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*A LABORATORY INVESTIGATION OF
AEROSOL AND EXTINCTION CHARACTERISTICS FOR SALTY DOG,
NWC 29 AND NWC 78 PYROTECHNICS*

by
J.T. Hanley and E.J. Mack

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Calspan is conducting a limited investigation of the efficiency of hygroscopic aerosols in restricting visibility at subsaturated humidity. The artificial fogs are produced by "SALTY DOG" and phosphorus pentoxide smoke in Calspan's 590 cubic meter chamber at controlled relative humidities of from 30 to 97 percent. Extinction at both visible and IR wavelengths, aerosol size spectra and pyrotechnic mass yield are compared as functions of humidity. Additionally, results of microscopically measured individual		

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particle growth as a function of humidity and numerical estimates of down-wind visibility reduction resulting from the burning of the Salty Dog pyrotechnic are presented.

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Section 1
INTRODUCTION AND SUMMARY

Under Contract No. N00019-80-C-0197 from the Naval Air Systems Command (AIR-310C), Calspan Corporation continued its experimental investigation of the feasibility of producing stable, optical-obscurant screens (smokes and fogs) with hygroscopic aerosols under conditions of subsaturated relative humidity. The objectives of this year's investigation were to (1) evaluate the physical, optical, and chemical properties of two new versions of the standard Salty Dog pyrotechnic, NWC 29 and NWC 78, as a function of humidity, (2) conduct a microscopic study of the growth characteristics of individual aerosol particles as a function of humidity, and (3) in support of planned NRL field trials of Salty Dog, provide estimates of the required pyrotechnic burn rate and upwind burn distance to achieve a desired visibility for prescribed meteorological conditions.

The laboratory investigation was carried out in Calspan's 590 m³ chamber. The facility's large size minimizes wall effects, provides relatively long path lengths for extinction measurements, and provides for a useful aerosol lifetime of many hours. A complete air handling capability permits the removal of virtually all particulate and gaseous contaminants prior to each experiment, the introduction of specified aerosols, and control of humidity from ~30 to 97% RH.

For comparison with the previous year's studies which focused on Salty Dog, a combined total of 36 chamber tests were conducted with the NWC 29 and 78 pyrotechnics over a humidity range of 33% to 97% RH. Additionally, one test each of Salty Dog and white phosphorus was made for comparison of resulting IR extinction spectra with those for NWC 29 and 78. The extinction measurements indicated that neither NWC 29 nor 78 produces greater extinction than Salty Dog and that NWC 78 may be slightly less effective due to its lower dry-yield factor. IR extinction spectra from ~2-12 μ m wavelength showed definite structure for all three screens which is presently attributed to absorption by liquid water deposited on the deliquescent aerosol.

Results from the laboratory investigation of individual particle growth indicate that the aerosol generated by NWC 78 has the most favorable growth characteristics of the three pyrotechnics. The NWC 78 specimens became completely dissolved at a RH of 70% as compared to 78% for NWC 29 and 81% for the Salty Dog.

Estimates of the required pyrotechnic burn rate and upwind burn distance for planned NRL field trials were made for the following conditions: 85% RH, 7 m/s wind speed, 32 km (20 mi) background visibility, and a desired visibility of 12.8 km (8 mi) measured over a 4 km path. The results indicate that, for a point-source, a minimum burn rate of ~ 1000 lb/hr and upwind burn distance of 11 km are required to achieve the desired 12.8 km (8 mi) visibility. These burn conditions are for a plume width which results in a $\geq 5\%$ reduction in background visibility at all points along the 4 km transmissometer path. For lesser plume widths, lower burn rates and upwind distances are possible.

All of the above topics are discussed in greater detail within the body of this report. Section 2 describes the chamber facility, instrumentation, and results of the chamber tests. Results of the laboratory growth measurement of microscopic particles and discussion of the apparatus are presented in Section 3. Section 4 contains the theory and results of dispersion computations related to the Salty Dog field trials. Section 5 presents specific conclusions and recommendations resulting from this study.

Section 2

RESULTS OF LARGE-SCALE LABORATORY EXPERIMENTS

2.1 Facilities, Procedures and Log of Experiments

Facilities and Instrumentation

The laboratory investigation was carried out in Calspan's 590 m³ chamber. The facility's large size (~9 m diameter by ~9 m high) minimized wall effects, allowed relatively long path lengths for extinction measurements, and provided for a useful aerosol lifetime of many hours. A complete air handling capability permitted the removal of virtually all particulate and gaseous contaminants prior to each experiment, the introduction of specified aerosols, and control of humidity from ~30 to 97% RH. A cut-away view of the chamber facility is presented in Figure 1.

In the chamber experiments, an isokinetic sampling inlet was employed for minimizing aerosol losses during sampling. Instrumentation used to monitor aerosol behavior within the chamber included visible and IR wavelength transmissometers, a Thermo Systems Model 3030 Electrical Aerosol Analyzer (EAA), an MRI Integrating Nephelometer, a Gardner Associates Small Particle Detector, and a Royco Optical Particle Counter. Specific details of the instrumentation and chamber facility may be found elsewhere (e.g., Mack et al, 1978).

Extinction Measurements

Extinction of electromagnetic radiation by aerosol sizes was measured at visible wavelengths over a folded path of about 18 m. A lens collimated beam from an incandescent bulb powered by a regulated power supply was focused on a photomultiplier after traversing the chamber twice (reflection by a mirror at the opposite chamber wall). The detector photomultiplier was an RCA-4440 which has a peak sensitivity in the range 0.4-0.5 μ m wavelength. The optical transmissometer systems have been used in the chamber for years and display good stability over periods of about 1 hour, with a resolution of about 2-3 percent.

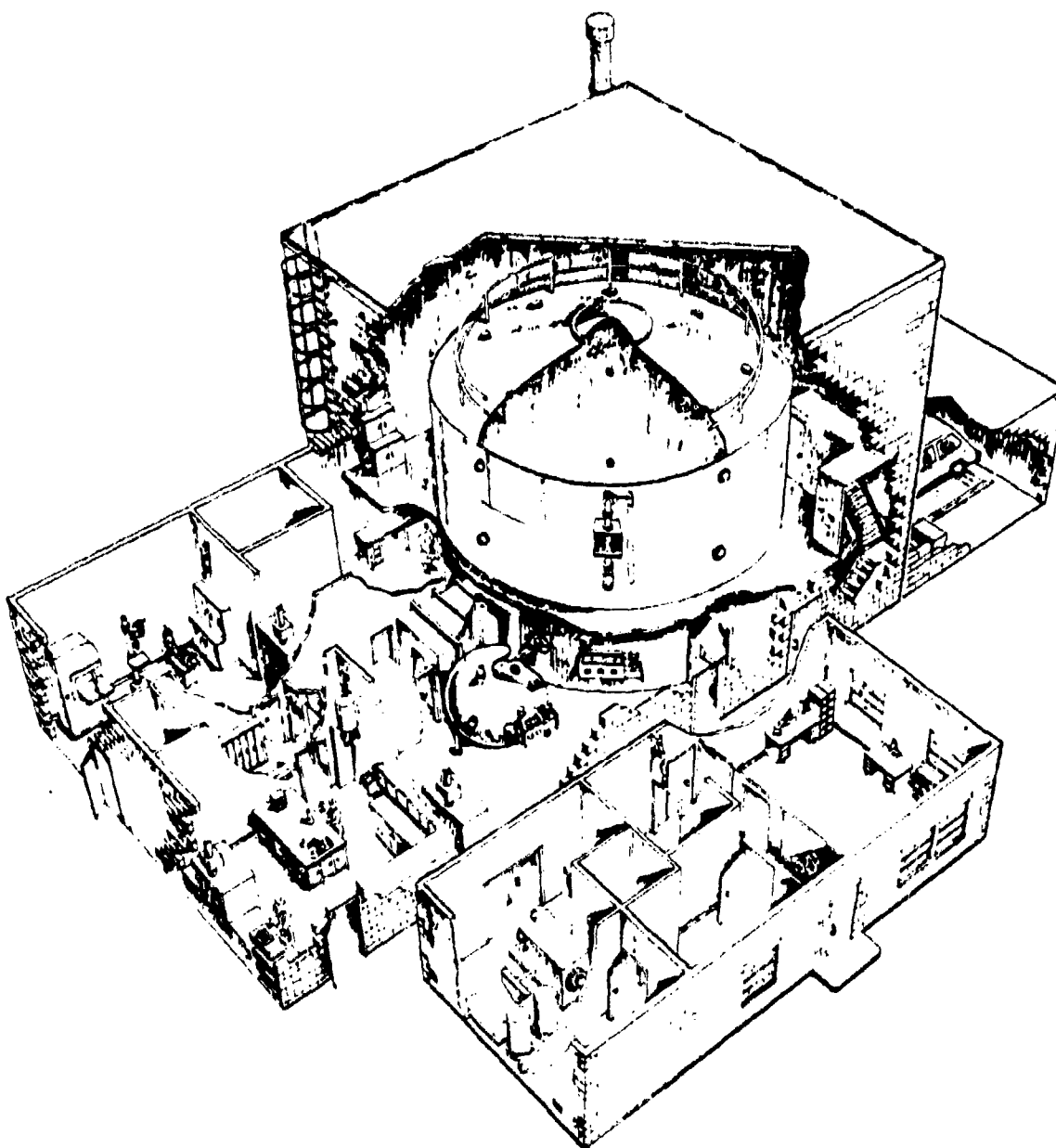


Figure 1. Cut-Away View of Calspan's Chamber facility.

The IR transmissometer utilized an 18.3 m path length, a 900°C black body source, and an HgCdTe detector operated at liquid nitrogen temperature. The chopped, collimated source beam was directed through the chamber and onto the detector by spherical front-silvered mirrors. Continuous measurements of extinction as a function of wavelength were obtained via a pair of variable wavelength filter wheels located in front of the detector. These filters covered the range from approximately 2-12 μm wavelength.

"Unattenuated" light intensities (i.e., I_0) were measured by both the visible and IR transmissometer systems prior to the introduction of aerosols into the chamber. Estimates of extinction were then obtained from the optical transmission data using the well-known Bouguer law:

$$I = I_0 e^{-\beta x}$$

where I_0 is the intensity of the incident light, I is the observed light intensity at some distance x through the aerosol medium, and β is the composite extinction coefficient of the aerosol.

Haze and Fog Generation

Production of the pyrotechnic hazes/fogs was generally accomplished as follows: After humidification of the chamber to greater than the desired relative humidity using a commercial nebulizer, all particulates were removed by absolute filters. The filtration process usually resulted in a decrease of relative humidity of about 5%. Subsequently, a specific quantity of the pyrotechnic (Salty Dog) was aerosolized in the chamber. To increase the uniformity of the burns, the pyrotechnic was ignited with a propane torch. Due to the hygroscopic nature of the resulting pyrotechnic smoke, the individual aerosol particles absorbed water until the vapor pressure of the aqueous droplets equalled that of the ambient air, producing a haze whose density at a given relative humidity was dependent upon the quantity of pyrotechnic burned. After allowing several minutes for the cloud to equilibrate, measurements were made of appropriate parameters. Among others, these parameters included the droplet size distribution, mass loading and extinction at both visible and IR wavelengths.

For the Salty Dog smokes, three different payloads were used during the test series to optimize the accuracy of the measurements. A low payload of 0.1 to 0.5 grams was used to provide an optimum chamber particle concentration for the aerosol sizing instrumentation. This payload, however, was not sufficient to provide reliable transmissometer extinction measurements, especially at low humidities. Therefore, a larger payload of 6 grams was employed for visible wavelength transmission measurements. For IR extinction measurements, a larger payload of 50 grams was required.

Log of Experiments

Table 1 presents a log of the chamber experiments performed. For each experiment, the pyrotechnic, payload and RH are presented along with the type of data obtained. These data include both visible and IR extinction measurements, yield measurements obtained from mass loading samples, size spectra measured by the aerosol sizing instruments, and samples collected for analysis by scanning electron microscopy (SEM). In all, 38 experiments were performed over a range of humidity from 33 to 97% RH.

2.2 Chemical Analyses of the Obscurant Aerosols

Low volume filter samples obtained for mass-loading requirements during Experiments 18 (NWC 29) and 34 (NWC 78) were analyzed for elemental composition of the aerosolized pyrotechnic. Analysis for K, Mg, Na, Ca and Li was performed by atomic absorption spectroscopy. Ion chromatography was used to determine Cl content. These results, together with the chemical composition of the bulk pyrotechnic (as provided by Dr. L. Mathews, NWC, China Lake) are presented in Table 2. As can be seen, the majority of the aerosol, by weight, for all the formulations is Cl. The remainder being primarily a mixture of Na and K for NWC 78 and Salty Dog, and Na for NWC 29.

Table 1
LOG OF CHAMBER TESTS

TEST PARAMETERS				DATA OBTAINED				
EXP #	PYROTECHNIC	PAYLOAD (g)	RH (%)	EXTINCTION		MASS YIELD	SIZE SPECTRA	SEM SAMPLE
				VIS	IR			
1	NWC 29	0.1	95				x	
2	NWC 29	0.1	82				x	
3	NWC 29	0.1	71				x	
4	NWC 29	0.5	97	x			x	
5	NWC 29	0.5	88	x			x	
6	NWC 29	0.5	78				x	
7	NWC 29	0.5	77				x	
8	NWC 29	0.5	64				x	
9	NWC 29	0.5	43				x	
10	NWC 29	0.5	33				x	
11	NWC 29	6.0	97	x		x		
12	NWC 29	6.0	93	x		x		
13	NWC 29	6.0	83	x		x		
14	NWC 29	6.0	78	x		x		
15	NWC 29	6.0	77	x		x		
16	NWC 29	6.0	64	x		x		
17	NWC 29	6.0	43	x		x		
18	NWC 29	6.0	33	x		x		x
19	NWC 78	0.5	97	x			x	
20	NWC 78	0.5	93	x			x	
21	NWC 78	0.5	92	x			x	
22	NWC 78	0.5	84	x			x	
23	NWC 78	0.5	76				x	
24	NWC 78	0.5	62				x	
25	NWC 78	0.5	35				x	
26	NWC 78	6.0	97	x		x		
27	NWC 78	6.0	92	x		x		
28	NWC 78	6.0	88	x		x		
29	NWC 78	6.0	84	x		x		
30	NWC 78	6.0	78	x		x		
31	NWC 78	6.0	76	x		x		
32	NWC 78	6.0	62	x		x		
33	NWC 78	6.0	48	x		x		
34	NWC 78	6.0	34	x		x		x
35	Salty Dog	50	92		x	x		
36	NWC 29	50	90		x	x		
37	NWC 78	50	91		x	x		
38	Phosphorus	6.0	93		x	x		

Table 2
CHEMICAL COMPOSITION OF ALKALI HALIDE PYROTECHNICS AND SMOKES (BY WEIGHT)

	STANDARD SALTY DOG	NWC #29	NWC #78
Bulk Pyrotechnic (NWC Analyses)	65% KClO_4 10% NaCl 5% Mg 2% Li_2CO_3 18% Binder	79% NaClO_4 5% Mg 2% LiCl 14% Binder	54% NaClO_4 25% KClO_4 5% Mg 2% LiCl 14% Binder
Measured Aerosol (Elemental) (Calspan Analyses)	51% Cl 33% K 10% Na 6% Mg <1% Li	68% Cl 27% Na 4% Mg <1% Li <1% K	75% Cl 12% Na 9% K 3% Mg <1% Li

2.3 Extinction Yield

Visible Wavelengths

The effectiveness of NWC 29 and 78 to produce visible wavelength extinction was measured with the chamber's transmissometer. Measurements were obtained in all 6 g and high humidity 0.5 g payload tests. For comparison to the extinction produced by Salty Dog, the data obtained from NWC 29 and 78 are plotted in Figure 2 along with Salty Dog extinction data from previous tests (Mack and Hanley, 1980). The results, on a per payload gram and per chamber basis, are shown in the figure as a function of humidity. From these

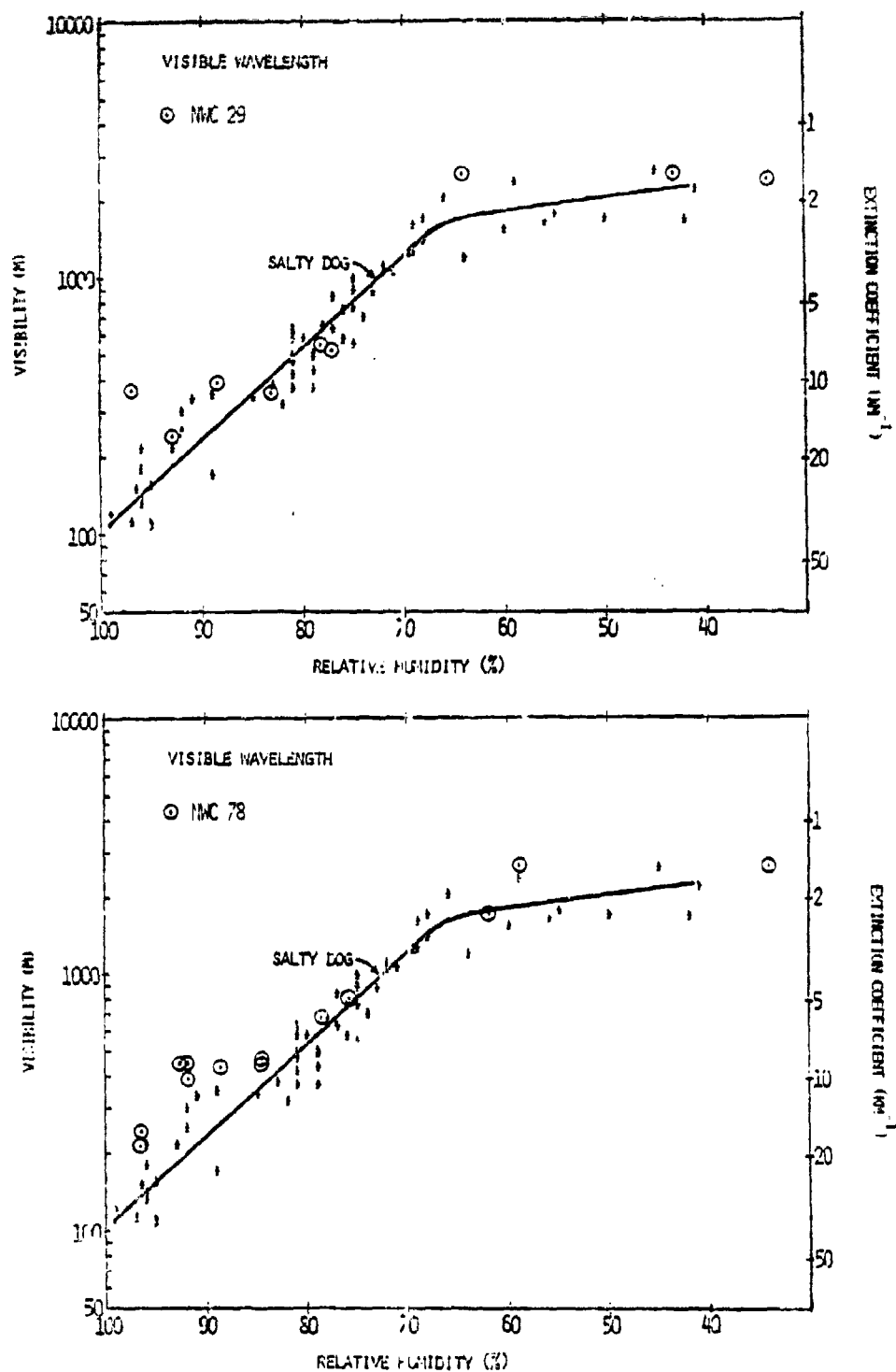


Figure 2 Chamber per-gran visibility and extinction as a function of humidity for Salty Dog, NWC 29 and NWC 78.

data, it is apparent that neither NWC 29 nor 78 produced greater extinction than Salty Dog, and the data suggest that NWC 78 may provide slightly less extinction per unit payload of pyrotechnic burned.

Extinction at IR Wavelengths

As described earlier, continuous IR extinction measurements from ~ 2 to $12\text{ }\mu\text{m}$ wavelength were made with an IR transmissometer over an 18.3 m path length. The instrument, designed and fabricated at Calspan, was installed in the chamber during the latter portion of the chamber tests, presenting an opportunity to obtain limited data on the IR extinction spectra of the pyrotechnics. The IR extinction measurements reported here, therefore, represent the first use of the system and, while believed to be reasonably reliable, should be regarded as preliminary data only. IR data were obtained during experiments 35, 36 and 37 where 50 g payloads of Salty Dog, NWC 29 and NWC 78, respectively, were aerosolized at a humidity of 90-92%. The larger payloads were required to provide a confident measure of IR extinction.

The resultant extinction spectra are presented in Figure 3A where chamber transmission (I/I_0) is plotted as a function of wavelength for the 50 g payload burns. Presently, the differences between the spectra are not considered significant, being attributed to the initial "break-in" drift of the IR system. The sharp decrease in transmission at $\sim 3.3\text{ }\mu\text{m}$ and the general decrease as the wavelength increases beyond $\sim 10\text{ }\mu\text{m}$ are believed to be due to liquid water (i.e., the deliquesced aerosol) absorption at those IR wavelengths.

To compare the extinction effectiveness of Salty Dog to that of phosphorus, Figure 3 B shows the extinction spectra resulting from a 6 g payload of phosphorus at 93% RH (exp. 38) and the 50 g Salty Dog payload at 92% RH previously shown (exp. 35). As can be seen, both burns resulted in approximately the same reduction in transmission, indicating that to achieve a comparable extinction relative to phosphorus at 93% RH, approximately eight times as much payload mass of Salty Dog is required.

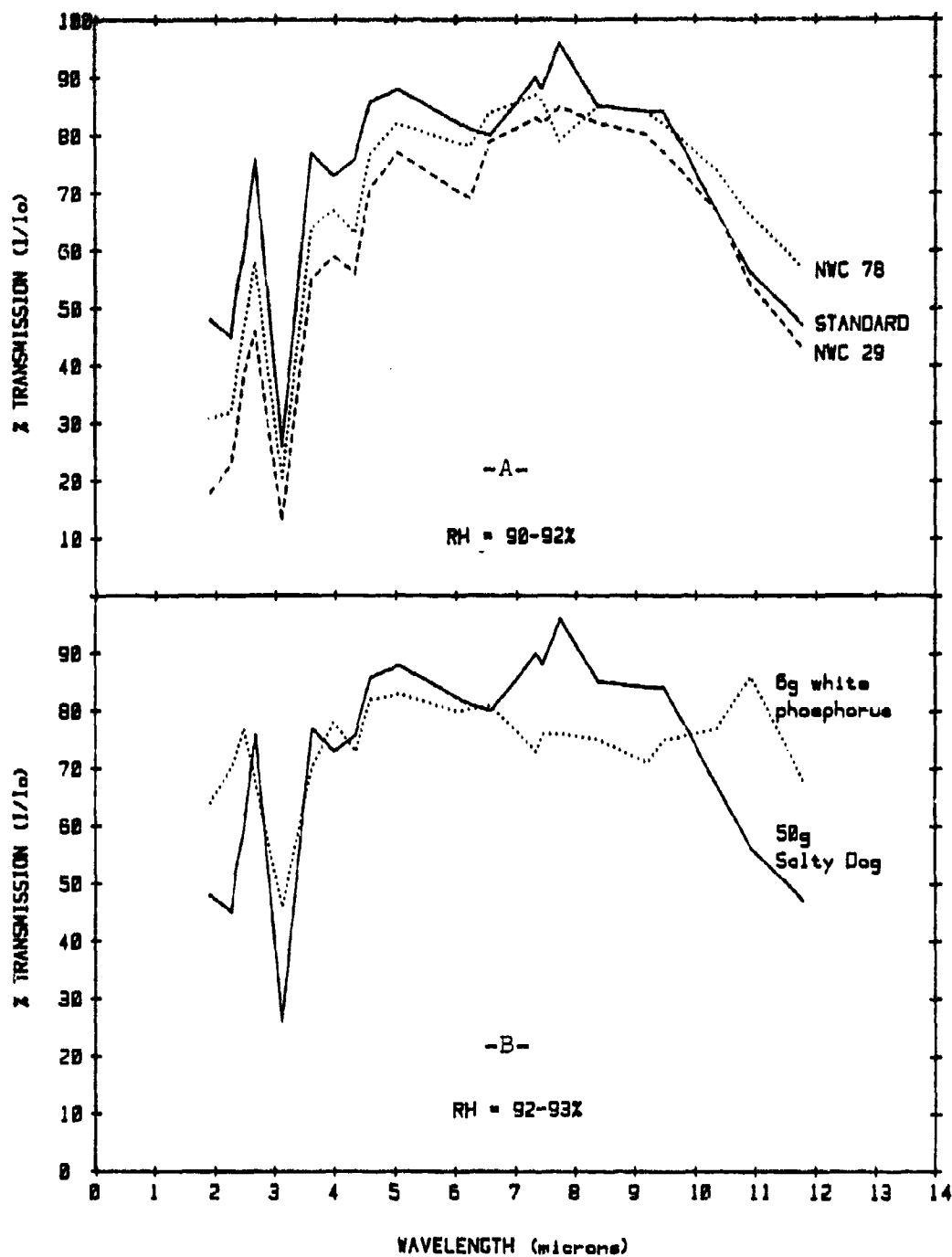


Figure 3. Chamber IR transmission spectra for (A) 50 g payloads of Salty Dog and NWC 29 and 78, and (B) a 6 g payload of White Phosphorus and a 50 g payload of Salty Dog.

2.4 Size Distribution as a Function of Humidity

During low payload experiments, size distribution data were obtained for the range of 0.01 to 3 μm diameter over a range of relative humidities from 35% to 93%. In previous tests, a 0.1 g payload was used to obtain size distribution data. However, for NWC 29, 0.1 g proved to be an insufficient quantity to provide a uniform burn, and thus, the payload was increased to 0.5 g. Still, NWC 29 often burned poorly leaving up to ~30% of its mass unburned. Incomplete aerosolization was not a problem for NWC 78 or Salty Dog, and is not expected to be a problem for any of the pyrotechnics under field conditions where much greater payloads would be used. Figure 4 presents the size distribution data for NWC 29 and 78, along with that for Salty Dog obtained from previous measurements (Mack et al, 1978). Note that the distributions are normalized on a per payload gram basis within the 590 m^3 chamber.

From the distributions of Figure 4, it is apparent that all of the pyrotechnics produce aerosols which undergo significant growth at humidities above ~70% RH. At lower humidities, little or no growth was measured. Additionally, Salty Dog appears to generate about twice the total number of particles as either NWC 29 or 78. However, NWC 29 and 78 generated a greater number of larger (i.e., $>1 \mu\text{m}$) particles.

2.5 Mass-Loading Yield of Pyrotechnics

The mass yield of a pyrotechnic may be defined as the ratio of the resultant cloud mass to the payload mass. For the chamber tests, the payload was always an accurately known quantity, being weighed shortly before burning. To obtain a measure of the cloud mass, mass-loading filter samples were obtained, and the mass of the filter sample was then related to the total cloud mass by the ratio of the chamber to sample volume.

To assure a known sample volume, the filter (Pallflex Products Corp., Type 2500 QAST) was used in conjunction with a 1 cfm critical orifice and vacuum pump. Additionally, a flow meter, placed behind the filter, was monitored to assure that filter loading did not reduce the sampling rate. In general, the sampling duration was 30 minutes (Experiment #12, and 35-38 had a 15 minute sample duration).

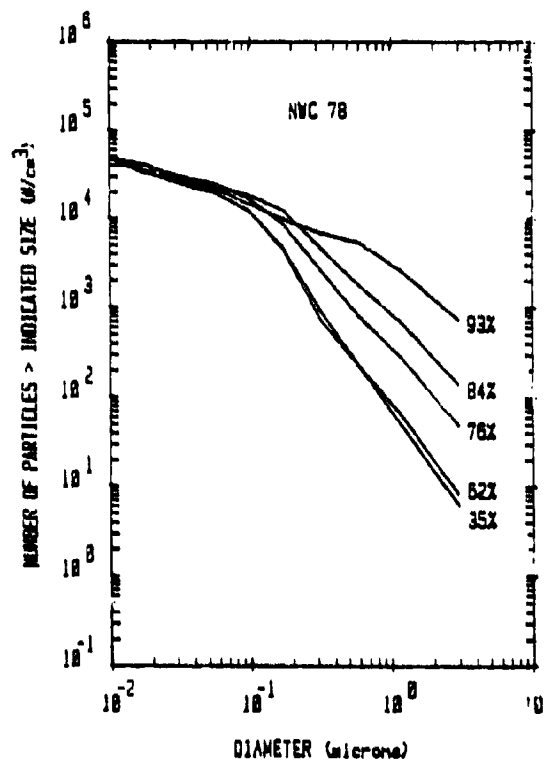
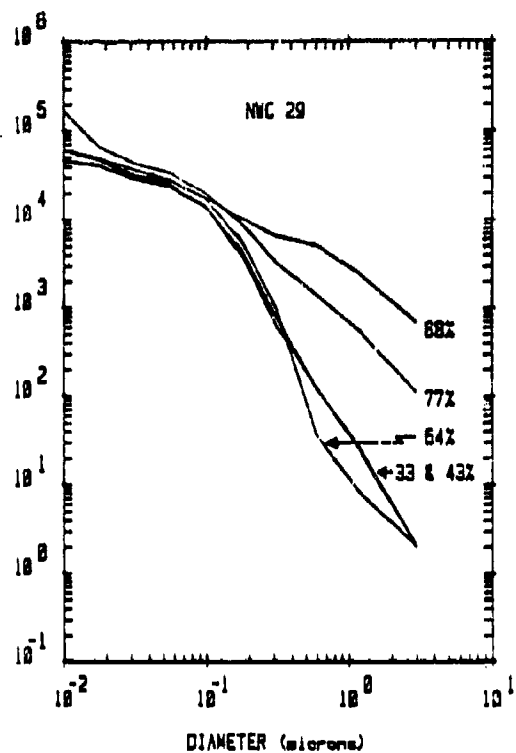
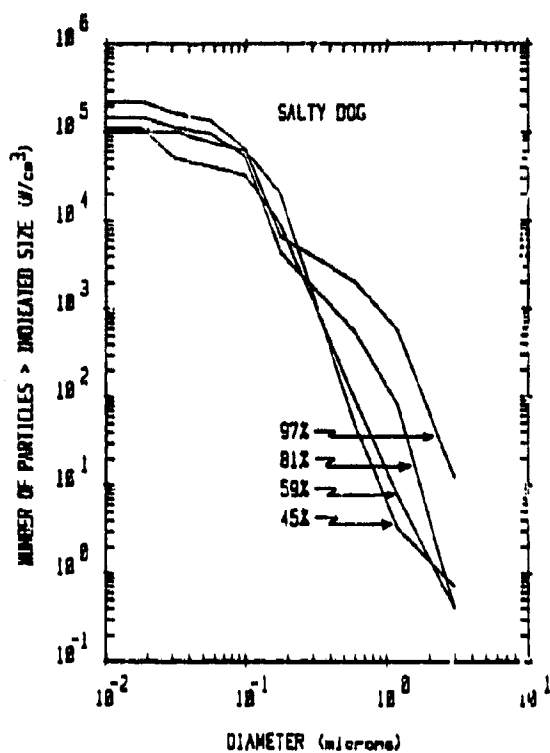


Figure 4
Chamber accumulative aerosol size distribution per payload gram of Salty Dog, NWC 29, and NWC 78 as a function of relative humidity.

Due to the hygroscopic nature of the pyrotechnic aerosols, precautions were taken to prevent the water content and, therefore, mass of the filter from changing prior to, and during, weighing. This was accomplished by obtaining the sample and sealing it in a small, light-weight, pre-weighed container prior to removal from the chamber environment. Upon removal from the chamber, the container and filter combination was immediately weighed and compared to the weight of the initial clean filter and container mass.

Figure 5 presents the resultant yield data for NWC 29 and 78 as a function of humidity. The dashed segment of the curves occur in the region of initial significant particle growth. For this region, the data base is insufficient to clearly define the shape of the curve.

As can be seen, the measured dry yields of NWC 29 and 78 were approximately 0.38 and 0.30, respectively. These values are somewhat lower than the expected theoretical dry yields of 0.48 for NWC 29 and 0.495 for NWC 78 reported by NWC. The "X" shown on the figures represents a mass yield measurement from a single Salty Dog test at 92% RH (exp. 35). By the relative position of the curves to the "X", it is readily seen that NWC 29 produced a greater yield than NWC 78 at higher humidities, apparently due to the initially greater dry yield of NWC 29. The single Salty Dog data point precludes a definite conclusion as to its yield relative to that of NWC 29 and 78, however, it appears that neither NWC 29 nor 78 produces a significantly greater yield than Salty Dog. The lower yield of NWC 78, relative to that of the Salty Dog data point, apparently accounts for the lower yield in extinction also observed for NWC 78 (see Figure 2).

In addition to the measured mass yield curve, a theoretical yield curve (Low, 1969) is shown based on the assumption that all of the pyrotechnic dry yield aerosol is composed entirely of pure NaCl. As can be seen, for both NWC 29 and 78, the measured yield was less than the theoretical at humidities above the deliquescent threshold of NaCl (76%). The differences between theoretical yields for NaCl and measured yields for the pyrotechnics are attributed to the fact that the generated aerosol was not pure NaCl but rather a combination of several salts and, additionally, may contain some insoluble material thereby reducing the effective mass yield and overall aerosol growth of the pyrotechnics.

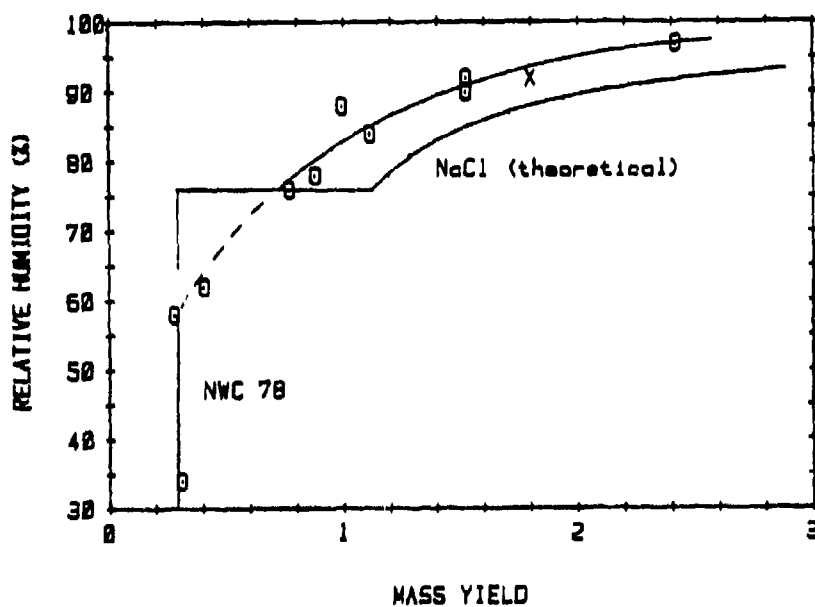
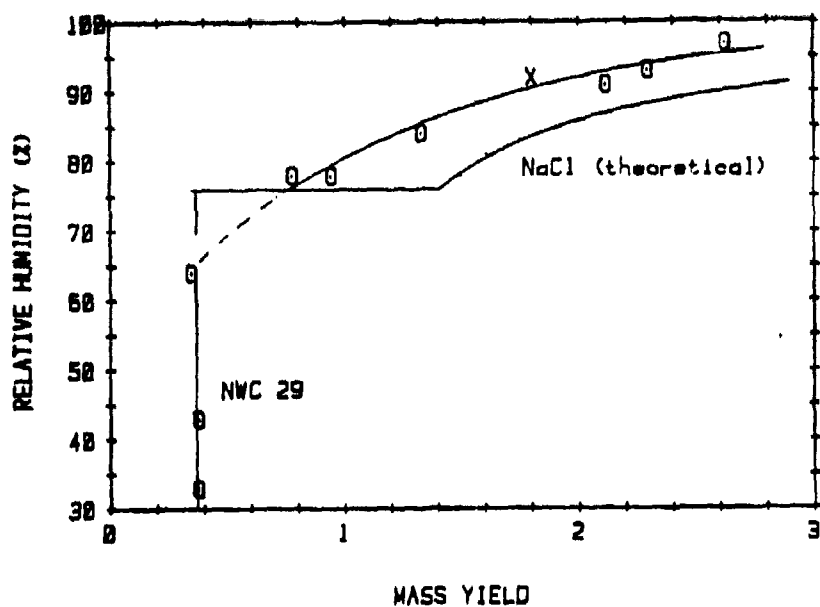
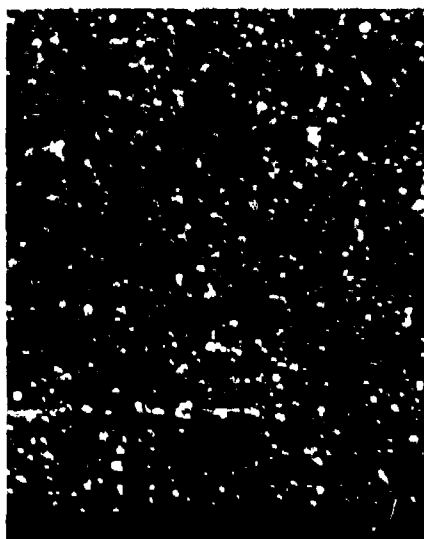


Figure 5 Mass yield for NWC 29 and NWC 78 as a function of humidity, and the theoretical yield of an NaCl aerosol having an assigned dry yield equal to that of the pyrotechnic.

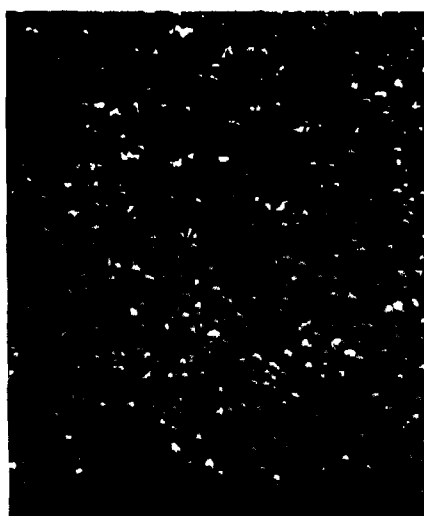
2.6 Aerosol Analysis by Scanning Electron Microscopy (SEM)

In addition to mass loading samples, filter samples were obtained in experiments 18 and 24 to examine particle shape, degree of coagulation, and particle composition as a function of size. The samples were collected upon Nuclepore polycarbonate membrane filters (0.1 μm pore diameter), which provide an excellent substrate for electron microscopy. Figure 6 shows two photomicrographs for each of the two filter samples: a lower magnification overall view of the sample and a higher magnification view to reveal particle shape and degree of coagulation. Upon close examination, it is seen that a large fraction of the particles appear to be composed of from 2 to 5 smaller particles and may, therefore, be small agglomerates. This is especially noticeable in the NWC 78 sample for which essentially all of the particles appear to be groupings of several smaller particles. An alternate possibility, however, is that the particles are not true agglomerates but rather nearly crystallized in irregular shapes giving the appearance of agglomerates.

The chemical composition of eleven particles from each sample was determined via SEM Dispersive X-ray analysis to provide initial information on composition vs. size relationships. The diameter of the analyzed particles ranged from 0.2 to 3 μm . The NWC 29 sample showed no significant evidence of a size-composition dependence with all particles being composed of Cl and Na followed by smaller amounts of Mg. The NWC 78 sample, however, did show definite evidence of a composition-size link. The analysis suggests that the larger particles ≥ 1.5 μm diameter, were primarily composed of Mg (possibly as MgO) with lesser amounts of Cl, K and Na. Particles in the range of ~ 0.4 to 1.5 μm diameter were a varying mixture of Cl, Na, K and Mg. The smaller particles, < 0.4 μm diameter, appeared to contain little Mg being primarily a mixture of Cl, Na and K. Due to the relatively small number of particles analyzed, these results should not be considered conclusive. However, they do indicate that different portions of the pyrotechnic aerosol distribution may grow at different rates due to potential variation of particle composition with size. Thus, a more thorough study of this relationship would be beneficial in understanding the overall growth characteristics of the Salty Dog smokes.



NWC 29



NWC 78



Figure 6. Photomicrographs of NWC 29 and 78 aerosol filter samples. Note the 1.0 micron sizing bar for each photo.

Section 3

RESULTS OF INDIVIDUAL PARTICLE GROWTH STUDIES

In an effort to gain further insight into the deliquescent growth characteristics of the aerosolized pyrotechnics, an apparatus was assembled which allowed the measurement of individual particle growth under controlled humidity conditions. The particles, observed through a microscope, were 20-40 μm in diameter and mounted on a stretched spider thread filament of approximately 1 μm diameter. The specimen particle was placed in a viewing chamber through which air of carefully controlled and measured humidity flowed.

A photograph of the apparatus is presented in Figure 7. Dry compressed air entered the apparatus through a regulator and coarse filter, followed by an additional fine (5 μm) filter. The flow then passed through a 1.0 cfm critical orifice to help maintain a constant flow through the system. By means of a single valve, the flow was divided into two streams; one stream was maintained dry while the other was brought to near 100% RH via passage through a saturator. The two streams were then recombined; by varying the percentage of the flow which passed through the saturator, the RH of the recombined flow was controlled. The flow was then again divided with a portion directed through the viewing chamber containing the sample particle and the remainder of the flow passing by dry and wet bulb thermometers to provide a measure of the RH. A video camera, viewing through the microscope, was also available for video taping and monitoring the actual particle growth. Examples of the thread mounted particles are shown in Figure 8 for pure KCl and for each of the aerosolized pyrotechnics.

To determine the ability of the apparatus to allow repeatable and accurate measurement of deliquescent particle growth, initial tests were conducted using particles of pure NaCl and pure KCl. Samples were collected on spider thread filaments by spraying a concentrated solution mist of the salt (dissolved in distilled water) over the thread, with some droplets being caught by the thread. When dried, the dissolved salt crystallized about the thread.

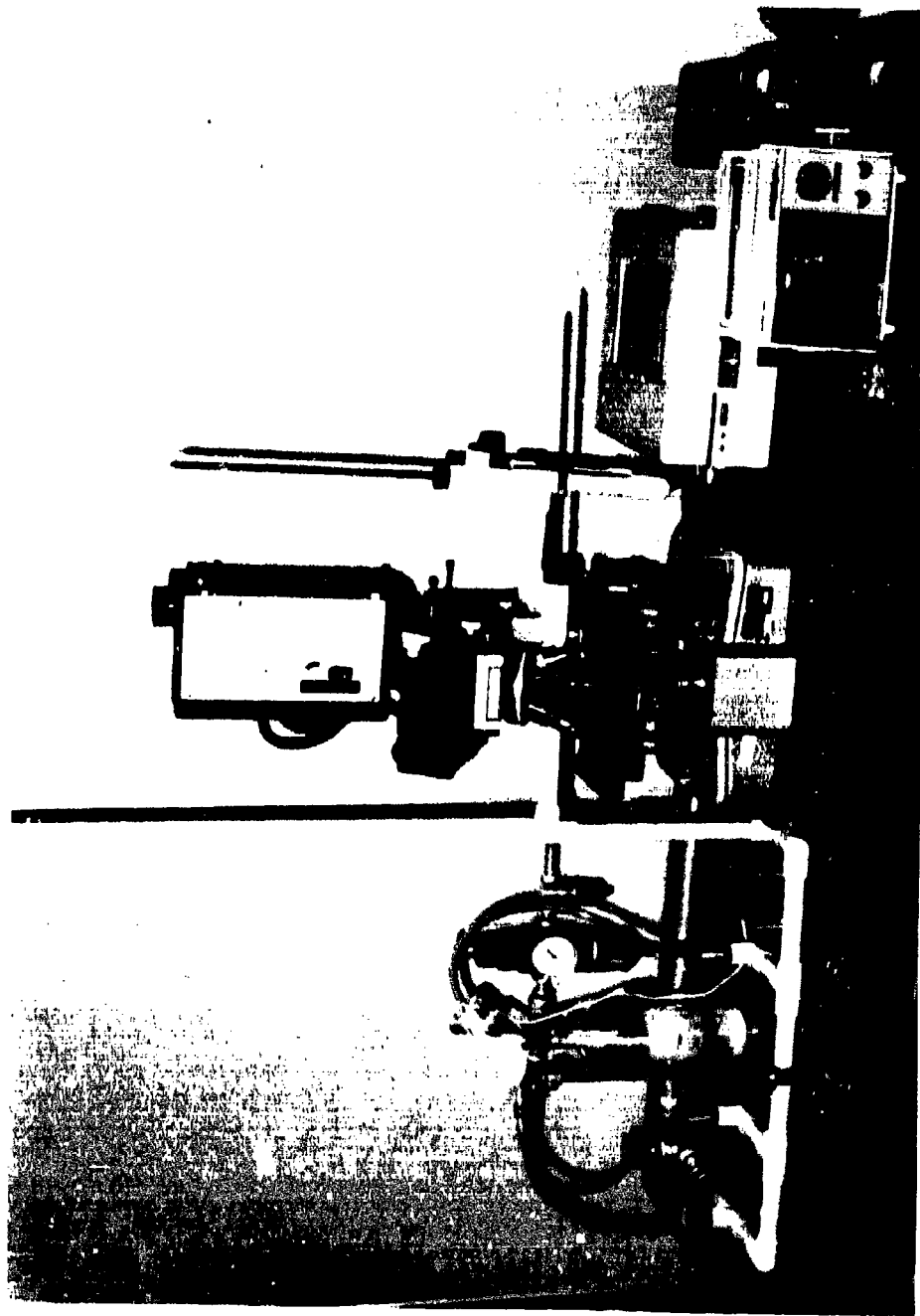


Figure 7. Photograph of Individual Particle Growth Apparatus.

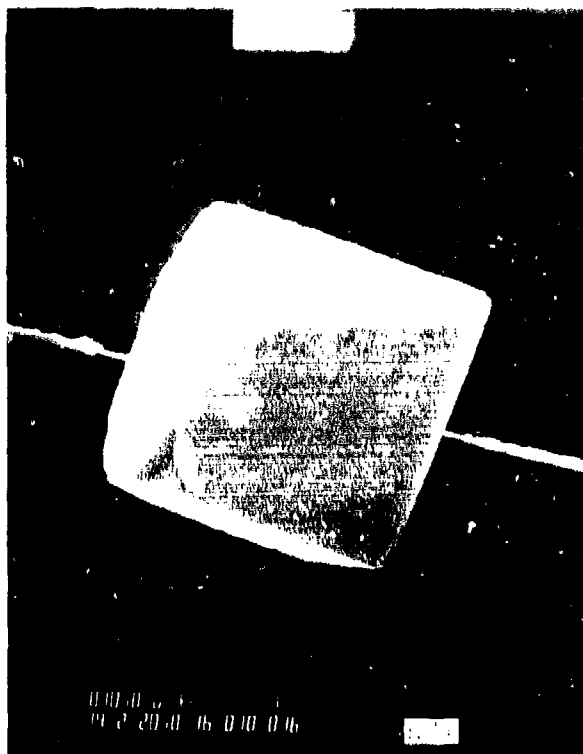
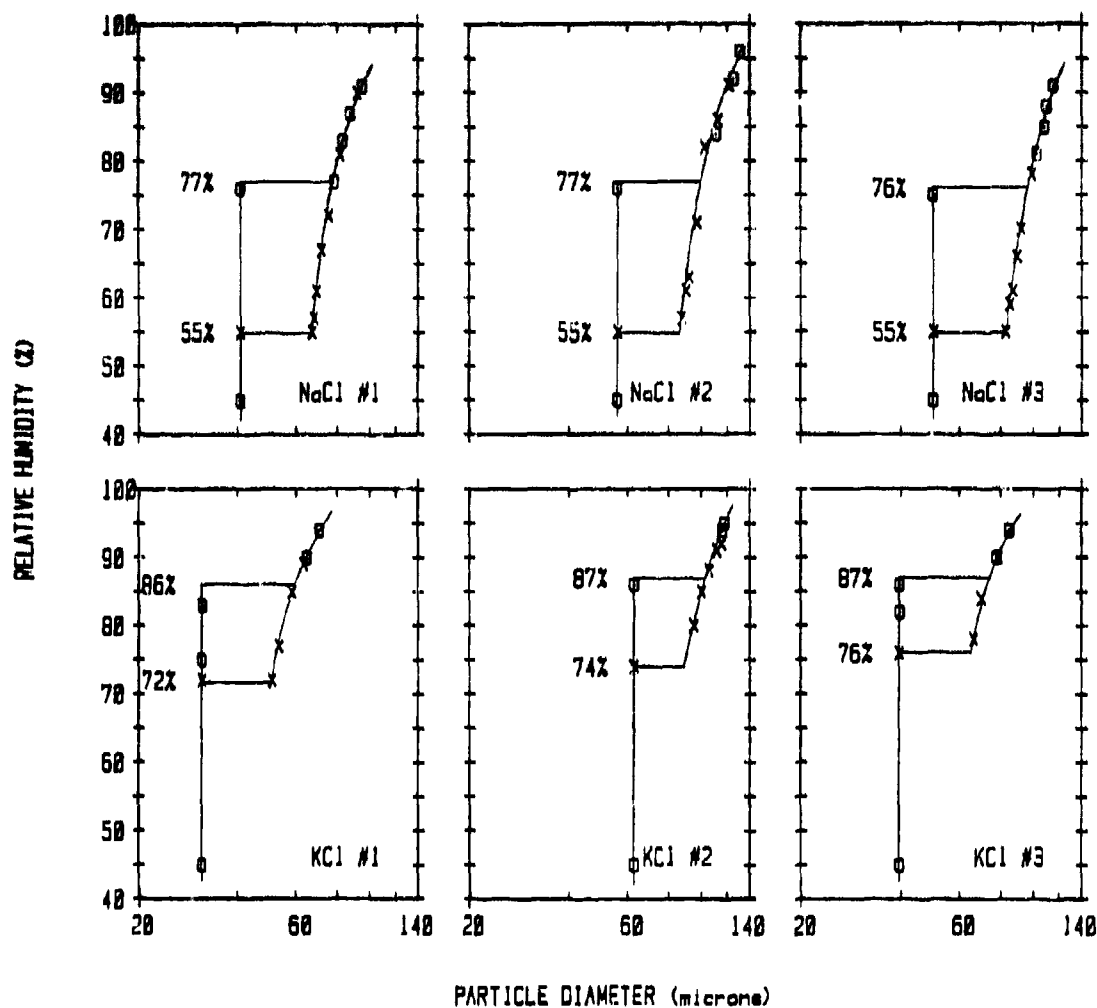


Figure 6. Photomicrographs of the solidified particles for 401 and 402, which are the aerosolized pyrotechnics. Note the 10 micron scale bar in the bottom left of each photo.

The growth of three NaCl and three KCl particles was measured as a function of RH, and the resultant growth curves are presented in Figure 9. Note for the NaCl particles, as the humidity was increased from a low value, the particles remained in the solid phase until reaching a deliquescence RH of ~77%. At this humidity, the particles completely dissolved, approximately doubling in diameter. As the RH was increased further, the droplets underwent additional growth. Upon lowering the RH, the hysteresis effect was observed where the particles existed as supersaturated solution droplets below their deliquescence humidity. When the humidity was decreased to ~55%, the supersaturation could no longer be maintained and the droplets crystallized. The repeatability of these growth characteristics can be evaluated by comparison of the growth curves for all three NaCl particles. A similar set of measurements was obtained for pure KCl particles again showing a high degree of repeatability. (Recrystallization of the droplet upon lowering humidity is a spontaneous nucleating event and thus it was not expected that this value would be highly repeatable.)

To ascertain the accuracy of the measured growth curves, comparison was made of the measured results to those predicted by theory (Low, 1969). This comparison is shown at the bottom of Figure 9 and indicates that the measured values agreed very well with the theoretical deliquescence humidity and relative growth upon deliquescence, and drop sizes were within 10% of the theoretical size expected at 90% RH.

Following the successful tests with the pure salts, samples of Salty Dog, and NWC 29 and 78 were prepared for testing. The particles were obtained by burning ~0.05 g of the selected pyrotechnic in an 0.01 m^3 chamber, allowing the smoke to collect naturally upon the spider thread. Since the vast majority of aerosol particles are $<1 \text{ }\mu\text{m}$, many particles were agglomerated to form a 20-40 μm diameter particle, the optimum size for measurement with the apparatus. The growth of two such agglomerated particles was studied for each of the three pyrotechnics. As was seen in Figure 8, the shape of pyrotechnic particles was very irregular in comparison to the near cubic shape of the pure KCl and NaCl specimens. Thus, measurement of the dry particle size was difficult and the values reported below are based on best estimates of the dry particle



		Deliquescent RH	GROWTH RELATIVE TO DRY DIAMETER AT:	
			Deliquescent RH	90% RH
NaCl	Theory	76%	1.90	2.43
	Measured	77%	1.89	2.22
KCl	Theory	85%	1.89	2.13
	Measured	87%	1.82	1.93

Figure 9. Measured and theoretical (Low, 1969) particle diameter as a function of humidity for NaCl and KCl. Measurements made for increasing humidity are denoted by "O" and for decreasing humidity by "X".

size and may well be overestimates due to the many voids in the particle structure. The resultant growth curves for two particles of each of the three pyrotechnics are presented in Figure 10. Referring to the Salty Dog particles, at low humidities, the particles are essentially all solid with no significant liquid present. (Apparently due to the presence of $MgCl_2$ and $LiCl$, minute quantities of liquid water were detected in each particle at humidities as low as 40%.) As the humidity was increased above ~73%, measurable growth was observed as the particles began to dissolve. In the RH range of 73-80%, the particles were a mixture of solid undissolved salt and liquid salt solution co-existing in an apparent equilibrium state. This differs from the growth of pure salts which completely dissolve upon deliquescence and hence do not exist at equilibrium in such a mixed state. At a RH of 81%, the Salty Dog particles completely dissolved. Upon lowering the humidity, the hysteresis effect was observed until ~69% RH when the droplets underwent a complete phase transition from a liquid supersaturated salt solution to a solid crystal such as shown in Figure 8. It should be noted that the mixed state of liquid salt solution and solid salt was not observed in the hysteresis region. As with the pure salts, the measurements were very reproducible.

In comparison to Salty Dog aerosol, the NWC 29 specimens became completely dissolved at ~78% RH and recrystallized at 55-57%. The NWC 78 particles completely dissolved at ~70%, significantly lower than the RH required for Salty Dog aerosols, and recrystallized at 55-57% RH.

In summary, the measurements indicate that, of the three formulations, NWC 78 produces the aerosol having the most favorable growth characteristics. While both NWC 78 and the Salty Dog particles began significant growth at approximately the same RH, NWC 78 completely dissolved at 70% as opposed to 81% for Salty Dog. Thus, it is expected that for the same dry size distribution, NWC 78 would produce larger droplets in the humidity range of 70 to 81% than would either NWC 29 or Salty Dog. Additionally, NWC 78 exhibited a much lower recrystallization humidity (55-57%) than did Salty Dog (69%) and, thus, would be expected to maintain larger droplet sizes than Salty Dog under decreasing humidities in the range 69-57%.

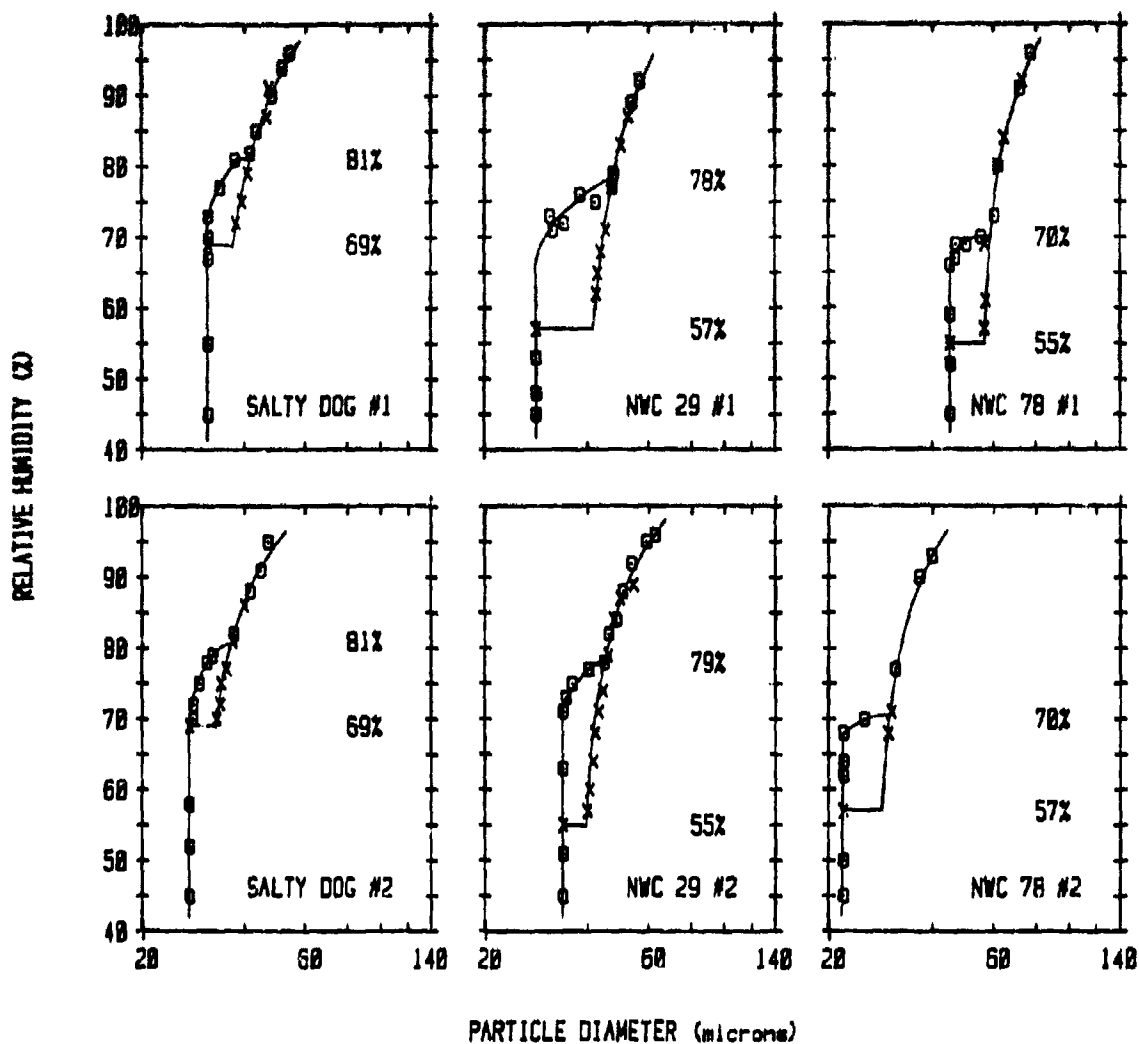


Figure 10. Measured particle diameter as a function of humidity for Salty Dog, NWC 29 and NWC 78. Measurements made for increasing humidity are denoted by "O" and for decreasing humidity by "X".

Section 4

DISPERSION COMPUTATIONS

In support of planned field trials of the Salty Dog pyrotechnic, conducted by the Naval Research Laboratory (NRL), estimates were made of the required upwind burn distance and burn rate to produce a prescribed visibility restriction measured by a 4 km path length transmissometer located on the northwest corner of San Nicolas Island, one of the Channel Islands off the coast of southern California. These estimates were made by combining experimentally derived mass extinction data and expected meteorological conditions through dispersion theory, assuming point-source emission.

The dispersion calculations are based on the theory presented by Turner (1969). Turner relates downwind aerosol mass concentration, x , to the emission burn rate, Q , wind speed, u , horizontal, σ_y and vertical, σ_z , dispersion coefficients (which are functions of atmospheric stability), sampling height, z , and effective emission height, H . (The effective emission height is the height at which the plume becomes essentially horizontal.) Following Turner, for a continuously emitting point source, the downwind aerosol mass concentration is given by

$$x = \frac{Q}{2\pi \sigma_y \sigma_z u} \exp \left[-0.5 \left(\frac{y}{\sigma_y} \right)^2 \right] \left\{ \exp \left[-0.5 \left(\frac{z-H}{\sigma_z} \right)^2 \right] + \exp \left[-0.5 \left(\frac{z+H}{\sigma_z} \right)^2 \right] \right\}.$$

Values of σ_y and σ_z are presented by Turner as a function of atmospheric stability and distance from the emission source based on a sampling time of approximately 10 minutes.

The presence of an inversion tends to "cap" the plume's vertical development, thereby preventing significant dispersion above the inversion base. To account for this, the following formulation is used when the plume has undergone sufficient vertical dispersion to be influenced by the inversion base at height L :

$$x = \frac{Q}{\sigma_y L u \sqrt{2\pi}} \exp \left[-0.5 \left(\frac{y}{\sigma_y} \right)^2 \right].$$

The expected meteorological conditions, as prescribed by NRL, are an 85% relative humidity, 7 m/sec (15 mph) wind, 500 m inversion base height, and a 32 km (20 mi.) background visibility. The transmissometer height is 15.24 m (50 ft) MSL with a 4.0 km path length perpendicular to the prevailing wind direction (Pacific Missile Test Center, 1977). The effective emission height, being a combination of burn height and plume rise is unknown and was, therefore, assigned a value of 10 m. The pyrotechnic burn was assumed to be a point source, and, for compatibility with Turner's theory, visibility computations are based on a 10-minute average value. Additionally, since under identical conditions all three salty dog formulations resulted in approximately the same extinction, the calculations are based on burning the Standard Salty Dog pyrotechnic.

It should be realized that the value assigned to the visibility will be dependent upon how it is measured. The 4 km path length transmissometer measures the visibility integrated over its total path. This measure will generally be different from that measured by a point visibility instrument such as a nephelometer. As an example, Figure 11 shows the downwind visibilities resulting from the continuous burning of 1000 lb/hr of Salty Dog under the stated conditions. Since the plume is horizontally symmetric about its centerline, two different quantities have been plotted in Figure 11. In the lower half of the figure, the point visibility at the grid location is shown. In the top half, the integrated visibility, as measured by a 4 km crosswind path length transmissometer centered at the grid point, is shown. The differences between the two measures is readily apparent.

By assuming the plume to be "on target" with the plume centerline perpendicular to the transmissometer beam and a desired visibility of 12.8 km (8 mi), the required burn rate can be plotted as a function of the upwind distance from the measuring location. Figure 12 shows such a plot for the stated conditions. In addition to burn rate, the percent of the 4 km path length occupied by plume, which results in a 25% reduction of the background visibility, is shown. The minimum burn time as a function of upwind distance is also shown and is based on a combination of the plume travel time and a 10-minute measuring period. As can be seen, it is not necessary to fill the entire 4 km path with

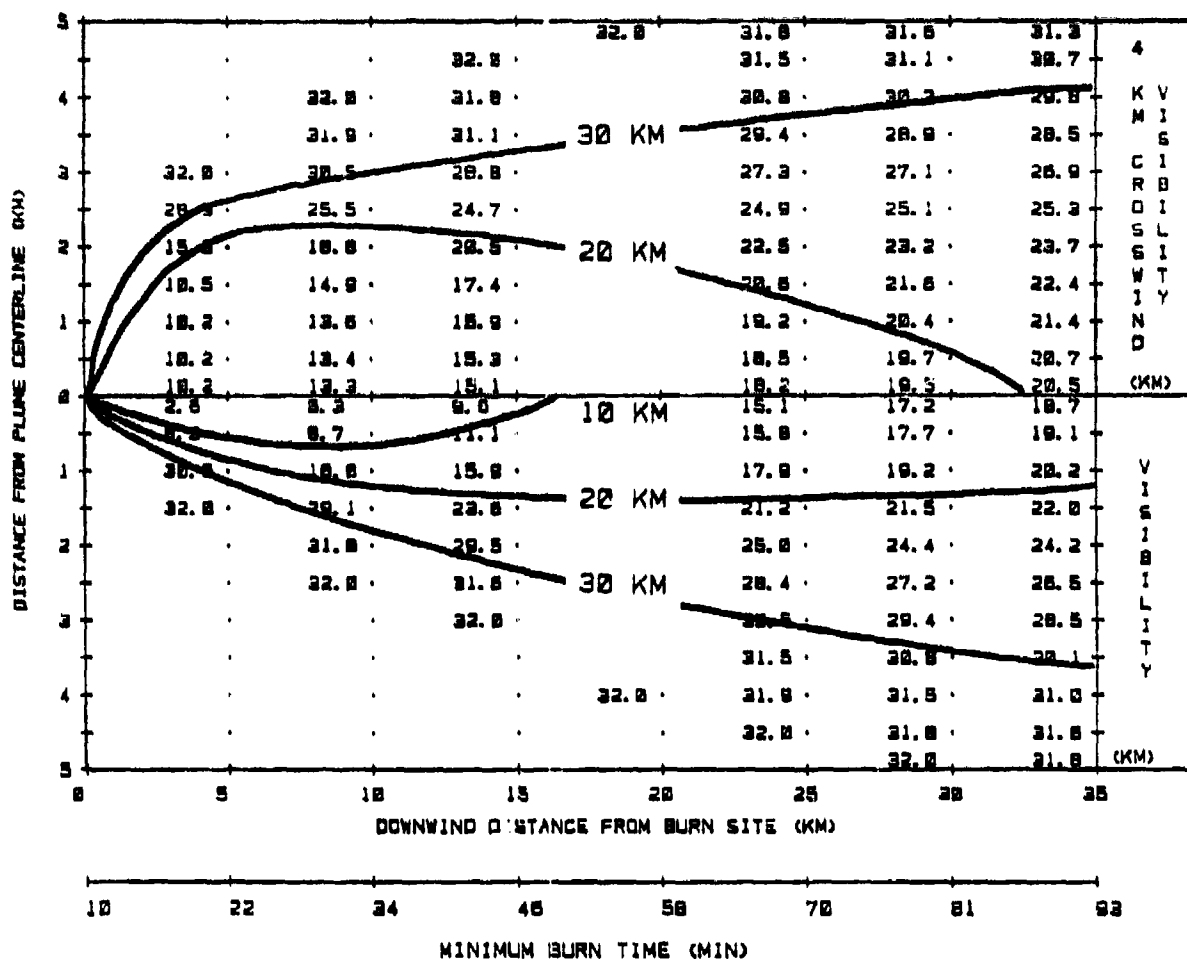
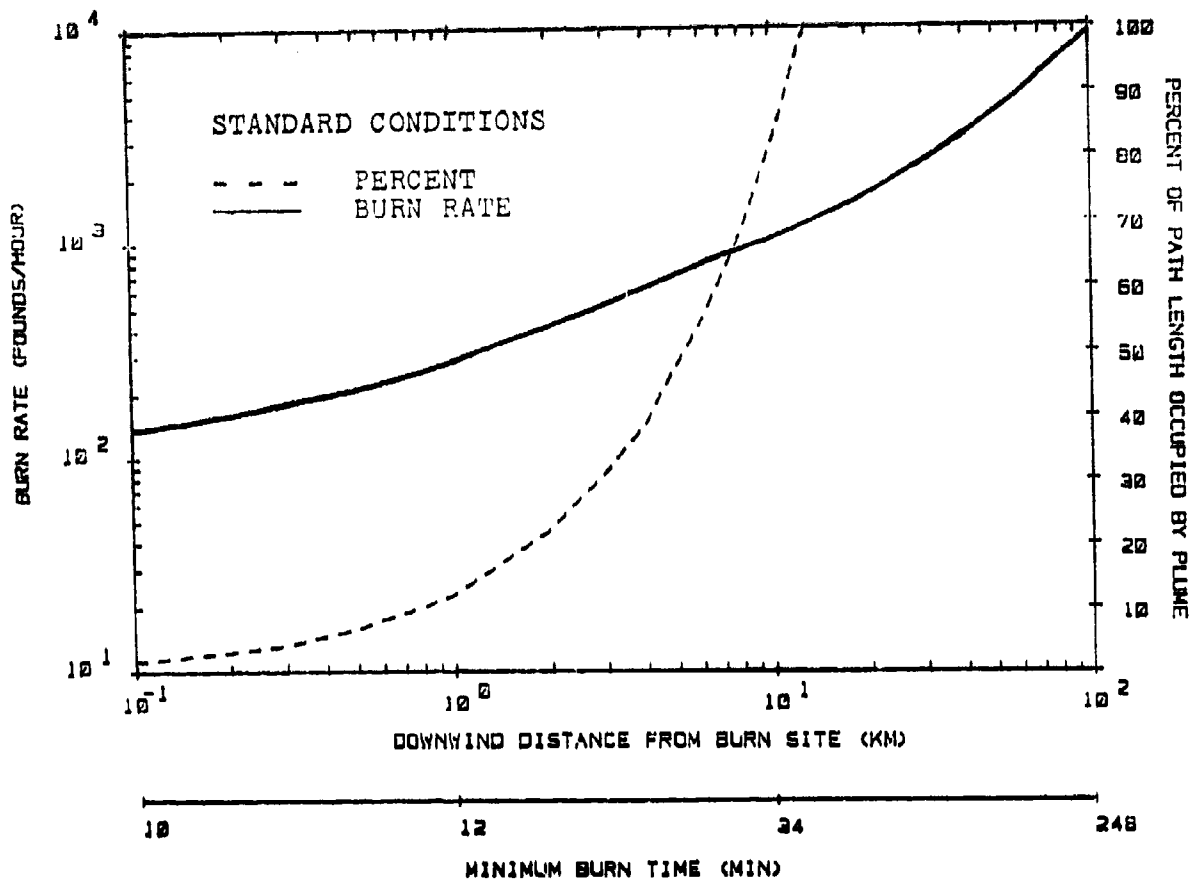


Figure 11. Numerical estimates of downwind visibility (point and 4 km crosswind) resulting from a point source burn of 1000 pounds/hour of Salty Dog under the indicated conditions.



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL:
 RELATIVE HUMIDITY 85 %
 WIND SPEED 7 M/S
 INVERSION BASE HEIGHT 500 M
 STABILITY: NEUTRAL
 EFFECTIVE EMISSION HEIGHT 10.0 M
 SAMPLING HEIGHT 15.2 M
 BACKGROUND VISIBILITY 32.0 KM
 SUBSTANCE BURNED: STANDARD SALTY DOG
 DESIRED VISIBILITY OVER 4 KM CROSSWIND PATH LENGTH: 12.8 KM

Figure 12. Numerical estimates of pyrotechnic burn rate, plume width, and minimum burn duration as a function of downwind distance from the burn site required to achieve a 12.8 km visibility measured over a 4 km crosswind path length for the indicated conditions.

plume to achieve a 12.8 km visibility. For example, a 12.8 km visibility can be achieved by burning at a rate of ~ 200 lb/hr, 1 km upwind. However, the plume will only be ~ 0.48 km wide when measured, occupying about 12% of the path length. For a truly large scale trial, it seems reasonable to require that the plume completely fill the transmissometer path. As shown in the Figure, this will occur at distances ≥ 11 km requiring a burn rate ≥ 1000 lb/hr for ≥ 36 min (assuming a stationary, point-source).

An investigation was made of the sensitivity of the required burn rate to changes in wind speed, relative humidity, inversion base height, effective emission height and atmospheric stability. These results are presented in Appendix A. Briefly summarizing these calculations, it is seen that a change in wind speed requires an approximately proportional change in burn rate. The burn rate is inversely related to humidity, allowing a 50% decrease in burn rate for a 10% increase of relative humidity, and is insensitive to inversion base heights at altitudes above ~ 300 m. Examination of the sensitivity to effective emission heights shows that, as expected, the most advantageous height is that equal to the transmissometer height, 15.2 m (50 ft). At heights less than (greater than) the measurement height, increased burn rates are required to enhance the upward (downward) vertical dispersion of the plume to compensate for the plume passing beneath (above) the transmissometer beam. It is also seen that increased stability allows for lower burn rates by decreasing both the horizontal and vertical dispersion.

From the above sensitivity analyses, it is apparent that for a 100% plume filled transmissometer path under neutral to stable conditions, a burn rate of 1000 lb/hr for at least 36 minutes, 11 km upwind of the transmissometer will be generally required. Because these values appear excessive, it may be prudent to redesign the experiment to allow for more reasonable burn rates and upwind burn distances, e.g., by using multiple or moving sources to simulate a line source.

Section 5
CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The tests performed on this program present a number of means by which the characteristics of aerosol produced by the NWC pyrotechnics may be compared. These include resultant mass yields, aerosol size distributions, extinction spectra, and growth measurements of individual specimen particles, all as functions of humidity. The data show that while a given formulation may possess superior characteristics for one of these measures, inferior performance in another aspect may eliminate any overall benefit in terms of extinction. For example, while NWC 78 showed superior growth characteristics in the particle growth studies, its lower mass yield for a given payload resulted in less extinction than provided by either Salty Dog or NWC 29.

Based upon theoretical considerations and the experimental data generated on this program, the following specific results and conclusions are drawn:

1. The relative elemental composition of NWC 29 aerosol by weight is 68% Cl, 27% Na, 4% Mg and <1% of K and Li. Similarly for NWC 78, the aerosol composition is: 75% Cl, 12% Na, 9% K, 3% Mg, and <1% Li. The composition of Salty Dog aerosol is 51% Cl, 33% K, 10% Na, 6% Mg and <1% Li.
2. The dry mass yields of NWC 29 and 78 were found to be 0.38 and 0.3, respectively, of the amount burned. At 92% RH, the respective yields of Salty Dog, NWC 29 and 78 were approximately 1.8, 2.0 and 1.6.
3. Compared to Salty Dog, NWC 29 and 78 produce lower numbers of particles, but of larger overall size.

4. Limited chemical analysis of individual particles suggests a variation of particle composition with size for NWC 78 aerosol which was not observed for the Salty Dog and NWC 29 formulations.
5. For the conditions of these tests, neither NWC 29 nor 78 produced greater extinction than Salty Dog; because of its lower dry mass yield, NWC 78 may provide less extinction than Salty Dog on a per unit payload basis.
6. Based on laboratory measurements of individual particle growth, the aerosol generated by NWC 78 exhibited the most favorable growth characteristics forming a completely liquid droplet at 70% RH, compared to 78% for NWC 29 and 81% for Salty Dog.
7. For point source field trials, dispersion calculations indicate that a minimum burn rate of ~ 1000 lb/hr and an upwind burn distance of 11 km are required to achieve a 12.8 km (8 mi.) visibility measured over a 4 km crosswind path for the ambient conditions of 85% RH, 7 m/s (~ 15 mph) wind speed, 500 m inversion base height and 32 km (20 mi) background visibility.

Recommendations

It is presently felt that pyrotechnic formulations which produce aerosols with lower deliquescence humidities than NaCl or KCl (e.g., CaCl_2 , MgCl_2 , LiCl, etc.) and yield greater aerosol mass per unit payload will be required to improve the extinction yield achieved by Salty Dog pyrotechnics. The addition of specific absorbers may improve extinction characteristics at infrared wavelengths but may also reduce the effective mass yield. Based on the above conclusions, it is recommended that future study include the following:

1. Evaluation of the growth characteristics of pure and mixed salts with low deliquescence humidities to aid in choosing optimum pyrotechnic salt mixtures for enhanced deliquescent growth of resultant aerosols.

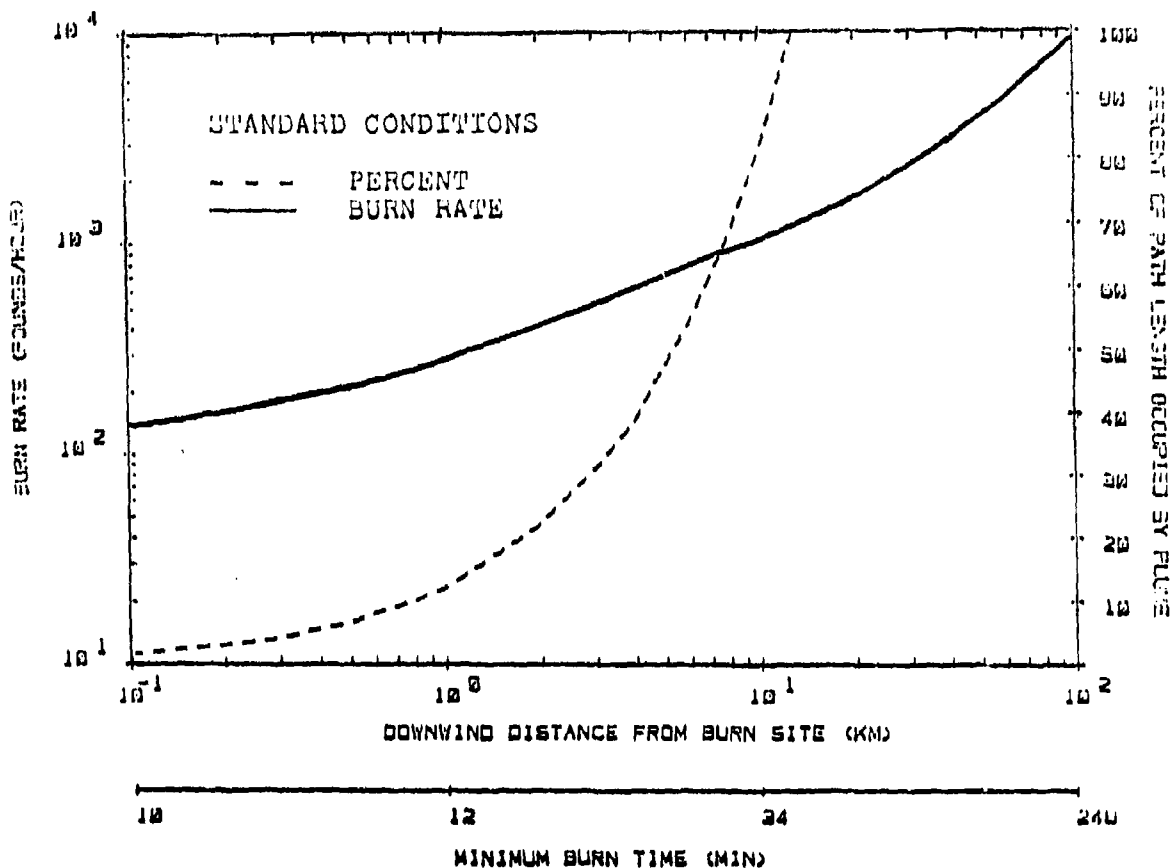
2. Development of pyrotechnic formulations which produce greater effective dry yields and more effective particle size spectra. New formulations should be thoroughly evaluated for extinction yield as functions of relative humidity and payload and the relative contributions to extinction by absorption and scattering.
3. Thorough definition of the particle size/composition relationship of the pyrotechnic aerosol to increase the understanding of the growth with humidity of Salty Dog smokes.
4. Development of IR extinction signatures as function of relative humidity for the NWC pyrotechnics so that their effectiveness as IR screens may be more thoroughly evaluated.
5. Evaluation of the effectiveness of stabilizers, such as cetyl alcohol, to reduce droplet evaporation by using individual-particle-growth-study techniques. By measuring the growth characteristics of a single particle before and after introduction of the stabilizer, the influence of the stabilizer on both droplet evaporation and growth should be readily measurable. To quantify the results, measurement should be made of the amount of stabilizer actually deposited upon the droplet.

REFERENCES

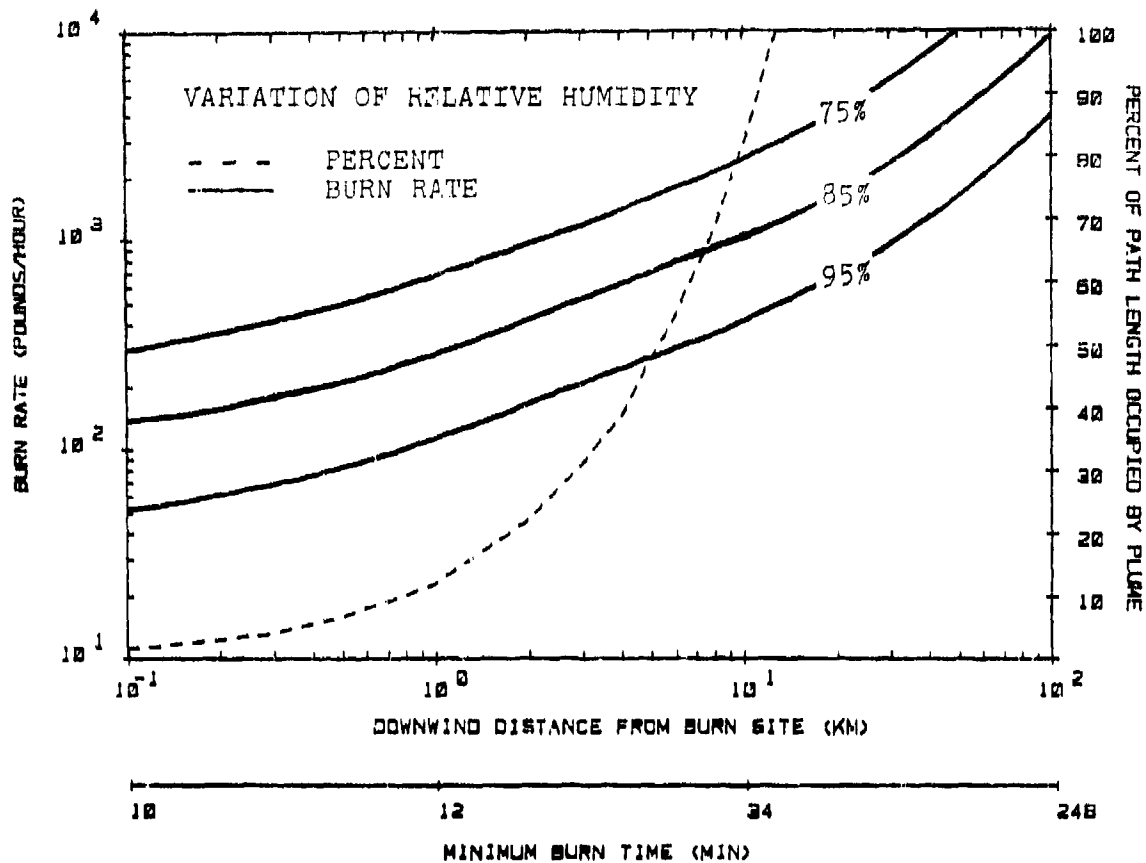
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APPENDIX A

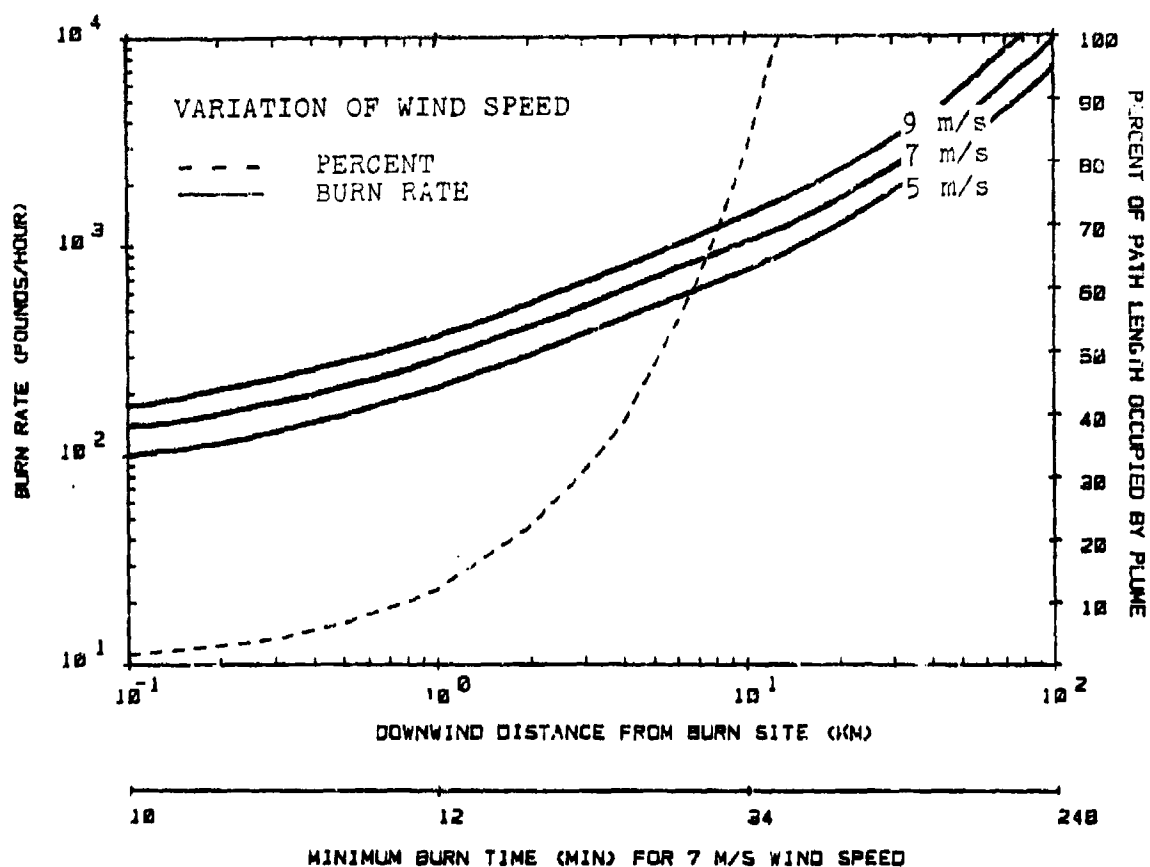
ESTIMATES OF PYROTECHNIC BURN RATE AND UPWIND
BURN DISTANCE REQUIRED TO ACHIEVE A 12.8 KM (8 MI) VISIBILITY
MEASURED BY THE 4 KM PATH LENGTH TRANSMISSOMETER ON SAN NICOLAS ISLAND
FOR A RANGE OF METEOROLOGICAL CONDITIONS



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL:
 RELATIVE HUMIDITY 85 %
 WIND SPEED 7 M/S
 INVERSION BASE HEIGHT 500 M
 STABILITY: NEUTRAL
 EFFECTIVE EMISSION HEIGHT 10.0 M
 SAMPLING HEIGHT 15.2 M
 BACKGROUND VISIBILITY 32.0 KM
 SUBSTANCE BURNED: STANDARD SALTY DOG
 DESIRED VISIBILITY OVER 4 KM CROSSWIND PATH LENGTH: 12.0 KM



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL:
 RELATIVE HUMIDITY AS INDICATED
 WIND SPEED 7 M/S
 INVERSION BASE HEIGHT 500 M
 STABILITY: NEUTRAL
 EFFECTIVE EMISSION HEIGHT 10.0 M
 SAMPLING HEIGHT 15.2 M
 BACKGROUND VISIBILITY 32.0 KM
 SUBSTANCE BURNED: STANDARD SALTY OGG
 DESIRED VISIBILITY OVER 4 KM CROSSWIND PATH LENGTH: 12.8 KM



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL:

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WIND SPEED AS INDICATED

INVERSION BASE HEIGHT 500 M

STABILITY: NEUTRAL

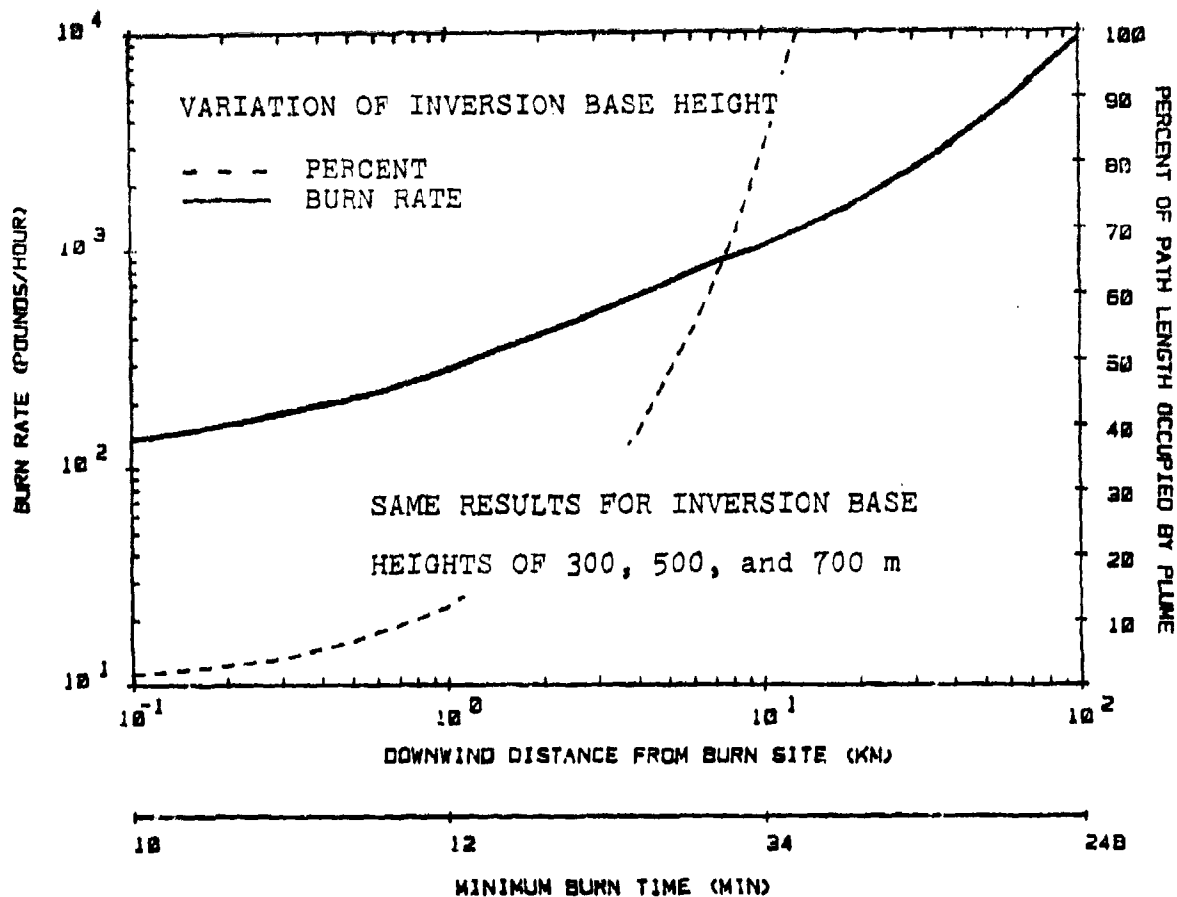
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SAMPLING HEIGHT 15.2 M

BACKGROUND VISIBILITY 32.0 KM

SUBSTANCE BURNED: STANDARD SALTY OGC

DESIRED VISIBILITY OVER 4 KM CROSSWIND PATH LENGTH: 12.0 KM



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL.

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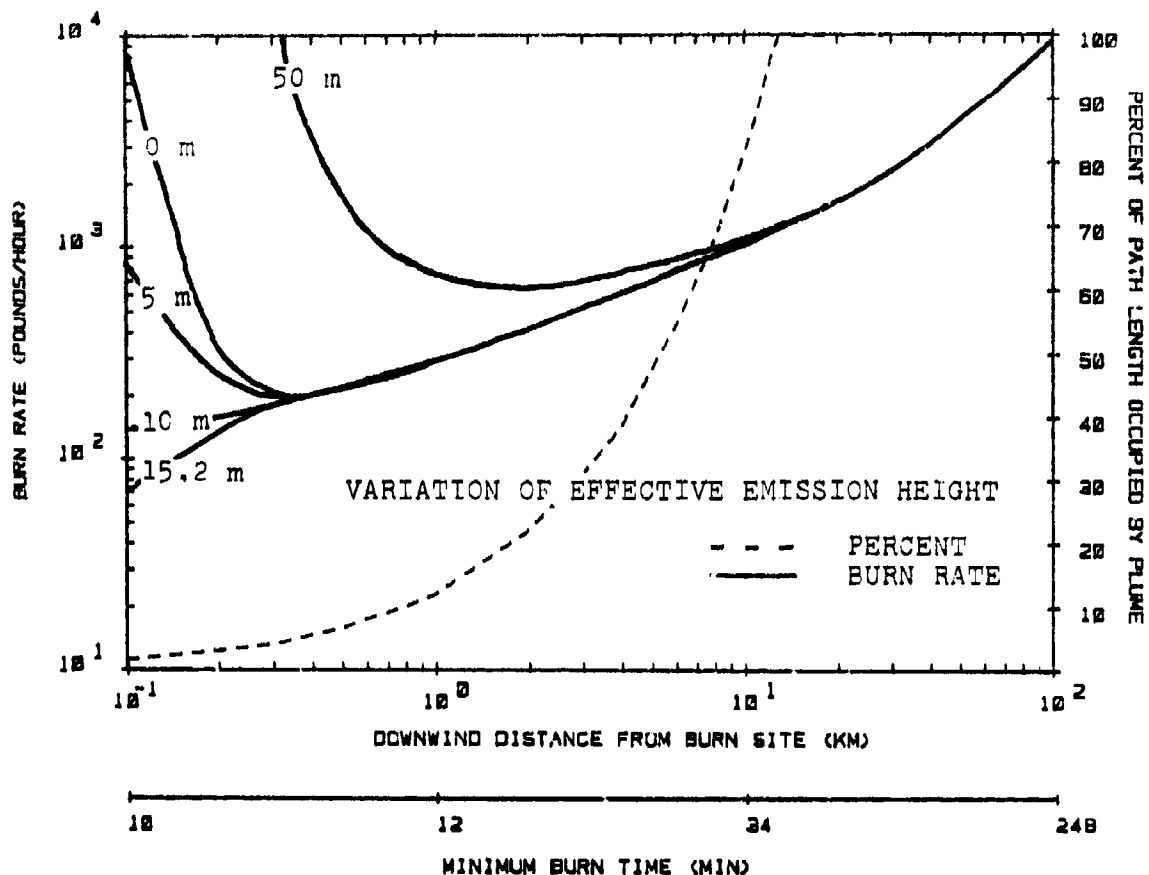
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SAMPLING HEIGHT 15.2 M

BACKGROUND VISIBILITY 32.0 KM

SUBSTANCE BURNED: STANDARD SALTY DOG

DESIRED VISIBILITY OVER 4 KM CROSSWIND PATH LENGTH: 12.0 KM



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL:

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WIND SPEED 7 M/S

INVERSION BASE HEIGHT 500 M

STABILITY: NEUTRAL

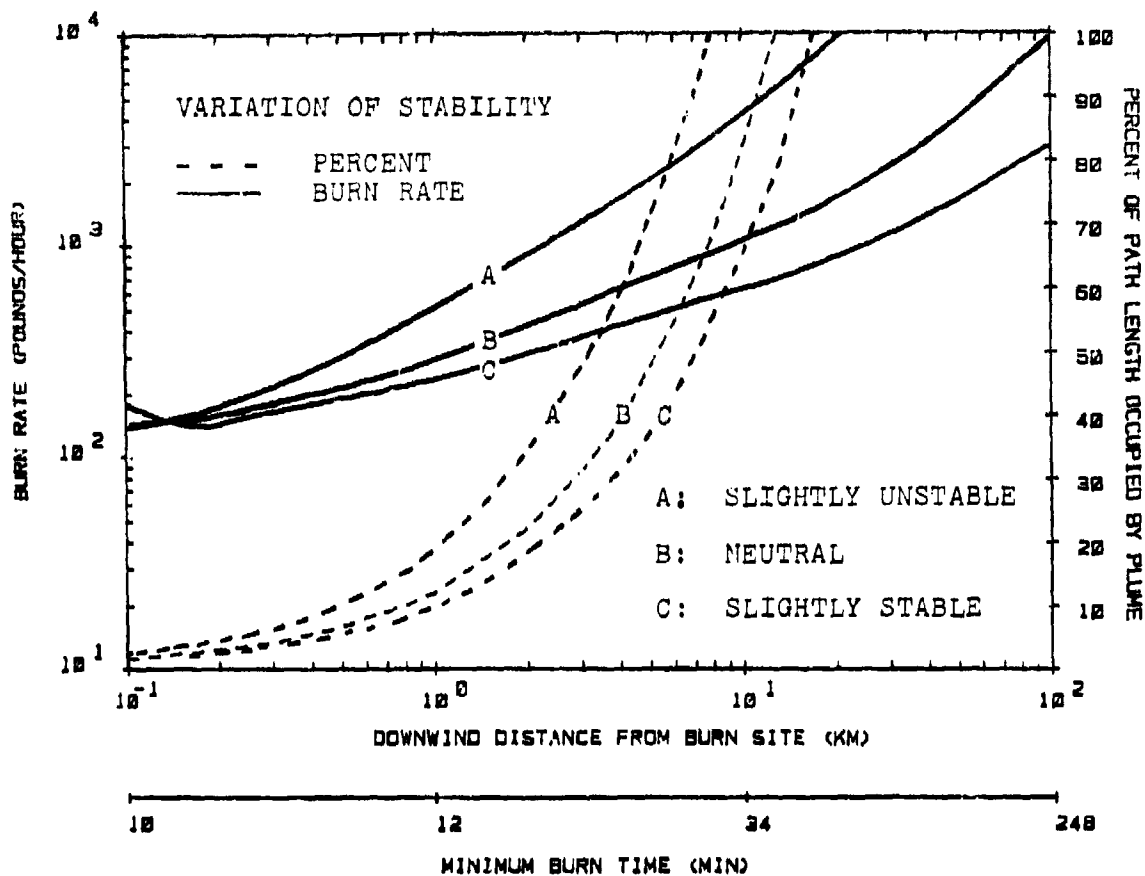
EFFECTIVE EMISSION HEIGHT AS INDICATED

SAMPLING HEIGHT 15.2 M

BACKGROUND VISIBILITY 32.0 KM

SUBSTANCE BURNED: STANDARD SALTY OIL

DESIRED VISIBILITY OVER 4 KM CROSSLAND PATH LENGTH: 12.0 KM



INPUT PARAMETERS TO ATMOSPHERIC DISPERSION MODEL:

RELATIVE HUMIDITY 85 %

WIND SPEED 7 M/S

INVERSION BASE HEIGHT 500 M

STABILITY: AS INDICATED

EFFECTIVE EMISSION HEIGHT 10.0 M

SAMPLING HEIGHT 15.2 M

BACKGROUND VISIBILITY 32.0 KM

SUBSTANCE BURNED: STANDARD SALTY DOG

DESIRED VISIBILITY OVER 4 KM CROSSWIND PATH LENGTH: 12.0 KM