Alternative Agent Combustion Product Formation, Flame Suppression and Flammability Characteristics

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Abstract

Flame suppression was measured with a tubular burner (RHR - 50-100 kW at a low Froude number) where the fuel and agent were mixed before they reached the burner outlet. The quantity of agent was increased until flame/extinction occurred. The ratio of the agent quantity to fuel quantity at extinction, the REMP-value (Required Extinguishing Media Portion) is used as a quantitative measure of efficiency of the agent.

In addition, a hood collected all the fire gases. In the exhaust duct from the hood the rate of heat release (using oxygen consumption calorimetry), temperature and concentration of toxic gases were measured on line. Emissions also were collected by grab samples from the duct and analyzed using wet chemistry methods and ion chromatography to determine the total ion concentration formed.

Some replacement agents usually considered as nonflammable actually increased the rate of heat release (acted as if they were a part of the fuel). The CO/CO_2 ratio and the measured ion concentration indicate the efficiency of the agent as a suppressant and of the toxicity of the gases.

The flammability limits of mixtures of propane and agent with air were determined in two explosion chambers, a sphere (vol. = 13 dm^3) and a cube (vol. = 8 dm^3). A spark of 1 - 150 Joule was produced across a 4 mm electrode gap. Measurements of explosive overpressure in the sphere and the cube and video recordings of the flame kernel growth in the cube were used as combustion criteria.

The motion of the flame kernel when the limit of flammability is approached is complex due to induced convection currents. After the limit of flammability has been passed, convection currents feed unburned gases to the residuum of the spark plasma in an additional heat release related to the size of the ignition source. Hence, flammability criteria should not be derived only from fixed overpressure (psi) in an explosion chamber, particularly for some replacement agents usually considered non-flammable.

Introduction

Studies of fire extinction have received more attention from the research community recently as a consequence of the involvement of halons in the depletion of the stratospheric ozone layer [1-4]. Although numerous chemical suppressants have been used for more than half a century, the mechanisms by which they inhibit combustion are not yet understood [1-8], i.e. fundamental criteria for the extinction of diffusion flames and premixed flames have not yet been established. In order to establish such criteria, attention has to be paid to gas-phase flames, aspects of turbulence, penetration of suppressants to gas-phase flames, etc.

The extinction models that have been presented range from more detailed theories for simplified burner configurations [9] to empirical relationships for diffusion flames and premixed flames which correlate and predict the fire-suppression effectiveness of a wide variety of gaseous, liquid and solid agents [1-4]. The empirical models, based either wholly on heat-absorption processes [2,3] or on a combination of heat-absorption processes and a chemical suppression factor [1,4], provide a criterion for extinction which can be expressed in terms of a critical adiabatic flame temperature chosen to fit the experiments. More recently a model which combines an energy-based approach with chemical-kinetic considerations has been published [10].

Many papers have been published on measurements of extinction limits. Considerably less research has been devoted to near-limit phenomena and to the mechanism of non-stationary flame extinction. A better understanding of the physical action of suppression is needed in the search for alternatives to halons.

In order to collect more data on extinguishment phenomena and agent performance more than 100 tests have been conducted using a tubular burner where the fuel and agent are mixed before they reach the burner outlet and explosion bombs.

Tubular Burner Tests

Introduction

The most common methodology for measuring the efficiency of different fire extinguishing agents against diffusion flames is to use a laboratory cup burner [11-16]. However, the results from a cup burner test depend on a lot of variables, i.e. fuel level, burner size, chimney size, temperature, air flow, operator. Even minor differences in equipment and technique can change cup burner values as much as 50% [11,16]. When comparing burner cup data with a developed fire scenario one has to consider differences between laminar and turbulent conditions in flames as well as differences in heat balance. For non-charring PMMA, for example, extinction was found at about 6% of Halon 1301 with FMRC 50 kW Scale Apparatus [17] contrary to a value of about 2.5% with NIST PMMA Burner [15].

Test Method

One limitation in most of the tests referred to above is that they have been performed in small scale and the results in most cases are difficult to translate to "real" fire situations. The introduction of the gas burner test was hoped to overcome these problems as the scale easily could be increased and quantitative results could be achieved. The method was originally developed by NBS for studying water spray extinction on large jet flames [18]. The method has been developed to a NORD-TEST Method NTFIRE 044 [19-23].

Testing is carried out using a tubular burner, where the propane gas and the extinguishing media are mixed prior to reaching the burner outlet, as seen in Figure 1. The agent is fed into the gas flow and the feeding rate ($\dot{m}e$) is determined by placing the entire pressure vessel with agent on a weighing device. The propane gas flow ($\dot{m}g$) is measured and controlled using a gas flow meter. The quantity of agent is increased until flame extinction occurs. The specific amount of extinguishing media requirement (Required Extinguishing Media Portion, REMP, the ratio of the agent quantity to fuel quantity consumed) is given as a quantitative measure of efficiency of the agent. Therefore $REMP = \dot{m}e/\dot{m}g$ where $\dot{m}e$ is the mass flow of the extinguishing agent and $\dot{m}g$ is the flow of the gaseous fuel. The lower the REMP value, the more efficient the agent. An important aspect is that the burner operates at a low Froude number, i.e. where gravity forces dominate the flame behavior.

Test results

Examples of various REMP values at low Froude numbers are given in Table 1. In Figure 2 the measured rate of heat release (RHR) is shown for Halon 1301 and two replacement candidates, 2320 and 2400. Three different RHR behaviors were observed dependent on halogen and hydrogen content of the agent.

- Halon 1301 reduces the RHR when a small amount is added and is then almost constant until extinction occurs.
- Halon 2320 gives the same characteristics as an inert gas i.e. the RHR is not affected until extinction occurs.
- Halon 2400 increases the RHR with increasing amounts of agent added until extinction occurs.

Some of these characteristics can be observed visually by the burner cup but not quantified. The result shows that some agents that normally are classified as non-flammable can together with the fuel become flammable under certain circumstances.

Reference tests carried out with the gas burner using twelve different types of power [22] show that the repeatability and reproducibility have in the majority of cases been better than ± 5% as shown in Figure 3 and Table 3. A similar repeatability was obtained with Halon 1301 and replacement candidates in these experiments. This must be seen as very satisfactory and similar values are impossible to achieve with conventional methods i.e. manual extinguishing tests with fire extinguishers.

In addition, tests indicate that the REMP value is independent of the RHR (between 50-500 kW) at low Froude numbers (≤ 100) [19] and that in general there seems to be a reasonably good correlation between gas burner tests and full scale testing [22].

Thermal Decomposition Product Testing

Samples for thermal decomposition analysis were collected (by grab sampling in the exhaust duct where the gases are well mixed) in two polypropylene gas washing bottles mounted in a sequence. The washing bottles were filled with 20 ml of sodium carbonate/sodium bicarbonate solution. The second bottle was used to check that all of the halides were recovered. The halides were determined by ionchromatography (IC).

The experimentally measured concentrations of Floride and Bromide ions produced from Halon 1301 and a blend used for the experiment (nitrogen + mixture of three replacement candidates) are summarized in Table 3. The concentration, μg per liter of gas, has been multiplied by the volume flow (at NTP) in the duct and normalized against the mass flow of propane and agent, respectively.

The results clearly indicate that the generation of fluorinated decomposition products is higher for most of the replacement candidates in agreement with references [24-28]. Since the generation of decomposition products is a function of the extinction time, it is important that systems with replacement candidates are optimized for the new agent.

Some favorable properties of the new agents have also been observed, i.e. a lower generation of carbon monoxide, Figure 3, and a much lower formation of soot.

Large scale tests utilizing an existing Halon 1301 system and equipment were conducted. The results verified that it is (at least with some systems) possible to bring extinguishing time down to "acceptable" levels. However, an increasing rapidity of function time requires also that engineering of an existing system has to be modified in order to be on the "safe" side in using new agents. Therefore, it is of major importance that the required amount of agent be sufficient to build a safe concentration in a variety of fire scenarios i.e. that the amount of agent needed can vary from a level of flame extinction to that of inertion.

Bomb Experiments

Introduction

Inertation tests and applications have one common objective: to prevent the ignition of a combustible gas mixture through the addition of a suppressing agent. Theories of ignition and flame propagation which include heat-transfer and diffusion processes lead to conservation equations which can in principle be solved to give a burning velocity if physical and chemical data are known. These equations do not, however, explain discontinuous phenomena such as limits of flammability. Since inertation capability cannot be predicted with certainty, one has recourse to experiments in which one aims at determining the limits in an apparatus-independent manner.

Test of inertation capability and limits of flammability are usually performed in burettes and bombs. From the results the minimum safe percentage of agent in an agent-air mixture at room temperature and atmospheric pressure can be derived in which all proportions of fuel and air are non-flammable. This limit usually occurs close to a stoichiometric proportions of fuel in air. The limit determined, however, depends on several parameters such as:

- The geometry of the enclosure
- The ignition source
- The combustion criteria used to indicate the occurrence of flammability

As shown in [Ref. 29-34] there is a considerable scatter in the experimental values of inertation concentrations. With Halon 1301, for example, [Ref. 29] the limit varies from 4 vol % (explosion burette, FMRC 1974, AC foil) to 40 vol % (DuPont 1972, 965 ml Bomb, AC spark 1300 /sec).

The present experiments have been carried out to determine the influence of the spark energy and combustion criteria on the inertation limit of different agents in three different enclosures; an 8 *l* cube, a 13 *l* sphere and a 784 *l* room (1/3 scale of the ASTM Room - Corner Test).

Test Method

The 8 *l* cube.

The 8 *l* (vacuum tight) cube (0.2 x 0.2 x 0.2 m) has circular Plexiglas windows (0.1 m in diameter) cut on two sides of the box. A 0.1m circular opening is cut out in the top of the box and covered with a pressure relief valve which opens at an overpressure of 0.5 atm. Three pair of electrodes are placed in the box, one at the lower level, a second in the geometric center, and a third at an upper level. The fuel (propane), agent and air are introduced in the cube by the standard partial pressure technique method of filling. After the gases are introduced into the box, the gases are mixed with a fan for 10 minutes. A spark of 0.7 - 150 Joule (1/2 C.V.^{2}) is produced across a 4 mm steel electrode gap. The spark is generated by charging capacitors (0.012, 0.5 and 2μF) with high voltage (10-15 kV). Once the capacitors are charged to the breakdown voltage in the gap they discharge automatically. Explosive overpressure is measured with a piezocapacitive transducer (sensitivity 1V/atm) and recorded on a storage oscilloscope. Video provides the visual records of the explosive event.

13 *l* sphere

One pair of steel electrodes is mounted in the geometric center. The fuel (propane) and agent are introduced in the evacuated sphere by the standard partial pressure technique method of filling. The air compressed to 10-20 atm in a 0.7 *l* cylinder is then introduced (a fast opening magnetic valve) through a series of mesh-covered orifices in order to get a very intense turbulent mixing. (The equipment has earlier been used to study dust explosions.) An attempt to ignite the mixture is made using a similar spark (4 mm) set and pressure recordings as described above.

784 *l* room

A 1/3 scale of the ASTM Room Corner Test is used. The door opening had been sealed hermetically with a Plexiglas slab and rubber sealant. The fuel (propane) and agent were mixed by weight (1 g accuracy) in a pressure vessel and homogenized by rotating the cylinder horizontally for 12 hours. A calculated mass of the dense fuel-agent mixture (measured by weight) is introduced in the lower part of the room at a slow rate and the excess air is ventilated out at the top of the room. After the fuel-agent mixture has been introduced, the gases are mixed with a fan placed on the floor of the room. The oxygen concentration in the room is then analyzed with a paramagnetic oxygen analyzer (Siemens oxymat). By adding more fuel-agent mixture or air and mix with the fan the mixture composition can be set to a predetermined value. An attempt to ignite the mixture is made using a similar spark (4 mm) set mounted in the center of the room 15 cm above the floor and pressure recordings as described above. Video tape provides the visual record of the explosive event.

Test Results

Examples of maximum pressure increase are given in Table 4 (Halon 1301) and Table 5 (Halon 2400). In Figure 5-6 examples of a pressure and a video record are shown for Halon 1301 and 2400, respectively. The uncertainty in the timing between the pressure and video record is estimated to be less than 10 msec. In Figure 7A a full sequence of a video record is shown for a mixture of 15.5 vol% Halon 2400 in a stoichiometric propane-air mixture which gave rise to a maximum pressure increase of 0.02 atm (0.3 psi). In Figure 7B sputtering from the electrodes is shown.

Discussion

The measured inerting concentration depends on the choice of the combustion criteria which is used to indicate the occurrence of flammability. If a maximum pressure increase of 0.068 atm (1 psi) is chosen as a criteria the following inerting concentrations are obtained from the data given in Table 4 and 5;

Halon 1301	sphere, 56 Joule	7.1-7.2 vol%
	cube, 0.7 Joule	6.0-6.5 vol%
	cube, 36 Joule	6.5 vol%
	cube, 144 Joule	8.0 vol%
	1/3 room, 144 Joule	< 7 vol%
Halon 2400	cube, 0.7 Joule	12.5-13.0 vol%
	cube, 30 Joule	15.0-15.5 vol%
	cube, 144 Joule	15.0-16.0 vol%

The inerting concentrations are given as vol% agent in a mixture of agent, air and fuel. Given on a fuel free basis one has to multiply the given values by 1.04. The measured inerting concentrations are in reasonable agreement with values given in Ref. 29; 6.2-7 vol% for Halon 1301 in propane-air mixtures, for experiments in bombs (5.6 - 7.9 *l* spark ignition and 1 psi criteria).

As shown above the inerting concentration increases with increasing spark energy, about 20-30% when the spark energy is increased from 0.7 to 144 Joule, in the 8 *l* bomb if 1 psi is used as a combustion criteria. In addition, the concentration range which will give only a small pressure increase (below 0.3 atm, or 5 psi) in small bombs will be extended with increasing spark energy.

In the 1/3 room scale tests (144 Joule), however, no pressure increase was recorded at an inerting concentration of 7 vol% even though a pressure increase above 0.3 atm was registered in the 8 *l* cube (144 Joule) with 7.0 and 7.5 vol% Halon 1301.

Video records give information of the flame area as a function of time, i.e. the burned volume. As shown in Figures 5-7 the flame shape is dominated by natural convection. It is known that the laminar burning velocity close to the extinction limit is small compared to connective currents and that the limits of flammability depend on the gravity force [33]. Two different kinds of flame shapes are observed:

- The flame expands rapidly both in the vertical and horizontal direction as in Figure 5.
- The flame expands more or less only in the vertical direction. The expansion in the horizontal direction depends mainly on the entrainment of air in the upward moving vertex ring (natural convection) as shown in Figure 6.

The question seems to be where the flame is quenched. In a small bomb the flame is quenched when it reaches the top of the bomb, if the spark energy is high enough as shown in Figure 6. In the 1/3 room test the flame is quenched by entrainment of cold gas mixtures (natural convection) at a distance approximately 0.2 m above the ignition source. Thus the use of a large ignition energy may heat and burn out a gas volume which will give a pressure increase above 0.068 atm (1 psi) in a small bomb but no measurable increase in a room scenario. An initial temperature increase of 250°C corresponds approximately to a 20% widening of the flammability limits.

The video recordings indicate that the burned gas volume is not repeatable for mixtures close to the inerting limit, as shown in Figure 7, due to the stochastic nature of the process which precedes the flame expansion, i.e. the spark chanel (0-1μs region), hydrodynamic puff (1μs - 10μs) and flame kernel (10μs - ms) development [35-36]. Other comments are that the burned volume varies with agent and that the spark power as a function of time is more important for the ignition process than the total energy stored in a capacitor [35].

Conclusions

Tubular burner tests provide

- A quantitative measure, the REMP value, of the extinction capacity for various agents.
- A quantitative measure of the generation of toxic products during various stages of the extinction process.
- In general, a reasonably good correlation for streaming agents with full scale testing. However, more experiments are needed.
- Excellent repeatability and reproducibility of the REMP-value, ± 5%.

Bomb Experiments

The combination of a relatively high spark energy in combination with small bomb volumes and a 1 psi combustion does

- overestimate the inerting concentration needed for room protection
- does not satisfy the demand for repeatability and reproducibility

Video recordings combined with pressure recordings in larger volumes (>0.5m^3) can provide better information on how to choose a combustion criteria and a spark energy level in smaller bombs. More large scale experiments are needed.

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Table 1 FIRE SUPPRESSION AGENT COMPARISON REMP VALUES FOR SOME TESTED AGENTS

AGENT	REMP $\dot{m}_e / \dot{m}_g$	SUITABLE APPLICATION
HALON 1301	4 - 5	FLOODING
HALON 1211	4 - 5	STREAMING, LOCAL APPL.
HALOTRON 1	6 - 7	STREAMING, LOCAL APPL.
HALON 2410	9 - 10	STREAMING,LOCAL APPL.
HALON 2400	13 - 15	FLOODING
PFC - 614	12 - 13	STREAMING

REMP = Required Extinguishing Media Portion

$\dot{m}_e$ = Mass flow rate of extinguishant

$\dot{m}_g$ = Mass flow rate of gas (fuel)

Table 2 The influence by the operator and ventilation on the REMP-value is within the method's repeatability

Powder no	1	1	5	5	1	1
	Operator 1	Operator 2	Operator 1	Operator 2	Low ventilation	High ventilation
REMP-value	2.89	2.66	2.83	2.78	2.74	2.64
Deviation % 1)	+ 7.0	- 1.5	+ 5.6	+ 3.7	+ 1.5	- 2.2
REMP-value min - max	2.72 -3.22	2.48 - 2.80	2.81 - 2.85	2.72 - 2.83	2.69 - 2.85	2.59 - 2.67
Deviation ±%	- 5.9 +11.4	-6.7 +5.3	-0.7 +0.7	-2.2 +1.8	-1.8 + 4.0	-1.9 +1.1
No of tests	3	3	2	2	3	3

1) Refers to the deviation from the mean REMP-value presented in figure 3 conducted by operator 1.
2) The tests conducted by operator 1.

1) Repeatability refers here to the possibility of achieving the same REMP-value during identical conditions, i.e. with the same operator and equipment during one and the same occasion. Reproducibility refers in this report to the possibility of achieving the same REMP-value during modified conditions, i.e. with different operators and ventilation conditions on different occasions. In order to provide a final measure of reproducibility the effect of different test equipment and tests at different laboratories should also be taken into account.

Table 3

Normalized generation of F$^-$, Br$^-$ and CO at different REMP-values for Halon 1301 and a test Blend.

Halon 1301

REMP	0.79	1.25	1.43	1.5	2.2
$\dot{F}$-/$\dot{m}$g	0.02	0.09	0.07	0.1	0.14
$\dot{F}$-/$\dot{m}$e	0.03	0.07	0.05	0.07	0.06
$\dot{B}$r-/$\dot{m}$g	0.02	0.06	0.06	0.06	0.07
$\dot{B}$r-/$\dot{m}$e	0.03	0.05	0.04	0.04	0.03
$\dot{C}$O/$\dot{m}$g	0.15	0.16	0.18	0.19	0.22
$\dot{C}$O/$\dot{m}$e	0.19	0.13	0.13	0.13	0.1

Blend

REMP	3.8	5.4	5.6	6.3	8.9
$\dot{F}$-/$\dot{m}$g	0.21	0.8	0.8	1.1	1.5
$\dot{F}$-/$\dot{m}$e	0.06	0.15	0.14	0.17	0.17
$\dot{C}$O/$\dot{m}$g	0.01	0.03	0.06	0.09	0.35
$\dot{C}$O/$\dot{m}$e	0.003	0.006	0.011	0.014	0.039

TABLE 4. HALON 1301

BOMB TYPE	**SPARK ENERGY** JOULE	**VOL.% AGENT** IN AGENT + AIR + PROPANE	**VOL.% PROPANE** IN PROPANE + AIR + AGENT	**PRESSURE INCREASE** ATM.
SPHERE	56	8,0	4,0	0
SPHERE	56	7,3	4,0	0
SPHERE	56	7,1	4,0	>0,5
SPHERE	56	6,3	4,0	>0,5
CUBE	0,7	7,5	3,9	0
CUBE	0,7	7,1	3,9	0
CUBE	0,7	6,5	3,9	0,01
CUBE	0,7	6,0	3,9	>0,5
CUBE	36	8,1	3,5	0
CUBE	36	8,0	3,9	0
CUBE	36	7,1	3,9	0,056
CUBE	36	6,5	3,9	0,056
CUBE	144	8,0	3,9	0,064
CUBE	144	8,0	4,2	0,16
CUBE	144	7,5	3,9	>0,5
CUBE	144	7,0	3,9	>0,5
ASTM 1/3 SCALE	144	7,0	3,7	0

TABLE 5 . HALON 2400

BOMB TYPE	**SPARK ENERGY** JOULE	**VOLUME % AGENT** IN AGENT + AIR + PROPANE	**VOLUME % PROPANE** IN PROPANE + AIR + AGENT	**PRESSURE INCREASE** ATM.
CUBE	0,7	14	3,6	0
CUBE	0,7	13	3,65	0
CUBE	0,7	12,5	3,7	0,3
CUBE	0,7	12	3,7	>0,5
CUBE	30	16	3,5	0,02
CUBE	30	15,5	3,5	0,02
CUBE	30	15	3,6	0,144
CUBE	30	14	3,6	0,15
CUBE	30	13	3,65	0,13
CUBE	30	12,5	3,7	>0,5
CUBE	144	16	3,5	0
CUBE	144	15	3,65	0,072
CUBE	144	14	3,6	0,14

FIRE SUPPRESSION AGENT TEST METHOD AT THE UNIVERSITY OF LUND

Figure 1 Experimental setup.

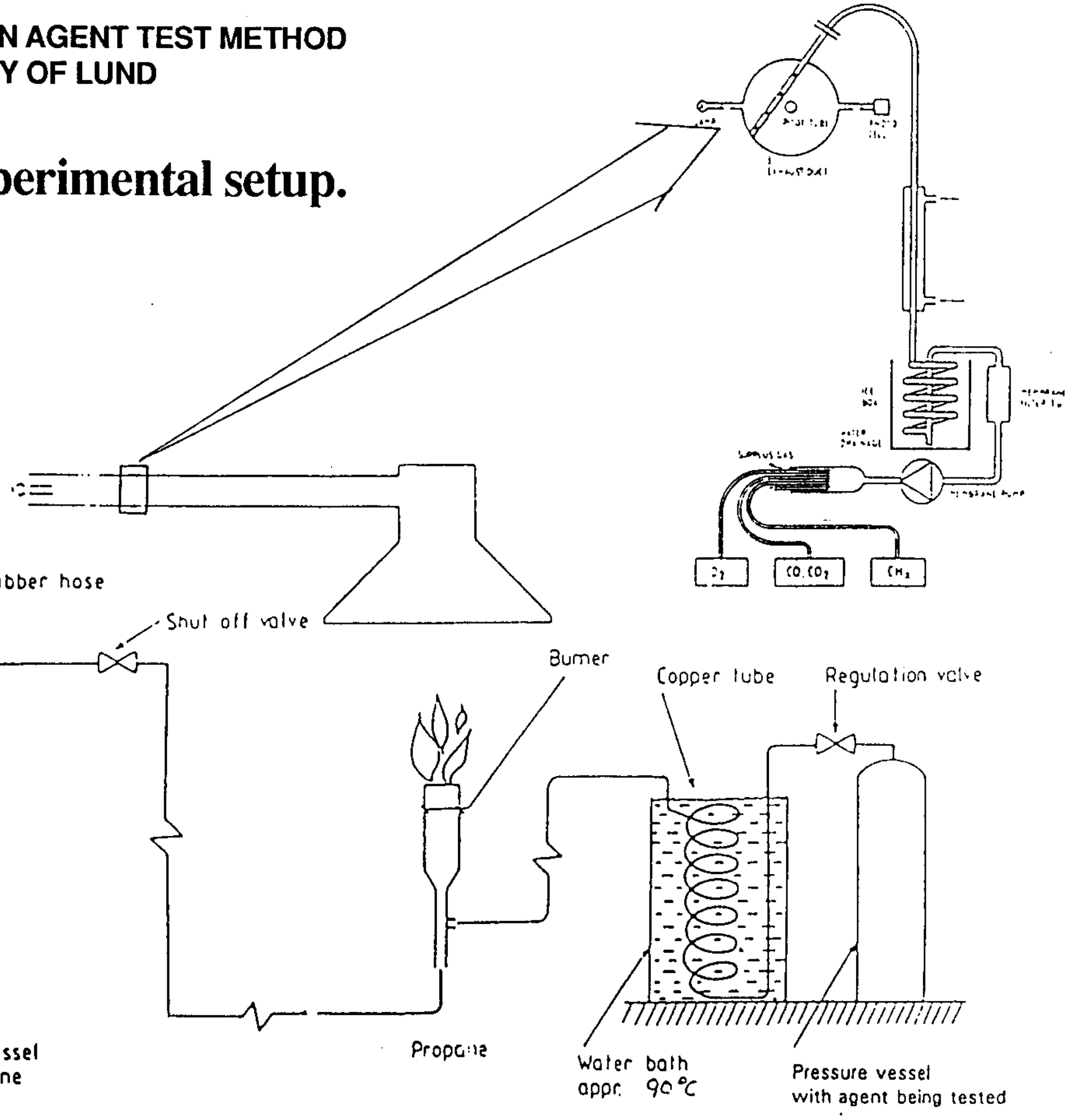
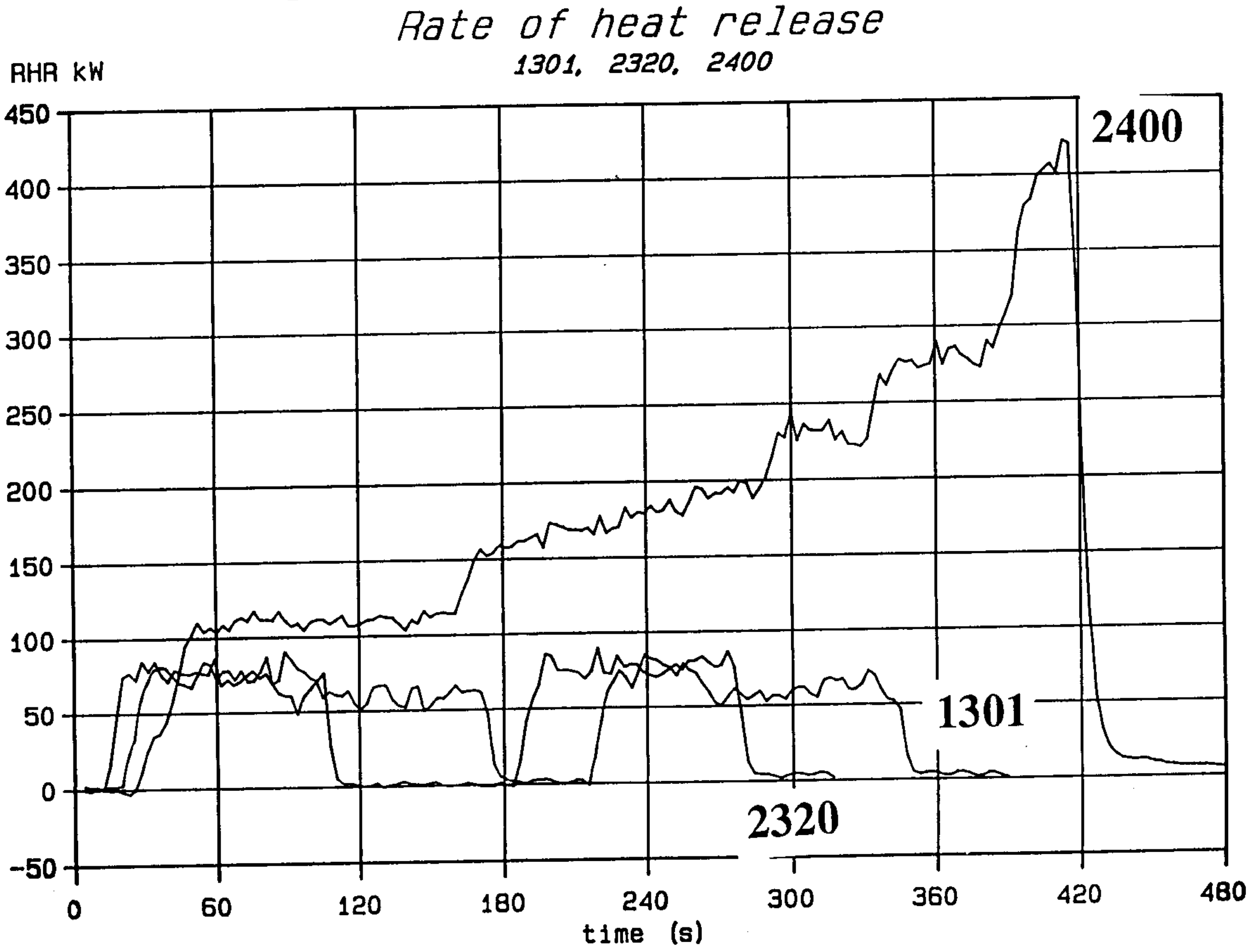


Figure 2 Rate of Heat Release (RHR),



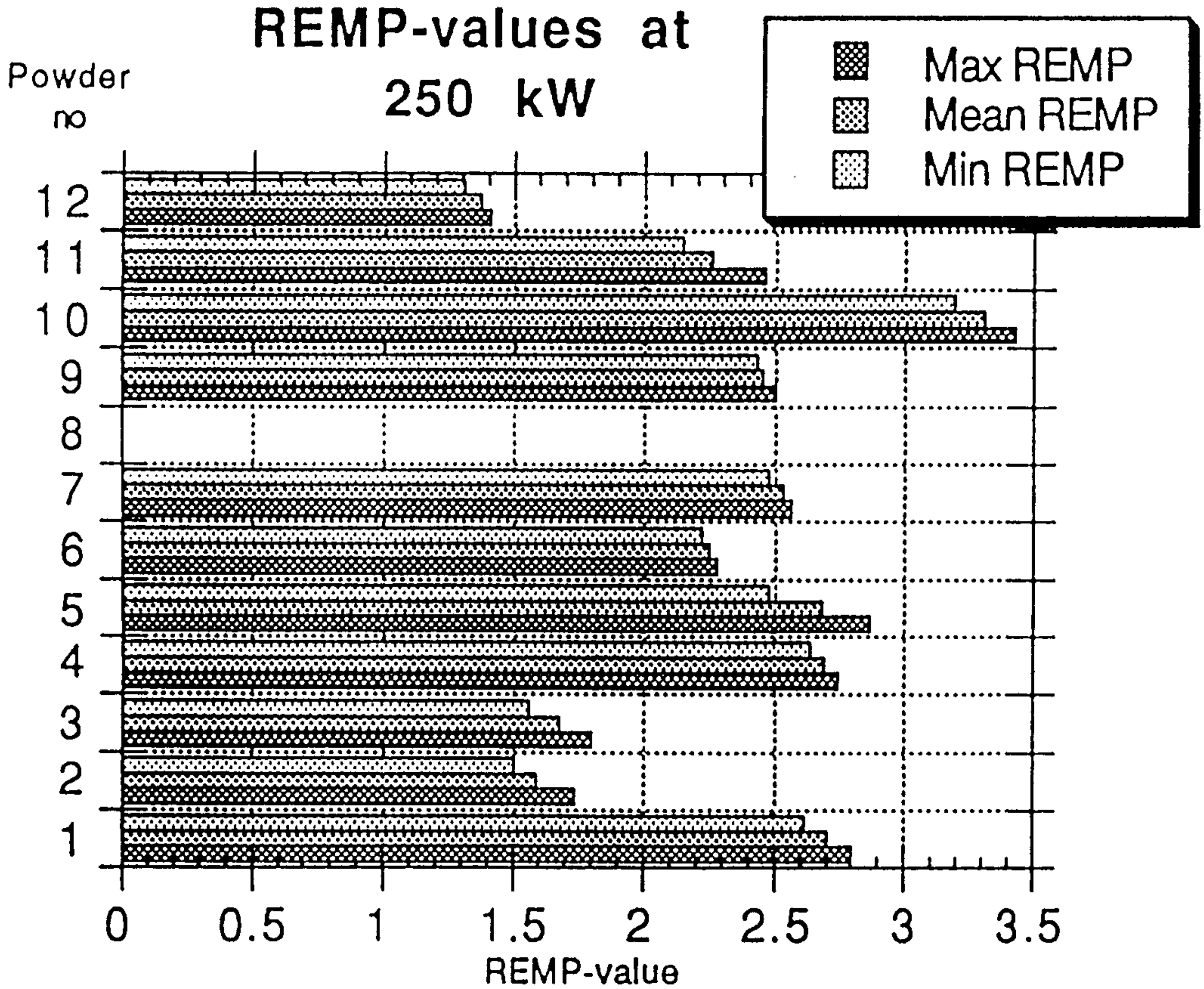


Figure 3

The REMP-value measured at 250 kW (11 different powders) with the gas burner test. The results provide a repeatability of 5.10%.

Figure 4

Generation of Carbon monoxide (CO) at different REMP-values for Halon 1301 and a test blend.

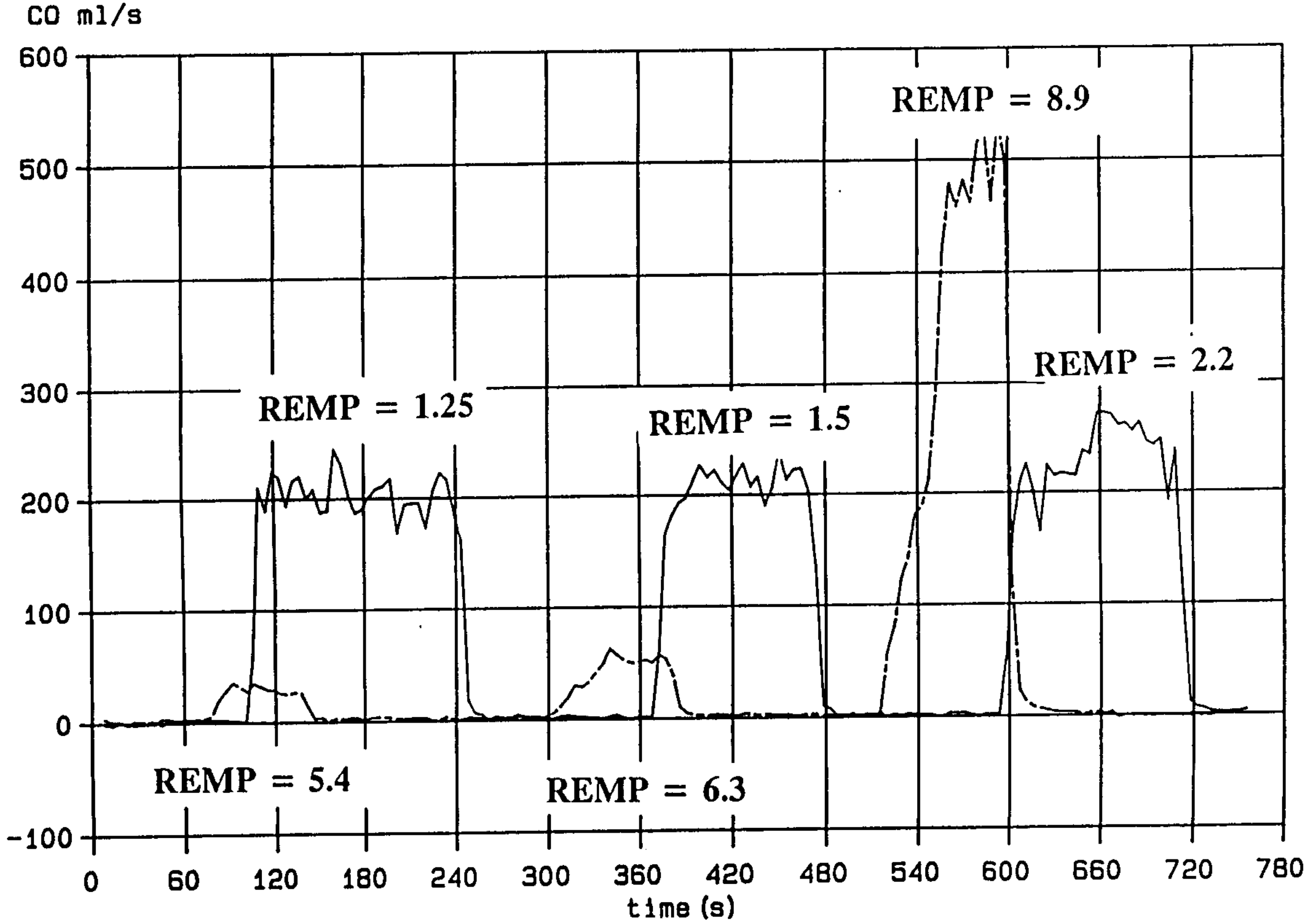


FIGURE 5 PRESSURE AND VIDEO RECORDINGS,
HALON 1301, .7 JOULE, 6 VOL% AGENT, 3.0% PROPANE

TIME AFTER IGNITION 40MS 120MS 200MS 280MS

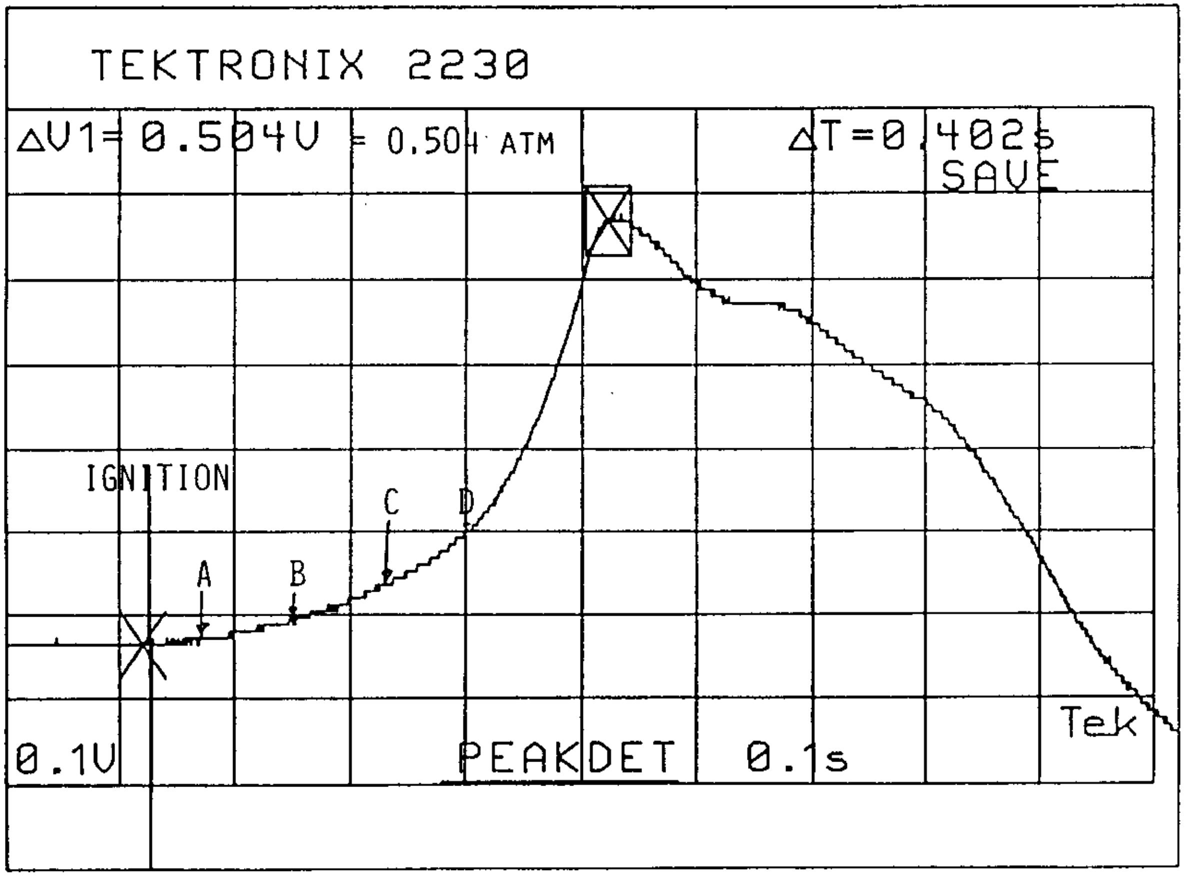
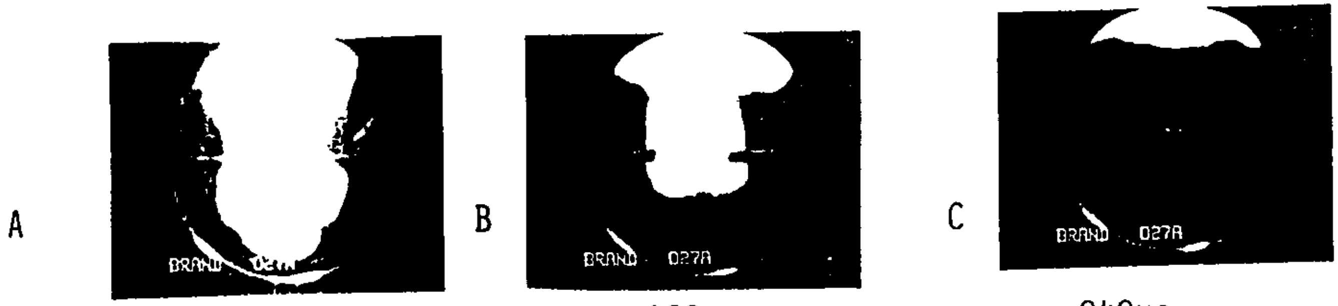


FIGURE 6 PRESSURE AND VIDEO RECORDINGS.
HALON 1301 ,144 JOULE, 7 VOL% AGENT 3.9 VOL% PROPANE



TIME AFTER IGNITION 80MS 160MS 240MS

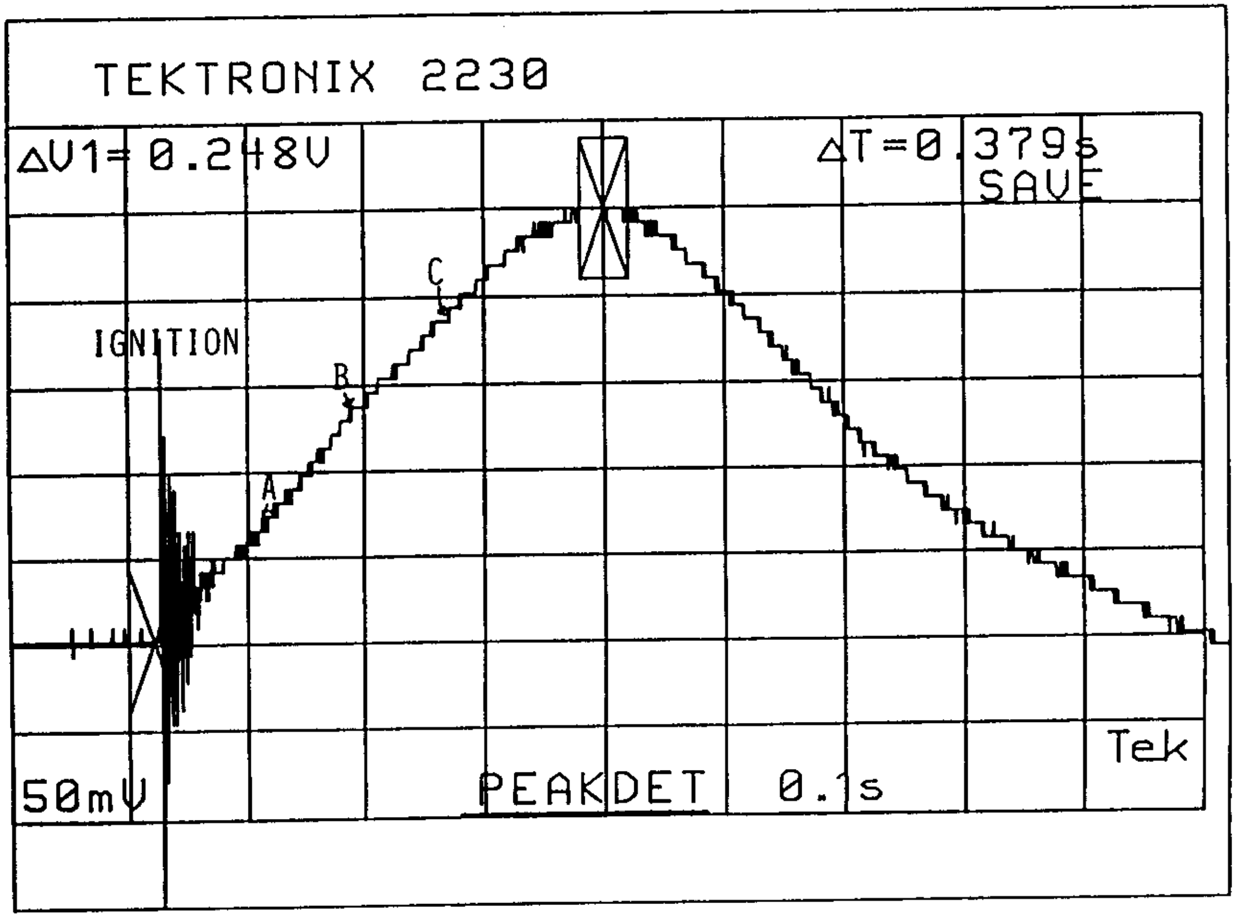
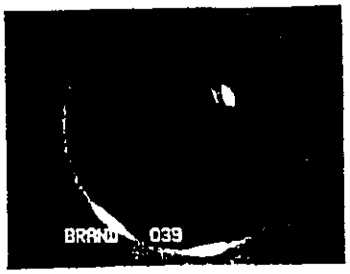


FIGURE 7
VIDEO RECORDINGS

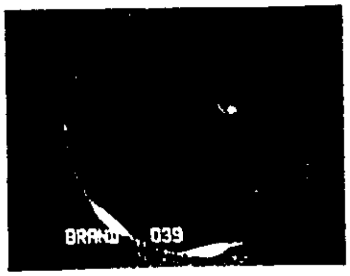
A: 2400 , 30 JOULE
15.5 VOL% AGENT
3.5 VOL% PROPANE

A

240MS

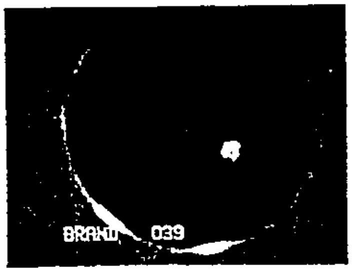


200MS

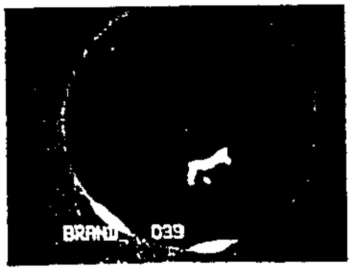


160MS

120MS



80MS



40MS

B: 42 JOULE
SPUTTERING FROM
ELECTRODES

B 40MS