination. For the post-extinguishment smoke, only small differences in the chemical properties were observed between specific extinguishing agents, water alone, agent solution, or foam. The specific extinguishing agent also did not appear to affect the physical properties of the smoke with the exception of the size distribution of the particulates. These changes in the distribution of smoke particulate sizes appear consistent with the appearance of “white smoke” after extinguishment (see section 4.7.2).

### 4.7.1 Chemical Properties

Extinguishing the crib fires causes a dramatic decrease in the concentrations of carbon dioxide, carbon monoxide, and nitrogen oxides. The oxygen concentrations also rapidly approach original levels as each fire was extinguished. This is not surprising since the burning fuel is producing the combustion gases and consuming the oxygen. Within the scatter of the different agents (water and agents A, B, C, and D), there does not appear to be any significant consistent difference in these gas concentrations that can be traced to a specific agent.

The different configurations (2 or 4 nozzle and 0.09, 0.1, or 0.13 l/s (1.4, 1.6, or 2.1 gpm) flow rate) do affect how quickly the gas concentrations return to their pre-burn levels. The lowest flow rate, 0.09 l/s (1.4 gpm), is not as effective in extinguishing the fire as the highest, 0.13 l/s (2.1 gpm), flow rate. Gas concentrations return to pre-burn values more slowly for the lowest flow rate as compared to the highest flow rate. This is not unexpected since fire continues to produce combustion gases until it is extinguished. The differences are a function of the ability of the given flow rate to extinguish the fire and do not appear related specifically to any one water/foam agent.

The pre-extinguishment concentrations of hydrogen cyanide dropped to essentially zero for most of the burns as the cribs were extinguished. The hydrogen cyanide resulted from the combustion of the ABS plastic sticks placed within the crib. The integrated nature of the sample, one sample collected over some period before or after extinguishment, precludes identification of any trends such as slowly decreasing concentrations as was observed in the other gas data. The specific flow rate and configuration did appear to affect the decrease in concentration of hydrogen cyanide. The lowest flow rate of water alone sprayed from the 2 nozzle configuration did not show as much of a decrease as the water was applied. This again appears to reflect the effect of configuration on the extinguishment process rather than being related to a specific extinguishing agent. The two nozzle configuration was less effective than the four nozzle set-up in extinguishing the crib fire. The fire continued to generate hydrogen cyanide until the fire was completely extinguished.

Extinguishment decreased the free burn concentrations of hydrogen chloride, but not quite as thoroughly as was observed with hydrogen cyanide. The hydrogen chloride resulted mainly from the combustion of the PVC plastic sticks placed within the crib. The integrated nature of the sample, one sample collected over some period before or after extinguishment, precludes identification of

any trends such as slowly decreasing concentrations as was observed in the other gas data. The specific flow rate and configuration did not appear to affect the decrease in concentration of hydrogen chloride. There did not appear to be any consistent differences between the specific agents in terms of reducing the hydrogen chloride concentrations.

The application of extinguishing agents to the crib fires reduced the mass concentration of the smoke from each of the crib burns. Qualitatively, the reduction appeared somewhat less for the 2 nozzle/0.09 l/s (1.4 gpm) configuration. This again reflected the inability of the lower flow rate to extinguish the fire as quickly as the higher flow rates/4 nozzle combinations. There were no apparent differences between the water alone and the agent solutions.

The agent solutions did appear to affect the size distribution of the smoke particulates. Extinguishment via water alone appeared to cause minor shifts in the aerodynamic mass mean diameter. But the agents consistently shifted the mean diameter toward smaller values. As the smoke cools, the water condenses on the smoke particulates. As the water collects on the smoke particulates and later evaporates through mixing with dry air, the loose aggregate structure observed in the electron microscopy work may collapse to form a more compact particulate. The surfactant found in the agents would allow the spray to wet the particulates better than water alone. This could result in slightly more compact particulates emerging from a fire extinguished using an agent. However, this does not reduce the hazard presented by the smoke particulates. The smaller particulates represent an increased hazard because the smaller smoke particles can penetrate further into the lungs than the larger particulates [11,12]. Therefore based on limited data, the most significant change in the physical properties of the smoke, the smaller mean diameter, may actually be a negative or undesirable effect.

The inorganic analysis via scanning electron microscopy and environmental scanning electron microscopy was not successful in identifying a “chemical marker” which could be used to differentiate between water and agent generated smoke. There were slight differences noted in several inorganic metals, but metals such as sodium, magnesium, or manganese could result from the water used to deliver the foam agent. It was not possible to differentiate between inorganic compounds originating in the agents and compounds originating in the water used to deliver the agents. The low concentrations of agent, typically 1 to 6% in the water and the dilution of the volatilized agent as it is entrained by the fire plume also makes it more difficult to isolate a compound unique to water or agent extinguished smoke.

The PAH analysis confirms the presence of organic “chemical markers” identifying the source or fuel as softwood. The PAH concentrations also indicate that the foam agents may reduce the formation of heavier polycyclic aromatic hydrocarbons. This is probably related to the ability of the agents to reduce surface tension and increase vaporization of water, which absorbs more energy from the region over the fire. Lower temperatures are less conducive to the formation of heavier PAHs. If additional water were used in the extinguishment process, then it is possible the formation of heavier PAHs would also be impeded as in the foam case.

#### **4.7.2 “White Smoke”**

During the extinguishment process, the fire suppressant is injected or sprayed into or around the

burning fuel. The fire suppressant may be water or a combination of fire suppression agent (1 - 6%) in water (94 - 99%). The energy released by the combustion of the fuel is absorbed by the water, and it undergoes a change in its physical state from liquid to vapor. The water vapor may be entrained by the fire plume and mixed with other combustion gases and smoke particulates. As the gases cool through radiation losses and mixing, the water vapor may condense on small particulates or condensation nuclei. As additional vapor condenses to form increasing numbers of small droplets, a cloud may appear. This cloud formation process requires that the gases be saturated in terms of water and that there be sufficient condensation nuclei present.

The agents could promote the formation of clouds by increasing the water content of the gases and by providing additional condensation nuclei. Surfactants and foam agents are designed to reduce the surface tension of the solution and encourage the formation of bubbles. The thin film of solution around a small volume of air or combustion gases can effectively increase the surface area of the solution. Increased surface area then translates into increased evaporation. As the water content increases, the air and/or combustion gases can become saturated with water vapor. The higher the degree of saturation or supersaturation, the quicker the water will condense to form droplets if condensation nuclei are present.

Additional condensation nuclei are provided by the salts, which are included in many surfactants and foam agents as water conditioners or softeners. As the agent is applied to the burning fuel, many small droplets of water/agent are sprayed on the fire. In the hotter regions of the fire, water evaporates from each droplet and the droplet collapses to form a small residue particle. The particles are the salts and other water conditioners added by the surfactant or foam agent as well as any impurities found in the water. These small particulates may provide additional condensation nuclei, which could promote the condensation of additional droplets.

#### **4.8 Conclusions**

The application of fire suppressant agents to crib fires did effect the chemical composition and size distribution of the smoke above the burning fuel. Most of the changes from pre- to post-extinguishment smoke were the result of the fire being extinguished. Extinguishment caused a significant reduction in the concentrations of carbon monoxide, carbon dioxide, hydrogen chloride, hydrogen cyanide, nitrogen oxides, and soot particulates in the post-extinguishment smoke. These reductions were observed for each of the fire suppressant agents, water alone, agent solution, and foam. With the exception of small shifts in smoke particulate size in the post-extinguishment smoke which was only observed with the foam, there did not appear to be significant differences in the post-extinguishment smoke between using water, agent solution, foam.

The agents, which reduce the surface tension of water and increase the surface area of a given mass of water, appear to expedite evaporation of the water. The agents also provide additional particulates, which may serve as condensation sites. Under the proper conditions, the additional water and particulates would promote the condensation of water into droplets, which may develop into a cloud of "white smoke".

## 4.9 References

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13. Andersen 2000 Cascade Impactor Operating Manual, Graseby Inc., Smyrna, reprinted with permission.

**Table 1. Size Distribution for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 2 nozzle/1.3 gpm/40 psi**

		Aerodynamic Mass Mean Diameter, $\mu\text{m}$
Pre- Extinguishment		1.6*
		1.4
Post-Extinguishment		
	Water	1.4
	Agent A	0.9
	Agent A (Repeat)	1.0
	Agent B	1.3
	Agent C	1.2
	Agent D	-
<p>Notes:</p> <p>Reported values for aerodynamic mass mean diameter are estimated to be +/- 0.2 <math>\mu\text{m}</math> (Combined Standard Uncertainty - <math>2\sigma</math> or 95% confidence level)</p> <p>*The same pre-extinguishment samples are reported for all three extinguishment configurations.</p>		

**Table 2. Size Distribution for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 4 nozzle/2.1 gpm/26 psi**

		Aerodynamic Mass Mean Diameter, $\mu\text{m}$
Pre- Extinguishment		1.6*
		1.4
Post-Extinguishment		
	Water	1.8
	Agent A	1.2
	Agent B	0.8
	Agent C	0.6
	Agent D	1.0
<p>Notes:</p> <p>Reported values for aerodynamic mass mean diameter are estimated to be +/- 0.2 <math>\mu\text{m}</math> (Combined Standard Uncertainty - <math>2\sigma</math> or 95% confidence level)</p> <p>*The same pre-extinguishment samples are reported for all three extinguishment configurations.</p>		

**Table 3. Size Distribution for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 4 nozzle/1.6 gpm/14 psi**

		Aerodynamic Mass Mean Diameter, $\mu\text{m}$
Pre- Extinguishment		1.6*
		1.4
Post-Extinguishment		
	Water	1.0
	Agent A	-
	Agent B	0.8
	Agent C	0.6
	Agent C	0.8
	Agent D	0.7
<p>Notes:</p> <p>Reported values for aerodynamic mass mean diameter are estimated to be +/- 0.2 <math>\mu\text{m}</math> (Combined Standard Uncertainty - <math>2\sigma</math> or 95% confidence level)</p> <p>*The same pre-extinguishment samples are reported for all three extinguishment configurations.</p>		

**Table 4. Hydrogen Chloride Concentrations for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 2 nozzle/1.3 gpm/40 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment Mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	520	300	0.4
Agent A	500	240	0.5
Agent A (Repeat)	520	-	
Agent B	550	100	0.8
Agent C	540	360	0.3
Agent D	440	100	0.8
<p>Notes:</p> <p>Reported values for hydrogen chloride concentrations are estimated to be +/- 100 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)</p>			

**Table 5 Hydrogen Chloride Concentration for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 4 nozzle/2.1 gpm/26 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment Mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	440	160	0.6
Agent A	270	120	0.6
Agent B	540	320	0.4
Agent C	550	410	0.3
Agent D	470	350	0.3

Notes:

Reported values for hydrogen chloride concentrations are estimated to be +/- 100 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)

**Table 6. Hydrogen Chloride for Smoke from Fire Suppressant Foam Agents  
Extinguishment Configuration - 4 nozzle/1.6 gpm/14 psi**

	Pre- Extinguishment mg/m <sup>3</sup>	Post- Extinguishment Mg/m <sup>3</sup>	Reduction ( <u>Pre-Ext. - Post-Ext.</u> ) Pre
Water	290	195	0.3
Agent A	450	150	0.7
Agent B	390	70	0.8
Agent C	490	210	0.6
Agent C (Repeat)	460	170	0.6
Agent D	520	290	0.4
<p>Notes:</p> <p>Reported values for hydrogen chloride concentrations are estimated to be +/- 100 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)</p>			

**Table 7. Hydrogen Cyanide Concentrations for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 2 nozzle/1.3 gpm/40 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	23	11	0.4
Agent A	13	3	0.8
Agent A (Repeat)	15	0	1.0
Agent B	12	3	0.8
Agent C	12	0	1.0
Agent D	21	0	1.0
<p>Notes:</p> <p>Reported values for hydrogen cyanide concentrations are estimated to be +/- 6 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)</p>			

**Table 8. Hydrogen Cyanide Concentration for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 4 nozzle/2.1 gpm/26 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment Mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	6	0	1.0
Agent A	25	0	1.0
Agent B	31	0	1.0
Agent C	24	0	1.0
Agent D	21	0	1.0

Notes:

Reported values for hydrogen cyanide concentrations are estimated to be +/- 6 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)

**Table 9. Hydrogen Cyanide for Smoke from Fire Suppressant Foam Agents  
Extinguishment Configuration - 4 nozzle/1.6 gpm/14 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment Mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	15	0	1.0
Agent A	17	0	1.0
Agent B	19	0	1.0
Agent C	31	0	1.0
Agent C (Repeat)	24	0	1.0
Agent D	17	0	1.0
<p>Notes:</p> <p>Reported values for hydrogen cyanide concentrations are estimated to be +/- 6 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)</p>			

**Table 10. Mass Concentrations for Smoke from Fire Suppressant Foam Agents  
Extinguishment Configuration - 2 nozzle/1.3 gpm/40 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	910	170	0.8
Agent A	850	230	0.7
Agent A (Repeat)	810	220	0.7
Agent A (Repeat)	840	-	-
Agent B	650	230	0.6
Agent C	670	260	0.6
Agent D	860	211	0.8
<p>Notes:</p> <p>Reported values for mass concentrations are estimated to be +/- 150 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)</p>			

**Table 11. Mass Concentration for Smoke from Fire Suppressant Foam Agents Extinguishment Configuration - 4 nozzle/2.1 gpm/26 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	850	30	1.0
Agent A	860	120	0.9
Agent B	911	90	0.9
Agent C	910	160	0.8
Agent D	951	140	0.9

Notes:

Reported values for mass concentrations are estimated to be +/- 150 mg/m<sup>3</sup>  
(Combined Standard Uncertainty - 2σ or 95% confidence level)

**Table 12. Mass Concentration for Smoke from Fire Suppressant Foam Agents  
Extinguishment Configuration - 4 nozzle/1.6 gpm/14 psi**

	Pre-Extinguishment mg/m <sup>3</sup>	Post-Extinguishment mg/m <sup>3</sup>	Reduction (Pre-Ext. - Post-Ext.) Pre
Water	890	100	0.9
Agent A	850	120	0.9
Agent B	830	120	0.9
Agent C	770	140	0.8
Agent C (Repeat)	720	-	-
Agent D	770	105	0.9
<p>Notes:</p> <p>Reported values for mass concentrations are estimated to be +/- 150 mg/m<sup>3</sup> (Combined Standard Uncertainty - 2σ or 95% confidence level)</p>			



Figure 1. Wood pallet fire suppression demonstration with water (foreground), foam solution (center) and compressed air foam (background).

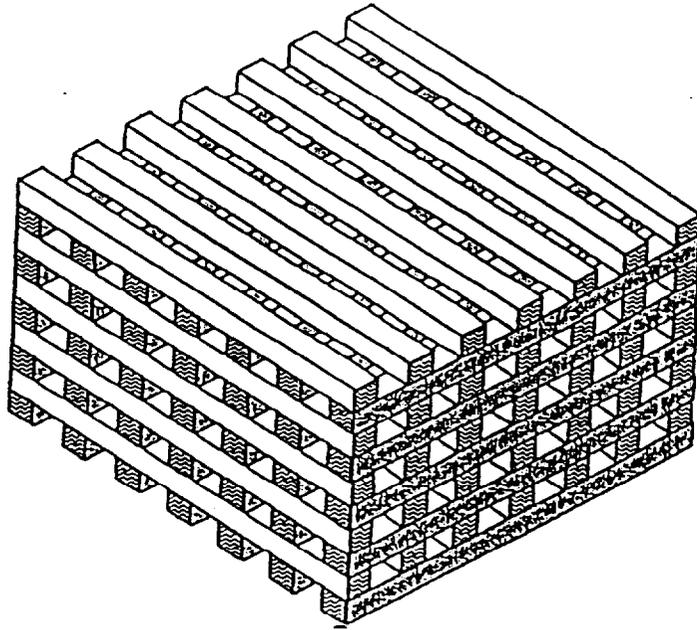


Figure 2. Diagram of crib (55.9 cm X 55.9 cm X 38 cm high) used for suppression experiments.

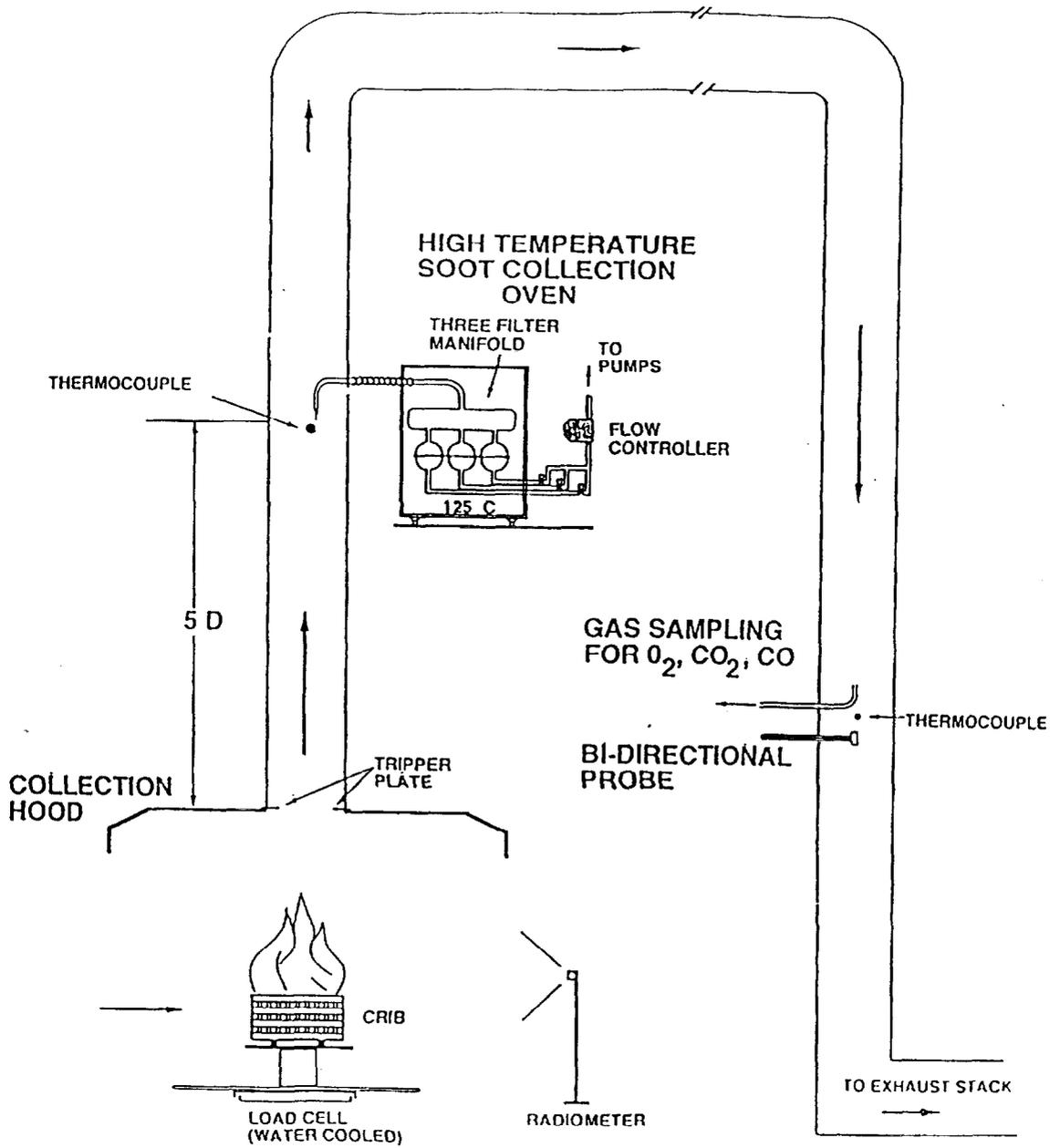


Figure 3. Diagram of furniture calorimeter and smoke sampling arrangement.

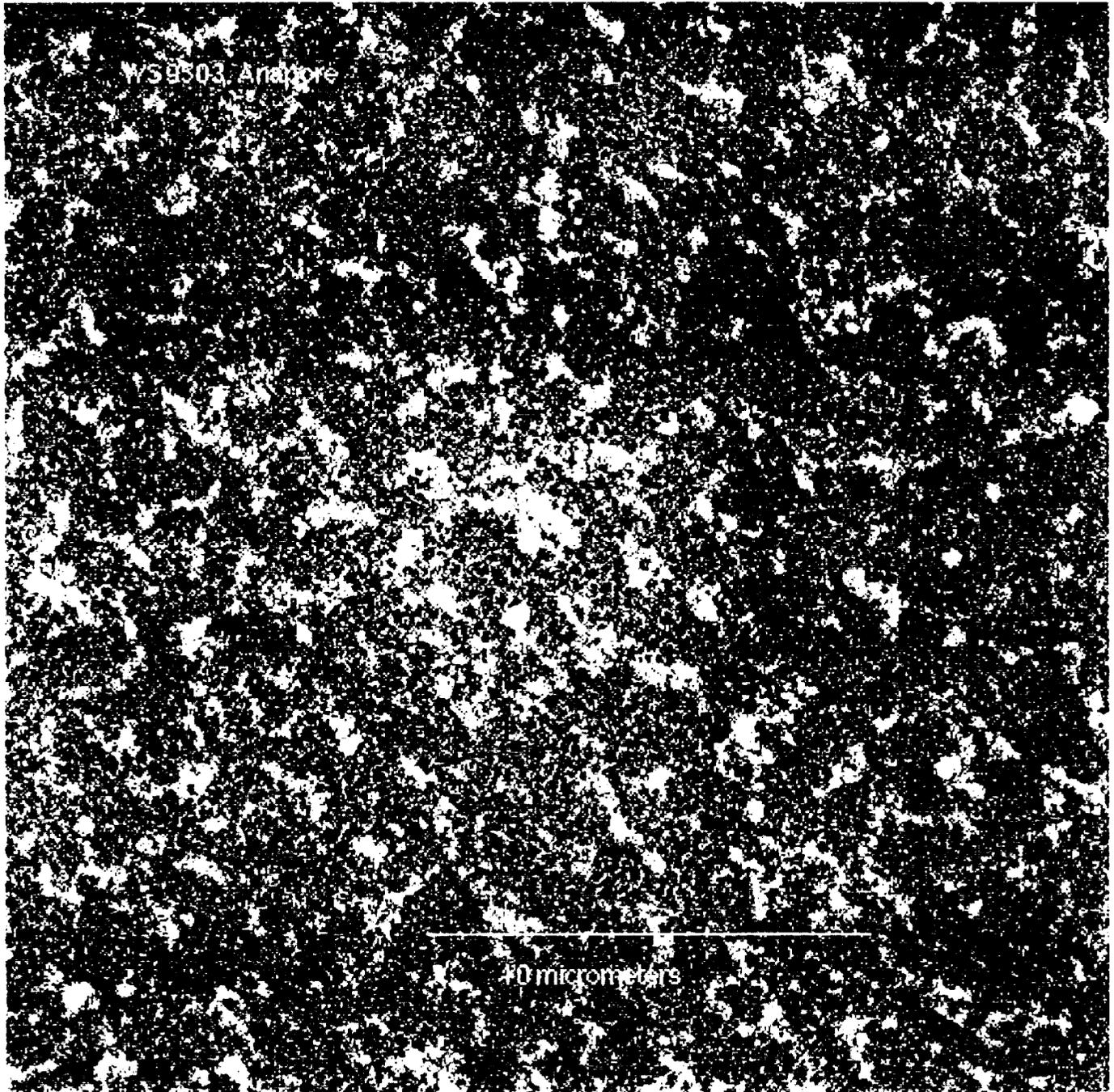


Figure 4. Electron micrograph of small aggregates on Anapore filter. Sample collected during extinguishment with foam.



Figure 5. Electron micrograph of single aggregate on Nucleopore filter. Sample collected during extinguishment with foam.

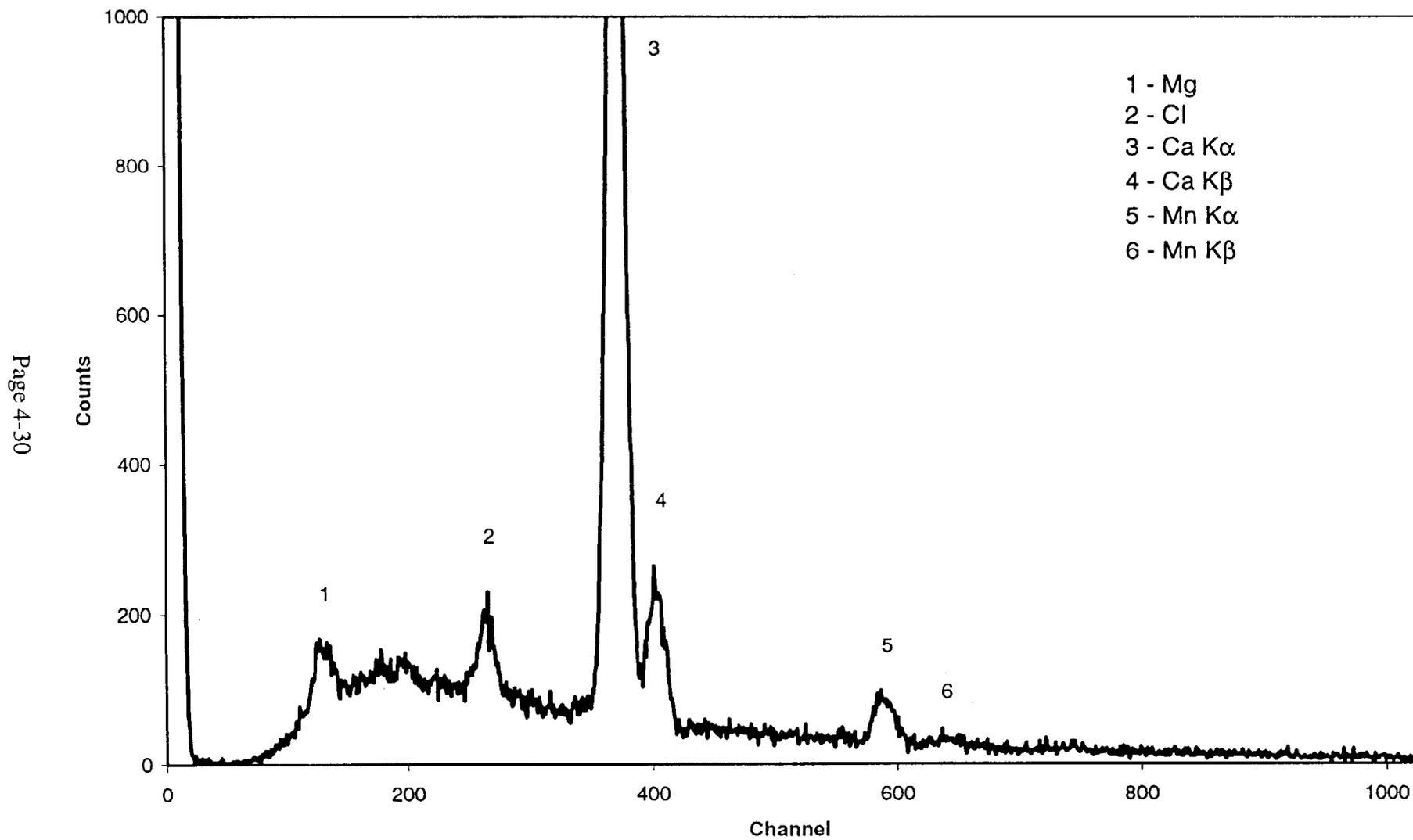


Figure 6. Spectrum from energy dispersive x-ray analysis of sample from Nucleopore filter collected during extinguishment with water. Peaks identified are magnesium, chlorine, calcium and manganese.



Figure 7. Electron micrograph of two aggregates (identified as particle 4 and 5) on Nucleopore filter. Sample collected during extinguishment with foam.

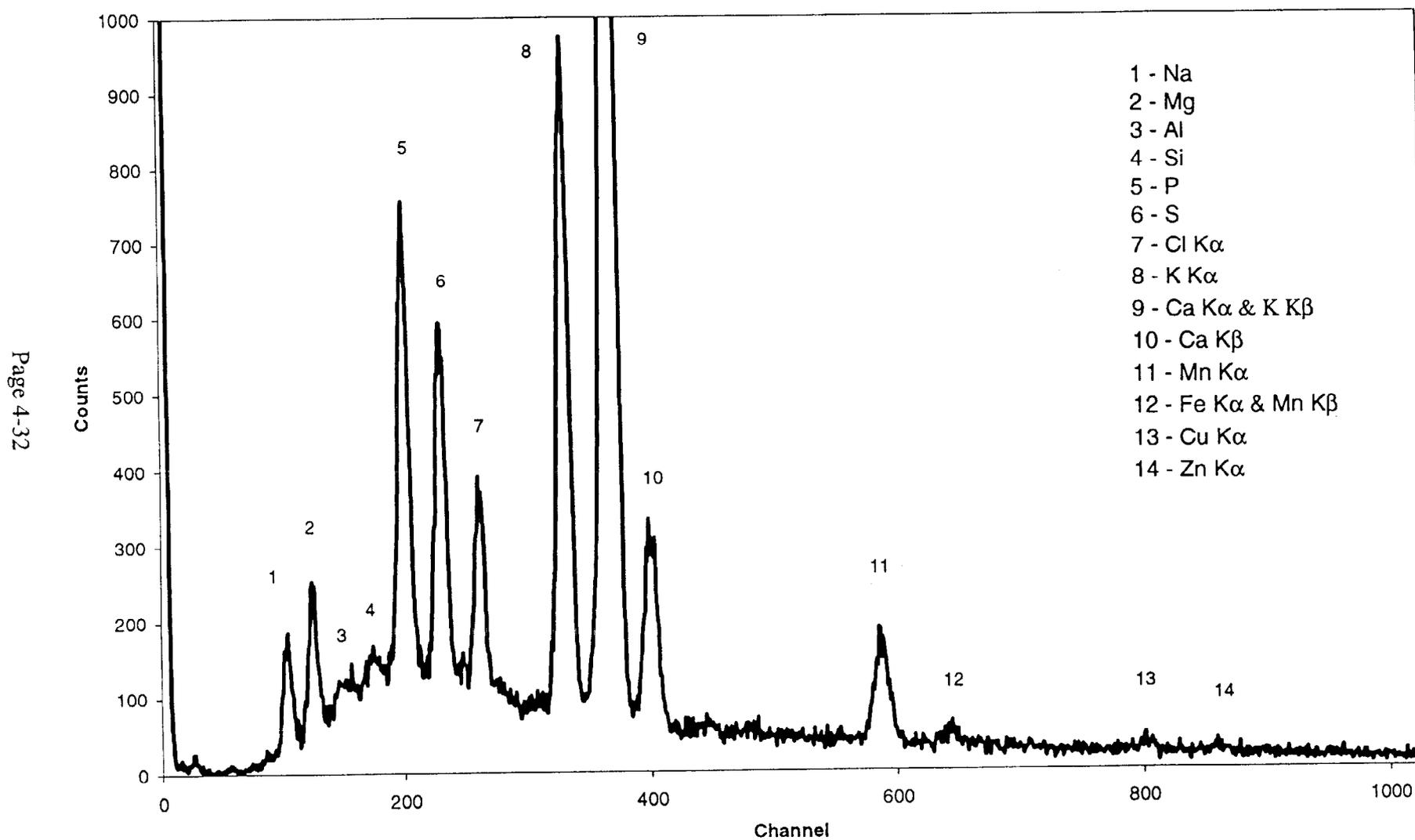


Figure 8. Spectrum from energy dispersive x-ray analysis of particle 4 from Nucleopore filter collected during extinguishment with foam. Peaks identified are sodium, magnesium, aluminum, silicon, phosphorous, sulfur, chlorine, potassium, calcium, iron, manganese copper and zinc.

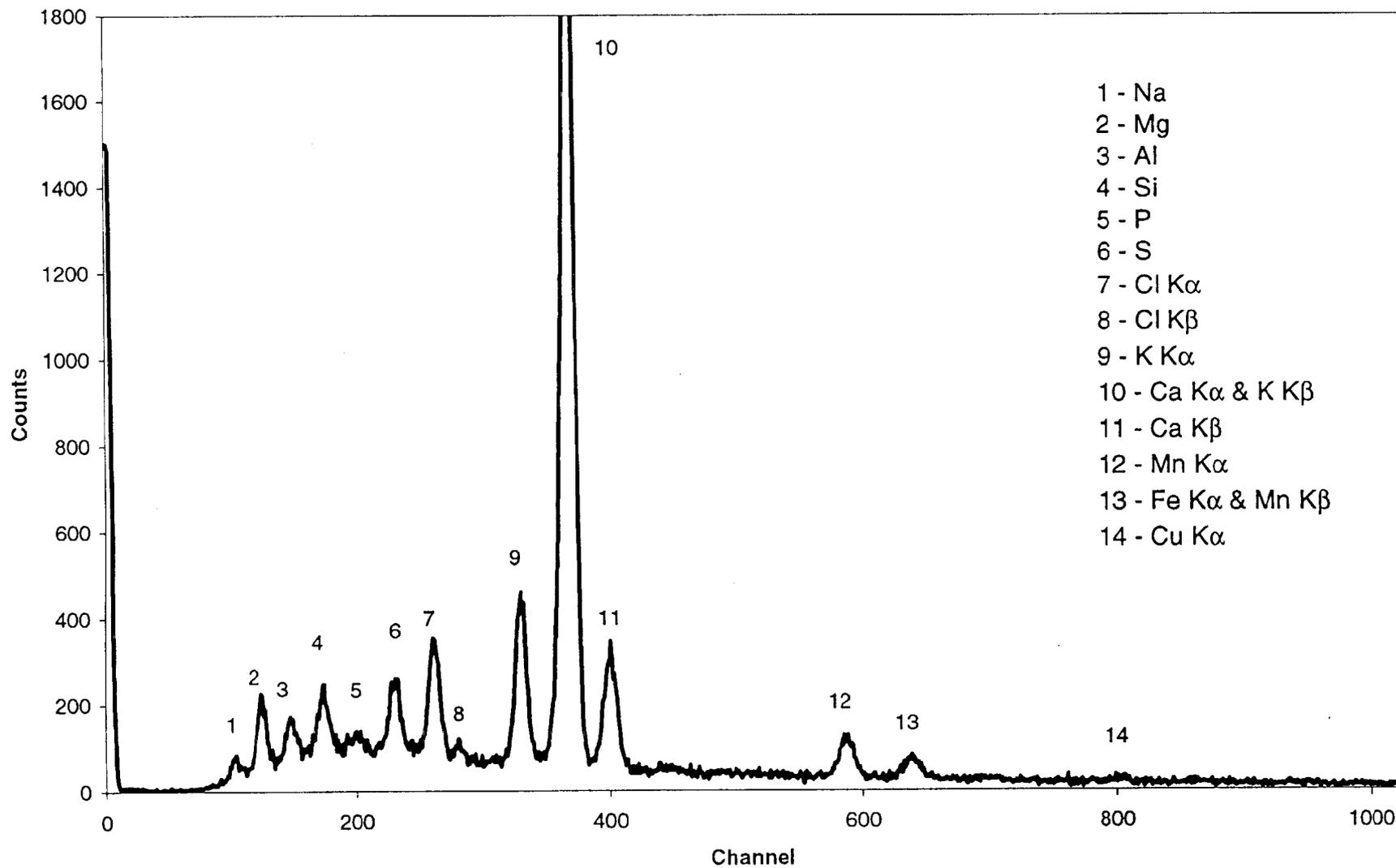


Figure 9. Spectrum from energy dispersive x-ray analysis of particle 5 from Nucleopore filter collected during extinguishment with foam. Peaks identified are sodium, magnesium, aluminum, silicon, phosphorous, sulfur, chlorine, potassium, calcium, manganese, iron, and copper.

Figure 10a. Foam Extinguished Wood Crib Fire.

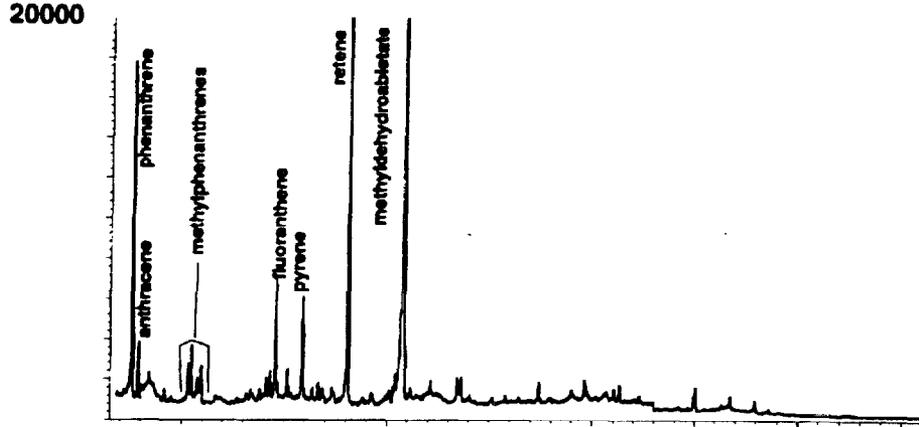


Figure 10b. Water Extinguished Wood Crib Fire.

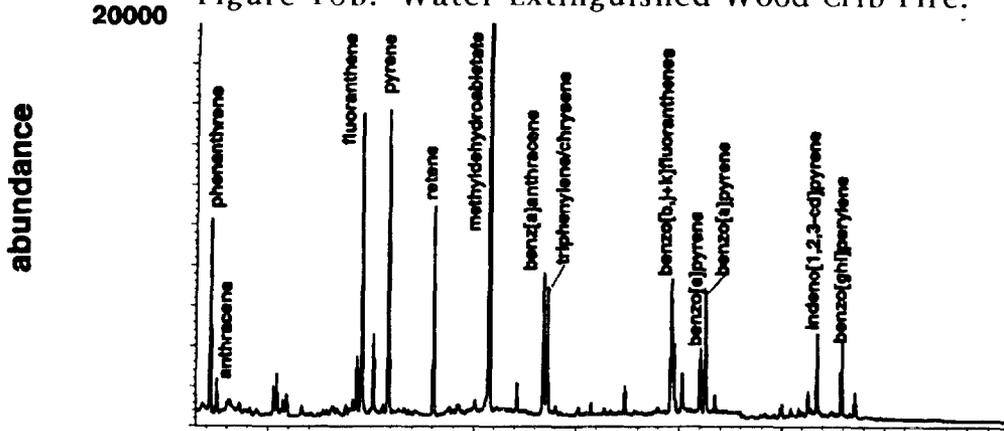
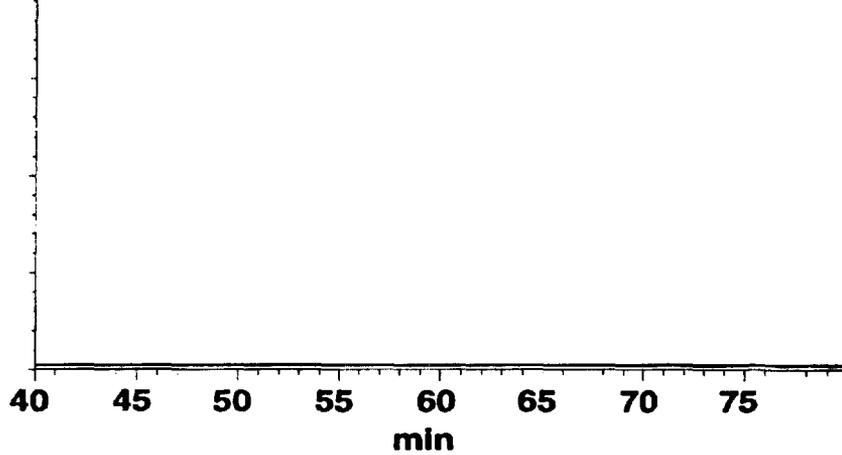


Figure 10c. Quartz Filter Blank.



Figures 10a-c. Gas chromatograms for combustion smoke.

Figure 11a. Before Extinguishment with Agent Solution.

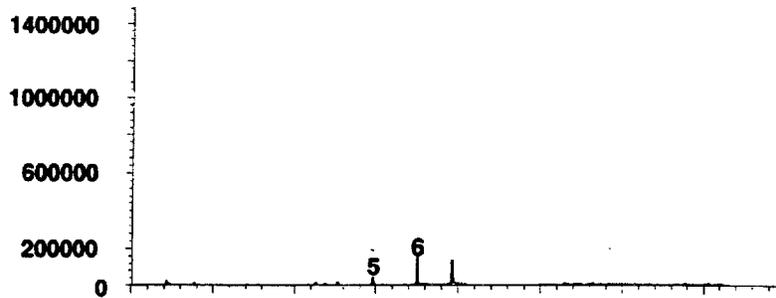


Figure 11b. After Extinguishment with Agent Solution.

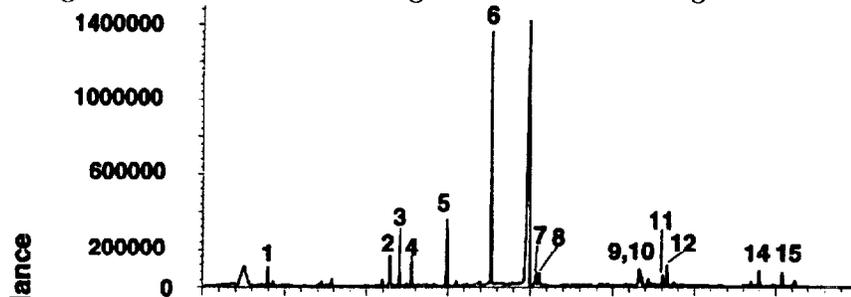


Figure 11c. Before Extinguishment with Agent Solution.

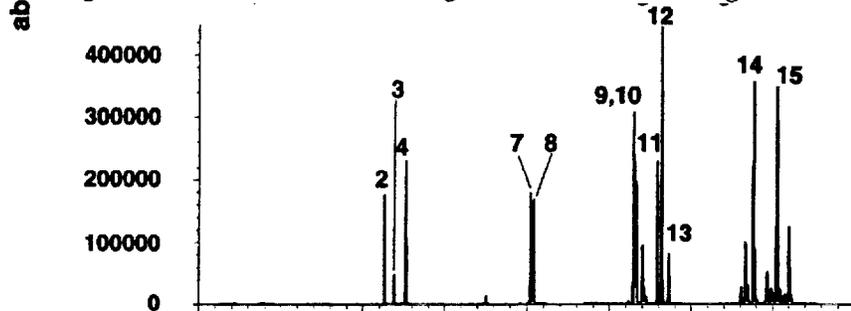
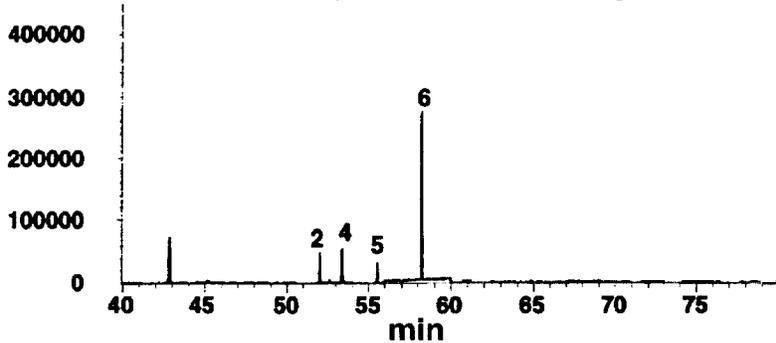


Figure 11d. After Extinguishment with Agent Solution.



Figures 11 a-d. Gas chromatograms for combustion smoke (each represents a different smoke sample).

Figure 12a. Before Extinguishment with Foam.

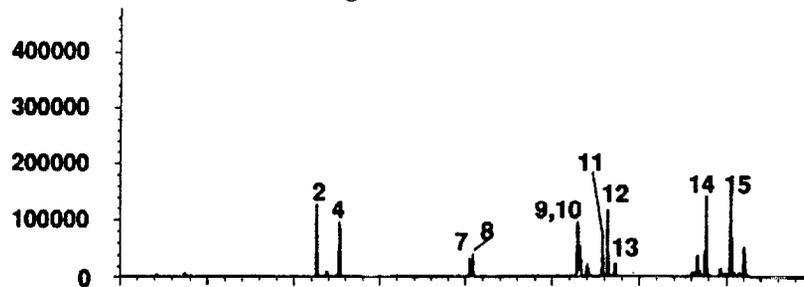


Figure 12b. After Extinguishment with Foam..

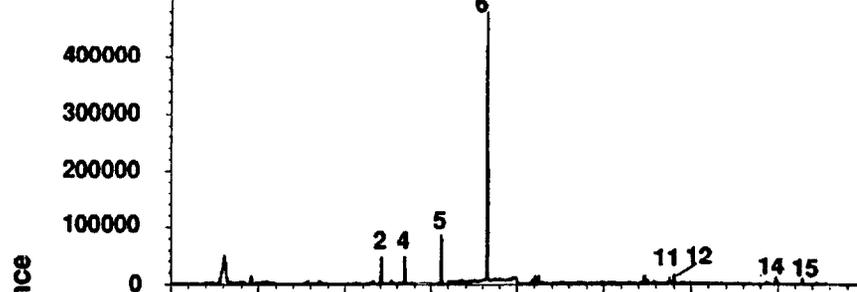


Figure 12c. Before Extinguishment with Water.

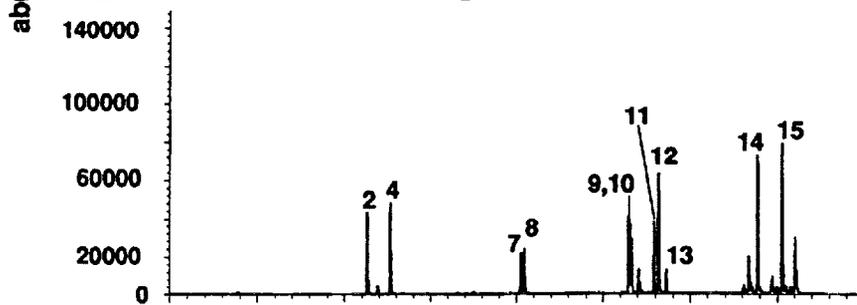
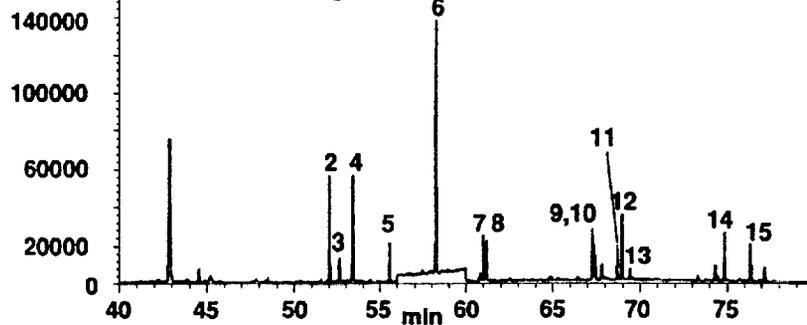


Figure 12d. After Extinguishment with Water.



Figures 12 a-d. Gas chromatograms for combustion smoke (each represents a different smoke sample).

Figure 13a. Before Extinguishment with Foam.

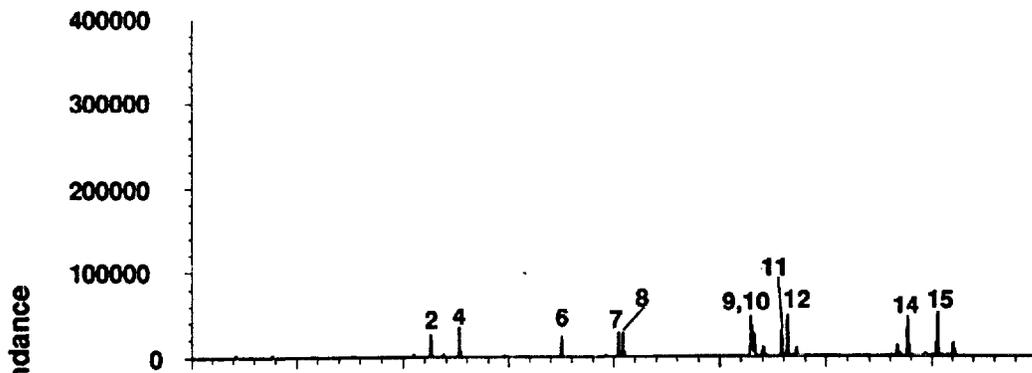
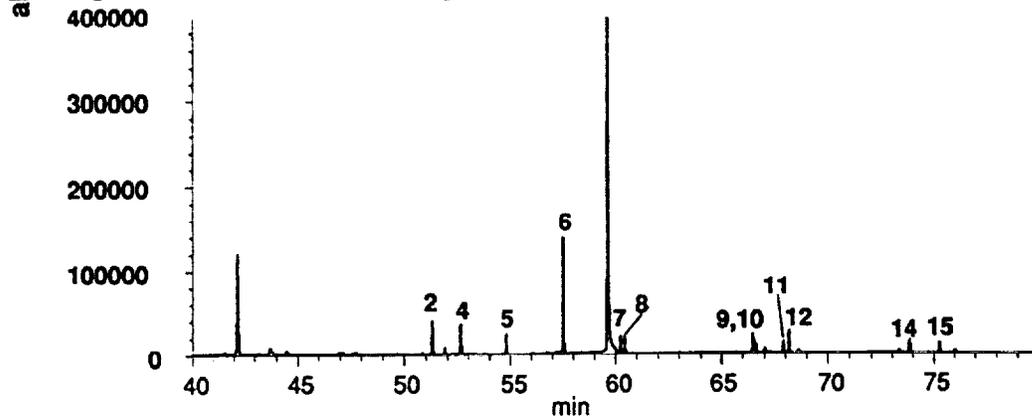


Figure 13b. After Extinguishment with Foam.



Figures 13 a-b. Gas chromatograms for combustion smoke (each represents a different smoke sample).

<u>Peak No.</u> <sup>1</sup>	<u>Identification</u>
1.	phenanthrene
2.	fluoranthene
3.	acephenanthrylene
4.	pyrene
5.	retene
6.	methyldehydroabietate
7.	benz[a]anthracene
8.	triphenylene/chrysene
9.	benzo[b]fluoranthene
10.	benzo[j] and benzo[k]fluoranthene
11.	benzo[e]pyrene
12.	benzo[a]pyrene
13.	perylene
14.	indeno[1,2,3-cd]pyrene
15.	benzo[ghi]perylene

Figure 13c. Key to polycyclic aromatic hydrocarbons identified in figures 10 –13.

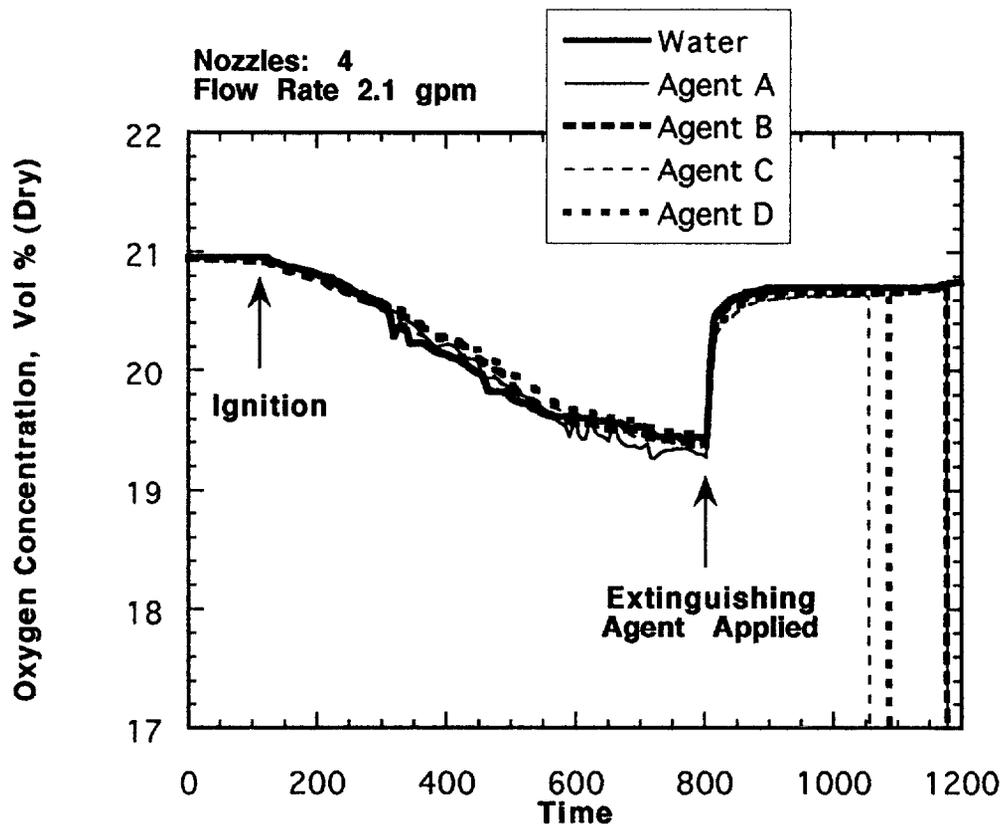


Figure 14. Oxygen concentration time history with four nozzles at 7.8 Lpm (2.1 gpm).

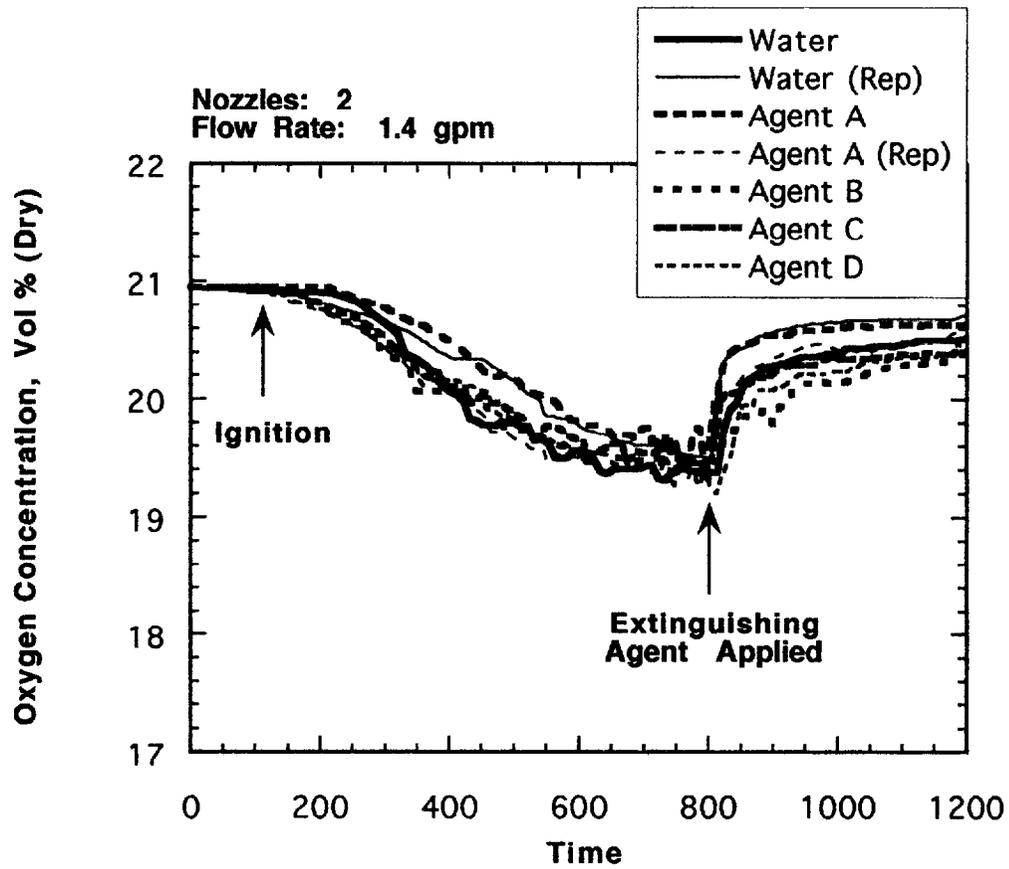


Figure 15. Oxygen concentration time history with two nozzles at 5.4 Lpm (1.4 gpm).

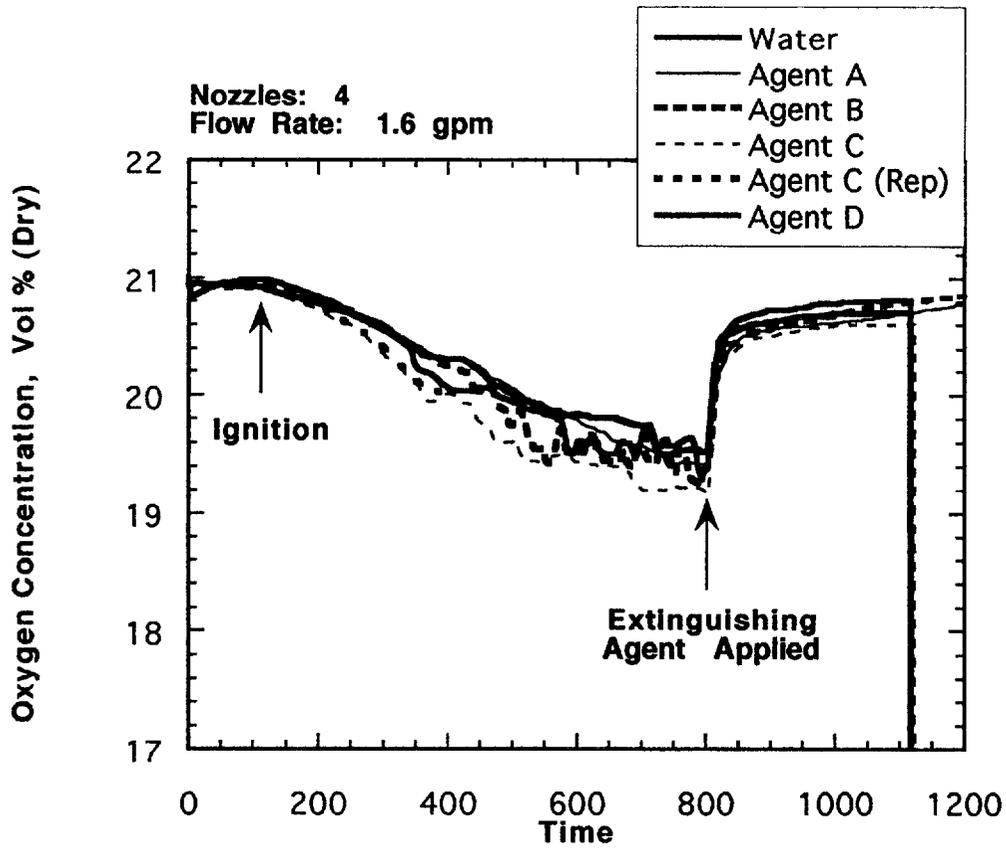


Figure 16. Oxygen concentration time history with four nozzles at 6 Lpm (1.6 gpm).

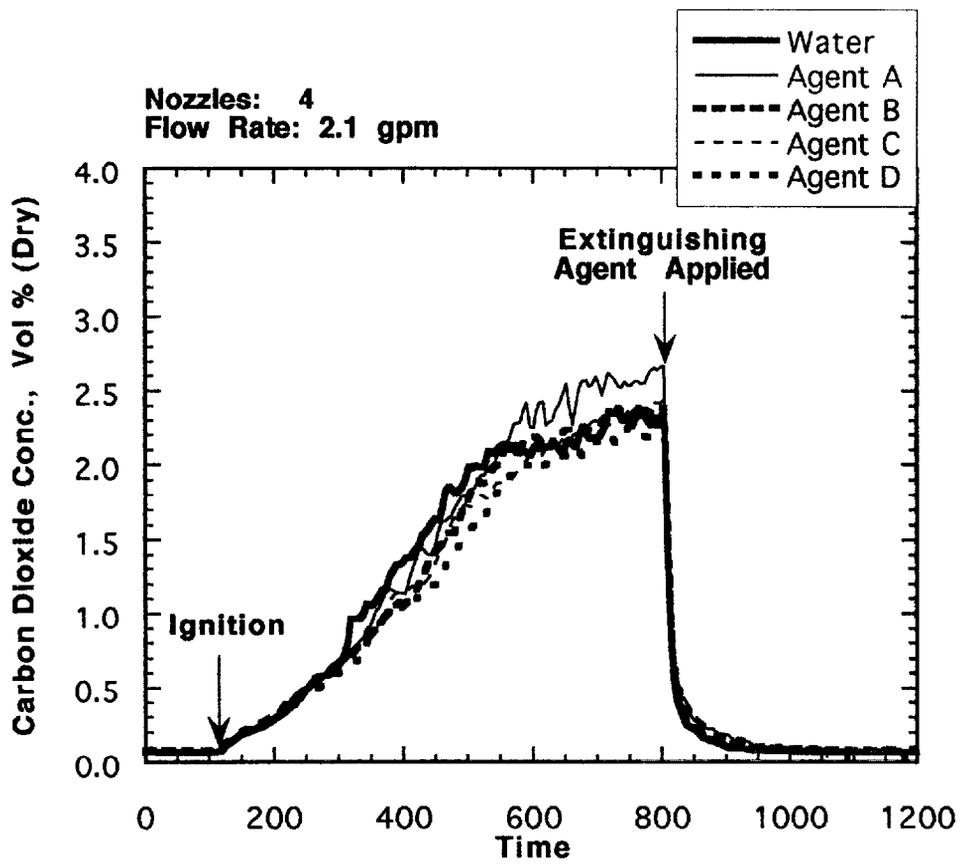


Figure 17. Carbon dioxide concentration time history with four nozzles at 7.8 Lpm (2.1 gpm).

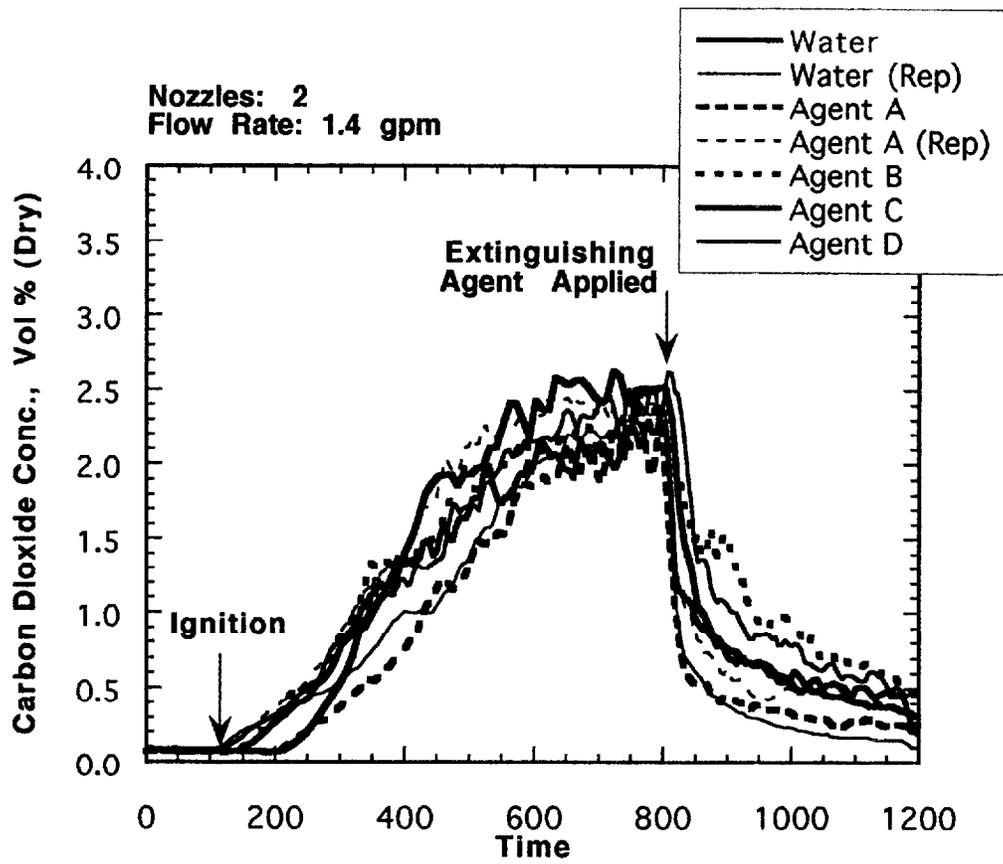


Figure 18. Carbon dioxide concentration time history with two nozzles at 5.4 Lpm (1.4 gpm).

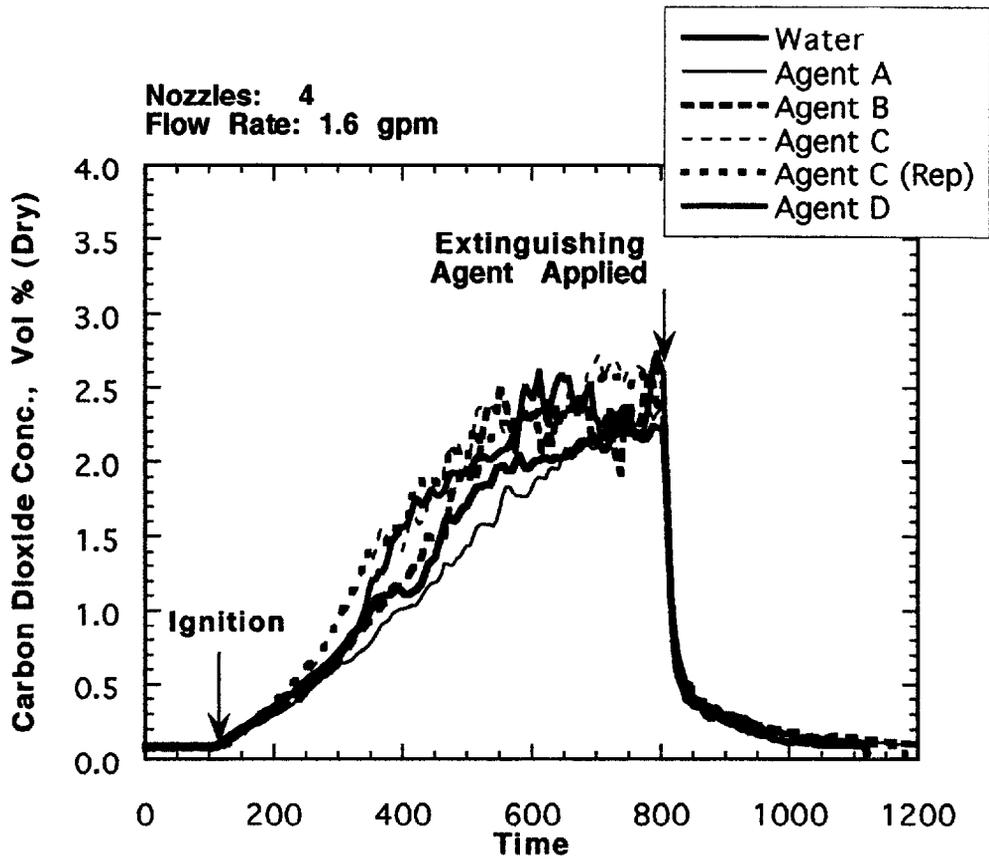


Figure 19. Carbon dioxide concentration time history with four nozzles at 6 Lpm (1.6 gpm).

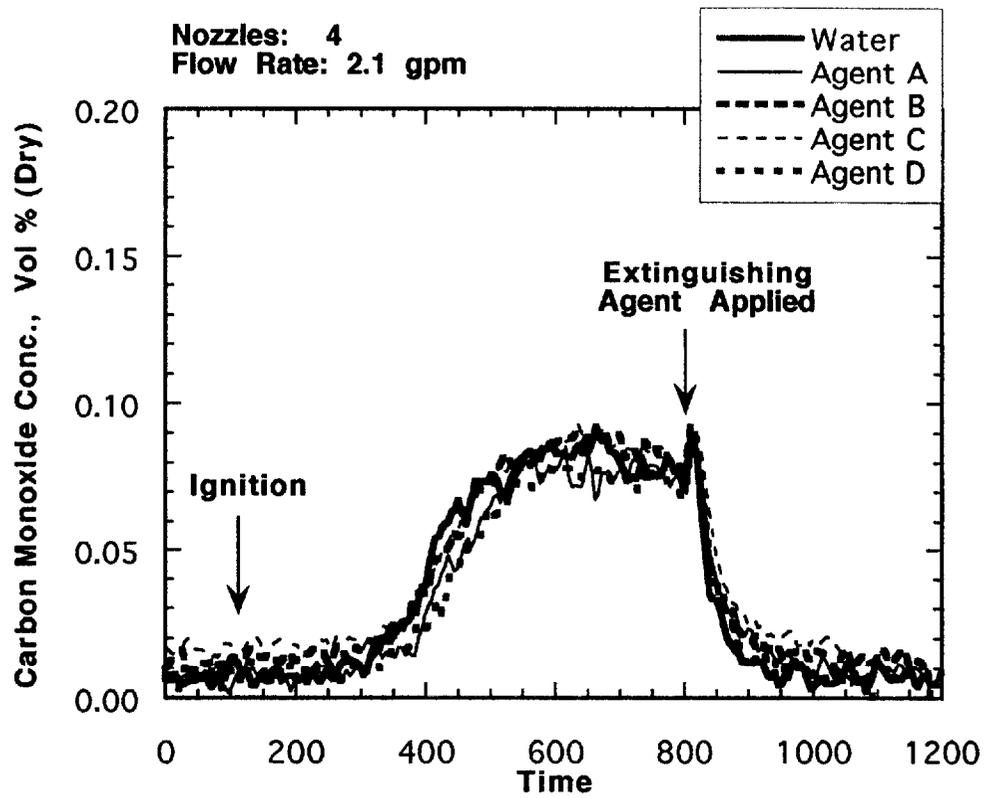


Figure 20. Carbon monoxide concentration time history with four nozzles at 7.8 Lpm (2.1 gpm).

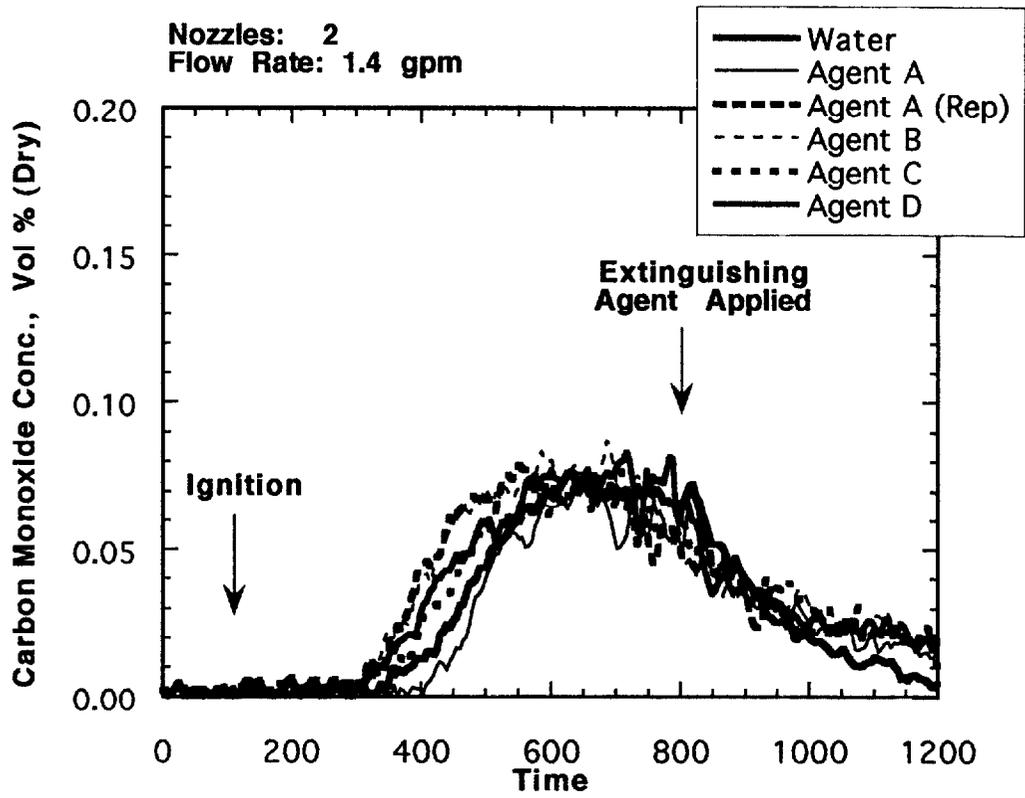


Figure 21. Carbon monoxide concentration time history with two nozzles at 5.4 Lpm (1.4 gpm).

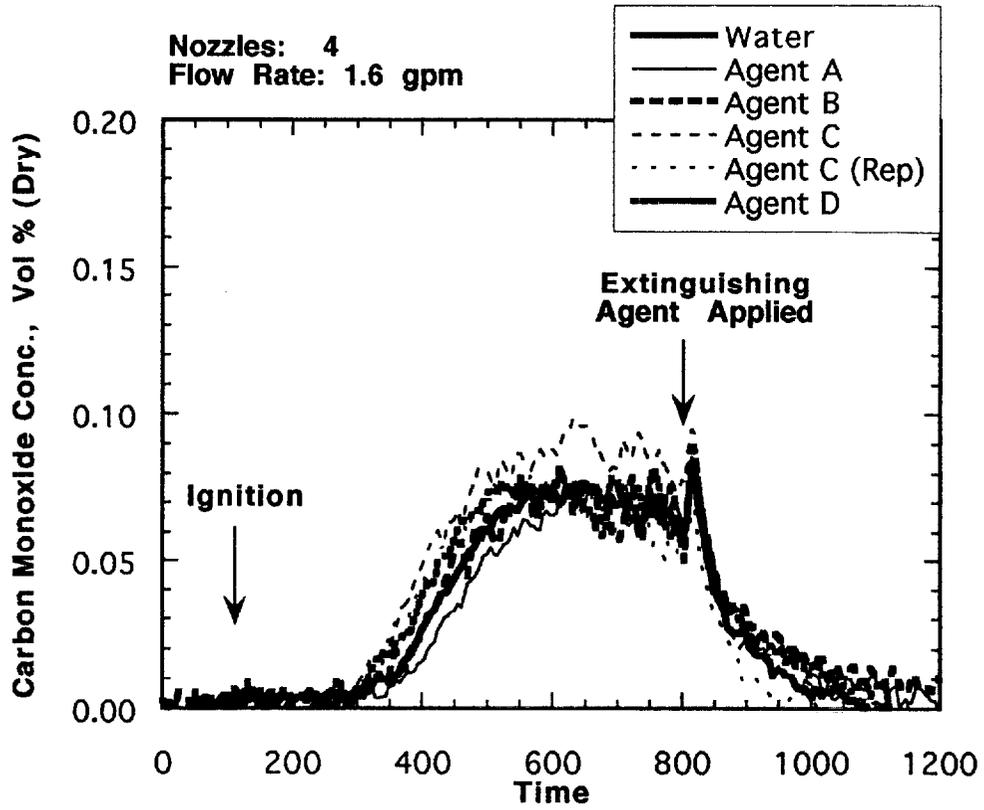


Figure 22. Carbon monoxide concentration time history with four nozzles at 6 Lpm (1.6 gpm).

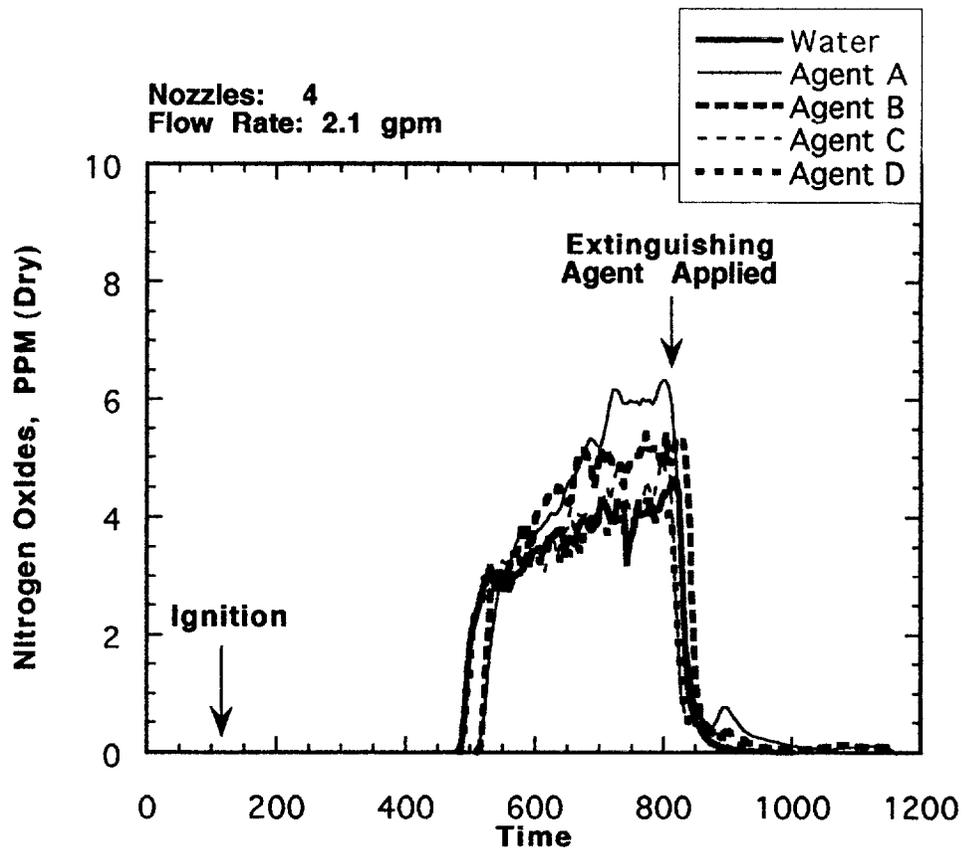


Figure 23. Nitrogen oxides concentration time history with four nozzles at 7.8 Lpm (2.1 gpm).

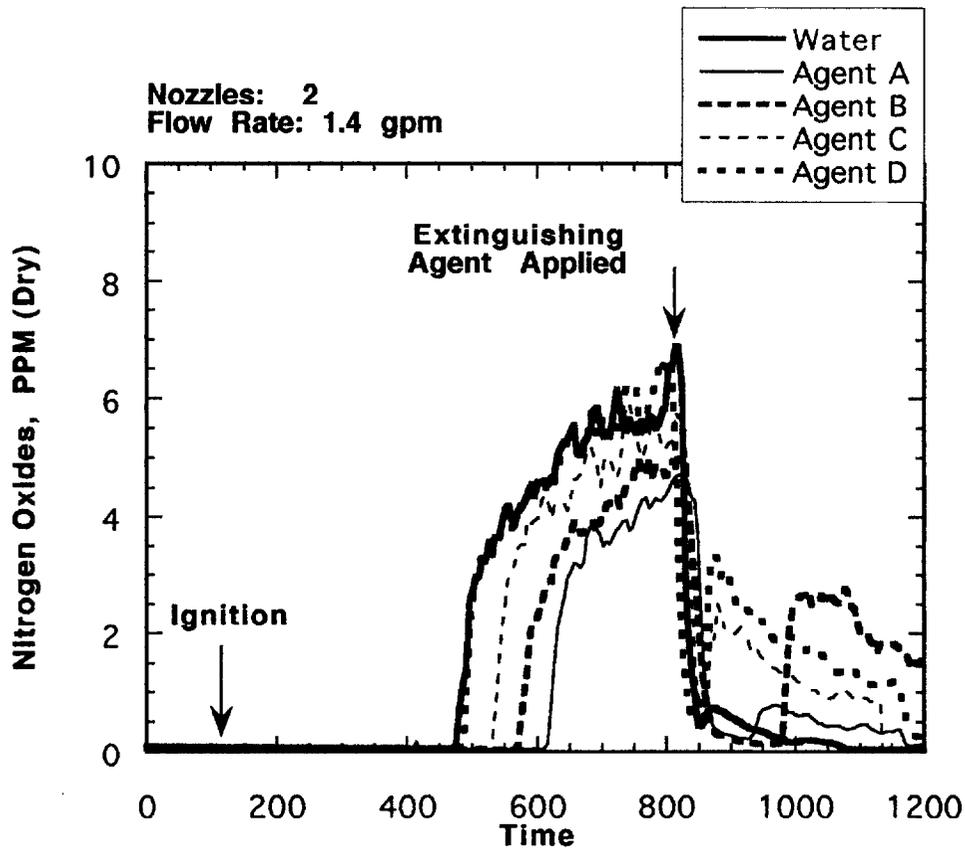


Figure 24. Nitrogen oxides concentration time history with two nozzles at 5.4 Lpm (1.4 gpm).

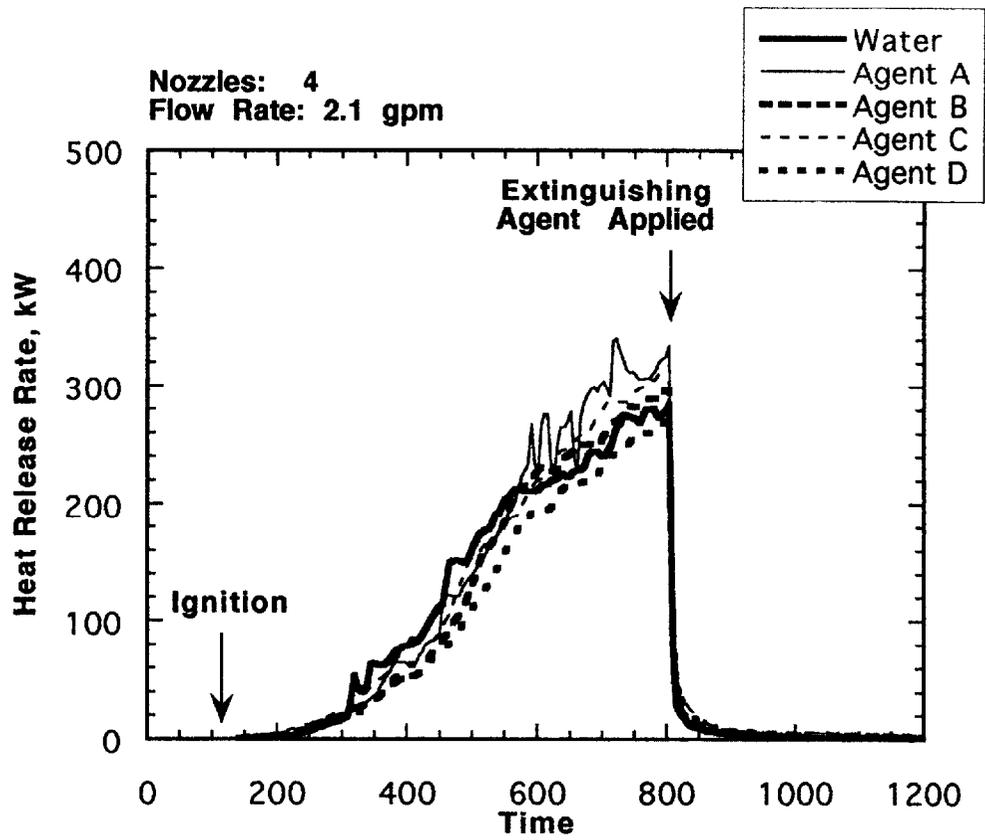


Figure 25. Heat release rate with four nozzles at 7.8 Lpm (2.1 gpm).

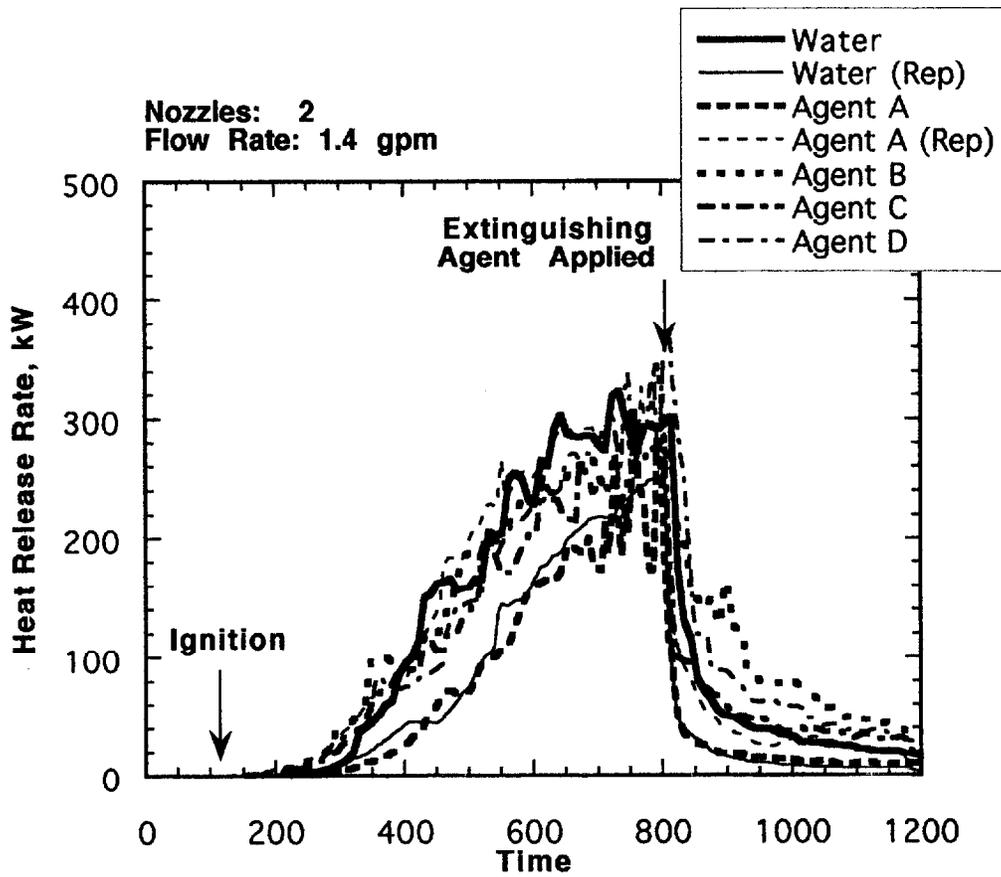


Figure 26. Heat release rate with two nozzles at 5.4 Lpm (1.4 gpm).

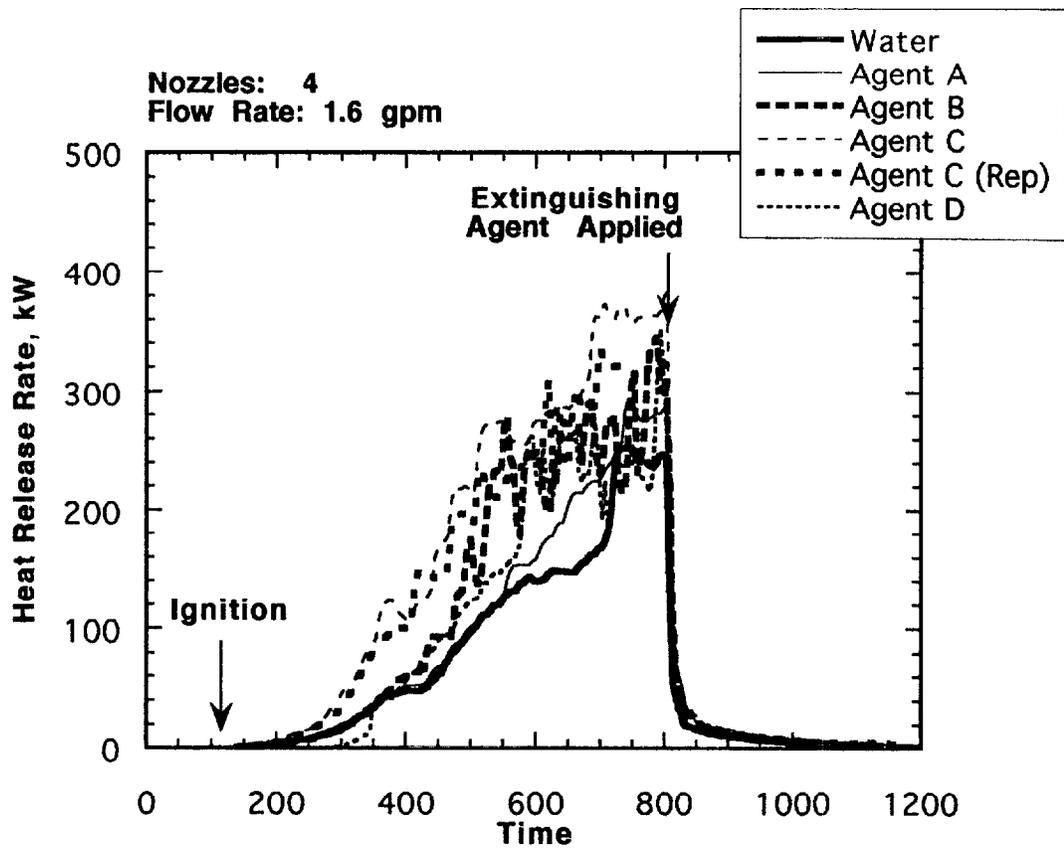


Figure 27. Heat release rate with four nozzles at 6 Lpm (1.6 gpm).