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Physical and Chemical Characterization of Hexachloroethane Smokes

Part 1 of 2

PHYSICAL AND CHEMICAL CHARACTERIZATION OF FOG OIL
SMOKE AND HEXACHLOROETHANE SMOKE

Final Report - January 1980

by

Sidney Katz
Alan Snelson
Raleigh Farlow
Roger Welker
Stephen Mainer

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Contract No. DAMD-17-78-C-8085

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The U.S. Army HC smoke generator has been studied, the investigation in- cluding the reagent materials, generation process, and the product gases and aerosol smoke. The reagent material consisted of hexachloroethane, zinc oxide, aluminum. In a series of chamber tests, variations in material composition did not appear to affect the characteristics of the product smoke, but small variations in the aluminum concentration did control the rate of the smoke generating reaction. Gases formed in the reaction included CO, HCl, COCl ₂ , C ₂ Cl ₄ , C ₂ Cl ₆ , C ₆ Cl ₆ , and Cl ₂ . Per gram of reagent, this amounted to 0.1-1 | | |

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mass % COCl_2 , 1-3 mass % CCl_4 , 3-17 mass % C_2Cl_4 , 0.3-5 mass % C_2Cl_6 , and 0.4-0.9 mass % C_6Cl_6 .

The HC smoke was predominantly zinc chloride, with 1-2% aluminum chloride. The diameter of the smoke particle was close to 0.3-0.4 μm initially. At a smoke concentration of 1 to 2×10^6 particles per cc, the aerosol was stable for 20-30 min. As the concentration increased, particle agglomeration reduced the stability. Particle concentration was controlled by the amount of reagent material allowed to react in the test chamber. Humidity did not appear to affect smoke formation size or composition. The principle impurities, lead and cadmium were present in the aerosol in the same proportions relative to zinc as in the reagent material.

Several miniature smoke generators were designed to control aerosol concentration during laboratory tests.

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EXECUTIVE SUMMARY

Hexachloroethane (HC) white smokes are an important class of military obscuration smokes. They are generated in military field operations in the thermochemical reaction of a mixture of reagents that includes zinc oxide, aluminum metal, and hexachloroethane. The present study dealt with the reagents, the reaction, and the reaction products, with especial reference to their compositions and persistence. It also examined the problems of reducing the field operation to laboratory scale for chemical and possible future biological investigations.

HC smokes were generated in a series of chamber tests. The smokes and their precursors were characterized physically and chemically to determine the particle size distribution of the smoke and the chemical composition of the smoke-generating materials and the gaseous and particulate products of smoke generation. The chemical studies particularly sought potentially hazardous materials. Only aerosol particles in the respirable region below 10 μm were chemically characterized.

Fifteen M5-HC 30-1b smoke generators were used in the study. Each generator consisted of a canister containing two layers of chemical mixtures of hexachloroethane, zinc oxide, and powdered aluminum of the following approximate compositions (given in parts by weight):

| Reagent | Upper Layer | Lower Layer |
|---------|-------------|-------------|
| HC | 45.5 | 46.5 |
| ZnO | 47.5 | 48.3 |
| Al | 7.0 | 5.2 |

The higher aluminum content of the upper layer facilitated ignition of the mixture.

The inorganic impurities in the reagent mixes were principally cadmium (50 to 1500 ppm by weight) and lead (30 to 900 ppm by weight), with traces of arsenic (a few ppm by weight) and mercury (fractional ppm).

The gaseous products of the smoke generating reaction were collected in a full-scale field operation and in a series of scaled down laboratory exper-

iments; they included:

| | |
|--|--|
| carbon monoxide (CO) | ethylene tetrachloride (C ₂ Cl ₄) |
| hydrogen chloride (HCl) | hexachloroethane (C ₂ Cl ₆) |
| carbonyl chloride (COCl ₂) | hexachlorobenzene (C ₆ Cl ₆) |
| carbon tetrachloride (CCl ₄) | chlorine (Cl ₂) |

Chemical analysis of the smokes indicated that they were predominantly zinc chloride (ZnCl₂), with 1-2% aluminum. Lead and cadmium were also present in concentrations closely similar to the levels present in the zinc oxide components of the original HC mixes.

A mean particle diameter of about 0.3 μm was observed for all aerosols. In typical chamber experiments, 5 min after generation the aerosol concentrations were 1 to 10 x 10⁶ particles cm⁻³, and the aerosol weights were 30-400 mg-m⁻³. With aging, aerosols tended to increase in mean particle size.

Assuming a mean aerosol particle diameter of 0.3 μm, aerosol loadings can be calculated as a function of particle number density. At loadings of 10⁶ particles cm⁻³ or less, half-lives in excess of 25 min can be expected:

| No. of Particles cm ⁻³ | Aerosol Loading | |
|--------------------------------------|--------------------|------------|
| | mg-m ⁻³ | ppm, wt/wt |
| 10 ⁴ | 0.28 | 0.23 |
| 5 x 10 ⁴ | 1.41 | 1.15 |
| 10 ⁵ | 2.82 | 2.3 |
| 5 x 10 ⁵ | 14.1 | 11.5 |
| 10 ⁶ | 28.2 | 23.0 |
| 5 x 10 ⁶ | 141.0 | 115.0 |

It is estimated that the HC generator functions at about 70% efficiency; that is, an aerosol of 142.0 mg total weight requires ≈200 mg of HC reagent.

FOREWORD

IIT Research Institute is pleased to submit this document as the Final Report on the Physical and Chemical Characterization of Hexachloroethane Smokes. This is one phase of a program titled "Physical and Chemical Characterization of Fog Oil Smoke and Hexachloroethane Smoke," U.S. Army Contract No. DAMD 17-78-C-8085. This phase was started on October 1, 1978 and the experimental work was completed on May 31, 1979. This report has been prepared prior to the conclusion of the entire program with the thought that it may be of value to the Army in its studies on the health-related effects of hexachloroethane smokes.

The many technical suggestions contributed by Mr. J. J. Barkley, Jr., the Contract Officer's Technical Representative are gratefully acknowledged.

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SYMBOLS AND ABBREVIATIONS

| | |
|----------------------|--|
| A, Å | Angstrom unit; 10^{-10} meter |
| ASAC | Active Scattering Aerosol Spectrometer, manufactured by the Particle Measuring Systems Co. |
| b | constant term in the linear regression equation, $Y = mx + b$ |
| BT | burn time |
| C | Celsius temperature scale |
| C_i | aerosol mass concentration in Stage i of the P/Z counter |
| cf | cubic foot |
| cm | centimeter, 10^{-2} meter |
| cm^3 , cc | cubic centimeter |
| cm^{-3} , / cm^3 | function per cm^3 , e.g., $g\ cm^{-3} = g/cm^3 =$ grams per cc |
| d | diameter |
| d_{av} | geometric mean particle diameter |
| d_i | midrange diameter of ASAS counter channel |
| \bar{d}_m | mass median particle diameter |
| $D_p 50$ | 50% cutoff size for each P/Z impactor stage |
| f_i | frequency in class i |
| ft | foot, unit of length in the foot-pound-second (fps) system of units |
| g | gram, unit of weight in the centimeter-gram-second (cgs) system of units |
| GC | gas chromatography |
| HC | hexachloroethane, C_2Cl_6 |
| Hz | hertz, frequency, vibrations per second |
| in. | inch, unit of length |
| kg | kilogram, 10^3 grams |
| kph | velocity, kilometers per hour |
| k_i | P/Z counter stage constant |
| l | liter, unit of liquid volume equal to 1000 ml |
| lb | pound, unit of weight in the foot-pound-second system of units |

| | |
|-----------------------------------|--|
| log | logarithm, common logarithm (base 10) |
| ln | logarithm, "natural" logarithm (base e) |
| LN ₂ | liquid nitrogen |
| M | molar |
| m. | constant term in linear regression equation equal to slope of the line |
| m | meter, unit of length in the meter-kilogram-second (mks) system of units |
| m ³ | cubic meter |
| m ⁻³ , /m ³ | function per cubic meter, e.g , g m ⁻³ = g/m ³ = gram per cubic meter |
| ma | milliamperce |
| mg | milligram |
| mgm ⁻³ | milligrams per cubic meter |
| M | midpoint cut off size between P/Z counter stages |
| min | minutes |
| ml | milliliter, unit of liquid volume, equal to 10 ⁻³ liter |
| mm | millimeter, 10 ⁻³ meter |
| MS | mass spectrometer |
| [n] | number of particles per unit volume |
| n _i | number of particles in class "i" |
| ppm | parts per million |
| P/Z | Piezoelectric particle measuring system |
| R | correlation coefficient |
| RH | relative humidity |
| sec | second |
| ss | stainless steel |
| t _{1/2} | time for reduction of aerosol by coagulation to ½ of original number |
| TCD | thermocouple detector |
| torr | barometric unit of pressure; 1 torr is equivalent to a barometric pressure of 1mm of mercury |
| TSP | total suspended particles, mass concentration per indicated volume |
| V | volume, flow rate of air sample in P/Z particle counter |
| wt | weight |
| X _i | mass fraction of aerosol per stage i in P/Z counter |

| | |
|--------------|---|
| Δf_i | change of frequency in class i |
| Δt | time interval |
| σ | standard deviation |
| σ_g | geometric standard deviation |
| σ_i | sensitivity factor for stage i of P/Z counter |
| μg | microgram, 10^{-6} gram |
| μl | microliter, 10^{-6} liter or 10^{-3} cc |
| μm | micrometer or micron, 10^{-6} meter or 10^{-3} mm |

1. INTRODUCTION

The present phase of this investigation involves hexachloroethane (HC) smokes and the physical and chemical characterization of the smokes and their precursor reagents. (A subsequent phase is concerned with fog oil smokes.) The primary objective was to obtain data so that HC aerosol smokes could be effectively generated for studies of mammalian health effects.

The physical characterization yielded information on the size distribution and number concentration of the smoke aerosol particles under conditions of normal use, as well as the possible effects of humidity, aging, concentration, and amount of smoke mix burned. From the chemical characterization it was possible to determine the gaseous and particulate products of the smoke generation. A qualitative and quantitative analysis was made of the gaseous products produced by burning varying amounts of smoke mix and of the aerosol composition of particles in the respirable region, below about 10 μm .

Initially, the physical and chemical properties of the HC smokes were to be determined by burning standard 30-lb field smoke pots in a suitably remote area and sampling the resultant aerosol. The idea, however, was rejected: (1) quantitative correlation between the gases evolved and the mass of aerosol burned would be extremely difficult; (2) the detection of trace gases would be difficult in the field; (3) aerosol size distribution would have to be determined against an uncontrolled natural background; (4) aerosol aging studies would be haphazard, if not impossible, depending on wind conditions; and (5) aerosol-humidity effects would be entirely dependent on atmospheric conditions.

Because of these limitations it was decided to perform virtually all of the studies in the laboratory. Field studies, though limited to a minimum test schedule, were conducted to provide a base for comparison with the laboratory studies.

2. CONCLUSIONS

The laboratory investigation of the composition of the materials used in the military M5-HC Smoke Generator and of the composition of the products of the smoke-generating reactions gave the following information.

M5-HC COMPOSITIONS

1. The HC mixtures are composed principally of hexachloroethane (HC), zinc oxide, and aluminum powder. Two formulations are used in a standard container: an upper layer, consisting of almost equal amounts of HC and zinc oxide and about 7% aluminum, and a similar lower layer, with about 5.2% aluminum. The lower layer forms the bulk of the material. The greater aluminum content of the upper layer induces a faster and hotter reaction and facilitates initiation of the reaction in the lower layer.
2. The principal impurities in the mix are cadmium and lead. Their levels vary widely from lot to lot, from 30 to over 1500 ppm by weight. Trace constituents include mercury and arsenic.

GASEOUS REACTION PRODUCTS

1. The reaction generated the following gases: carbon monoxide (CO), hydrogen chloride (HCl), carbonyl chloride (COCl₂), carbon tetrachloride (CCl₄), ethylene tetrachloride (C₂Cl₄), hexachloroethane (C₂Cl₆), hexachlorobenzene (C₆Cl₆), and chlorine (Cl₂).
2. The most abundant in the laboratory tests was C₂Cl₄, 3-17% of the reagent weight under various reaction conditions, followed by CCl₄ (1-3%), C₂Cl₆ (0.3-5%), COCl₂ (0.1-1%), and C₆Cl₆ (0.4-0.9%).

AEROSOL FORMATION AND PARTICLE SIZE DEPENDENCE

Aerosols were generated in various concentrations and under different humidity conditions.

1. The initial aerosol median particle diameter measured about 0.3 μm.

2. Aerosols tend to grow, depending on concentration. At a concentration of about 1 to 2×10^6 particles cm^{-3} , the aerosol is stable for 20 to 25 minutes. With increasing concentration, aerosol growth accelerates.
3. Aerosol formation and growth appears to be independent of humidity.
4. At low concentrations, aerosols obey a log normal particle size distribution. At higher concentrations, this changes to a multimodal distribution.

AEROSOL COMPOSITION

1. The aerosol particle is predominantly zinc chloride with small amounts of aluminum chloride and traces of lead and cadmium chlorides. The aluminum content is about 1.7% of the zinc. The lead and cadmium concentrations are in approximately the same ratios as in the initial mix.

3. GENERAL DESCRIPTION OF THE HC SMOKE GENERATING COMPOUND

The HC smoke mixture consists of grained aluminum, zinc oxide, and hexachloroethane. The military formula for the HC mixture specifies the following approximate composition¹:

| <u>Ingredient</u> | <u>Wt % (approx.)</u> |
|-------------------|-----------------------|
| Grained aluminum | 6.68 |
| Zinc oxide | 46.66 |
| Hexachloroethane | 46.66 |

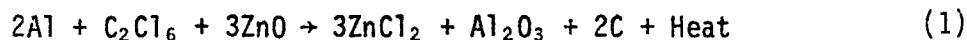
The ratio of zinc oxide to hexachloroethane is maintained between 1.00 and 1.04. The aluminum content may be varied slightly to regulate burning time. The following comparative data are given:

| <u>Aluminum Content, %</u> | <u>Burning Time, sec</u> |
|----------------------------|--------------------------|
| 9.0 | 55 |
| 8.4 | 64 |
| 8.0 | 65 |
| 7.5 | 71 |
| 7.0 | 84 |
| 6.5 | 96 |
| 6.0 | 107 |
| 5.5 | 147 |

The burning rate is clearly sensitive to small variations in the aluminum content of the mixture.

The standard M5-HC smoke generator utilizes two formulations, White Smoke-I, which contains 7-11% aluminum and White Smoke-II, which contains 5-7% aluminum¹ (Table 1). The generator is assembled with Mix I in an upper layer adjacent to the ignition system to facilitate the initiation of the reaction. Mix II forms the bulk of the mix.

The basic chemical reaction taking place in the HC mixture is:



in which the ZnCl_2 leaves the reaction zone as a hot vapor and, on cooling below the condensation point of ZnCl_2 , produces the desired aerosol.

¹ Field Manual: Military Chemistry and Chemical Compounds. Army FM 3-9/Air Force AFR 355-7, October 1975.

Table 1

NATIONAL MILITARY ESTABLISHMENT FORMULA FOR WHITE SMOKE-I

| Ingredient | Hexachloroethane ¹ | Zinc oxide | Aluminum, grained |
|--|-------------------------------|------------------------------|---------------------|
| Specification No. | JAN-M-235 (class a) | JAN-Z-291 (grade I, class a) | JAN-A-512 (grade I) |
| Particle size (U.S. Standard sieve sizes--Fed. Spec. RR-S-366) | | | |
| Percentage Passing | (Residue to Pass) | | |
| No. 25 sieve | 95 minimum | | |
| No. 50 sieve | | | |
| No. 100 sieve | | | |
| No. 200 sieve | | | |
| No. 270 sieve | 99.9 minimum | | 100 minimum |
| No. 325 sieve | 99.0 minimum | | 97 minimum |
| Parts by weight | 45.5 ± 0.2 | 47.5 ± 0.2 | 7.0 |

¹Any hexachloroethane which is discolored, emits acid fumes, or has a wet, oily appearance, shall not be used in the manufacture of the smoke mixture, even if the material has previously passed the acceptance tests.

The ratio of grained aluminum to the other ingredients in the smoke mixture may be varied, between a minimum of 7.0 parts and a maximum of 11.0 parts, to meet the delay and burning time requirements specified. However, the ratio of zinc oxide to hexachloroethane shall be maintained in the proportion prescribed in the table. Before loading the mixture into smoke munitions, test the mixture as follows: Prepare at least five M8 grenades in accordance with United States Army Specifications 96-111-69, using 500 grams of smoke mixture, and pressing in one or more increments at a total pressure of 2,000 pounds, dead load. Ignite the grenade and burn. The average burning time of the grenade shall be between 1½ and 2 minutes. Not more than one of the grenades shall burn outside these limits.

Toluoline red toner (Fed. Spec. TT-T-562), in a quantity not exceeding 20 percent of the total mix, may be added to the smoke mixture to facilitate inspection.

All of the zinc oxide and hexachloroethane are roughly premixed and put through a high-speed hammermill provided with a discharge screen. This operation is performed to give an intimate mixture of hexachloroethane and zinc oxide and reduce the tendency for the zinc oxide to "ball up" in the subsequent blending operation. All of the base mixture and aluminum are added together in a baffled tumbling mixer and blended for 20 minutes.

The above formulation replaced standard JAN-STD-500 dated 5 August 1948 and was incorporated into Cmil. Dwg. No. 8143-1-1, March 1962.

WHITE SMOKE-II

| Ingredient | Hexachloroethane ¹ | Zinc oxide | Aluminum, grained |
|--|-------------------------------|------------------------------|---------------------|
| Specification No. | JAN-M-235 (class a) | JAN-Z-291 (grade I, class a) | JAN-A-512 (grade I) |
| Particle size (U.S. Standard sieve sizes--Fed. Spec. RR-S-366) | | | |
| Percentage Passing | (Residue to Pass) | | |
| No. 25 sieve | 95 minimum | | |
| No. 50 sieve | | | |
| No. 100 sieve | | | |
| No. 200 sieve | | | |
| No. 270 sieve | 99.9 minimum | | 100 minimum |
| No. 325 | 99.0 minimum | | 97 minimum |
| Parts by weight | 46.5 ± 0.2 | 48.3 ± 0.2 | 5.2 |

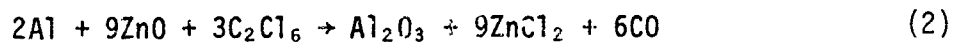
¹Any hexachloroethane which is discolored, emits acid fumes, or has a wet, oily appearance, shall not be used in the manufacture of the smoke mixture, even if the material has previously passed the acceptance tests.

²The ratio of grained aluminum to the other ingredients in the smoke mixture may be varied between a minimum of 5.0 parts and a maximum of 7.0 parts, to meet the delay and burning time requirements specified. However, the ratio of zinc oxide to hexachloroethane shall be maintained in the proportion prescribed in the table. Zinc borate (U.S. Army Spec. 96-111-112), in a quantity not exceeding 1.5 percent of the total mixture, may be added to the smoke mixture as follows: The zinc borate shall be mixed intimately with a portion of the zinc oxide, in the ratio of one part of zinc to two parts of zinc oxide, and then blended with the balance of the mixture.

The balance of the zinc oxide and the hexachloroethane are rough mixed and put through a high-speed hammermill provided with a discharge screen. This operation is performed to give an intimate mixture of the chloroethane and zinc oxide and reduce the tendency for the zinc oxide to "ball up" in the subsequent blending operation. All of the base mixture and the zinc borate submixture, and the aluminum are added together in a baffled tumbling mixer and blended for 20 minutes.

The above formulation replaced standard JAN-STD-501 dated 5 August 1948 and was incorporated into Cmil. Dwg. No. 8143-1-2.

With the stoichiometry indicated, the reaction produces substantial amounts of carbon, which tends to darken the smoke. To minimize free carbon formation, the following stoichiometry may be considered:



This gives a mixture composed of Al, 3.6% by weight, ZnO, 48.94%, and C_2Cl_6 , 47.46%, which does not differ much from that specified for White Smoke Mixes I and II. However, both laboratory and field studies with HC smoke mixes indicated considerable carbon formation and the actual stoichiometry is probably intermediate between reactions 1 and 2.

Field pots of HC smoke require the use of a starter mix to provide the initial heat to get the mixture well ignited. The following mixture¹ is typical of the variety of starter available: silicon, potassium nitrate, charcoal, iron oxide, grained aluminum, cellulose nitrate, and acetone. This mixture has some of the burning properties of both thermite and black powder.

As noted earlier, the zinc chloride is vaporized in the hot reaction and on cooling below the condensation point nucleates to form the aerosol, which absorbs water rapidly from the surrounding atmosphere to produce a particle size distribution ideal for obscuration in the visible. Small amounts of aluminum trichloride and hexachloroethane are also lost as vapor.¹ In a differential thermal analysis study of the reactions between hexachloroethane and zinc oxide,² the data suggested the formation of carbon tetrachloride, ethylene tetrachloride, phosgene, and a zinc oxychloride, $2\text{ZnO} \cdot \text{ZnCl}_2$. In this study reaction temperatures below 800°C were used, which are considerably lower than those occurring in the HC smoke pot reaction. The present studies showed that temperatures in the smoke pot during combustion rose above 1500°C .

Zinc chloride has a strong affinity for water and without stringent precautions it is difficult to obtain it completely moisture free. The $\text{ZnCl}_2 - \text{H}_2\text{O}$ phase diagram is shown in Figure 1. At least two basic chlorides have been identified, ZnOHCl and $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$.³ Both are thermally unstable, and decompose at temperatures as low as 65°C to give ZnCl_2 , ZnO , and H_2O .

² A. Jarvis. The Combustion Reactions of Pyrotechnic White Smoke Composition. *Combustion and Flame*, 14, 313 (1970).

³ J.W. Hoffman and I. Lauder. *Austr. J. Chem.*, 21, 1439 (1968).

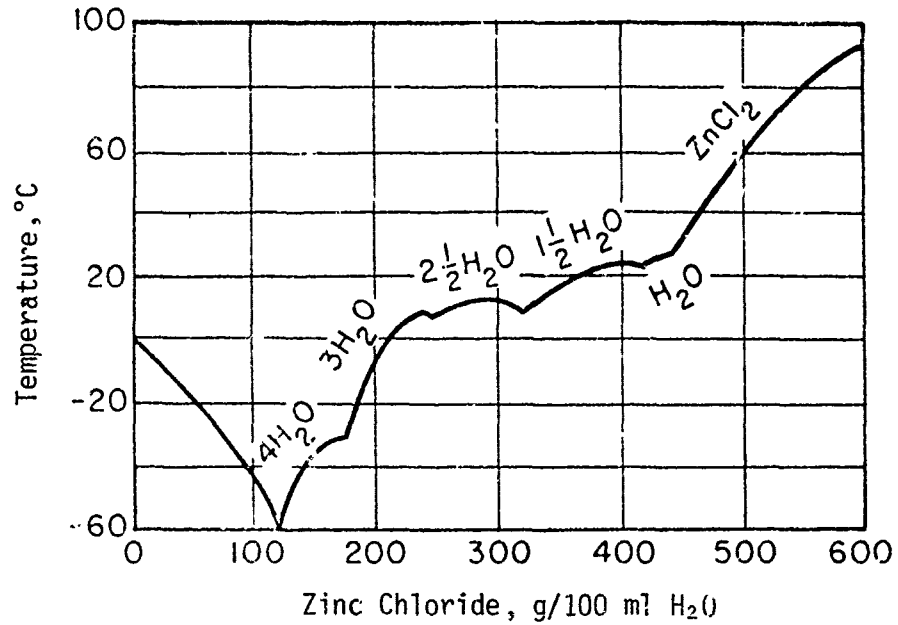
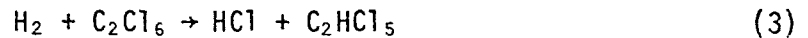


Figure 1. The hydrates of zinc chloride. The hydrates do not separate from the solution unless the temperature is 28°C or lower. Above 28°C the anhydrous salt is in equilibrium with the solution.¹

Finally, HC mixtures containing up to 0.6% moisture are considered reasonably stable.¹ Above this level decomposition is said to occur. It is hypothesized that the water dissolves some chloride from impurities in the zinc oxide or hexachloroethane. The chloride solution then slowly attacks the aluminum, producing nascent hydrogen, which reacts with the HC according to the equation:



This produces more HCl, which further attacks the aluminum and induces more decomposition. Although this mechanism seems reasonable, it does not appear to have been verified.

4. THE HC AEROSOL GENERATORS

Fifteen standard M5-HC 30-lb smoke pots delivered by the Army were used as aerosol generators in this study. They arrived in five lots, three HC smoke pots per lot.

The lot designations and dates of loading, taken from the labeling on the canisters, are given in Table 2. Each canister was assigned an IITRI sample number to assure identification of individual canisters in each lot. The gross weight of each pot was then recorded. The net weight of pyrotechnic mix was calculated from the weight of an empty canister retrieved after firing one of the smoke pots.

TABLE 2. HC SMOKE POT DATA

| Lot No. | Canister No. | Weight, kg (lb) | | Density** g/cm ³ |
|----------------------------|--------------|-----------------|-------------|--------------------------------|
| | | Gross | Net* | |
| PB 06003-11 Loaded 9/59 | 1.1 | 15.8 (35.0) | 14.4 (31.8) | 1.8 |
| | 1.2 | 15.0 (35.25) | 14.5 (32.0) | 1.8 |
| | 1.3 | 15.8 (35.0) | 14.4 (31.8) | 1.8 |
| PB 5467-3 Loaded 12/54 | 2.1 | 16.1 (35.5) | 14.6 (32.3) | 1.8 |
| | 2.2 | 15.8 (35.0) | 14.4 (31.8) | 1.8 |
| | 2.3 | 16.1 (35.5) | 14.6 (32.3) | 1.8 |
| PB 96003-12 1/59 | 3.1 | 16.1 (35.5) | 14.6 (32.3) | 1.8 |
| | 3.2 | 16.3 (36.0) | 14.8 (32.8) | 1.9 |
| | 3.3 | 15.8 (35.0) | 14.4 (31.8) | 1.8 |
| PB 96003-1 12/58 | 4.1 | 16.7 (36.75) | 15.2 (33.6) | 1.9 |
| | 4.2 | 16.4 (36.25) | 15.0 (33.0) | 1.8 |
| | 4.3 | 16.1 (35.5) | 14.8 (32.8) | 1.8 |
| PB 5467-6 12/54 | 5.1 | 16.7 (36.75) | 15.2 (33.6) | 1.9 |
| | 5.2 | 16.3 (36.0) | 14.8 (32.8) | 1.8 |
| | 5.3 | 16.1 (35.5) | 14.8 (32.3) | 1.8 |

* Estimated from the weight of the can (1.462 kg or 3.2 lb); this was derived by measuring the weight of a can after firing, including residue (3.990 kg), then subtracting the weight of the residue (2.528 kg or 5.57 lb, ≈17% of the original charge).

** Estimated from the calculated volume of HC mix and the net weight.

SAMPLE EXTRACTION

To obtain access to the contents of the smoke pots, it was necessary to disarm and open each container. The construction of the pot and the ignition system and the sequence of events in the opening process are detailed in Appendix C.

Although the HC mix was packed firmly in the pot, it proved to be very friable. Samples for analysis were obtained by drilling vertically through the mix with a 19-mm (3/4-in.) manually operated auger wood bit. Samples were drawn up from different levels and were stored for analysis in polyethylene bags.

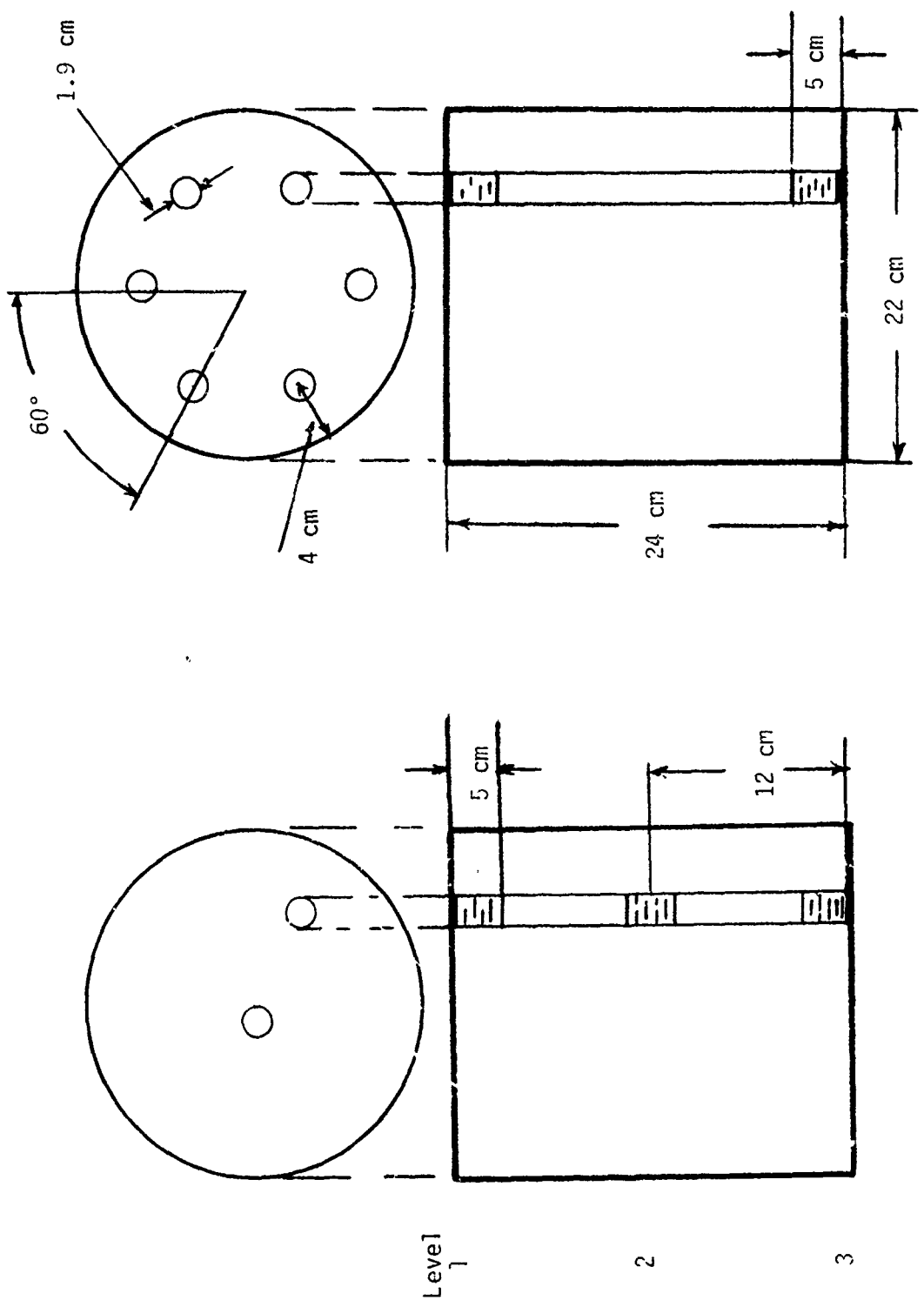
To extract a sample from a pot, a site was selected at the surface of the exposed mix and drilled vertically. Samples were removed at the top, midpoint, and bottom of the channel. Figure 2-A illustrates the procedure. A numbering sequence was adopted to designate each level (Table 2). For example, in Canister No. 1.1, the three sample levels, from top to bottom, are numbered 1.1.1, 1.1.2, and 1.1.3.

In addition, one pot, Canister No. 2.1, was sampled at six radial positions at the top and bottom levels to determine angular distribution in composition. The sampling pattern is shown in Figure 2-B. In all cases a core approximately 5 cm long was extracted at each site.

CHEMICAL ANALYSIS OF THE HC REAGENT MIXTURE

The chemical analysis determined the presence of aluminum, zinc oxide, and hexachloroethane (the major constituents) and lead, cadmium, mercury, and arsenic (the minor constituents). The minor constituents were selected because they are elements frequently associated with zinc as impurities.

The major constituents were analyzed in 10 of the 15 smoke pots, using two canisters from each of the five lots (Table 2). Each canister was analyzed at three levels, top, middle, and bottom. In addition, Canister No. 2.1 was analyzed in six radial positions, at top and bottom levels.



(A)

(B)

Figure 2. Vertical and radial locations of HC canister sampling sites for sampling analysis. Sampling shown in B was limited to canister 2-1.

The Major Constituents: Aluminum, Zinc Oxide, and Hexachloroethane

Analytical Procedures--

For the inorganic analyses, the organic material was first extracted from the HC mixture. One gram of the HC sample was weighed in a capped centrifuge tube. The organics were extracted in three 5-ml washings with methylene chloride and one 5-ml washing with pentane. After each washing, the solution was centrifuged at 2300 rpm for 5 min to ensure that no suspended ZnO or Al particles remained in the discarded liquid. After separation, the sample was dried at 100°C for 1 hr and weighed to determine the percent inorganics in the sample. The percent of total inorganics is shown in Table 3.

The ZnO and Al were dissolved by weighing a 100-mg sample of the inorganic material into a beaker and adding 5 ml of 50% (vol/vol) HCl in deionized water. In some cases, 50% HNO₃ was used and was found to give the same results as obtained when using HCl. The beaker was covered, heated, and allowed to reflux for 2 hr. A ZnO and Al standard was prepared by weighing 83 mg of dry ZnO (Fischer ACS Certified Reagent) and 17 mg of 30 mesh Al (Fischer) into a beaker and dissolving it in the same manner as the HC samples. The dissolved samples and standards were filtered to remove insoluble material and then diluted to 100 ml with deionized water. (An insoluble black residue was often found in the HC samples, hence the filtering procedure.)

Atomic absorption spectroscopy was used to determine the major inorganic constituents. For the ZnO determination, 10 ml of the solution was diluted to 100 ml three successive times to give a final dilution of 1:1000. Five, 10, 15 ml, and 15 ml of this ZnO standard were each diluted to 100 ml. Thus the ZnO standards contained 1.245, and 0.830, and 0.415 µg ZnO/ml (1.0, 0.67, and 0.33 ppm Zn). Two ml of HCl (or HNO₃) were added at the last dilution so that the samples and standards were in 2% HCl (or HNO₃).

A 20-ml aliquot of the sample solution plus 2 ml 12.7% NaCl was diluted to 100 ml with deionized water for the Al determination. The Al standards were prepared by diluting 30, 20, and 10 ml aliquots of the dissolved Al standard with 2 ml of the NaCl solution to 100 ml. The resulting Al standards contained 51, 34, and 17 µg Al/ml with 1000 ppm Na to control the ionization of Al in the flame.

Table 3
COMPOSITION OF THE MAJOR COMPONENTS IN THE HC SMOKE POT SAMPLES
TAKEN FROM THE TOP, MIDDLE AND BOTTOM OF MIX

| Sample | % Inorganic | No. | % Al in Inorganic | % ZnO in Inorganic | % Al in HC | % ZnO in HC | % C ₂ O ₆ by Difference | % C ₂ O ₆ by GC |
|--------|-------------|-----|-------------------|--------------------|------------|-------------|---|---------------------------------------|
| 1.1.1 | 50.7 | a | 10.1 | 89.9 | 5.0 | 45.1 | 49.3 | 43.0 |
| | | b | 9.6 | 87.9 | | | | |
| 1.1.2 | 53.3 | a | 10.0 | 89.1 | 5.3 | 47.4 | 46.7 | 44.5 |
| | | b | 9.9 | 88.7 | | | | |
| 1.1.3 | 52.7 | a | 9.0 | 89.4 | 4.7 | 47.2 | 47.3 | 44.3 |
| | | b | 9.0 | 89.7 | | | | |
| 1.2.1 | 54.0 | a | 10.2 | 89.1 | 5.6 | 48.1 | 46.0 | 42.0 |
| | | b | 10.3 | 88.9 | | | | |
| 1.2.2 | 51.8 | a | 9.7 | 87.2 | 5.0 | 45.5 | 43.2 | 45.0 |
| | | b | 9.5 | 88.6 | | | | |
| 1.2.3 | 51.7 | a | 9.8 | 88.4 | 5.0 | 46.0 | 43.3 | 43.5 |
| | | b | 9.6 | 89.0 | | | | |
| 2.1.1 | 50.4 | a | 11.0 | 87.8 | 5.9 | 47.0 | 46.6 | 44.5 |
| | | b | 11.0 | 88.1 | | | | |
| 2.1.2 | 50.1 | a | 9.8 | 88.2 | 4.9 | 44.3 | 49.9 | 44.5 |
| | | b | 9.8 | 88.6 | | | | |
| 2.1.3 | 49.3 | a | 9.7 | 87.8 | 4.8 | 43.0 | 50.7 | 43.0 |
| | | b | 9.8 | 86.7 | | | | |
| 2.2.1 | 53.3 | a | 11.3 | 85.1 | 6.1 | 45.7 | 46.7 | 45.5 |
| | | b | 11.5 | 86.4 | | | | |
| 2.2.2 | 50.4 | a | 10.3 | 86.4 | 5.2 | 43.9 | 49.6 | 48.5 |
| | | b | 10.2 | 87.8 | | | | |
| 2.2.3 | 50.7 | a | 10.3 | 87.5 | 5.2 | 44.4 | 49.3 | 47.0 |
| | | b | 10.3 | 87.5 | | | | |
| 3.1.1 | 54.3 | a | 11.3 | 87.3 | 6.0 | 47.3 | 45.7 | 46.0 |
| | | b | 11.1 | 86.9 | | | | |
| 3.1.2 | 52.3 | a | 10.4 | 87.6 | 5.3 | 45.7 | 47.7 | 45.0 |
| | | b | 9.8 | 87.3 | | | | |
| 3.1.3 | 53.7 | a | 9.3 | 89.0 | 5.2 | 47.8 | 46.3 | 47.0 |
| | | b | 10.0 | 88.9 | | | | |
| 3.2.1 | 54.6 | a | 14.2 | 85.4 | 7.7 | 46.6 | 45.4 | |
| | | b | 14.1 | 85.2 | | | | 42.5 |
| 3.2.2 | 53.2 | a | 12.0 | 88.3 | 6.3 | 46.9 | 46.8 | |
| | | b | 11.8 | 88.0 | | | | 42.0 |
| 3.2.3 | 53.8 | a | 9.7 | 97.2 | 5.2 | 46.9 | 46.2 | 45.0 |
| | | b | 9.7 | 87.2 | | | | |
| 4.1.1 | 53.3 | a | 8.7 | 99.9 | 4.6 | 47.7 | 46.7 | 45.5 |
| | | b | 9.9 | 89.1 | | | | |
| 4.1.2 | 52.9 | a | 9.5 | 90.9 | 4.9 | 48.0 | 47.1 | 48.5 |
| | | b | 9.0 | 90.6 | | | | |
| 4.1.3 | 52.0 | a | 9.4 | 90.7 | 5.0 | 47.2 | 48.0 | 48.0 |
| | | b | 10.0 | 90.7 | | | | |
| 4.2.1 | 54.4 | a | 10.2 | 86.1 | 5.6 | 47.1 | 45.6 | 46.5 |
| | | b | 10.3 | 87.0 | | | | |
| 4.2.2 | 51.2 | a | 8.4 | 88.8 | 4.4 | 45.3 | 48.8 | 46.5 |
| | | b | 9.0 | 88.2 | | | | |
| 4.2.3 | 50.2 | a | 9.0 | 88.0 | 4.6 | 44.5 | 49.8 | 47.5 |
| | | b | 9.0 | 89.1 | | | | |
| 5.1.1 | 50.8 | a | 10.2 | 90.4 | 5.2 | 45.8 | 49.2 | 49.0 |
| | | b | 10.3 | 90.0 | | | | |
| 5.1.2 | 52.4 | a | 10.3 | 89.2 | 5.3 | 47.0 | 47.6 | 46.0 |
| | | b | 9.9 | 90.2 | | | | |
| 5.1.3 | 53.7 | a | 10.2 | 90.0 | 5.5 | 48.2 | 46.3 | 46.0 |
| | | b | 10.2 | 89.7 | | | | |
| 5.2.1 | 54.9 | a | 11.7 | 89.0 | 6.3 | 49.1 | 45.1 | 46.5 |
| | | b | 11.2 | 89.8 | | | | |
| 5.2.2 | 53.7 | a | 10.0 | 89.5 | 5.5 | 47.9 | 46.3 | 44.5 |
| | | b | 10.5 | 89.0 | | | | |
| 5.2.3 | 52.4 | a | 10.7 | 89.7 | 5.6 | 46.8 | 47.6 | 47.0 |
| | | b | 10.6 | 89.0 | | | | |

Estimated uncertainties in the various measurements; % Inorganic ±2%; % Al in Inorganic ±2%; % ZnO in Inorganic ±2%; % C₂O₆ by GC ±2%.

Results--

The results of the inorganic analysis of 10 smoke pots are presented in Table 3. The additional digit (1, 2, or 3) appended to the pot identification numbers indicates that the particular sample was obtained from the top, middle, or bottom, respectively, of the smoke pot mixture (Figure 2). Two samples of the extracted inorganic material designated (a) and (b), were used in the analyses at each level. The amount of C_2Cl_6 in the mixture was determined by difference, Column 8 (100 - % inorganic) and also by gas chromatography, Column 9. The details of the gas chromatography are described later.

In summary, a given mass of the HC mix was extracted with methylene dichloride and a known volume of the extracted material was injected into the chromatograph. Duplicate analyses were run on different smoke pot samples using different standards for each series of experiments. These results for the duplicate analyses are presented in Table 4 together with their overall estimated experimental uncertainties. It is apparent that the two essentially independent analyses, as far as the samples and standards are concerned, are identical within the error limits of the determinations. The average of the two sets of determinations is shown in Table 3 together with the overall estimated error associated with each determination. In comparing the HC fraction determined by difference and by GC in Table 3, agreement in many cases is within the estimated uncertainties of the determinations. However, in some instances, there are substantial differences. In these cases the GC values are generally preferred since in the centrifuging procedure it was possible that some of the insoluble material may have been decanted in the extracting medium, which would have the effect of making the HC concentration larger than it should be. Indeed, the general trend is for the GC determination of the HC content to be smaller than that obtained by difference.

In 7 of the 10 canisters, the Al analyses indicated a higher concentration of the metal in the top layer than in the lower layers. According to the specifications for the HC mixes given in Table 1, the top layer should contain a higher proportion of the metal, $\approx 7\%$, than the lower layer, $\approx 5.2\%$. Since our data did not show an Al content consistently higher in the top layer than in the lower layers, the possibility exists that inhomogeneities in the mix might be responsible. To test this, two samples were taken from Canister 2.1 at each

TABLE 4. HEXACHLOROETHANE CONTENTS OF HC SMOKE PCTS,
WEIGHT PERCENT OBTAINED BY GAS CHROMATOGRAPHY

| Canister No. | 1st Analysis | 2nd Analysis |
|--------------|--------------|--------------|
| 1.1.1 | 42 ± 3 | 44 ± 2 |
| 1.1.2 | 44 ± 3 | 45 ± 2 |
| 1.1.3 | 43 ± 3 | 45 ± 2 |
| 1.2.1 | 42 ± 3 | 42 ± 2 |
| 1.2.2 | 43 ± 3 | 47 ± 2 |
| 1.2.3 | 45 ± 3 | 42 ± 2 |
| 2.1.1 | 43 ± 3 | 46 ± 2 |
| 2.1.2 | 44 ± 3 | 45 ± 2 |
| 2.1.3 | 40 ± 3 | 46 ± 2 |
| 2.2.1 | 44 ± 2 | 47 ± 2 |
| 2.2.2 | 48 ± 2 | 49 ± 2 |
| 2.2.3 | 48 ± 2 | 46 ± 2 |
| 3.2.1 | 42 ± 3 | 43 ± 2 |
| 3.2.2 | 42 ± 3 | 42 ± 2 |
| 3.2.3 | 47 ± 3 | 45 ± 2 |
| 4.1.1 | 42 ± 2 | 49 ± 2 |
| 4.1.2 | 49 ± 2 | 48 ± 2 |
| 4.1.3 | 47 ± 2 | 49 ± 2 |
| 4.2.1 | 47 ± 2 | 46 ± 2 |
| 4.2.2 | 46 ± 2 | 47 ± 2 |
| 4.2.3 | 46 ± 2 | 49 ± 2 |
| 5.1.1 | 48 ± 2 | 50 ± 2 |
| 5.1.2 | 47 ± 2 | 45 ± 2 |
| 5.1.3 | 43 ± 2 | 49 ± 2 |
| 5.2.1 | 46 ± 2 | 47 ± 2 |
| 5.2.2 | 46 ± 2 | 43 ± 2 |
| 5.2.3 | 48 ± 2 | 46 ± 2 |

of the six radial positions at levels 2.1.1 and 2.1.3 (Figure 2-B) and Al analyses were made according to the following analytical procedures:

A 250-mg HC sample was placed in a beaker and the HC was allowed to sublime over a weekend. The small amount of residual organic material was oxidized by 10 ml of 50% nitric acid used to dissolve the Al and ZnO. The solution was filtered and diluted to 100 ml. The Al standards were prepared by diluting a 1000 ppm Al atomic absorption standard. The ionization of the Al was controlled by adding 4 ml of 9.4M $Zn(NO_3)_2$ and 5 ml HNO_3 to the standard. In this way both the samples and the standards were of similar concentration, approximately 1000 ppm Zn and 5% HNO_3 . The results of these analyses are presented in Table 5.

TABLE 5. ALUMINUM ANALYSIS FROM CANISTER 2.1, SAMPLED RADially AT THE TOP AND BOTTOM

| Top Samples | % Al | Bottom Samples | % Al |
|-------------|------|----------------|------|
| A a* | 6.4 | A a | 5.2 |
| b* | 6.2 | b | 5.1 |
| B a | 6.6 | B a | 4.7 |
| b | 6.9 | b | 4.2 |
| C a | 7.1 | C a | 5.2 |
| b | 6.8 | b | 5.3 |
| D a | 5.9 | D a | 5.0 |
| b | 6.0 | b | 5.7 |
| E a | 6.3 | E a | 5.5 |
| b | 6.4 | b | 5.2 |
| F a | 6.4 | F a | 5.5 |
| b | 5.7 | b | 5.4 |
| Mean | 6.39 | Mean | 5.17 |
| σ | 0.40 | σ | 0.38 |

* a and b designate duplicate samples at each site.

Generally, analyses a and b agree with each other to within the estimated precision of 2%, thus giving credence to our estimated error for the measurement. However, in a given layer, the aluminum content covers quite a large range, 7.1-5.7% in the top layer and 4.2-5.7% in the bottom layer. These data appear to indicate inhomogeneity in the mix. From the radial analyses, the mean Al contents of the top and bottom layers are $6.39 \pm 0.4\%$ and $5.17 \pm 0.38\%$, respectively. These numbers compare satisfactorily with the values reported in Table 3 for Samples 2.1.2 and 2.1.3 at 5.9% and 4.8%, respectively.

The Minor Constituents--Lead, Cadmium, Mercury, and Arsenic

Analytical Procedures--

The HC canisters were analyzed for four trace elements--lead, cadmium, mercury, and arsenic. The lead and cadmium were analyzed by IITRI personnel. The preliminary analyses for arsenic and mercury indicated concentrations below 5 ppm; the final analyses were made by Trace Elements, Inc., Park Ridge, Illinois.

The Pb and Cd analyses were performed on duplicate samples taken at three levels from nine canisters so that members of all five lots were included. Sample preparation was essentially the same as described above for ZnO, except that the solution was not highly diluted. Both nitric and hydrochloric acid were used to dissolve the sample mix to determine if the limited solubility of $PbCl_2$ had any effect on the final analytical results. As was subsequently found, the results were the same, irrespective of the acid used. Atomic absorption spectroscopy (described later) was used for the quantitative determination of the metals.

Results--

Complete analytical data on the Pb and Cd are given in Appendix B. A representative summary of the results for all four components is given in Table 6.

The results of the As and Hg analyses presented in Table 6 reflect an analytical error of about 10%.

TABLE 6. ARSENIC, MERCURY, CADMIUM, AND LEAD CONTENTS IN HC CANISTERS

| Canister | As | Hg ppm (% by weight) | Cd | Pb |
|----------|-------------------------------|------------------------------|--------------|---------------|
| 1.1 | 0.134(0.13x10 ⁻⁴) | 0.478(4.8x10 ⁻⁵) | 53.3(0.005) | 858.0(0.086) |
| 2.1 | 3.33 (3.3 x10 ⁻⁴) | 0.524(5.2x10 ⁻⁵) | 1523.0(0.15) | 50.7(0.005) |
| 3.1 | 4.98 (5.0 x10 ⁻⁴) | 0.441(4.4x10 ⁻⁵) | 299.0(0.03)* | 631.7(0.063)* |
| 4.1 | 4.48 (4.5 x10 ⁻⁴) | 0.601(6.0x10 ⁻⁵) | 296.7(0.03) | 678.7(0.068) |
| 5.1 | 1.39 (1.4 x10 ⁻⁴) | 0.346(3.5x10 ⁻⁵) | 805.7(0.08) | 50.2(0.005) |

* Canister 3.2 was used in these tests.

No identifiable trends were observed in the distributions of the Cd and Pb in single canisters or among the members of each of the five lots. However, the concentrations varied widely from lot to lot in a somewhat consistent pattern. In qualitative terms, the occurrence of high levels of Cd is invariably associated with low levels of Pb and vice versa.

A relation between the Pb and Cd concentrations was examined.* When concentrations are expressed in ppm by weight, the data are described by the linear relation,**

$$\text{Pb} = -0.632\text{Cd} + 817.98$$

which fits the experimental data from nine canisters with a correlation coefficient of 0.914.

* Appendix B

** This correlation was suggested by Mr. J. J. Barkely, Jr. of the U.S. Army Medical Bioengineering R&D Laboratory.

5. M5-HC CANISTER FIELD TEST

GENERAL FIELD TEST OBSERVATIONS

Essentially all the physical and chemical characterization studies of the HC smokes were performed in the laboratory. It was, however, considered desirable to obtain some physical and chemical data on a smoke generated under field conditions. Accordingly, Canister No. 2.3 was taken to our Kingsbury facility and was ignited in an open outdoor area.

The day was overcast with a temperature of -2°C . The wind was from the south-southwest, variable, blowing at 5-13 kph. The ground had a thin covering of snow. No measurement of relative humidity was available. The smoke pot was laid on its side (the standard operating procedure) and ignited. A distinct cyclic variation in the vigor of the burning was apparent, as judged by the size of the flame issuing from the smoke pot orifice and the density of the dirty white smoke issuing from the pot. The smoke paled in color as it moved away from the pot. At the termination of the burn, a dark patch was evident on the ground, extending about 2 m in front of the orifice. This dark material appeared to be unburned carbon.

A linear burning rate of about 1 cm/min was estimated from the change in the color of the paint on the smoke pot exterior. It was also noted that the mix did not burn evenly, progressing more rapidly in some places along the length of the canister than in others. In some places, the exterior of the canister became red hot. A thermocouple probe in the pot failed at about 1500°C . A rather voluminous residue remained in the canister at the conclusion of the burn. Subsequent weighing determined that about 17% of the initial charge or about 252 g was residue. The total burn time was 22 min. Photographs of the burning HC canister are shown in Figure 3.

CHEMICAL ANALYSIS OF FIELD TEST VAPORS

During the first 5 min of the smoke pot burn, samples of the atmosphere containing the aerosol were collected using five 3-liter Pyrex flasks fitted with high-vacuum stopcocks. The flasks were evacuated to about 10^{-3} torr

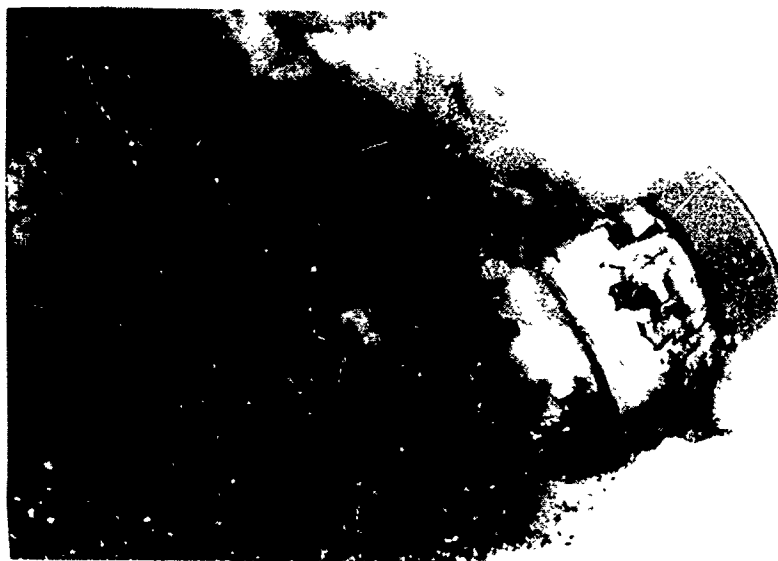


Figure 3. HC smoke generation.

in the laboratory and sealed on the day of the tests prior to their transport to the test site. Four of the flasks were filled by inserting the open end of the 7.5 cm glass tube connected to the stopcock into the dense smoke column about 15 cm from the orifice of the canister and opening the stopcock, allowing the gas and aerosol to be aspirated into the flask. After filling, the stopcock was closed. One sample was obtained about 2 m from the burning pot orifice. The samples were returned to the laboratory for analysis.

The details of the analytical procedures are described in Section 5; the results are shown in Table 7.

PARTICLE SIZE ANALYSIS OF FIELD TEST AEROSOL

Two instruments were used to obtain particle size distribution on the HC smoke aerosol: a Royco light scattering particle counter and an Anderson impactor. The useful particle size ranges of these instruments are 5-0.3 μm and 9-0.65 μm (diameters) respectively. They were selected without benefit of prior information on the likely size distribution of the HC aerosol.

The instrumentation was mounted in the back of an open "pickup" truck using a portable generator to provide electrical power. Ambient background aerosol levels were rather high, seriously complicating interpretation of the data. Because of the mobility of the cloud it was necessary to follow it. Sampling with the Royco was further complicated since the particle concentrations were greater than its upper range of about 1000 cm^{-3} .

Analysis of data from the impactor studies indicated that about 71% of the sample was collected on the after absolute filter, indicating that instrumentation with capabilities to measure smaller particles would be needed for the laboratory studies. Data obtained with the Royco are shown in Figure 4. Details of the particle size analysis and its relationship to the laboratory studies are presented later. For the present, it is noted that the data shown in the figure are almost certainly biased to a larger particle size distribution than applies to the true HC aerosol, a consequence of two factors: the ambient background levels and the inability of the instrumentation to measure particles below the 0.5-0.3 μm range. Subsequent laboratory studies showed this lower region to be important in the total aerosol size distribution pattern.

TABLE 7. CHEMICAL ANALYSIS OF VAPOR REACTION PRODUCTS
FROM FIELD TEST OF 30-LB MILITARY HC SMOKE POT
IITRI Pot No. 2.3*

| Distance from Mount of Pot, cm | CO ppm** | HCl ppm | COCl ₂ ppm | CCl ₄ ppm | C ₂ Cl ₄ ppm | C ₂ Cl ₆ ppm | C ₆ Cl ₆ ppm |
|-----------------------------------|-------------|------------|--------------------------|-------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ~15 | <1 | 1128 | 30 | 33 | 36 | (nd)*** | (nd) |
| ~15 | <1 | 1958 | 16 | 8 | 9 | (nd) | (nd) |
| ~15 | <1 | 5693 | 30 | 57 | 192 | 40 | 103 |
| ~15 | <1 | 6822 | 20 | 36 | 81 | 40 | 95 |
| ~200 | <1 | 1137 | 1 | 1 | 2 | (nd) | (nd) |

*Analytical procedures are described in Section 5. Experimental errors for HCl are estimated at ±7%. The error for COCl₂, based on calibration measurements, is ±12%, for C₂Cl₄, ±8%, and for the others, ±4 to 6%. (See Table 8).

**Parts per million by volume.

***(nd) - not determined

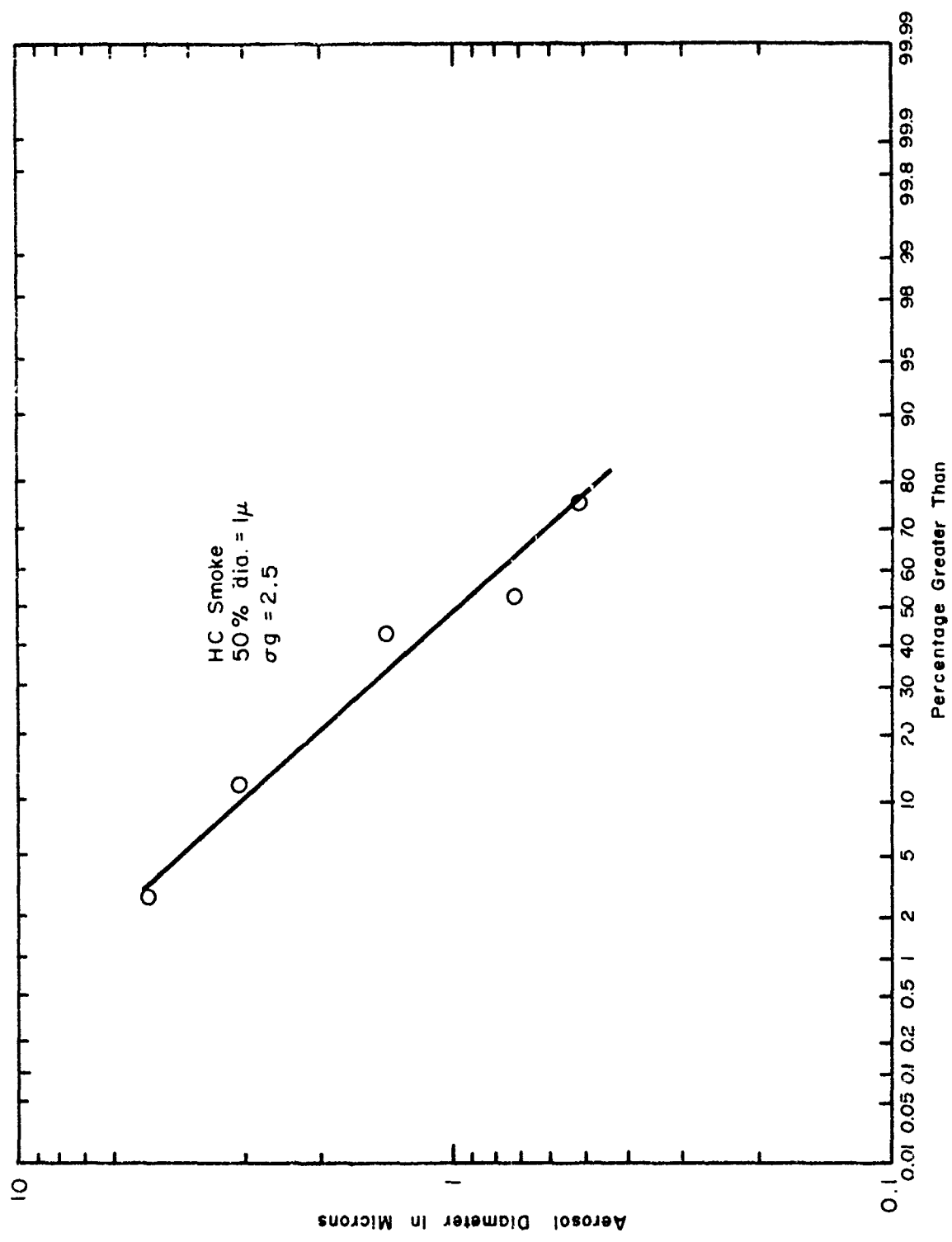


Figure 4. Aerosol size distribution data from field tests.

6. LABORATORY STUDIES OF THE HC REACTION

The major reactions taking place in the HC smoke mix to produce the $ZnCl_2$ aerosol were discussed in Section 3 of this report. However, because of incomplete mixing of the reactants and the heterogeneous nature of the reaction, several trace gas species would be expected to form in the reaction. Thus the very presence of relatively easily pyrolyzable materials such as C_2Cl_6 in the mixture should almost surely produce C_2Cl_4 and CCl_4 at the temperature of the reaction and some of these materials will escape from the combustion zone intact. A series of experiments was therefore initiated to analyze the trace gas species formed during the burning of the HC smoke mix.

EXPERIMENTAL PROCEDURES

The object of this phase was to obtain both qualitative and quantitative data on the trace gas species formed during the combustion of the HC mix. Accordingly, small samples of HC mixtures (0.5-2 g) were burned in a sealed 5-liter flask. The experiments were initiated before the delivery of the M5-HC smoke pots, and the first reagents used were laboratory mixtures consisting of 44.5% C_2Cl_6 , 9% Al, and 46.5% ZnO. Later experiments used the M5-HC mix (Section 5, Table 11).

The experimental combustion reactor is shown in Figure 5. HC samples were weighed into a suitable container. In some experiments an 8-mm diameter Pyrex test tube about 5 cm long was used; in others, a small stainless steel reactor with a restricted opening, fabricated for easy assembly and disassembly, was used. The stainless steel reactor more nearly simulated the military smoke pot design. The HC mixture was ignited electrically using a short nichrome wire spiral embedded in the top of the mix. The flask was sealed with a standard 45/50 taper joint and Teflon sleeve. Provision was made to fill the flask with air at known humidity using vacuum line procedures.

ANALYTICAL PROCEDURES

The HC smoke trace gases were analyzed by gas chromatography. The gases included carbon monoxide (CO), phosgene (carbonyl chloride, $COCl_2$), trichloroacetyl chloride (CCl_3COCl), carbon tetrachloride (tetrachloromethane, CCl_4), tetrachloroethylene (C_2Cl_4), hexachloroethane (C_2Cl_6), hexachlorobenzene (C_6Cl_6),

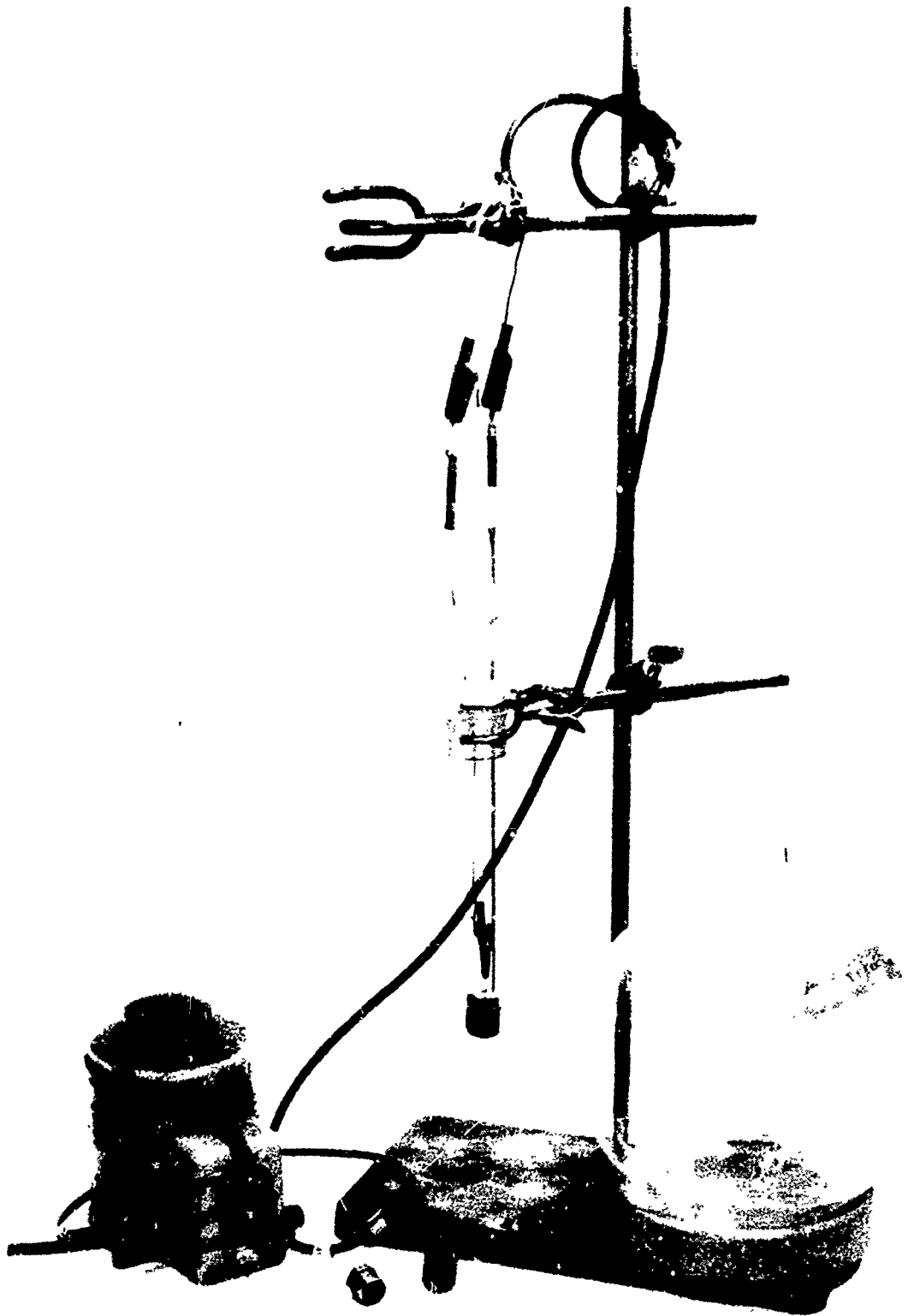


Figure 5. Laboratory glass reactor system used for collecting trace gases from HC smoke mix combustion.

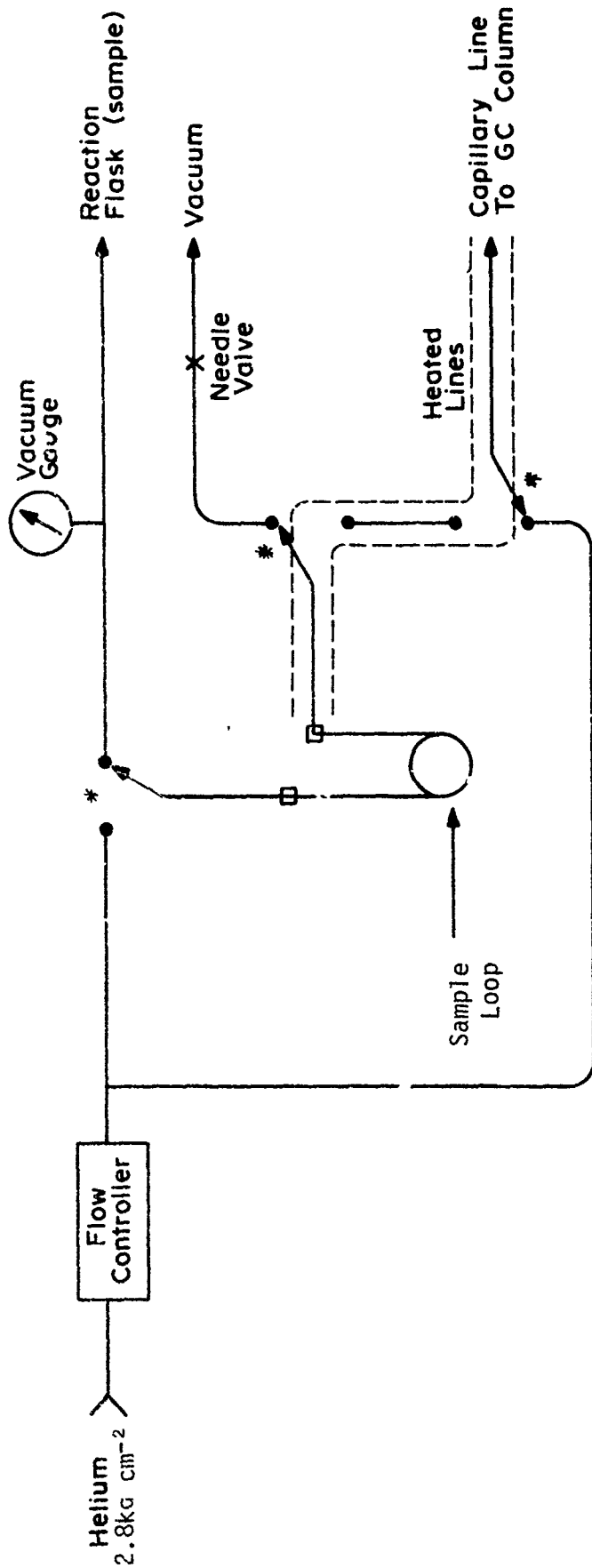
and chlorine (Cl_2). Hydrogen chloride (HCl) was measured from its infrared spectrum.

A Hewlett Packard Model No. 5710A gas chromatograph with thermal conductivity detection was used for the analyses in conjunction with the sampling loop shown in Figure 6.

Carbon monoxide was quantitated by analyzing a 3-5 ml gas sample on a gas chromatograph equipped with a thermal conductivity detector and a 6m x 3mm stainless steel column packed with 5 Å molecular sieve held at 120°C.

The analysis of COCl_2 , CCl_4 , and C_2Cl_4 was accomplished by trapping approximately 5% of a 5-liter reaction flask gas sample in a stainless steel loop held at -176°C. In this procedure the sealed reaction flask was connected to a vacuum line that was linked to a compact stainless steel tubular loop via a vacuum stopcock. The entire line, external to the reaction flask was evacuated. The loop was cooled in liquid nitrogen (LN_2) and the flask stopcock was opened, causing its contents to condense in the loop. The loop was then "warmed" to -130°C with a LN_2 - pentane mixture and the air, CO_2 , and HCl were pumped off. The stainless steel loop containing the remaining components from the flask was then connected to the gas chromatograph and heated to approximately 100°C. For this analysis the gas chromatograph was fitted with a thermal conductivity detector and a 3 m x 3 mm. stainless steel column packed with a diatomaceous support coated with 3% polytrifluoropropyl silane (SP-2401). The column was temperature programmed (linearly) from -10° to 150°C at 16°/min. Trace amounts of trichloroacetyl chloride (CCl_3COCl) and possibly dichloroacetylene (C_2Cl_2) were seen in all samples. The estimates of C_2Cl_6 and C_6Cl_6 in the smoke were obtained by analyzing on the same column a methylene chloride wash of the reaction flask. The reaction flasks were washed with three 100-ml portions methylene chloride. The extracts were combined, filtered through prewashed glass wool, and concentrated to 3-ml volumes with a N_2 gas stream at room temperature. Two-five μl aliquots were injected into the gas chromatograph for analysis.

Hydrogen chloride gas was quantified from its infrared spectrum. A sample of gas from the reactor was introduced into a 10 cm path length absorption cell and the HCl vibration-rotation bands were monitored at 3100-2700 cm^{-1} . The HCl analyses have an estimated error of $\pm 7\%$.



All 304 Stainless Steel Construction

Sample Loop:

3.8mm x 40cm SS Line; 3.8cm Turns In Line To Form A 3.8cm Dia. Circle And Two 12cm Long Arms; End Of Arms Inserted Into The Valve Fittings.

* Valves In Sample Position
 (Valves In Alternate Position During Analysis)
 3 Valves Required, Whitey Stainless Steel
 3-Way Ball Valves 1/4" Compression Fittings

Figure 6. Schematic diagram of sampling loop used in the GC analysis of HC combustion products.

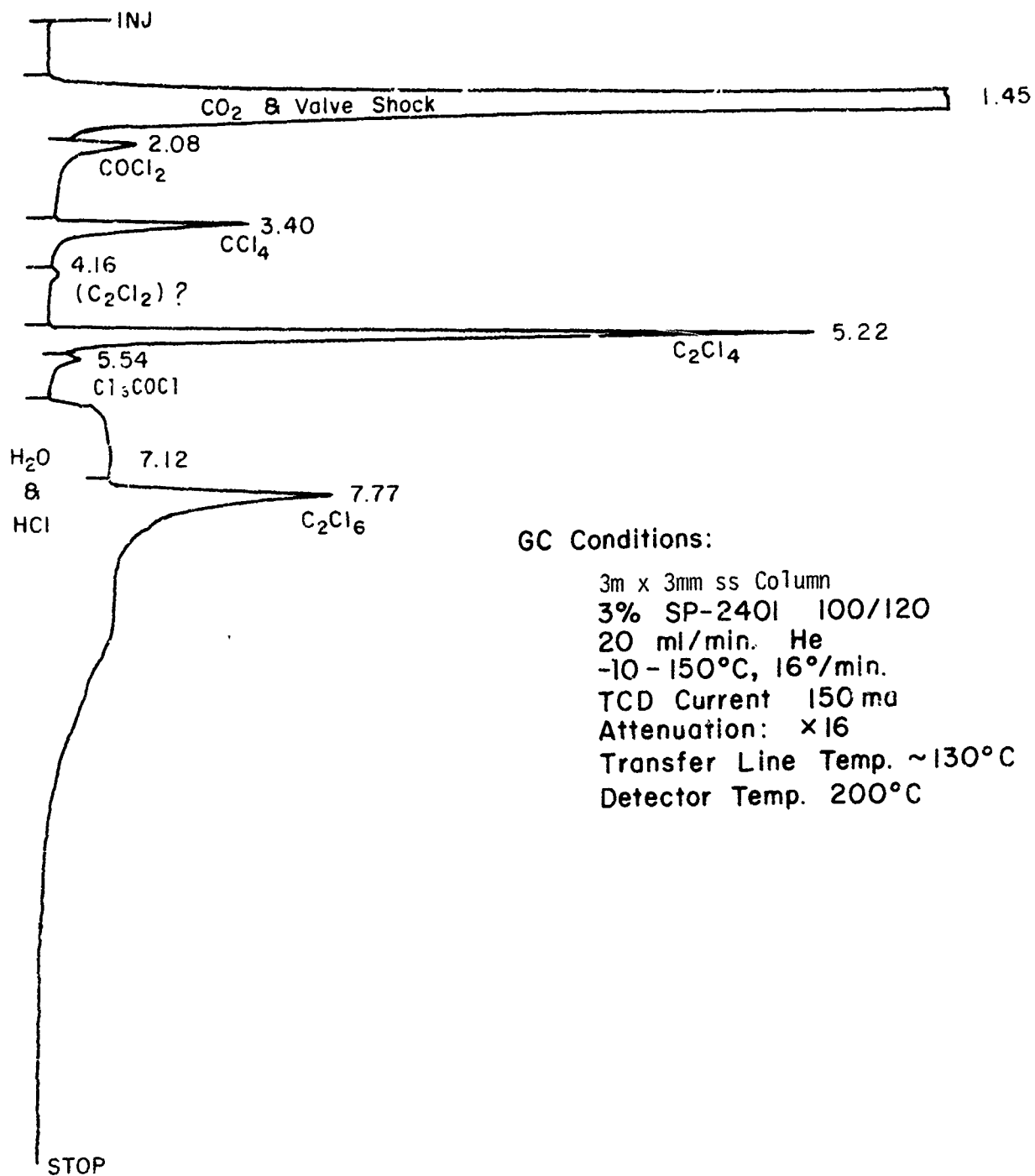


Figure 7. Typical gas chromatogram of the trace gas constituents of the HC smoke mix combustion.

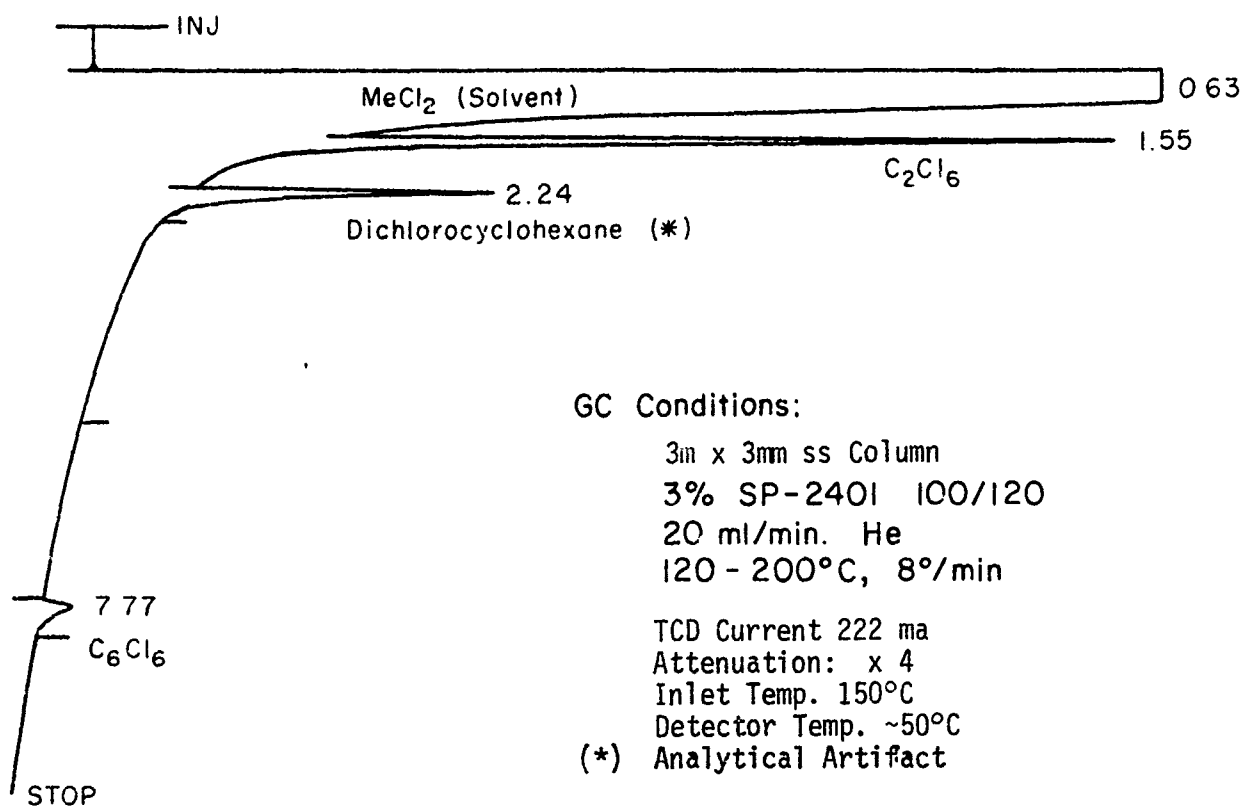


Figure 8. Typical gas chromatogram of the extracted material from HC smoke mix combustion.

TABLE 8. STANDARD CURVE CALIBRATION AND DEVIANCES FOR GC ANALYSIS

| Compound | x | y | % Deviance From Calculated Line |
|--------------------------------|--------|--------|---------------------------------|
| COCl ₂ | 24606 | 11758 | -7 |
| | 25469 | 11636 | -11 |
| | 58374 | 32044 | +12 |
| | 121824 | 57293 | -2 |
| | | | (±12%) $x = (y - 1126)/0.47$ |
| CCl ₄ | 32672 | 43174 | +1 |
| | 33818 | 41894 | -5 |
| | 77510 | 103460 | +2 |
| | 161760 | 212632 | 0 |
| | | | (±5%) $x = (y + 611)/1.32$ |
| C ₂ Cl ₄ | 32168 | 30946 | -1 |
| | 33205 | 32773 | +1 |
| | 75514 | 80256 | 0 |
| | 159264 | 173831 | -8 |
| | | | (±8%) $x = (y + 4840)/1.12$ |
| C ₂ Cl ₆ | 12 | 11273 | 0 |
| | 16 | 16490 | +3 |
| | 26.5 | 34103 | -4 |
| | 41 | 52432 | +1 |
| | | | (±4%) $C = (y + 5763)/1438$ |
| C ₆ Cl ₆ | 10 | 1040 | 0 |
| | 14 | 5590 | +6 |
| | 22.5 | 21443 | -4 |
| | 35 | 39002 | +1 |
| | | | (±6%) $C = (y + 14874)/1553$ |

x = pressure (mm Hg) x concentration (ppm)
 C = concentration (micrograms)
 y = response (integrator tics)

Typical chromatograms are shown in Figures 7 and 8 and calibration data in Table 8. In Figure 8, the presence of dichlorocyclohexane ($C_6H_{10}Cl_2$) is indicated. This material was identified from GC/MS studies and was not expected as a reaction product of the HC combustion. Investigation of this situation eventually led to the discovery that the dichlorocyclohexane was being formed by chlorine attack on the Apiezon hydrocarbon stopcock grease used in sealing the 5-liter reaction flask. To further test these findings, Cl_2 was deliberately added to the reaction flask and indeed dichlorocyclohexane was formed. Once this fact was established, subsequent studies were made with halocarbon grease on the stopcock and this eliminated the formation of the dichlorocyclohexane. It was noted the the dichlorocyclohexane peak was found in the chromatograms obtained from the HC smoke field test trace gas analyses, indicating the presence of free chlorine.

Studies were initiated to allow quantitation of the evolved chlorine from the HC smoke combustion. Initially, HC smoke and chlorine gas standard samples were introduced into a mass spectrometer through a batch inlet system. The chlorine was not seen in any of the samples; however, hydrogen chloride was produced as a result of chlorine degradation. The chlorine was found to be too reactive in the stainless steel batch inlet system for an analysis to be made.

A second attempt to quantitate chlorine was made by the use of a gas chromatographic system similar to that used for the analysis of the other gas constituents in the HC smoke. The gas chromatographic system consisted of a stainless steel cryogenic inlet trap with associated valves, a thermal conductivity detector, and a 2.5 m x 6 mm stainless steel column packed with 10% SF-96 on 60/80 mesh Chromosorb T. The helium carrier flow rate was 80 ml/min and the column temperature was maintained at 30°C. Repeated injections of chlorine gas were required to saturate reactive or catalytic sites prior to the analysis of the calibration standard and HC smoke samples each working day. This system was found to be linear and reproducible for the quantitation of chlorine gas. In Figure 9 a typical chlorine gas analysis chromatogram is presented.

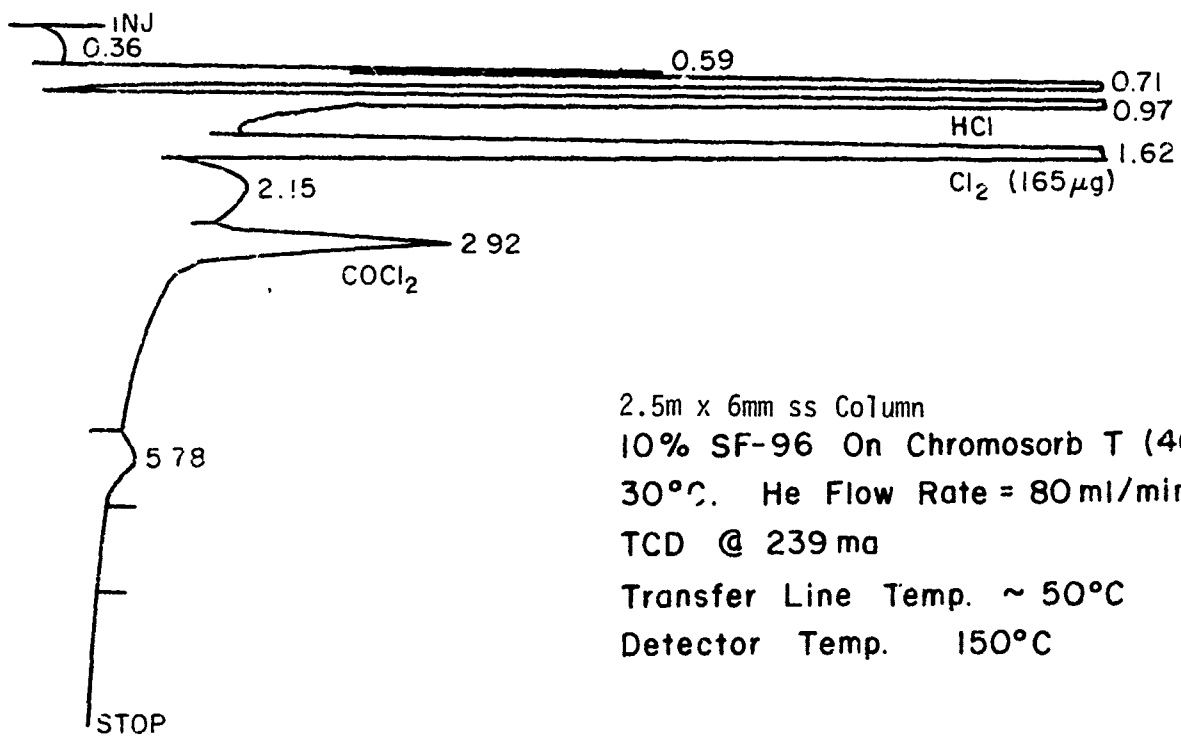


Figure 9. Typical gas chromatogram obtained for the chlorine analysis in the combustion of the HC smoke mixture.

ANALYTICAL RESULTS

The results of some typical analyses on the combustion products of the HC smoke mixes are shown in Tables 9, 10, and 11.* The data shown in Tables 9 and 10, obtained before we received the military smoke pots, used the laboratory simulated smoke mix (see Section 6). In the first series of experiments (Table 9), open glass reactors were used to contain the HC mix and only marginal humidity control was maintained. The values quoted may be regarded at best as a qualitative guide to the actual humidity. Comparison of data for the various experiments indicates a considerable variation in the product yields. In a qualitative sense this is not surprising since the visual appearance of the reaction was somewhat erratic. In some cases, small lumps of the burning mix were ejected from the container, whereas in others this was not observed. Consequently, the data does not allow us to draw any conclusions about product yield and humidity. In Table 10, similar data for the combustion of the laboratory smoke mix in the restricted opening steel container are presented. Again, the indicated humidity should only be taken as a qualitative guide to the actual value. In general, there is less variability in the product yield in these experiments than in those run previously in the open glass containers, probably reflecting a more uniform combustion process. The chlorocarbon concentrations are somewhat lower than in the former experiments, possibly indicating better overall combustion. The yields of CO in the steel container experiments appear to be generally higher than in the glass, suggesting that a somewhat higher temperature prevailed in the earlier experiments.

Table 11 shows the combustion product analysis obtained from burning the military HC mix (Sample No. 3.1) in restricted opening steel reactors. In these experiments, the humidity values are reliable since vacuum line techniques were used to meter gases into the reaction flask. Also, infrared analysis was used to estimate the amount of water vapor in the gas phase after the aerosol combustion. The chlorocarbon yields are generally higher and CO yields are lower than in the comparable experiments using the laboratory mix. This may be attributed to a lower burning temperature in the military mix (Al content $\approx 6\%$) than in the laboratory mix (Al content $\approx 9\%$).

* The indicated precision of the analyses is calculated from the calibration measurements (Section 6, Table 8).

TABLE 9. ANALYSIS OF GASEOUS COMBUSTION PRODUCTS FROM H₂ SMOKE IN OPEN GLASS REACTION

| HC Reagent* g | Relative Humidity % | Product Collected, mg/g of reagent | | | | | | C ₆ Cl ₆ |
|---------------------|---------------------------|------------------------------------|--------|-------------------|------------------|--------------------------------|--------------------------------|--------------------------------|
| | | CO | HCl | COCl ₂ | CCl ₄ | C ₂ Cl ₄ | C ₂ Cl ₆ | |
| 0.69 | 41 | 23 | 9 | 1.3 | 2 | 12 | 49 | 11 |
| 1.33 | 41 | 23 | 4 | 1.0 | 3 | 8 | 44 | 5 |
| 2.16 | 44 | 31 | 2 | 1.0 | 4 | 9 | 8 | 3 |
| 2.17 | 44 | 43 | (nd)** | 0.2 | 0.4 | 1 | 3 | 3 |
| 1.04 | 70 | 44 | 14 | 1.0 | 0.6 | 4 | 11 | 6 |
| 0.62 | 72 | 51 | 19 | 1.9 | 1.6 | 6 | 20 | 11 |
| 2.16 | 82 | 66 | 22 | 0.4 | 0.8 | 2 | 4 | 3 |
| GC Analysis error % | | | | ±12 | ±5 | ±8 | ±4 | ±6 |

* Laboratory HC mixture = 44.5% C₂Cl₆, 46.5% ZnO, 9% Al.

** (nd) - not determined

TABLE 10. ANALYSIS OF GASEOUS REACTION PRODUCTS FROM HC REACTION IN RESTRICTED OPENING STEEL REACTOR

| HC Reagent* g | Relative Humidity % | Product Collected, mg/g of reagent | | | | | | | |
|------------------|---------------------------|------------------------------------|-----|-------------------|------------------|--------------------------------|-----------------------|--------------------------------|--------------------------------|
| | | CO | HC1 | COC1 ₂ | CC1 ₄ | C ₂ Cl ₄ | CC1 ₃ COCl | C ₂ Cl ₆ | C ₆ Cl ₆ |
| 1.70 | 39 | 62 | 14 | 0.2 | 0.4 | 1.2 | (nd) | (nd) | <0.1 |
| 1.70 | 40 | 108 | 25 | 1.6 | 4.7 | 9.2 | 2.4 | 15 | 6 |
| 1.70 | 48 | 57 | 3 | 0.2 | 1.1 | 3.1 | <0.03 | 4 | 6 |
| 1.70 | 48 | 52 | 0 | 0.1 | 0.3 | 0.7 | <0.03 | 3 | 3 |
| 1.70 | 48 | 51 | 0 | 0.1 | 0.1 | 0.4 | <0.03 | 3 | <0.1 |
| 1.70 | 49 | 68 | 4 | 0.3 | 0.6 | 2.0 | <0.03 | 4 | 4 |
| 1.06 | 78 | 63 | 6 | 0.5 | 1.0 | 3.0 | 0.2 | 8 | 5 |
| 1.70 | 78 | 80 | 25 | 0.3 | 0.2 | 0.2 | <0.03 | 3 | <0.1 |
| 1.70 | 80 | 78 | 10 | 0.1 | 0.2 | 0.5 | 0.06 | 4 | <0.1 |
| 1.04 | 82 | 54 | 7 | 0.4 | 2.1 | 4.1 | 0.2 | (nd) | 6 |

* Laboratory HC mixture = 44.5% C₂Cl₆, 46.5% ZnO, 9% Al.

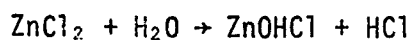
** (nd) - not determined

TABLE 11. ANALYSIS OF GASEOUS REACTION PRODUCTS FROM HC REACTION
IN RESTRICTED OPENING STEEL-REACTOR

| HC Reagent* g | Relative Humidity % | Product Collected, mg/g of reagent | | | | | | | |
|------------------|---------------------------|------------------------------------|------|-------------------|------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| | | CO | HCl | COCl ₂ | CCl ₄ | C ₂ Cl ₄ | C ₂ Cl ₆ | C ₆ Cl ₆ | C ₆ Cl ₆ |
| 1.61 | 0 | 37 | 34 | 11 | 20 | 59 | 3 | 4 | 4 |
| 1.60 | 0 | 21 | 16 | 0.6 | 14 | 36 | <1 | 4 | 4 |
| 1.60 | 0 | 29 | 16 | 1 | 12 | 35 | 3 | 4 | 4 |
| 1.60 | 24 | 9 | 4 | 1 | 9 | 32 | 3 | 4 | 4 |
| 1.60 | 24 | 21 | <0.3 | 4 | 19 | 48 | 7 | 4 | 4 |
| 1.60 | 24 | 31 | 14 | 2 | 18 | 49 | 8 | 4 | 4 |
| 1.60 | 48 | 27 | <0.3 | 3 | 20 | 47 | 10 | 5 | 5 |
| 1.60 | 48 | 24 | <0.3 | 2 | 19 | 64 | 11 | 5 | 5 |
| 1.60 | 48 | 18 | <0.3 | 2 | 25 | 56 | 31 | 9 | 9 |
| 1.60 | 71 | 25 | <0.3 | 3 | 33 | 108 | 49 | 9 | 9 |
| 1.60 | 71 | 15 | 0.3 | 4 | 16 | 142 | 3 | 4 | 4 |
| 1.60 | 71 | 22 | <0.3 | 1 | 11 | 130 | 3 | 4 | 4 |

* Military HC Mixture No. 3.1.

It should be noted that in this last series of experiments, HCl yields were highest at zero relative humidity and decreased markedly to essentially zero at the higher humidity. This observation was at first a little puzzling since it was originally thought that the HCl formation might be due to a high-temperature gas-phase reaction of the type:



in which high humidity would favor HCl production; alternatively, it might be due to the hydrolysis of COCl_2 , where high humidity again favors HCl production. The observed lack of HCl at high humidity does not appear to support such possibilities. Subsequent investigation of this phenomenon provided a likely answer. It was found that if the HCl analysis was made directly after ignition of the mix at 24% relative humidity, an HCl level could be established, but that if a period of time elapsed this level would decrease. At 48% relative humidity, unless the HCl analyses were obtained immediately after ignition of the sample all the HCl essentially disappeared. It thus appears likely that at moderate relative humidities, the HCl initially formed is absorbed by the zinc chloride-water aerosol particles, and based on the available data, an equilibrium is attained quite rapidly. In view of these findings, it is not possible to determine if the ambient humidity has any effect on the amount of HCl produced in the combustion of the smoke mix.

TABLE 12. CHLORINE GAS ANALYSIS IN MILITARY HC SMOKE

| Reaction* | Cl_2 Concentration** |
|-----------|---|
| 2-23 | (11 ± 1 mg Cl_2 /1.60 g reagent) 7 mg Cl_2 /g reagent |
| 3-9 | (30 ± 3 mg Cl_2 /1.60 g reagent) 19 mg Cl_2 /g reagent |
| 3-12 | (7.5 ± 1 mg Cl_2 /1.60 g reagent) 5 mg Cl_2 /g reagent |
| 3-13 | 5.0 ± 0.5 mg Cl_2 /1.60 g reagent 3 mg Cl_2 /g reagent |

* Analyses of smokes of four different laboratory reactions of 1.60 g samples of IITRI Sample 3.1 at a relative humidity of approximately 0%.

** Chlorine concentration errors are estimated from calibration data, which indicated an analytical precision ± 10%.

In Table 12 some typical chlorine analyses are presented. Since the presence of chlorine in the combustion products was not established until near the end of the investigation, Cl analyses were not made in the experiments presented in Tables 9, 10, and 11. However, the peak in the chromatograms subsequently identified as dichlorocyclohexane was observed in all these experiments in which Apiezon grease was used on the stopcock of the reaction flask, indicating the formation of chlorine in these experiments as well.

ANALYSES

A straightforward comparison of the analyses of the combustion products found in the field test reported earlier and in the laboratory studies is not possible. The laboratory results are in essence absolute quantities, the amount of a given species formed per unit mass of HC smoke mix burned, whereas the field measurements give the concentrations of a given species found in the ambient air close to the mouth of the burning smoke pot. Under these circumstances, the best that can be done is to make qualitative observation about the relative amounts of materials formed.

For convenience, the average concentrations and product yields obtained in the field test and laboratory reactor studies are presented in Table 13.

TABLE 13. COMPARISON OF FIELD TEST AND LABORATORY REACTOR ANALYSES OF COMBUSTION GASES FROM HC SMOKE MIX

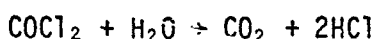
| Component | Relative Concentrations Normalized to C ₂ Cl ₄ | | Volumetric Gravimetric | | Absolute Laboratory Concentrations** |
|--------------------------------|--|------------|------------------------|------------|--------------------------------------|
| | Field* | Laboratory | Field* | Laboratory | |
| CO | <0.016 | 1.89 | <0.003 | 0.32 | 23 |
| HCl | 52.3 | 1.38 | 11.5 | 0.31 | 22 |
| COCl ₂ | 0.30 | 0.07 | 0.18 | 0.04 | 3 |
| CCl ₄ | 0.42 | 0.27 | 0.39 | 0.25 | 18 |
| C ₂ Cl ₄ | 1.0 | 1.0 | 1.0 | 1.0 | 72 |
| C ₂ Cl ₆ | 0.625 | 1.17 | 0.85 | 0.17 | 12 |
| C ₆ Cl ₆ | 1.55 | 0.04 | 0.27 | 0.07 | 5 |
| Cl ₂ | - | 0.28 | - | 0.12 | 9 |

* Calculated from data in Table 7.

** Averages of values given in Table 11.

For purposes of comparison, both the field test and laboratory reactor data have been normalized to $C_2Cl_4 = 1$. On this basis, for CCl_4 , and C_2Cl_6 the relative amounts found in the field test and the laboratory studies agree to within a factor of two. With the other components, however, the relative quantities differ by larger amounts, CO (>100), HCl (40), $COCl_2$ (4), and C_6Cl_6 (40). Two factors may be responsible for some of the discrepancies, 1.) the very high temperature in the HC canister during the reaction, and 2.) the different sequence of events between experiment and analysis. The HC canister is estimated to have reached a temperature near $1500^\circ C$, as indicated by the partial fusion of the container and the failure of a thermocouple. The smaller laboratory experiments possibly reached comparable temperatures at the center but not at the reaction borders or the container walls. The gases collected in the M5-HC canister experiment were stored for several days prior to analysis. The laboratory-generated gases were analyzed immediately after generation.

The apparent absence of CO in the field sample could possibly be due to the reaction $CO + Cl_2 \rightarrow COCl_2$. This reaction is used commercially at $200^\circ C$ in the presence of activated charcoal to produce $COCl_2$. As noted earlier, a considerable amount of carbon was formed in the HC smoke combustion, and indeed the inside surfaces of all the sampling flasks were darkened. It is possible that over the time period involved significant amounts of $COCl_2$ could have been formed. In the presence of water vapor, a significant amount of the phosgene could be expected to hydrolyze to HCl, thus:



This mechanism would also qualitatively account for the increased amount of $COCl_2$ found in the field test compared to the laboratory reactor. A possible problem with the above rationalization is that it requires about 100-fold greater amounts of chlorine to be formed in the reaction in the field than the laboratory studies would indicate. It is possible that zinc chloride absorbed on the carbon may promote the reaction, $ZnCl_2 + H_2O \rightarrow ZnOHCl + HCl$. Indeed, assuming a relative humidity of $\approx 50\%$, more than enough water vapor would be available to account for the observed HCl.

The relative amount of hexachlorobenzene found in the field test was considerably greater than that found in the laboratory study. This finding could possibly be attributed to the higher temperature in the military smoke pot than in the small laboratory reactor, since higher temperatures would be expected to produce more dichloroacetylene, the most likely precursor of hexachlorobenzene. A peak on the GC chart shown on Figure 7 has been tentatively assigned to C_2Cl_2 . However, this is at best speculative. Perhaps more reasonably, the high temperature in the HC canister may have led to the formation of more free chlorine.

In conclusion, it must be admitted that agreement between the gaseous product analyses from the field test and laboratory HC combustion studies is not very good. Unfortunately, the results obtained from the field test study were probably compromised by the long interval between actual sample collection and analysis, and so the observed differences between CO, HCl, and $COCl_2$ may be more apparent than real. The results for C_6Cl_6 appear to indicate a higher reaction temperature in the field than in the laboratory. Qualitatively, however, there can be little doubt that HC combustion does result in the formation of all the species shown in Table 13.

7. CHAMBER STUDIES OF THE HC AEROSOL

In this series of experiments, HC smokes were generated using reduced scale "minipot" reactors charged with HC mixture taken from the M5-HC military pots. Aerosol generation and aerosol aging experiments were performed in a spherical chamber with a volume of 96.5 m³ (3000 cf). The aerosols were removed from the chamber and chemically analyzed to determine their inorganic components, including the two major impurities, lead and cadmium, and characterized to establish the effects of aerosol concentration, humidity, variations in the source reagents, and aging.

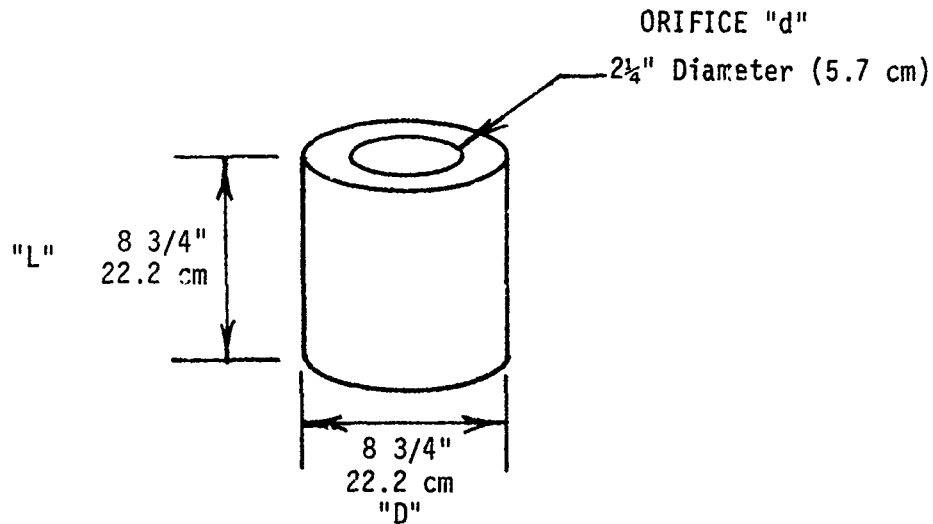
EXPERIMENTAL PROCEDURES

There were basically two constraints in designing the miniature smoke pots: (1) the aerosol loadings in the chamber were to amount to 10⁶- 10⁷ particles cm⁻³, a range in which the lower end would be expected to be fairly stable, whereas the higher end would show rapid agglomeration; and (2) the minipot geometry should be suitably scaled in relation to the M5-HC 30-lb pot.

In the absence of detailed information about the burning behavior of the smoke pots, it was decided to scale them geometrically. Assuming that the burning rate is sensitive to pressure, it should scale approximately as the ratio of the burning area to the nozzle area. It was further assumed that the mix would exhibit "cigarette" burning,* and that the burning area would be proportional to the square of the inside diameter of the can. The nozzle area would be proportional to the square of the diameter of the small opening in the center of the can. This is shown schematically in Figure 10 with the derived scaling factors. The design of the model smoke pots is shown in Appendix D, Drawings SP-A-1 through 3. The assembled and disassembled smoke pots are shown in Figures 11 and 12, respectively. This construction was found durable and a given pot was used repeatedly after disassembly and cleaning. Eventually the nozzle orifice showed signs of erosion and at that point was replaced.

Direct ignition of the HC composition was difficult. The procedure adopted in this study utilized two elements. An igniter mix of 18% by weight of Al powder and 82% of WO₃ were placed on top of the HC mix. The upper layer

* "Cigarette" burning was observed in the field experiment with the M5-HC Pot Number 2.3 (Section 5).



Scale Factors

Weights of HC reagent mix in the scale-down minipots were selected to yield reasonable smoke concentrations. These weights were used to derive the minipot inside dimensions by assigning a constant ratio of pot to orifice area and using the density of 1.8 g/ml for the density of HC. Then $L = D$, $D^3 = W/1.4$, and $D^2/d^2 = 15.2$, where W is the weight of reagent in the pot. Four minipot sizes were fabricated in approximate conformity with these dimensions.

MINIPOT DIMENSIONS

| Pot No. | Diameter, D cm | Height, L cm | Orifice, d cm | Volume cm ³ | Estimated Aerosol Concentration in Sphere, mg/m ³ |
|---------|-------------------|-----------------|------------------|---------------------------|--|
| 1 | 2 | 4.0 | 0.5 | 12 | 200 |
| 2 | 3 | 3.3 | 0.8 | 25 | 400 |
| 3 | 3.8 | 4.4 | 1.1 | 50 | 800 |
| 4 | 8.4 | 9.2 | 2.5 | 500 | 8000 |

Figure 10. Design parameters of the miniaturized smoke pots.



Figure 11. The assembled miniaturized smoke pot.

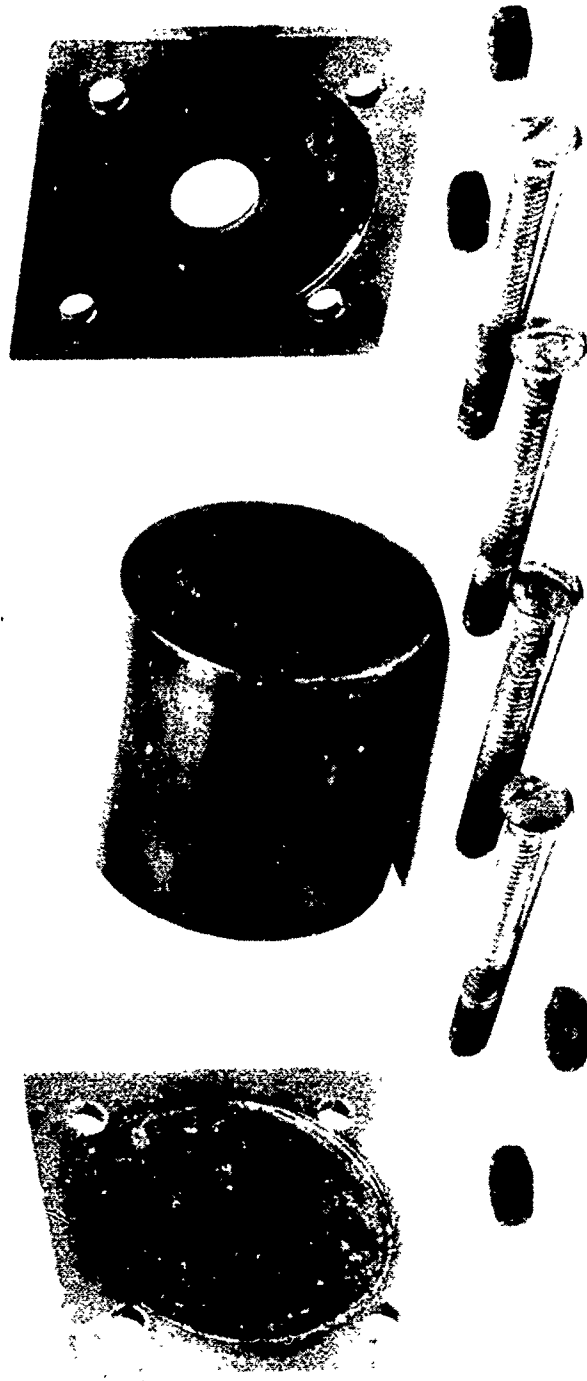


Figure 12. The disassembled miniaturized smoke pot.

of the HC mix was always extracted from the top starter layer of the canister, i.e., Smoke Mix I of Table 1. The remainder of the HC mix was either the same "starter" mix or an admixture of 50% each from the top and a lower stratum of the canisters. The igniter mix reaction was initiated with a nichrome wire spiral immersed in the mix, electrically heated to bring it to red heat.

In some of the early experiments, the HC mix was placed in the smoke pot and compacted to a density of 1 g cm^{-3} (Table 16, p. 49). In most of the experiments, however, the mix was compacted to a density of about 1.5 g cm^{-3} to approach more nearly the density in a military canister.

The charged minipot was placed in a tray on an extension arm which could be controlled from a glove box on the side of the chamber. The extension arm allowed the pot to be placed about 3 ft inside the chamber for ignition. After ignition, the pot was retracted into the glove box and the chamber was sealed from the glove box. Once the pot was installed in the chamber ready for ignition, the temperature and humidity of the system were allowed to come to equilibrium. To facilitate this process, a large circulating fan installed in the center of the chamber was turned on. About 20 minutes before ignition, the circulating fan was turned off, temperature and humidity readings were taken, and the background aerosol level was established.

During ignition the aerosol cloud tended to concentrate in the upper third of the chamber. After the burn was completed, the circulating fan was turned on to mix the aerosol uniformly throughout the chamber. Sampling for aerosol analysis was started 5 min after ignition. At the conclusion of the experiment the chamber was washed and purged with fresh air. Humidity in the chamber was controlled by removing excess moisture with a small refrigeration unit.

ANALYTICAL INSTRUMENTATION

The aerosol sampling and dilution system is shown in Figure 13. An important function of this system was to reduce the chamber aerosol concentration to a level suitable for measurement by the two aerosol monitors. A dilution of $1000(\pm 10) : 1$ was used with a total transit time from chamber to detector of less than 1 min. The aerosol particles were analyzed using the two instruments described below.

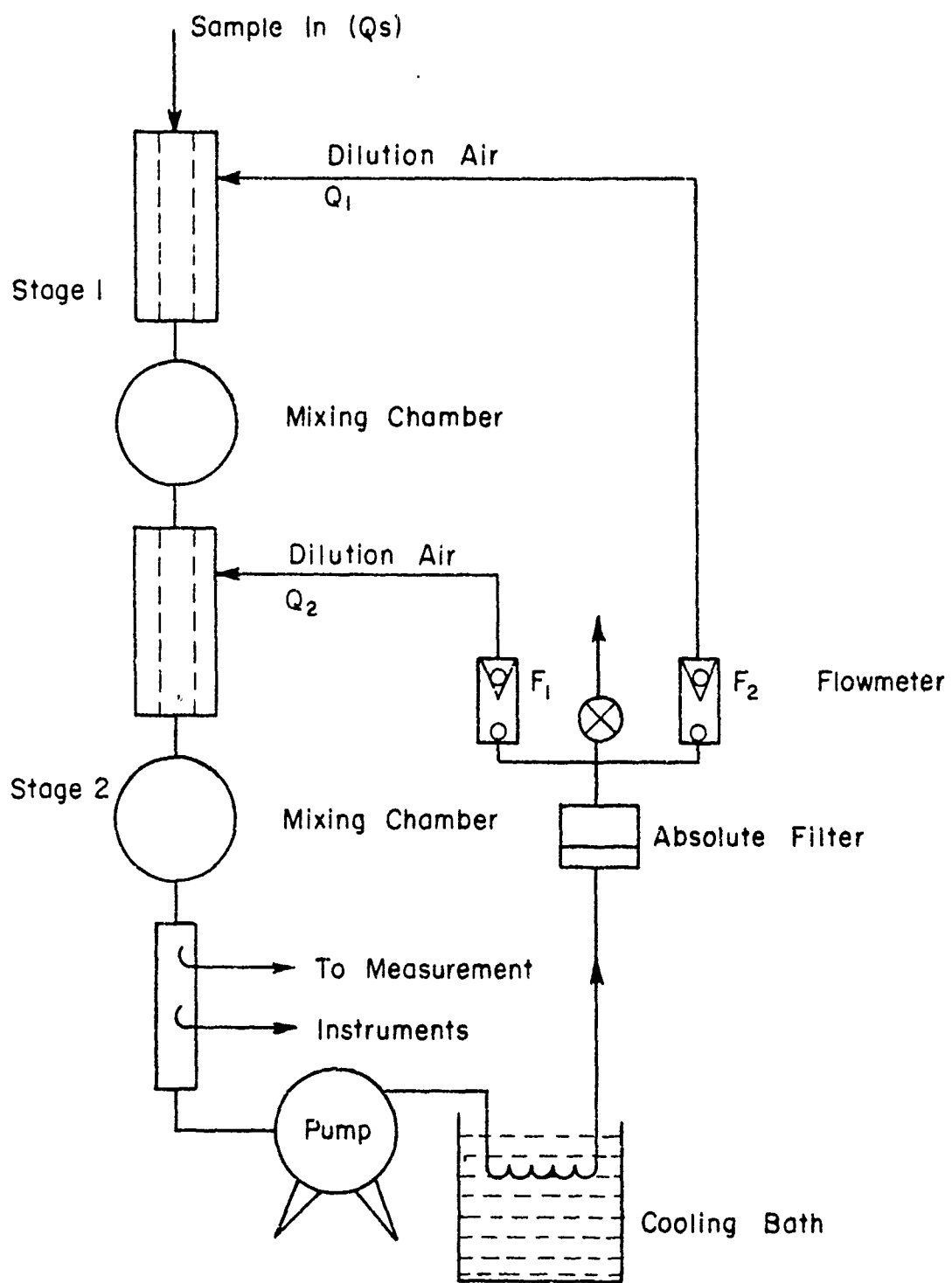


Figure 13. Aerosol sampling line and dilution system.

A California Measurements, Inc. Piezo Electric (P/Z) Particle Cascade Impactor Model PC-Z was used for the direct measurement of the mass concentration of air-suspended particles between 0.05 and 25 μm . The aerosol laden air stream, sampled at 240 ml/min, is impacted sequentially on 10 quartz crystal impactor stages. The mass accumulated by each stage causes a proportional frequency shift on each impactor crystal, which is electronically compared to a matching clean reference crystal. Table 14 lists the 50% cutoff sizes (D_{p50}) for the ten stages with a particle density of 2 g cm^{-3} . The values of M_i are the between-stage midpoint diameters used to compute the aerodynamic equivalent mass median diameter for each distribution.

TABLE 14. PIEZOELECTRIC COUNTER STAGES

| Stage | D_{p50} μm | M_i μm |
|-------|----------------------------|------------------------|
| 1 | 25.0 | - |
| 2 | 12.5 | 18.75 |
| 3 | 6.4 | 9.6 |
| 4 | 3.2 | 4.8 |
| 5 | 1.6 | 2.4 |
| 6 | 0.80 | 1.20 |
| 7 | 0.40 | 0.60 |
| 8 | 0.20 | 0.30 |
| 9 | 0.10 | 0.15 |
| 10 | 0.05 | 0.075 |

After passing through the 10th, lowest, stage, the air flows through a flowmeter to a pump where it is exhausted to the atmosphere. The rate of frequency shift in each stage is related to the mass concentration of aerosol particles captured in that stage, and can be expressed by the following equation:

$$\frac{\Delta f_i}{\Delta t} = \sigma_i V C_i$$

where

Δf_i = frequency shift for stage 1, Hz

Δt = sample time, min

σ_i = sensitivity factor for stage 1

V = volume flow rate of air sample, 240 ml/min

C_i = aerosol mass concentration in stage 1, $\mu\text{g}/\text{m}^3$

The sensitivity factor, σ_i , depends on the resonant frequency of the crystal and the area of the sensitive portion of the crystal compared to the area of the impinging air jet, but is otherwise a constant for each stage. The concentration may therefore be calculated from the measured frequency shift by the equation:

$$C_i = k_i \frac{\Delta f_i}{\Delta t}$$

where

$$k_i = \text{stage constant}$$

The data reported from the P/Z cascade impactor are the total suspended particles (TSP) in mg/m^3 and the mass median diameter, \bar{d}_m , in μm . The TSP is determined by adding the masses per stage and multiplying by the dilution factor:

$$\text{TSP} = 1000 \sum C_i$$

The \bar{d}_m are computed by summing the products of the mass fractions per stage, X_i , times the midpoint cutoff size between stages, M_i :

$$\bar{d}_m = \sum X_i M_i$$

where

$$X_i = C_i / \sum C_i$$

$$M_i = \text{as indicated in Table 14}$$

The Particle Measuring Systems, Inc. Active Scattering Aerosol Spectrometer (ASAS) Model ASAS-300-PMT was used for sizing particles within the size range of 0.088 to 3.00 μm . Particles passing through the laser cavity of a continuous He-Ne laser produce pulses of light proportional only to their size and position in the beam. A pair of photomultiplier detectors image the light impulses and select pulses produced by particles in the correct sample space. A pulse height analyzer then determines the particle sizes.

The output of the ASAS is grouped into size classes as shown in Table 15; the data are in the form of numbers of particles per size range, n_i .

TABLE 15. ASAS SIZE RANGE DATA

| ASAS Range | ASAS Channel | Size Interval μm | Interval Width μm | d_j , Midrange Diameter, μm |
|---------------|-----------------|--------------------------------|---------------------------------|---|
| 3 | 1-15 | 0.088-0.208 | 0.120 | 0.148 |
| 2 | 4-15 | 0.210-0.390 | 0.180 | 0.300 |
| 1 | 4-8 | 0.388-0.503 | 0.120 | 0.448 |
| 1 | 9-15 | 0.508-0.676 | 0.168 | 0.592 |
| 0 | 2 | 0.690-0.855 | 0.165 | 0.772 |
| 0 | 3 | 0.855-1.020 | 0.165 | 0.938 |
| 0 | 4 | 1.020-1.185 | 0.165 | 1.102 |
| - | - | - | - | - |
| 0 | 15 | 2.835-3.000 | 0.165 | 2.918 |

The data reported from the ASAS include the number concentration, number of particle per cm^3 , $[n]$, computed by multiplying the sum of nonoverlapping interval counts by the dilution factor, thus:

$$[n] = 1000 \sum n_j$$

and the count mean diameter, d_{av} , is computed by:

$$d_{av} = \frac{\sum n_j d_j}{\sum n_j}$$

AEROSOL STUDIES WITH MINIPOT GENERATORS

Aerosol Size Dependence on Generator Charge Size

It was important at this stage to determine if any significant change in aerosol size distribution could be related to particle clouds generated in the different size miniature smoke pots. The experimental conditions are presented in Table 16 and the corresponding aerosol analyses are shown in Table 17.

From the linear burning rates shown in Table 16 it is evident that the starter mix (Experiments 1 and 2) burns at about twice the rate of the composite mixture containing both the starter mix and the material from the lower part of the canister. The burning rates in Experiments 3-5 and 6-9 are very similar; only the largest pot, Experiment 10, shows a marked reduction in burn rate, 2.3 cm min^{-1} . The burning rate of the M5-HC 30-1b pot was in a similar range,

TABLE 16. SUMMARY OF HC SMOKE GENERATION EXPERIMENTS*

| Run No. | Pot | HC Charge g | Ratio 3.1.1:mix** | Density | Burn Time sec | Burn Rate cm/min | Weight Loss, % |
|---------|-----|-------------|-------------------|---------|---------------|------------------|----------------|
| 1 | 1 | 12 | 3.1.1 only | 1.0 | 16 | 7.5 | 79 |
| 2 | 1 | 12 | 3.1.1 only | 1.0 | 15 | 8.0 | 87 |
| 3 | 1 | 12 | 2:10 | 1.0 | 32 | 3.7 | 75 |
| 4 | 1 | 12 | 2:10 | 1.0 | 29 | 4.1 | 73 |
| 5 | 1 | 12 | 2:10 | 1.0 | 28 | 4.1 | 69 |
| 6 | 2 | 37 | 7:30 | 1.5 | 55 | 3.5 | 76 |
| 7 | 2 | 37 | 7:30 | 1.5 | 53 | 3.8 | 75 |
| 8 | 3 | 75 | 15:60 | 1.5 | 70 | 3.8 | 76 |
| 9 | 3 | 75 | 15:60 | 1.5 | 67 | 4.1 | 76 |
| 10 | 4 | 700*** | 100:600 | 1.5 | 220 | 2.3 | 87.4 |

* Smoke mix taken from HC pot number 3.1.

** The 3.1.1 layer is the faster burning layer; the mix is a mixture of 50% reagent each from the 3.1.1 and 3.1.3 layers; the 3.1.1 layer is superimposed on the mix in the mini-canisters.

*** A "one of a kind" smoke pot, scaled in the same way as the others with the object of providing an order of magnitude higher aerosol concentration than that obtained with the other miniature pots.

TABLE 16-A. STATISTICAL ANALYSIS FOR BURN RATES AND WEIGHT LOSSES, Run Numbers 1-9

| Runs No. | Burn Rates, cm/min | | Weight Loss, % | |
|----------|--------------------|------------------------------|-----------------|------------------------------|
| | Mean, \bar{x} | Standard Deviation, σ | Mean, \bar{x} | Standard Deviation, σ |
| 1-2 | 7.75 | 0.25 | 83 | 4 |
| 3-5 | 3.97 | 0.19 | 73.7 | 4.1 |
| 6-9 | 3.8 | 0.21 | 75.7 | 0.4 |
| 3-9 | 3.7 | 0.59 | | |
| 1-9 | 4.7 | 2.83 | 76.2 | 4.58 |

TABLE 17. SUMMARY OF INITIAL PARTICLE SIZE AND CONCENTRATION MEASUREMENTS AT FIVE MINUTES AFTER IGNITION, HC Lot 3.1

| No. | Weight Loss g | P/Z Cascade Impactor | | Aerosol Spectrometer | |
|-----|------------------|------------------------|-----------------------------|-----------------------|--------------------------|
| | | TSP, mg/m ³ | \bar{d}_m , μm | [n] / cm ³ | d_{av} , μm |
| 1 | 9.5 | 253.2 | 0.476 | 1.139×10^6 | 0.271 |
| 2 | 10.4 | 181.2 | 0.484 | 1.727×10^6 | 0.375 |
| 3 | 9.0 | 228.4 | 0.463 | 1.286×10^6 | 0.410 |
| 4 | 8.7 | 156.3 | 0.437 | 1.035×10^6 | 0.425 |
| 5 | 8.3 | 129.0 | 0.351 | 0.706×10^6 | 0.381 |
| 6 | 28.1 | 292.0 | 0.439 | 3.094×10^6 | 0.446 |
| 7 | 27.6 | 285.3 | 0.612 | 6.023×10^6 | 0.516 |
| 8 | 57.1 | 297.0 | 1.063 | 7.731×10^6 | 0.646 |
| 9 | 56.5 | 315.0 | 1.083 | 4.610×10^6 | 0.542 |
| 10 | 612.1 | 418.4 | 1.403 | 10.940×10^6 | 0.708 |

TABLE 17-A. ANALYSIS OF PARTICLE SIZE DATA OF TABLE 17

| Runs No. | Mass Median Diameter, μm | | Count Mean Diameter, μm | |
|-------------|-------------------------------------|----------|------------------------------------|----------|
| | \bar{d}_m | σ | d_{av} | σ |
| 1, 2 | 0.48 | 0.0056 | 0.323 | 0.0735 |
| 3, 4, 5 | 0.417 | 0.0586 | 0.405 | 0.0223 |

as discussed in Section 5 around 1 cm min^{-1} . Apparently both pot size and charge density are controlling factors. Means and standard deviations for the burn rates and weight loss of Runs No 1-9 are given in Table 16-A, which further emphasizes the fair agreement of the weight losses, and also of the burn rates for Runs 3-9 the runs with uniform compositions.

The aerosol analysis data (Table 17) shows the general kinds of trends that would be expected; as the initial mass and number concentration of the particles increase there is an increase in both the mass mean diameter and the count mean diameter. In the five experiments using the 12 g smoke pot charge, the average number concentration is $\approx 1.6 \times 10^6 \text{ particles cm}^{-3}$ with a count mean diameter of $0.37 \mu\text{m}$. At the particle number density of $1-2 \times 10^6 \text{ cm}^{-3}$, agglomeration of the aerosol in the time interval between ignition and the actual aerosol measurement would be expected to be minimal and hence the mean particle diameter of $0.37 \mu\text{m}$ may be regarded as typical of the sizes to be formed with the HC smoke mix.

The first five members of Table 17 were examined further. The means and standard deviations of the particle sizes of Runs No 1 and 2 and of 3, 4 and 5 are given in Table 17-A.

A comparison of the data for this relatively small number of experiments indicates that, the starter reagents used in Runs No 1 and 2 produce larger aerodynamically sized particles. The count mean diameter data are inconclusive, the standard deviation of Runs 1 and 2 being almost 25% of the mean diameter.

The data of Runs No 3-10, all of which have the same mixture compositions were examined. In this case, a correlation of particle sizes, \bar{d}_m and d_{av} , was tested with the reagent weight loss, W . Since weight is related to volume, it seems reasonable to relate diameter to $W^{1/3}$, and linear regression curves were calculated using the relation.

$$\text{Size } d = m W^{1/3} + b$$

where for $d = \bar{d}_m$ and d_{av} , m , b and the correlation coefficient, R , are:

| Variable | m | b | R |
|-------------|--------|--------|-------|
| \bar{d}_m | 0.1616 | 0.1576 | 0.875 |
| d_{av} | 0.0480 | 0.3388 | 0.871 |

The close correlation of particle size with reagent weight, combined with the indication of an initial mean particle diameter of 0.37 μm gives strong support to the occurrence of progressive particle growth through agglomeration as the aerosol concentration increases.

The correspondence between aerosol concentration and reagent weight loss has also been compared, using the data of Table 17. Good agreement occurs in Runs No. 1-5 between the average mass loading obtained with the P/Z mass monitor, $\sim 189 \text{ mg/m}^3$, with the ASAS aerosol spectrometer, $\sim 212 \text{ mg/m}^3$ and the charge weight loss (106 mg/m^3 + water of hydration).* In Runs No. 6-10, however, the P/Z means are consistently less than the levels estimated from charge weight loss while the ASAS measurements are higher. Possible explanations are:

1. Not all the material ejected from the larger minipots is in aerosol form. During Run No. 10, in particular, a considerable amount of material was deposited on the floor of the chamber

2. High localized agglomeration in the initial unmixed aerosol cloud might lead to the formation of larger particles which settle before sampling. This could remove significant mass from the aerosol cloud.

3. If the individual particles are solids, agglomeration might form structures of lower density than individual particles, invalidating the assigned density based on ZnCl_2 .

Aerosol Generation and Humidity

The next series of experiments, Numbers 11-17, was made with the 12 g mini pots. Table 18 summarizes the results of the ignition process, which again employed a hot wire igniter and the Al-WO_3 first fire mix. Each pot was charged with approximately one gram of first fire mix layered over 2 grams of the starter composition 3.1.1 below which were 10 grams of a 50:50 blend of the 3.1.1 and 3.1.3 HC compositions. The mixing fan in the aerosol chamber was left on during ignition to prevent formation of a concentrated cloud of the aerosol in the immediate vicinity of the smoke pot as appeared to be the case in the previous experiments (Nos. 1-10). In addition the humidity in the chamber was varied from 75% down to 9.5%. Humidity control was obtained by saturating the chamber with a water spray and removing the excess moisture with a refrigerated coil.

* A spherical aerosol particle and a density of 1.6 was assumed.

TABLE 18. SUMMARY OF HC SMOKE GENERATION EXPERIMENTS USING 12 g OF HC MIX IN MINI-POT NUMBER 1

| No. | Ratio 3.1.1 to Mix | Burn Time sec | Burn Rate cm/min | Weight Loss g | % Relative Humidity |
|-----|-----------------------|------------------|---------------------|------------------|------------------------|
| 11 | 2:10 | 20 | 12.0 | 8.0 | 75 |
| 12 | 2:10 | 20 | 12.0 | 8.5 | 45 |
| 13 | 2:10 | 33 | 7.3 | 9.0 | 25 |
| 14 | 2:10 | 33 | 7.3 | 9.0 | 24 |
| 15 | 2:10 | 32 | 7.5 | 8.8 | 15 |
| 16 | 2:10 | 31 | 7.7 | 9.0 | 24 |
| 17 | 2:10 | 30.5 | 7.9 | 8.8 | 9.5 |

The possibility of a dependence of burn time on relative humidity was examined. A linear dependence of burn time on relative humidity was derived:

$$B.T. = m(RH) + b$$

where B.T. and RH are, respectively, burn time and relative humidity. The data from Table 18 yielded values for m and b of -0.224 and 35.5 with a correlation coefficient of 0.849 indicating the high probability of the dependence of burn time and its reciprocal, burn rate on relative humidity.

The aerosol data for Runs 11-17 are shown in Table 19. There appears to be no obvious correlation between ambient relative humidity and mean par-

TABLE 19. INITIAL AEROSOL PARTICLE SIZE AND CONCENTRATIONS
HC Lot 3.1 Smokes

| No. | Relative Humidity % | Weight Loss g | Min. After Ignition | P/Z Cascade TSP, mg/m ³ | Impactor d _m , μm | Aerosol Spectrometer [n]/cm ³ | d _{av} , μm |
|-----|---------------------------|---------------------|---------------------------|---------------------------------------|---------------------------------|---|----------------------|
| 11 | 75 | 8.0 | 8 | 74.8 | 0.352 | 0.866 x 10 ⁶ | 0.320 |
| 12 | 45 | 8.5 | 4 | 44.8 | 0.428 | 2.320 x 10 ⁶ | 0.304 |
| 13 | 25 | 9.0 | 4 | 99.8 | 0.404 | 2.281 x 10 ⁶ | 0.315 |
| 14 | 24 | 9.0 | 4 | 97.2 | 0.389 | 1.935 x 10 ⁶ | 0.321 |
| 15 | 15 | 8.8 | 4 | 147.0 | 0.416 | 6.541 x 10 ⁶ | 0.218 |
| 16 | 24 | 9.0 | 4 | 109.5 | 0.399 | 1.871 x 10 ⁶ | 0.306 |
| 17 | 9.5 | 8.8 | 4 | 63.0 | 0.456 | 0.913 x 10 ⁶ | 0.341 |

ticle size. This was tested quantitatively, again by attempting a linear regression. The low correlation coefficient of -0.234 indicates that humidity probably has little or no effect on particle size. Since the aerosol particles are largely composed of $ZnCl_2$, which is very hygroscopic, this was somewhat unexpected.

It should be noted, however, that at relative humidities of 9.5 and 75% at $25^\circ C$, the chamber air contains 0.12 mol m^{-3} (2.2 g) and 0.95 mole m^{-3} (17.0 g) of water vapor, respectively. An aerosol loading of 150 mg m^{-3} would correspond to $\approx 1.1 \times 10^{-3} \text{ mole}$ of $ZnCl_2$ so that even at the lowest humidity investigated there are approximately two orders of magnitude more water present on a molar basis than zinc chloride. It may reasonably be assumed that each zinc chloride molecule is associated with only a few molecules of water at best, and hence the independence of the aerosol size with respect to the humidity range investigated is reasonable.

A further observation from these studies indicates that operation of the circulating fan during ignition results in slightly higher average number concentrations of aerosol and smaller particles sizes. These data are summarized in Table 20 and are consistent with the previous suggestion, that without stirring the chamber during the ignition process, locally high aerosol loadings occur with increased particle agglomeration.

TABLE 20. COMPARATIVE PARTICLE SIZES AND CONCENTRATIONS, HC Lot 3.1

| Fan Condition | Off During Ignition | On During Ignition |
|-----------------------------|---------------------|--------------------|
| Experiments | nos. 1 through 5 | Nos. 11 through 17 |
| Weight Loss, g | 9.2 | 8.7 |
| TSP*, mg/m^3 | 189.6 | 90.7 |
| \bar{d}_m , μm | 0.442 | 0.406 |
| $[n]/\text{cm}^3$ | 1.58×10^6 | 2.39×10^6 |
| $d_{a,7}$, μm | 0.463 | 0.304 |

* Total suspended particles

Aerosol Dependence on Generating Reagent

The final series of experiments on HC smoke generation is summarized in Table 21. In this series, HC samples from the top layers of two cans selected from each of the five lots of military HC canisters were burned in the smallest miniature smoke pot (12g). The circulation fan was left

TABLE 21. SUMMARY OF HC SMOKE GENERATION EXPERIMENTS USING
12 g HC IN MINIPOT NUMBER 1

| No. | HC Composition | Burn Time sec | Burn Rate cm/min | Weight Loss g | % Relative Humidity |
|-----|----------------|------------------|---------------------|------------------|------------------------|
| 18 | 100% Lot 1.1.1 | 33.5 | 7.2 | 7.8 | 27 |
| 19 | 100% Lot 1.1.1 | 11.0 | Incomplete | 3.1 | 24 |
| 20 | 100% Lot 1.1.1 | 44.5 | 5.4 | 7.8 | 24 |
| 21 | 100% Lot 1.1.1 | 49.0 | 4.9 | 7.5 | 22 |
| 22 | 100% Lot 1.2.1 | 25.0 | 9.6 | 8.3 | 24 |
| 23 | 100% Lot 2.1.1 | 38.0 | 6.3 | 8.6 | 24 |
| 24 | 100% Lot 2.2.1 | 28.0 | 8.6 | 7.5 | 30 |
| 25 | 100% Lot 4.1.1 | 14.0 | 17.1 | 9.0 | 41 |
| 26 | 100% Lot 3.2.1 | 18.0 | 13.3 | 9.5 | 36 |
| 27 | 100% Lot 4.2.1 | 17.0 | 14.1 | 9.1 | 36 |
| 28 | 100% Lot 5.1.1 | 20.0 | Incomplete | 3.7 | 41 |
| 29 | 100% Lot 5.2.1 | 15.0 | Incomplete | 4.2 | 41 |

on during ignition of the samples and the experiments were run at ambient humidity. Table 22 contains initial particle size and concentration data. The primary object of these experiments was to determine if there were any significant variations in the aerosol size distribution as a function of different samples of the military HC formulations.

TABLE 22. SUMMARY OF INITIAL PARTICLE SIZE AND CONCENTRATION MEASUREMENTS

| No. | Weigh. Loss g | Time After Ignition | Piezoelectric Impactor | | Aerosol Spectrometer | |
|-----|------------------|------------------------|------------------------|-----------------------------|----------------------|--------------------------|
| | | | TSP mg/m ³ | \bar{d}_m , μm | [n]/cm ³ | d_{av} , μm |
| 18 | 7.8 | 4 min | 230.3 | 0.442 | 5.40 $\times 10^6$ | 0.236 |
| 19 | 3.1 | 4 min | 33.1 | 0.476 | 0.477 $\times 10^6$ | 0.279 |
| 20 | 7.8 | 4 min | 82.2 | 0.442 | 1.027 $\times 10^6$ | 0.319 |
| 21 | 7.5 | 8 min | 119.9 | 0.393 | 0.865 $\times 10^6$ | 0.362 |
| 22 | 8.3 | 6 min | 117.9 | 0.381 | 1.566 $\times 10^6$ | 0.290 |
| 23 | 8.6 | 4 min | 132.2 | 0.414 | 2.144 $\times 10^6$ | 0.333 |
| 24 | 7.5 | 4 min | 31.7 | 0.274 | 2.093 $\times 10^6$ | 0.315 |
| 25 | 9.0 | 8 min | 69.5 | 0.361 | 2.019 $\times 10^6$ | 0.253 |
| 26 | 9.5 | 4 min | 113.2 | 0.360 | 1.085 $\times 10^6$ | 0.301 |
| 27 | 9.1 | 4 min | 114.2 | 0.463 | 4.356 $\times 10^6$ | 0.238 |
| 28 | 3.7 | 4 min | 69.8 | 0.455 | 0.816 $\times 10^6$ | 0.322 |
| 29 | 4.2 | 4 min | 56.4 | 0.419 | 0.756 $\times 10^6$ | 0.339 |

A comparison of the mean particle sizes of Table 19 (Runs No. 11-17) and Table 22 (Runs No. 18-29) has been summarized in Table 23. The close agreement of the particle size data among these groups indicates that aerosols generated by the different M5-HC lots are indistinguishable so far as particle size is concerned.

TABLE 23. COMPARISON OF PARTICLE SIZE DATA OF RUNS NO 11-17

| | \bar{d}_m | (σ) | d_{av} | (σ) |
|---------------------------|-------------|--------------|----------|--------------|
| Table 19 (Runs No. 11-17) | 0.406 | (0.030) | 0.304 | (0.04) |
| Table 22 (Runs No. 18-29) | 0.407 | (0.054) | 0.299 | (0.039) |

An attempt was made to establish a correlation between the relative humidities of Table 21 and the corresponding particle sizes recorded in Table 22. Incomplete Runs 19, 28 and 29 were omitted from this test which yielded the very poor correlation coefficient of -0.1672, reinforcing the previous conclusions, based on the data of Table 19, that humidity is a minor factor in size control.

A comparison of weight loss with particle size in Table 22 also yielded a poor correlation coefficient, 0.2295. This appears to indicate the absence of coagulation in the time frame of these experiments. It should be noted that the mean d_{av} in this series is $0.299\mu\text{m}$ and the average $[n]/\text{cm}^2$ is 1.97×10^6 .

SIZE DISTRIBUTION AND TIME HISTORIES OF HC SMOKES

In experiments 1 through 10 it was shown that the mean and geometric mean diameters of the HC smokes varied as a function of the initial concentration of the smoke generated. Table 24 lists the cumulative size distributions of selected HC smokes as determined by the ASAS five minutes after ignition. HC smokes having initial concentrations below approximately 3×10^6 particles per cm^3 tend to be log normally distributed. A typical plot is shown in Figure 14. However, at higher concentrations the distributions become bimodal or multimodal and do not conform to a log-normal plot and are better represented by relative frequency histograms, as depicted in Figures 15-20. The relative frequencies are computed from the counts per interval divided by the interval width and the total counts for each distribution.

TABLE 24. CUMULATIVE SIZE DISTRIBUTIONS OF SOME LOG-NORMALLY DISTRIBUTED HC SMOKES

| | Experiment | 2 | 3 | 4 | 5 |
|-------------------------------------|--|-------|-------|-------|-------|
| Percent Greater than, μm | Initial Conc. $n \times 10^6/\text{cm}^3$ | 1.727 | 1.286 | 1.035 | 0.706 |
| 0.208 | | 87.0 | 94.7 | 93.9 | 84.4 |
| 0.390 | | 42.7 | 55.7 | 56.8 | 43.5 |
| 0.508 | | 14.9 | 19.0 | 23.2 | 17.1 |
| 0.676 | | 5.2 | 4.3 | 7.8 | 7.5 |
| 0.855 | | 0.58 | 0.39 | 1.4 | 1.0 |
| 1.020 | | 0.23 | 0.08 | 0.19 | 0.28 |
| 1.185 | | 0.06 | | | |
| 1.350 | | | | | |
| Count Median, μm | | 0.36 | 0.38 | 0.40 | 0.34 |
| σ | | 1.44 | 1.39 | 1.40 | 0.42 |

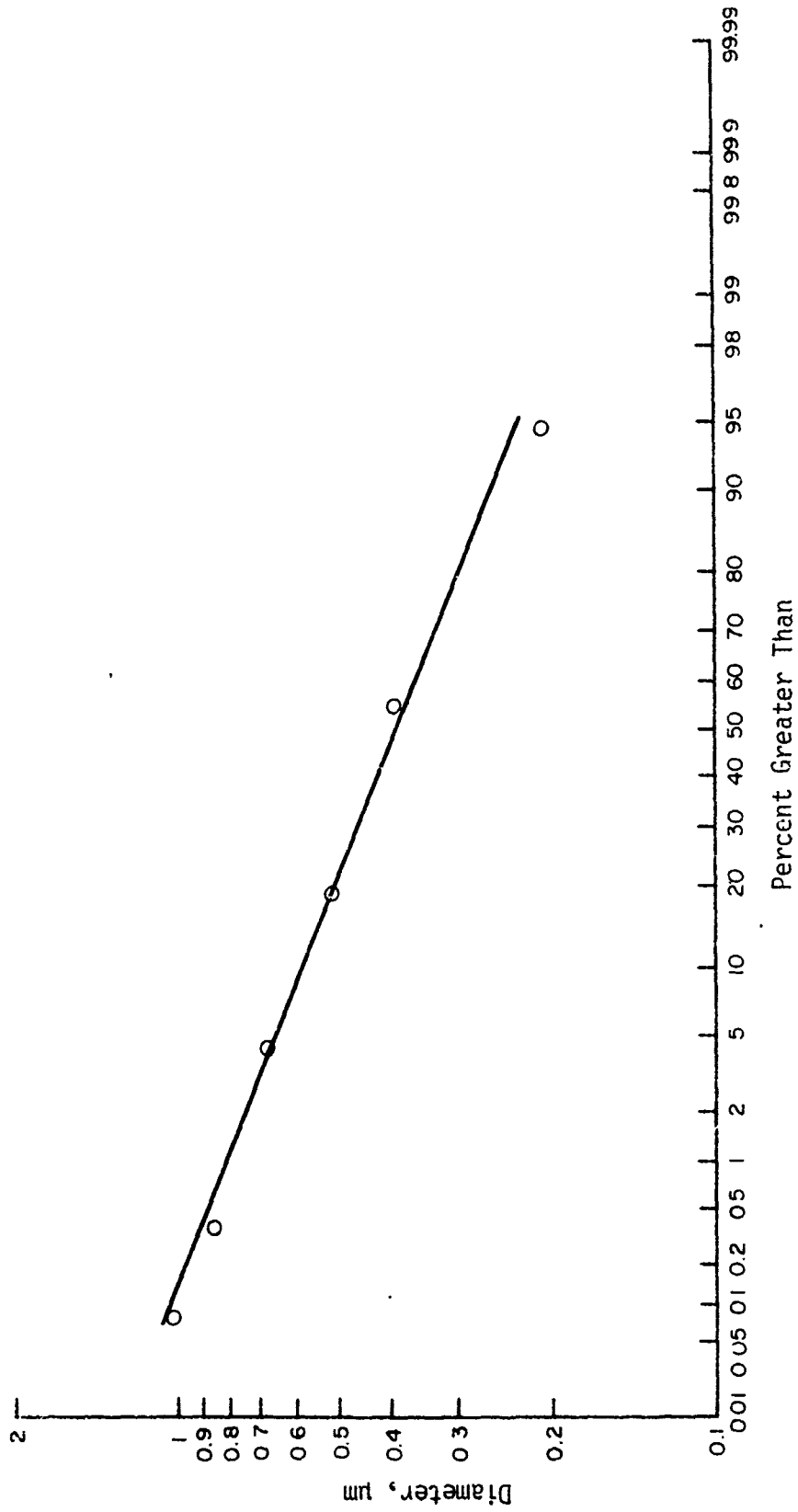


Figure 14. Log normal plot of HC smoke size distribution. Experiment 3, HC lot 3.1.

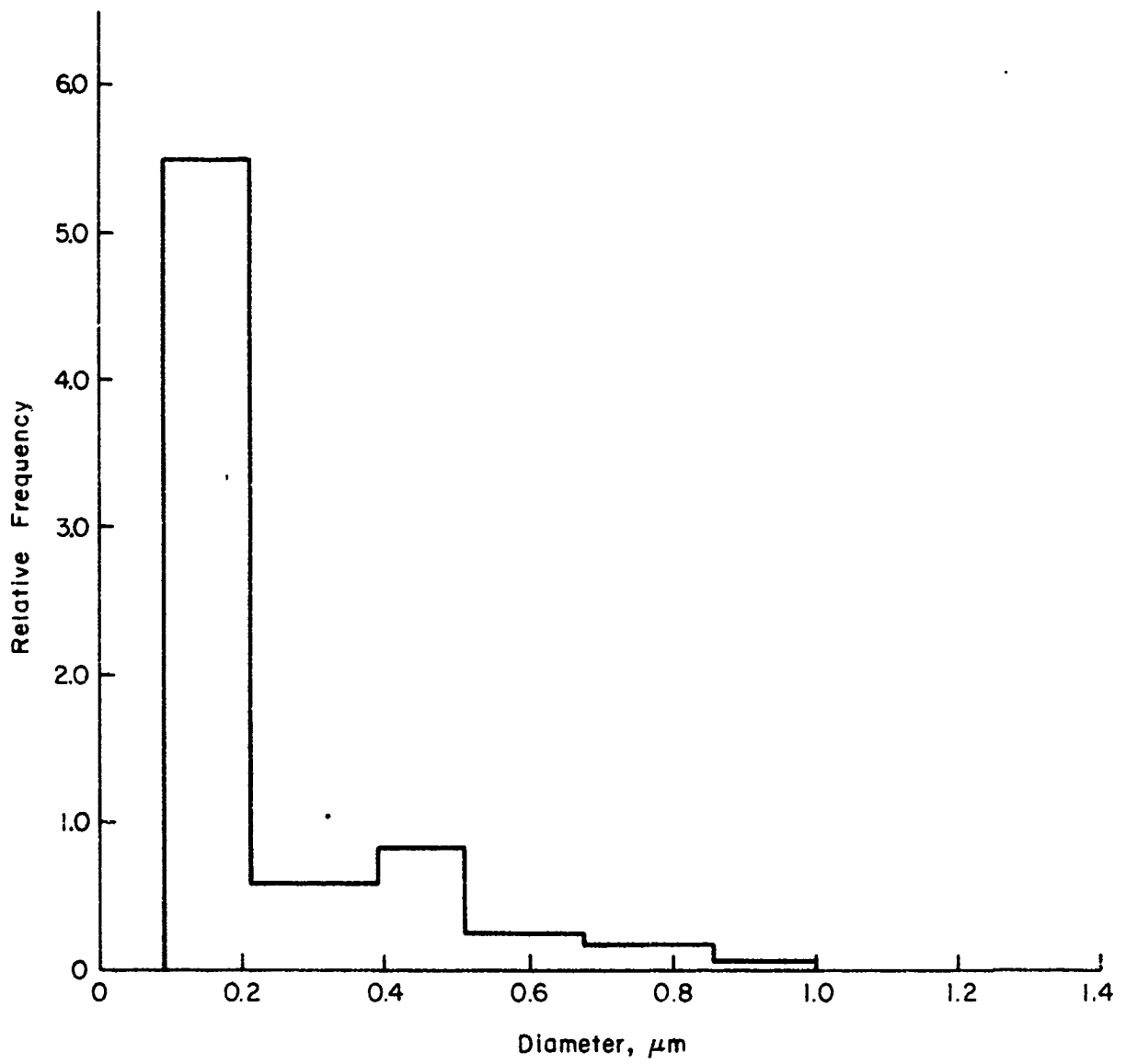


Figure 15. Relative frequency distribution by ASAS of HC. Experiment 1.

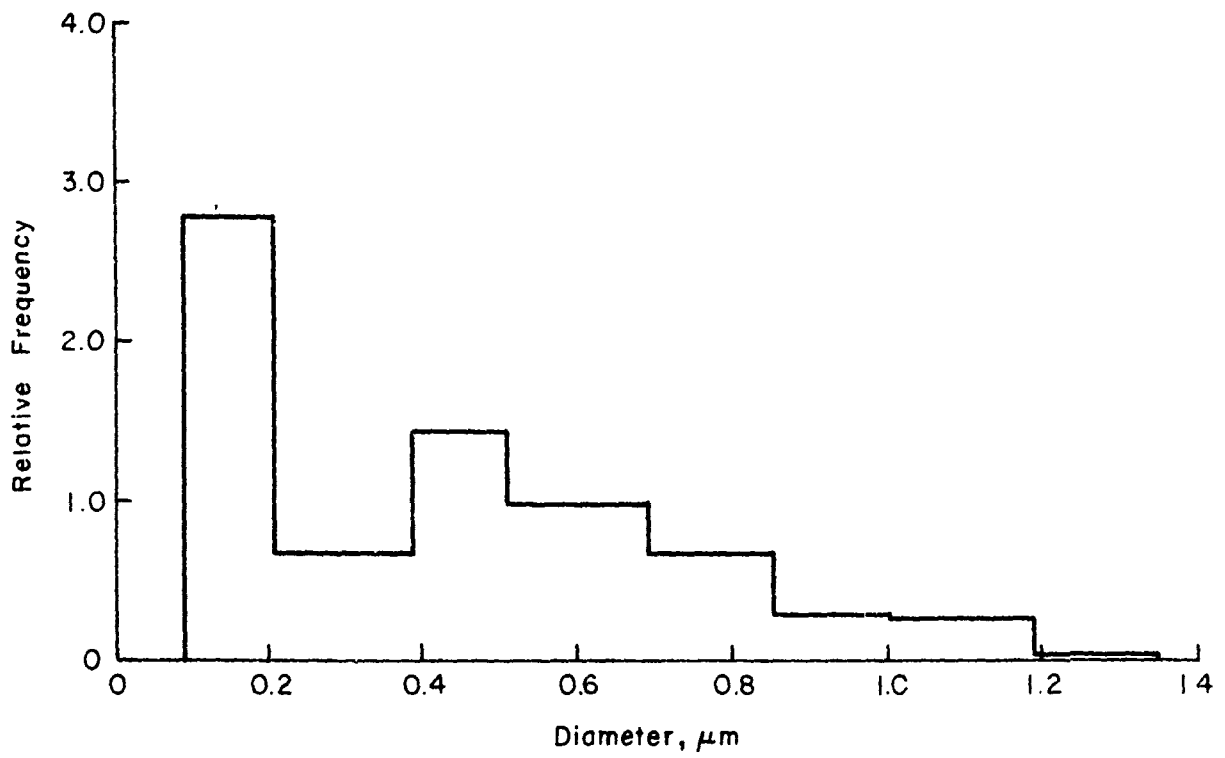


Figure 16. Relative frequency distribution as determined by ASAS of HC fog. Experiment 6.

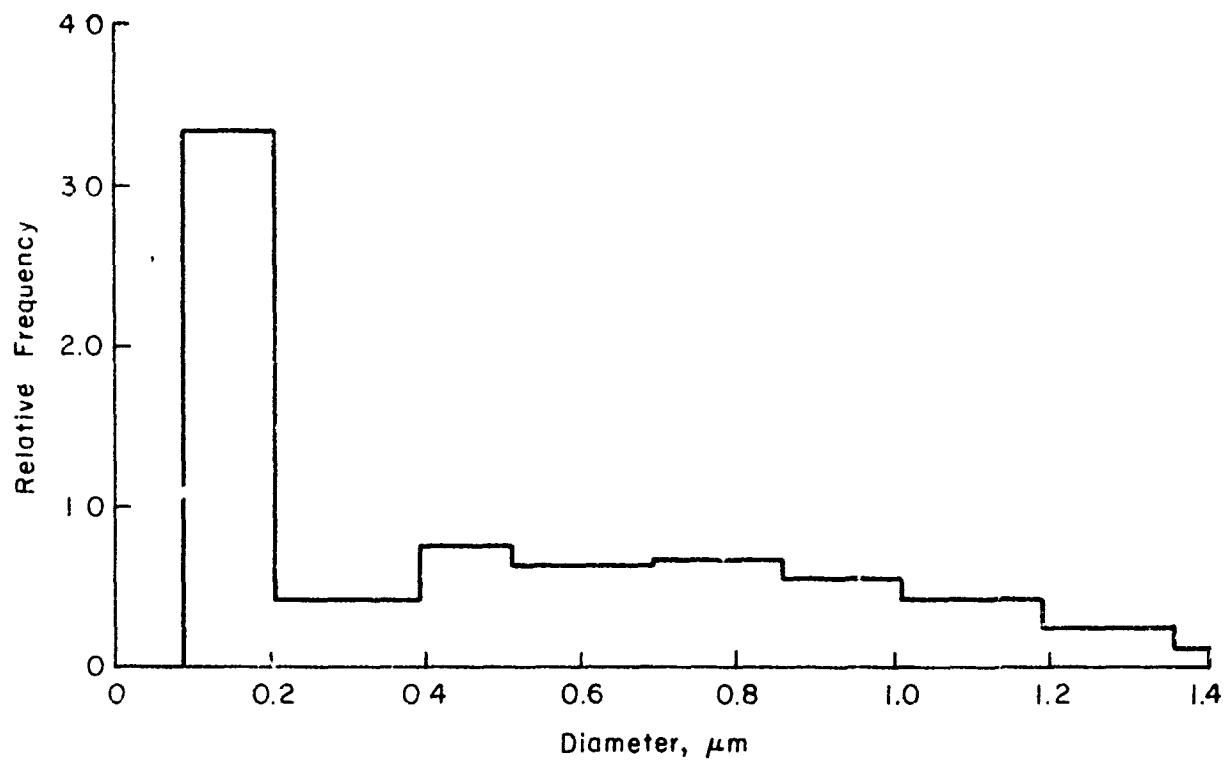


Figure 17. Relative frequency distribution as determined by ASAS of HC fog. Experiment 7.

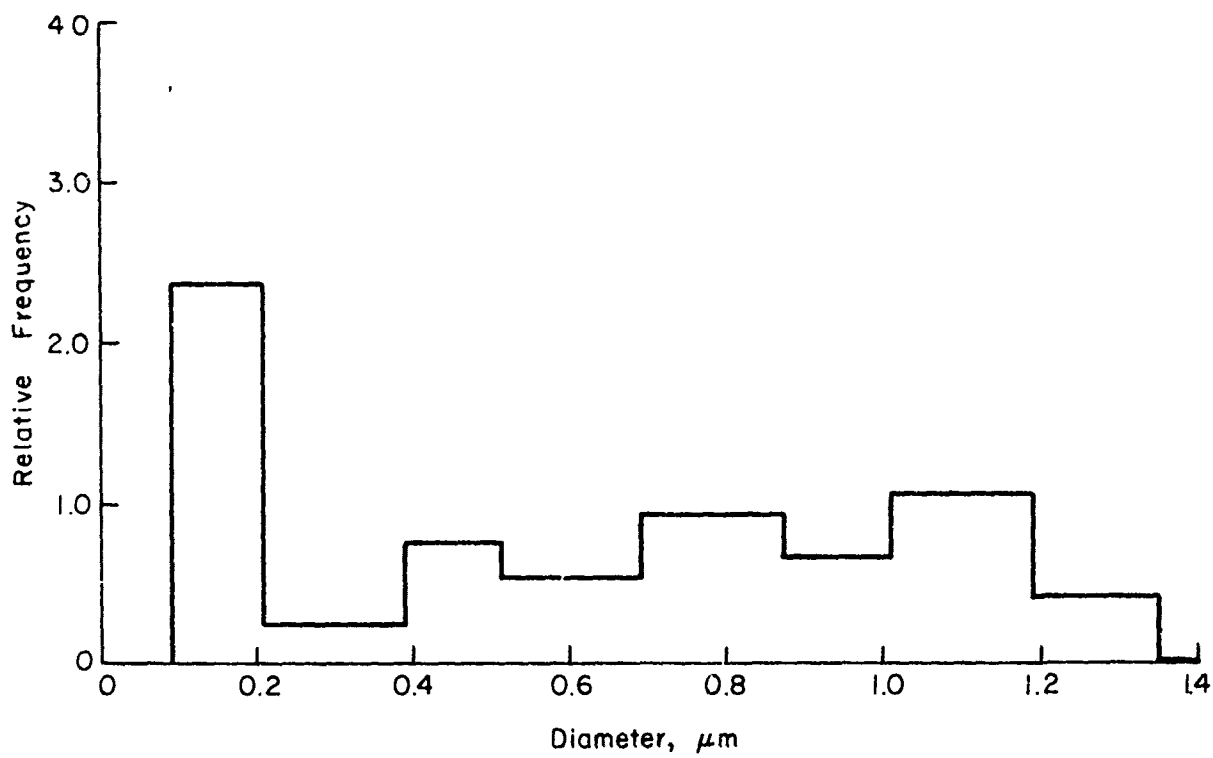


Figure 18. Relative frequency distribution as determined by ASAS of HC fog. Experiment 8.

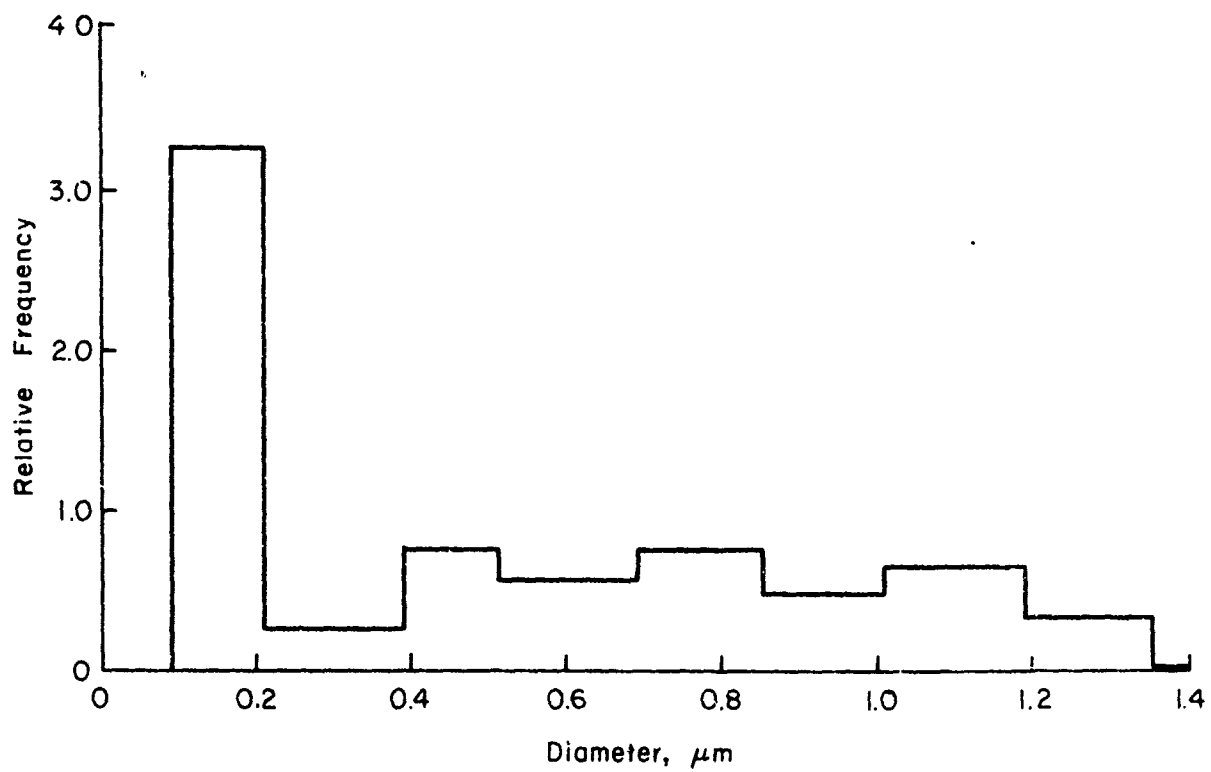


Figure 19. Relative frequency distribution as determined by ASAS of HC fog. Experiment 9.

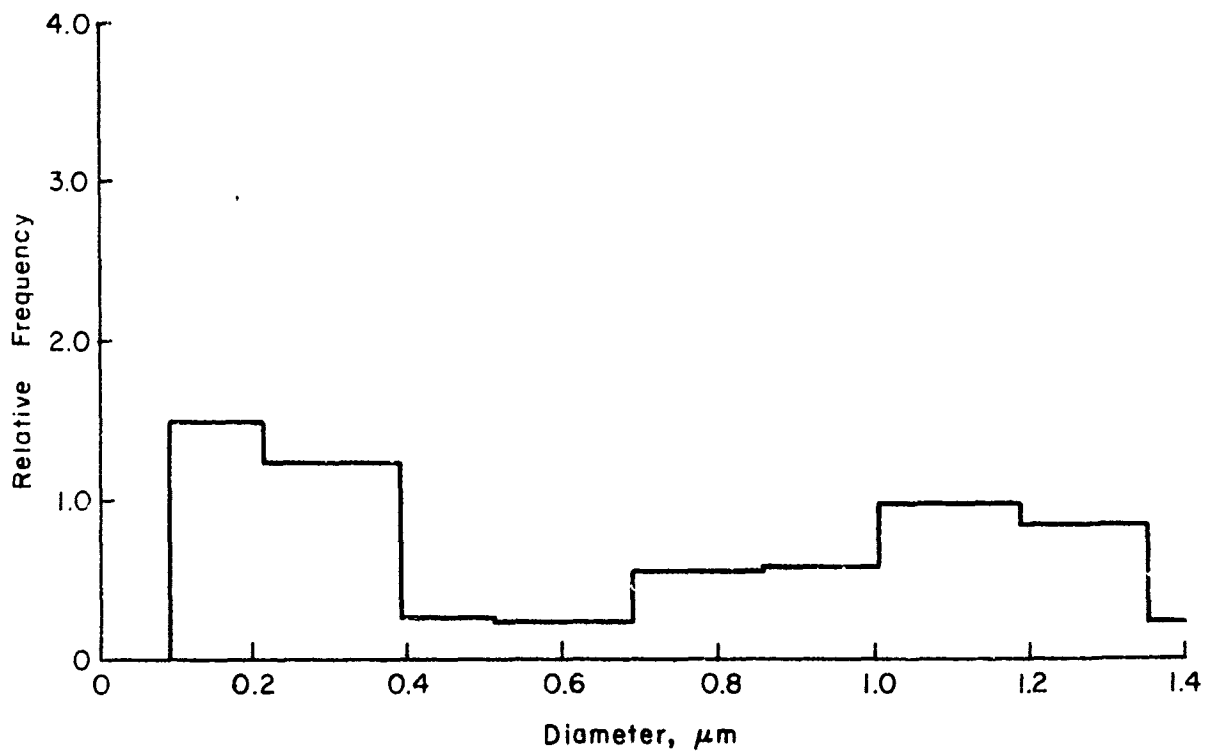


Figure 20. Relative frequency distribution as determined by ASAS of HC fog. Experiment 10.

Time histories of geometric (count) mean diameter, mass median diameter and concentration (particles per cm^3), were obtained for experiments 11 through 29. As an example, complete data obtained up to two hours after ignition in HC Experiment 13 are shown in Table 25. The decrease in number concentration and the growth in particle mass median and count mean diameter are plotted versus the log of time in Figure 21 for these data. The average

TABLE 25. TIME HISTORY OF HC FOG EXPERIMENT 13

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|--|-----------------------------|-----------------------------|----------------------|---|--------------------------|
| Time Min:Sec | TSP, mg/m^3 | \bar{d}_m , μm | Time Min:Sec | $[n]$, $/\text{cm}^3$ $\times 10^6$ | d_{av} , μm |
| 2 | 45.9 | 0.403 | 2:00 | 2.285 | 0.270 |
| 4:35 | 99.8 | 0.404 | 4:00 | 2.281 | 0.315 |
| 8:00 | 97.7 | 0.396 | 8:00 | 2.250 | 0.297 |
| 11:00 | 105.3 | 0.438 | 11:00 | 1.859 | 0.340 |
| 15:00 | 100.8 | 0.423 | 14:00 | 1.486 | 0.357 |
| 30:00 | 78.9 | 0.466 | 30:00 | 1.358 | 0.426 |
| 45:00 | 74.1 | 0.496 | 45:00 | 0.983 | 0.465 |
| 60:00 | 73.2 | 0.568 | 60:00 | 0.762 | 0.513 |
| 75:00 | 59.6 | 0.581 | 75:00 | 0.707 | 0.505 |
| 91:00 | 65.1 | 0.544 | 90:00 | 0.727 | 0.550 |
| 106:15 | 50.6 | 0.604 | 106:00 | 0.606 | 0.545 |
| 120:00 | 41.3 | 0.605 | 120:00 | 0.392 | 0.555 |
| b | | 0.311 | | 3.200 | 0.181 |
| m | | 0.130 | | -1.317 | 0.176 |
| R | | 0.922 | | 0.988 | 0.974 |
| $t_{1/2}$ | | | | 23 min | |
| \bar{d}_m at $t_{1/2}$, μm | | 0.48 | | | |
| d_{av} at $t_{1/2}$, μm | | | | | 0.42 |

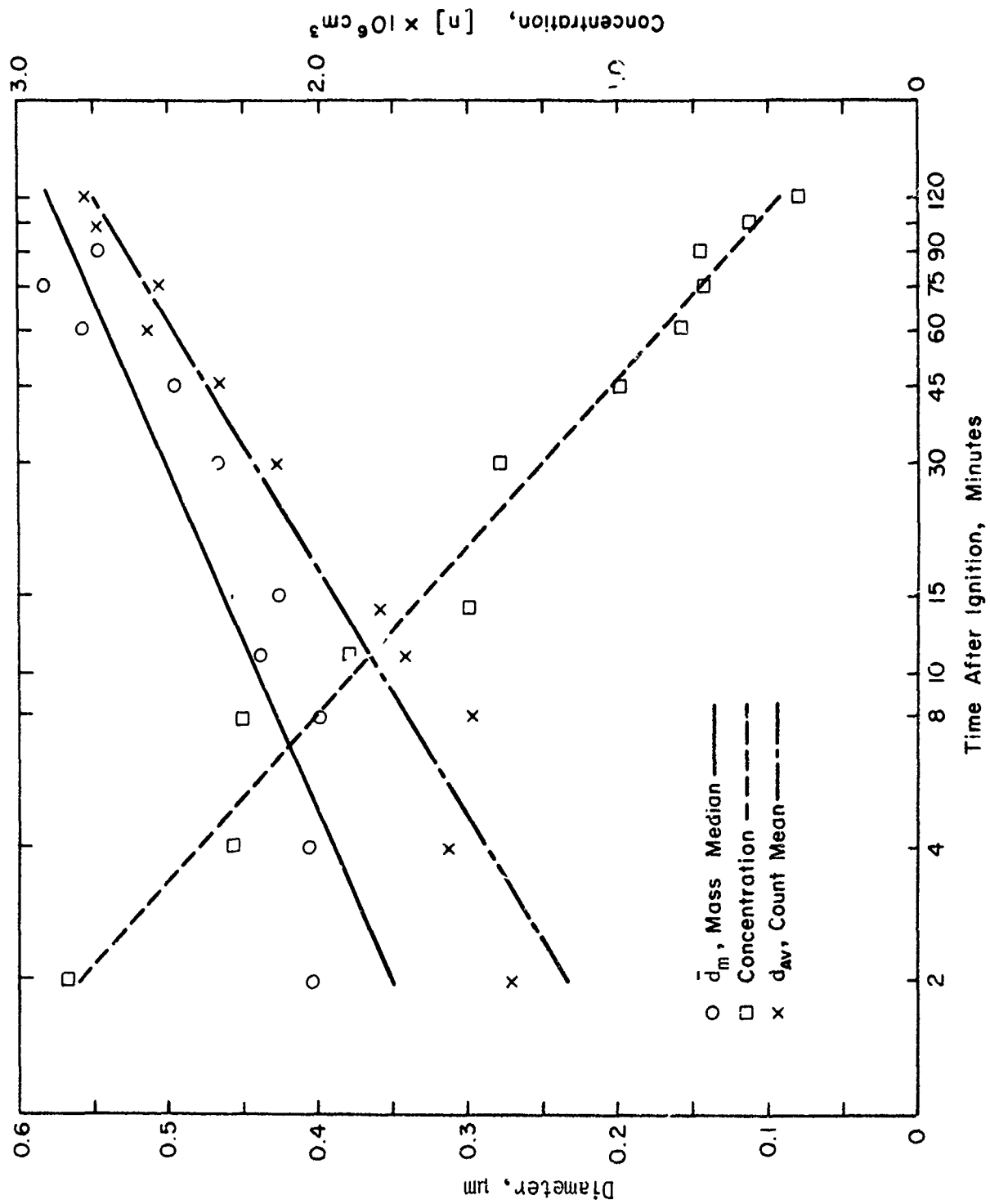


Figure 21. HC aerosol size and concentration as a function of time.

diameter increase and the number concentration decrease linearly as a function of log time. Also shown in Table 25 are the slope, m, intercept b and the correlation coefficients, R for the equation:

$$y = m \log \text{ time} + b$$

where y is \bar{d}_m in μm , $[n] \times 10^6/\text{cm}^3$ or d_{av} in μm as appropriate. Inspection of these data also indicate the time, $t_{1/2}$, when the concentration is half that measured at $t = 2\text{min}$ and the corresponding diameters. For HC fog experiment 13, $t_{1/2}$ is 23 minutes, at which time \bar{d}_m has grown to $0.48 \mu\text{m}$ and d_{av} to $0.42 \mu\text{m}$.

Table 26 summarizes the time histories for HC fog experiments 11 through 29. The regression coefficients obtained from Aerosol Spectrometer data generally indicate excellent data fit with the regression equation. Conversely for experiments resulting in low mass loading (incomplete burns) regression coefficients for the cascade impactor are low, possibly due to the low mass loadings obtained which results in greater data scatter.

However, in all cases the tendency for the particle size to grow and concentration to decrease as a function of time prevails as expected.

In the majority of experiments the particle concentration is halved in 20 to 25 minutes. Fogs with initial concentrations greater than 3.5×10^6 particles/ cm^3 tend to coagulate to half initial concentration in less than 20 minutes. Table 27 shows how particle growth relates to a particle count reduction of a half. Particle diameter growth over the $t_{1/2}$ time span for HC experiments 11 through 29 average 44% for d_{av} and 24% for \bar{d}_m .

CHEMICAL ANALYSES OF AEROSOLS

In this phase of the program aerosol samples generated in the 86 cu meter chamber were collected and analyzed for their major constituents, Zn, chloride ion, and Al. Because it was not practical to obtain large aerosol samples from the chamber, the trace species Pb and Cd were analyzed from samples burned in a 5 liter glass flask.

TABLE 26. TIME HISTORIES OF HC EXPERIMENTS*

| No. | Aerosol Spectrometer | | | | | | P/Z Cascade Impactor | | | | | |
|-----|--------------------------|--------|-------|-----------------|--------------------|-------|----------------------|-----------------|-------|-------|--------------------------|------|
| | $\ln I/cm^3 \times 10^6$ | | | $t_{1/2}$, min | d_{av} , μm | | | d_m , μm | | | \bar{d}_m at $t_{1/2}$ | |
| | b | m | P | | b | m | R | b | m | R | | |
| 11 | 1.188 | -0.431 | 0.927 | 34 | 0.209 | 0.140 | 0.934 | 0.42 | 0.403 | 0.011 | 0.059 | 0.42 |
| 12 | 2.798 | -1.126 | 0.986 | 25 | 0.221 | 0.167 | 0.978 | 0.45 | 0.375 | 0.083 | 0.597 | 0.49 |
| 13 | 3.200 | -1.137 | 0.988 | 23 | 0.181 | 0.176 | 0.974 | 0.42 | 0.311 | 0.130 | 0.922 | 0.48 |
| 14 | 2.664 | -1.079 | 0.994 | 24 | 0.226 | 0.136 | 0.975 | 0.41 | 0.346 | 0.055 | 0.759 | 0.53 |
| 15 | 8.917 | -4.348 | 0.984 | 15 | 0.237 | 0.054 | 0.948 | 0.30 | 0.359 | 0.083 | 0.913 | 0.46 |
| 16 | 2.347 | -0.977 | 0.929 | 22 | 0.231 | 0.120 | 0.948 | 0.39 | 0.334 | 0.108 | 0.882 | 0.48 |
| 17 | 1.078 | -0.412 | 0.959 | 29 | 0.268 | 0.103 | 0.899 | 0.42 | 0.404 | 0.043 | 0.706 | 0.47 |
| 18 | 9.570 | -5.341 | 0.953 | 11 | 0.125 | 0.181 | 0.861 | 0.31 | 0.378 | 0.118 | 0.973 | 0.50 |
| 19 | 0.604 | -0.153 | 0.898 | 133 | 0.259 | 0.028 | 0.856 | 0.32 | 0.289 | 0.134 | 0.715 | 0.57 |
| 20 | 1.286 | -0.415 | 0.936 | 48 | 0.276 | 0.081 | 0.924 | 0.41 | 0.417 | 0.035 | 0.579 | 0.48 |
| 21 | 1.052 | -0.189 | 0.774 | 860 | 0.285 | 0.093 | 0.929 | 0.56 | 0.435 | 0.028 | 0.226 | 0.52 |
| 22 | 2.440 | -0.955 | 0.870 | 27 | 0.245 | 0.095 | 0.904 | 0.38 | 0.269 | 0.102 | 0.899 | 0.41 |
| 23 | 2.769 | -1.11 | 0.961 | 25 | 0.274 | 0.103 | 0.959 | 0.42 | 0.462 | 0.084 | 0.573 | 0.58 |
| 24 | 2.651 | -1.007 | 0.968 | 29 | 0.271 | 0.081 | 0.967 | 0.39 | 0.255 | 0.008 | 0.164 | 0.27 |
| 25 | 3.901 | -1.905 | 0.953 | 15 | 0.166 | 0.092 | 0.963 | 0.27 | 0.395 | 0.061 | 0.405 | 0.38 |
| 26 | 1.248 | -0.468 | 0.840 | 30 | 0.291 | 0.037 | 0.786 | 0.35 | 0.349 | 0.079 | 0.795 | 0.47 |
| 27 | 6.114 | -3.014 | 0.930 | 15 | 0.169 | 0.116 | 0.853 | 0.30 | 0.310 | 0.145 | 0.811 | 0.48 |
| 28 | 1.009 | -0.314 | 0.928 | 57 | 0.303 | 0.031 | 0.925 | 0.35 | 0.467 | 0.064 | 0.341 | 0.58 |
| 29 | 1.001 | -0.365 | 0.967 | 33 | 0.314 | 0.044 | 0.973 | 0.38 | 0.435 | 0.001 | 0.011 | 0.43 |

* The data on which this table is based are presented in Appendix A.

TABLE 27. PARTICLE GROWTH OF HC FOGS
WHEN CONCENTRATION IS HALVED

| No. | t = 2 min | | t _{1/2} , min | d _{av} , μm | d _m , μm |
|-----|----------------------|---------------------|------------------------|----------------------|---------------------|
| | d _{av} , μm | d _m , μm | | | |
| 11 | 0.25 | 0.40 | 34 | 0.42 | 0.42 |
| 12 | 0.27 | 0.40 | 25 | 0.45 | 0.49 |
| 13 | 0.23 | 0.35 | 23 | 0.42 | 0.48 |
| 14 | 0.27 | 0.37 | 24 | 0.41 | 0.53 |
| 15 | 0.25 | 0.38 | 15 | 0.30 | 0.46 |
| 16 | 0.27 | 0.37 | 22 | 0.39 | 0.48 |
| 17 | 0.30 | 0.42 | 29 | 0.42 | 0.47 |
| 18 | 0.18 | 0.41 | 11 | 0.31 | 0.50 |
| 19 | 0.27 | 0.33 | 133 | 0.32 | 0.57 |
| 20 | 0.30 | 0.43 | 48 | 0.41 | 0.48 |
| 21 | 0.31 | 0.44 | 860 | 0.56 | 0.52 |
| 22 | 0.27 | 0.30 | 27 | 0.38 | 0.41 |
| 23 | 0.30 | 0.49 | 25 | 0.42 | 0.58 |
| 24 | 0.29 | 0.26 | 29 | 0.39 | 0.27 |
| 25 | 0.19 | 0.32 | 15 | 0.27 | 0.38 |
| 26 | 0.30 | 0.37 | 30 | 0.35 | 0.47 |
| 27 | 0.20 | 0.35 | 15 | 0.30 | 0.48 |
| 28 | 0.31 | 0.48 | 57 | 0.35 | 0.58 |
| 29 | 0.32 | 0.435 | 33 | 0.38 | 0.437 |

Analytical Procedures

The aerosol samples from the large test chamber were collected on 9 cm diameter 0.45 μ m cellulose acetate membrane filters. About 1.5 m³ of air were aspirated through the filter over a period of about 3 minutes. The filter was weighed before and after collection to get an approximate idea of the amount of sample collected (50-100 mg). The resultant filters on which the aerosol was collected were quite black, presumably due to carbon particles in the smoke. They were cut in half and both halves were analyzed. The following analytical procedures were followed. The filter was placed in a beaker and 20 ml 5% HNO₃ added. The beaker was covered and placed on a hot plate, and the solution allowed to reflux for two hours. The filter was broken up and stirred, and the mixture washed and filtered into a 100 ml volumetric flask and diluted to volume. (After the material had been extracted from the filter, two of the filters were washed with 20 ml 5% HNO₃ and 80 ml deionized water. Less than 0.25% of the zinc remained on the filter and the amount of chloride and aluminum were below the detection limit.) First the chloride concentration was determined, then the dilution for the zinc analysis was calculated. Dilutions of 1:100, 1:200, and 1:400 were used. The Al standards were made with 150 ppm Zn to control ionization in the flame.

The details of the chloride analyses follow. Ten and twenty milliliter aliquots of the sample solution are diluted to 75 ml with deionized water. The contents of a diphenyl carbazone buffered indicator pillow* was dissolved in the solution. The resulting yellow solution was titrated with standard 0.0141 M mercuric nitrate until the solution turned blue. Blanks containing 1% HNO₃ and prepared in the same manner as the samples were also titrated. The volume of titrant required for the blanks was subtracted from the volume for the sample to give a corrected volume. The mercuric nitrate standard contained the equivalent of 0.5 mg chloride/ml. The detection limit of the method was estimated at 0.05 mg chloride.

The metal analyses were conducted as follows using a Perkin Elmer Model 360 atomic absorption spectrometer. For the ZnO and Al determinations the standards were prepared by dissolving solid ZnO and Al in acid and diluting

* Hach Chemical Company

with deionized water. For the Zn, Al, Pb and Cd determinations, atomic absorption standard solutions (1.000 mg/ml) were diluted with deionized water. The standards were prepared in the same acid matrix as the sample. For Al, either Na was added to both the sample and standards or enough Zn added to the standards made with Na and those with Zn showed that both Na and Zn adequately controlled the aluminum ionization in the flame.

Aluminum was analyzed with a nitrous oxide-acetylene flame, using the 209.27 and 209.28 nm aluminum lines for analysis. Zn, ZnO, Pb and Cd were analyzed with an air-acetylene flame. The wavelengths used were 213.9 nm for Zn and ZnO, 217.0 nm for Pb and 228.8 for Cd. The minimum detection limits (twice the average noise level) are 10 μ g/100ml for Pb and Al, and 2 μ g/100 ml for Cd and Zn.

All samples and standards were diluted to levels such that the calibration curve of absorbance versus concentration was linear. Also the standards were made so that at least one of the standards had a lower metal concentration than the sample. A least squares straight line was constructed for the calibration curve and the sample concentrations were determined by interpolation.

Analytical Data for Major Components of Aerosols

The analytical data for the HC samples used in the aerosol size analysis shown in Table 21 are presented in Table 28. The aluminum content of the aerosols ranged from 4.06% to 0.49% of the zinc concentration, with a mean of 1.79 ($\sigma = 1.06$). In column 5 of Table 28, headed % d, the excess or deficit of chloride ion is given, assuming that zinc and aluminum are present only as ZnCl₂ and VAlCl₃. With three exceptions, the first 3.2.1 b and the 4.1.1 pair, the results all lie between 4 and -4%. The 3.2.1 b figure was not confirmed in the second analyses and it and the other two are believed to involve analytical errors.

A small amount of one of the aerosols was prepared for qualitative infrared analysis using a cesium iodide pellet as a matrix. The resulting spectrum was compared with reference spectra of ZnCl₂, ZnOHCl and Zn(OH)₂ previously obtained in the laboratory using the same pelleting technique. Only one strong absorption band appeared at ≈ 255 cm⁻¹, clearly identifiable

TABLE 28. CHEMICAL ANALYSIS FOR Zn^{+2} , Cl^{-} and Al^{+3} IN HC AEROSOLS GENERATED IN THE TEST CHAMBER

| Sample* | Cl^{-} mg | Al^{+3} mg | Zn^{+2} mg | Total mg | % d** | $\frac{Al}{Zn} \times 100$ |
|---------|----------------|-----------------|-----------------|-------------|-------|----------------------------|
| 1.1.1a | 44.4 | 0.61 | 38.0 | 83.0 | 1.75 | 1.61 |
| 1.1.1b | 45.6 | 0.63 | 38.8 | 85.0 | 2.26 | 1.62 |
| 1.2.1a | 27.4 | 0.265 | 25.1 | 52.8 | -3.18 | 1.06 |
| 1.2.1b | 24.1 | 0.215 | 20.6 | 44.9 | 3.77 | 1.04 |
| 2.1.1a | 21.5 | 0.439 | 18.3 | 40.2 | -0.37 | 2.40 |
| 2.1.1b | 17.8 | 0.352 | 15.0 | 33.2 | 0.80 | 2.35 |
| 2.2.1a | 9.9 | 0.090 | 8.42 | 18.4 | 4.16 | 1.07 |
| 2.2.1b | 10.4 | 0.096 | 8.95 | 19.4 | 3.02 | 1.07 |
| 3.1.1a | 56.6 | 0.47 | 49.4 | 106.5 | 2.06 | 0.95 |
| 3.1.1b | 55.9 | 0.45 | 48.4 | 104.8 | 2.91 | 0.93 |
| 3.2.1a | 8.2 | 0.116 | 7.44 | 15.8 | -3.99 | 1.56 |
| 3.2.1b | 19.1 | 0.200 | 10.9 | 30.2 | 3.40 | 1.83 |
| 3.2.1a | 23.0 | 0.355 | 20.7 | 44.1 | -3.71 | 1.71*** |
| 3.2.1b | 20.2 | 0.310 | 17.7 | 38.2 | -1.09 | 1.75*** |
| 4.1.1a | 14.0 | 0.052 | 9.65 | 23.7 | 23.8 | 0.54 |
| 4.1.1b | 16.6 | 0.059 | 12.0 | 28.7 | 28.7 | 0.49 |
| 4.2.1a | 18.8 | 0.180 | 16.0 | 35.0 | 3.91 | 1.13 |
| 4.2.1b | 21.0 | 0.232 | 18.4 | 39.6 | 0.61 | 1.26 |
| 5.1.1a | 9.9 | 0.330 | 8.12 | 18.4 | -2.11 | 4.06 |
| 5.1.1b | 9.3 | 0.307 | 7.77 | 17.4 | -3.64 | 3.95 |
| 5.2.1a | 9.2 | 0.258 | 7.58 | 17.0 | -0.42 | 3.40 |
| 5.2.1b | 11.7 | 0.345 | 9.84 | 21.9 | -2.85 | 3.51 |

* The designations a and b refer to the two halves of the filter used to collect the sample.

** % d (chloride ion deficit or excess)
= $100 [(mole Cl^{-}) - 3(mole Al^{+3}) - 2(mole Zn^{+2})] / (mole Cl^{-})$

*** Rerun

Aerosol Analysis for Trace Species

Finally an investigation was made of the aerosol material to determine the ultimate disposition of the Pb and Cd, the major impurities in the HC reagent materials. It was noted in Sec. 3.2.3 and Table 6 that the concentrations of these materials varied considerably in the few different families of HC canisters.

The investigation consisted of sampling the HC mixtures from each of the five M4-301b canisters. Each sample was separated into three portions. One portion was analyzed by solution in 5% HCl and another with 5% HNO₃ to determine if the different acids had any effect on the analysis. The third portion, 1-2 g was burned in a minipot in a 5-liter flask. The smoke was allowed to settle for 30 min and the flask was then rinsed three times with 25 ml of 5% HCl and the rinse solutions were combined and diluted to 100 ml with 5% HCl. All three fractions were analyzed by the procedure given on pp. 67 and 70.

The results of the analyses are shown in Table 29. It is seen that the alternative procedures for the HC mixtures using HCl or HNO₃ yield similar results.

In comparing the analyses of the combined HC mix and of the aerosol, particular attention is directed to the last two columns in which the mass ratios of Pb/Zn and Cd/Zn are presented. It is seen that the results of the duplicate analyses of the unburned samples and the one duplicate aerosol analysis (1.1.1) are consistently in close agreement. Also comparison of the mass ratios, Pb/Zn and Cd/Zn in the unburned mix and the aerosol materials shows very good agreement. It is noted that in all cases the Pb and Cd show a slightly higher relative concentration in the aerosol than in the starting HC mixture. There is no obvious explanation for this increase. One may speculate on the possibility of differences in the chemical kinetics of the aerosol forming process, with the zinc, cadmium and lead oxides undergoing in complete reduction or subsequent halogenation at different rates.

However, it seems clear that the Cd and Zn are associated with the Zn in both the initial mix and the final aerosol compositions.

TABLE 29. ANALYSIS FOR Zn, Pb, AND Cd IN HC MIXTURES AND HC AEROSOLS

| Sample No. | Acid | Zn, mg | Pb, µg | Cd, µg | $\frac{\text{Pb, } \mu\text{g}}{\text{Zn, mg}}$ | $\frac{\text{Cd, } \mu\text{g}}{\text{Zn, mg}}$ |
|----------------------|-----------------|--------|--------|--------|---|---|
| Unburned HC Mixtures | 1.1.1 | 67.8 | 147 | 12 | 2.17 | 0.18 |
| | | 67.6 | 146 | 12 | 2.16 | 0.18 |
| | 2.1.1 | 68.3 | 9 | 343 | 0.13 | 5.02 |
| | | 67.8 | 9 | 341 | 0.13 | 5.03 |
| | 3.2.1 | 68.8 | 125 | 53.1 | 1.82 | 0.77 |
| | | 69.1 | 125 | 52.7 | 1.81 | 0.76 |
| | 4.1.1 | 70.0 | 136 | 57.0 | 1.94 | 0.81 |
| | | 69.0 | 136 | 55.9 | 1.97 | 0.81 |
| | 5.1.1 | 70.1 | 7 | 150 | 0.10 | 2.14 |
| | | 69.1 | 7 | 147 | 0.10 | 2.13 |
| HC Aerosols | 1.1.1A* | 33.5 | 84 | 7 | 2.51 | 0.21 |
| | 1.1.1B* | 130 | 328 | 29.4 | 2.52 | 0.23 |
| | 2.1.1 | 136 | 28 | 780 | 0.21 | 5.73 |
| | 3.1.1 | 184 | 353 | 179 | 1.92 | 0.97 |
| | 4.1.1 | 79.9 | 179 | 69.2 | 2.24 | 0.87 |
| | 5.1.1 | 73.2 | 11 | 159 | 0.15 | 2.17 |
| | Estimated Error | ±1 | ±2 | ±2 | | |

* 1.1.1A and B were two separate samples.

APPENDIX A

TIME HISTORIES OF HC FOG EXPERIMENTS

The Tables which follow summarize the time histories of HC fog experiments 11 through 29. The Tables include the mass concentration, TSP, in mg/m^3 and mass median diameter, \bar{d}_m , in μm as determined by the P/Z cascade impactor and the number concentration, $[n]$, particles per cm^3 and geometric mean particle diameter, d_{av} , in μm as determined by the aerosol spectrometer at various times after ignition.

Table A1
 SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 11

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min:sec | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| -- | -- | -- | 4 | 0.822 | 0.327 |
| -- | -- | -- | 6 | 0.892 | 0.314 |
| 8:15 | 74.8 | 0.352 | 8 | 0.866 | 0.320 |
| 10:45 | 42.2 | 0.476 | 10 | 0.822 | 0.337 |
| -- | -- | -- | 12 | 0.739 | 0.342 |
| 15:50 | 107.1 | 0.405 | 14 | 0.644 | 0.364 |
| 18:20 | 110.2 | 0.475 | -- | -- | -- |
| 20:45 | 104.3 | 0.402 | 20 | 0.629 | 0.386 |
| 23:25 | 95.1 | 0.426 | -- | -- | -- |
| 25:50 | 95.7 | 0.443 | 25 | 0.609 | 0.405 |
| 28:10 | 108.1 | 0.433 | -- | -- | -- |
| 30:45 | 76.8 | 0.350 | 30 | 0.534 | 0.421 |
| 33:20 | 123.3 | 0.425 | -- | -- | -- |
| 35:50 | 76.5 | 0.416 | 35 | 0.480 | 0.448 |
| 38.25 | 105.2 | 0.420 | -- | -- | -- |

Table A2

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 12

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|---------------------|----------------------|---|------------------|
| Time, min:sec | TSP mg/m ³ | \bar{d}_m , um | Time, min:sec | conc. [n] (x10 ⁶ /cm ³) | d_{av} , um |
| 2:00 | 39.2 | 0.386 | 2:00 | 2.32 | 0.305 |
| 4:30 | 44.8 | 0.428 | -- | -- | -- |
| 15:00 | 44.2 | 0.512 | -- | -- | -- |
| -- | -- | -- | 20:30 | 1.233 | 0.404 |
| 30:00 | 57.9 | 0.511 | 30:00 | 1.318 | 0.467 |
| 45:00 | 57.6 | 0.445 | 45:00 | 0.970 | 0.473 |
| 50:00 | 48.6 | 0.493 | 60:00 | 0.900 | 0.533 |
| 75:00 | 35.2 | 0.457 | 75:00 | 0.574 | 0.543 |
| 90:00 | 39.8 | 0.607 | 90:00 | 0.602 | 0.539 |
| 105:00 | 35.2 | 0.526 | 105:00 | 0.436 | 0.562 |
| 120:00 | 30.6 | 0.606 | 120:00 | 0.466 | 0.583 |

Table A3

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 13

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min:sec | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2:00 | 45.9 | 0.403 | 2 | 2.825 | 0.270 |
| 4:35 | 99.8 | 0.404 | 4 | 2.281 | 0.315 |
| 8:00 | 97.7 | 0.396 | 8 | 2.250 | 0.297 |
| 11:00 | 105.3 | 0.438 | 11 | 1.859 | 0.340 |
| 15:00 | 100.8 | 0.423 | 14 | 1.486 | 0.357 |
| 30:00 | 78.9 | 0.466 | 30 | 1.358 | 0.426 |
| 45:00 | 74.1 | 0.496 | 45 | 0.983 | 0.465 |
| 60:00 | 73.2 | 0.568 | 60 | 0.762 | 0.513 |
| 75:00 | 59.6 | 0.581 | 75 | 0.707 | 0.505 |
| 91:00 | 65.1 | 0.544 | 90 | 0.727 | 0.550 |
| 106:15 | 50.6 | 0.604 | 105 | 0.606 | 0.545 |
| 120:00 | 41.3 | 0.605 | 120 | 0.392 | 0.555 |

Table A4

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 14

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 55.4 | 0.415 | 2 | 2.207 | 0.308 |
| 5 | 97.2 | 0.389 | 4 | 1.935 | 0.321 |
| 7 | 116.6 | 0.389 | 6 | 1.930 | 0.325 |
| 9 | 105.0 | 0.381 | 8 | 1.691 | 0.335 |
| 11 | 103.8 | 0.419 | 10 | 1.668 | 0.349 |
| 13 | 103.8 | 0.419 | 12 | 1.617 | 0.349 |
| 15 | 105.4 | 0.407 | 14 | 1.418 | 0.359 |
| 32 | 87.4 | 0.427 | 32 | 1.087 | 0.419 |
| 47 | 72.8 | 0.436 | 47 | 0.832 | 0.443 |
| 77 | 69.2 | 0.437 | 77 | 0.607 | 0.496 |
| 92 | 58.5 | 0.449 | 92 | 0.510 | 0.511 |
| 107 | 54.7 | 0.532 | 107 | 0.434 | 0.510 |
| 121 | 50.5 | 0.541 | 122 | 0.382 | 0.520 |

Table A5

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 15

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min:sec | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2:00 | 87.2 | 0.393 | 2 | 6.749 | 0.212 |
| 4:20 | 147.0 | 0.416 | 4 | 6.541 | 0.218 |
| 7:00 | 161.2 | 0.425 | 6 | 6.114 | 0.228 |
| -- | -- | -- | 8 | 5.369 | 0.236 |
| 10:00 | 161.5 | 0.434 | 10 | 4.707 | 0.249 |
| -- | -- | -- | 12 | 4.466 | 0.257 |
| 15:00 | 166.5 | 0.446 | 14 | 4.020 | 0.268 |
| 20:00 | 156.3 | 0.468 | -- | -- | -- |
| 30:00 | 234.8 | 0.508 | 32 | 1.805 | 0.389 |
| 45:00 | 133.3 | 0.467 | 47 | 1.219 | 0.474 |
| 60:00 | 110.4 | 0.473 | 62 | 0.926 | 0.515 |
| 75:00 | 96.1 | 0.537 | 77 | 0.810 | 0.524 |
| 90:00 | 86.5 | 0.543 | 92 | 0.662 | 0.541 |

Table A6

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 16

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. \bar{n} ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 44.4 | 0.394 | 2 | 1.788 | 0.285 |
| 4 | 109.5 | 0.399 | 4 | 1.871 | 0.306 |
| 6 | 117.6 | 0.402 | 6 | 1.680 | 0.321 |
| 8 | 119.1 | 0.406 | 8 | 1.623 | 0.317 |
| 10 | 119.1 | 0.427 | 10 | 1.520 | 0.339 |
| 12 | 128.7 | 0.450 | 12 | 1.313 | 0.341 |
| 14 | 104.3 | 0.464 | 14 | 1.307 | 0.370 |
| -- | -- | -- | 16 | 1.142 | 0.367 |
| -- | -- | -- | 18 | 1.104 | 0.388 |
| 20 | 119.7 | 0.449 | 20 | 1.001 | 0.398 |
| 22 | 113.6 | 0.497 | 22 | 0.930 | 0.402 |
| 24 | 110.1 | 0.507 | 24 | 0.868 | 0.412 |
| 26 | 105.8 | 0.467 | | | |
| 28 | 108.9 | 0.518 | | | |

Table A7

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 17

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 41.6 | 0.414 | 2 | 0.808 | 0.336 |
| 4 | 63.0 | 0.456 | 4 | 0.913 | 0.341 |
| 6 | 81.9 | 0.396 | 6 | 0.786 | 0.347 |
| 8 | 76.7 | 0.464 | 8 | 0.747 | 0.353 |
| 10 | 78.2 | 0.437 | 10 | 0.673 | 0.363 |
| 12 | 67.7 | 0.465 | 12 | 0.654 | 0.367 |
| 14 | 91.5 | 0.432 | 14 | 0.613 | 0.379 |
| -- | -- | -- | 20 | 0.562 | 0.394 |
| -- | -- | -- | 22 | 0.543 | 0.387 |
| -- | -- | -- | 24 | 0.511 | 0.413 |
| -- | -- | -- | 26 | 0.507 | 0.409 |
| -- | -- | -- | 28 | 0.536 | 0.407 |
| 30 | 63.6 | 0.497 | 30 | 0.468 | 0.416 |
| -- | -- | -- | 40 | 0.397 | 0.445 |
| 45 | 61.2 | 0.473 | 45 | 0.353 | 0.465 |
| 60 | 57.7 | 0.481 | 60 | 0.283 | 0.474 |
| 75 | 52.5 | 0.471 | 70 | 0.303 | 0.482 |

Table A8

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 18

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 140.9 | 0.407 | 2 | 7.010 | 0.255 |
| 4 | 230.3 | 0.442 | 4 | 6.407 | 0.236 |
| 6 | 229.5 | 0.459 | 6 | 5.708 | 0.241 |
| 8 | 210.3 | 0.495 | 8 | 5.190 | 0.250 |
| 10 | 210.6 | 0.501 | 10 | 4.798 | 0.255 |
| 12 | 202.2 | 0.517 | 12 | 4.136 | 0.274 |
| 14 | 192.3 | 0.532 | 14 | 4.480 | 0.307 |
| 16 | 190.1 | 0.518 | -- | -- | -- |
| -- | -- | -- | 22 | 1.238 | 0.421 |
| 30 | 105.5 | 0.538 | 32 | 0.874 | 0.421 |
| 45 | 73.8 | 0.565 | 47 | 0.654 | 0.460 |

Table A9

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 19

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min:sec | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2:00 | 18.6 | 0.255 | 2 | 0.536 | 0.271 |
| 4:15 | 33.1 | 0.476 | 4 | 0.477 | 0.279 |
| 7:00 | 36.6 | 0.412 | 6 | 0.527 | 0.277 |
| -- | -- | -- | 8 | 0.479 | 0.282 |
| -- | -- | -- | 10 | 0.496 | 0.284 |
| 12:30 | 23.8 | 0.417 | 12 | 0.460 | 0.294 |
| -- | -- | -- | 14 | 0.419 | 0.282 |
| -- | -- | -- | 16 | 0.435 | 0.282 |
| 19:00 | 27.1 | 0.472 | 18 | 0.413 | 0.289 |
| 21:00 | 30.0 | 0.455 | 20 | 0.386 | 0.294 |
| -- | -- | -- | 22 | 0.378 | 0.299 |
| -- | -- | -- | 24 | 0.377 | 0.298 |
| 26:00 | 30.0 | 0.455 | 26 | 0.375 | 0.311 |

Table A10

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 20

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 28.2 | 0.419 | 2 | 1.063 | 0.319 |
| 4 | 82.2 | 0.442 | 4 | 1.027 | 0.319 |
| 6 | 72.3 | 0.474 | 6 | 1.044 | 0.338 |
| 8 | 97.1 | 0.416 | 8 | 0.900 | 0.341 |
| 10 | 77.0 | 0.481 | 10 | 0.933 | 0.353 |
| 12 | 91.5 | 0.432 | 12 | 0.904 | 0.358 |
| 14 | 86.0 | 0.450 | 14 | 0.835 | 0.355 |
| 16 | 78.2 | 0.468 | --- | -- | -- |
| 20 | 82.5 | 0.459 | 20 | 0.785 | 0.366 |
| 25 | 100.9 | 0.481 | 25 | 0.679 | 0.383 |
| 30 | 72.9 | 0.477 | 30 | 0.597 | 0.417 |
| 35 | 81.3 | 0.472 | 35 | 0.593 | 0.416 |

Table A11

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 21

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|---|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] (x10 ⁶ /cm ³) | d_{av} , μm |
| 6 | 13.7 | 0.504 | 6 | 0.924 | 0.371 |
| 8 | 119.9 | 0.393 | 8 | 0.865 | 0.362 |
| 10 | 72.3 | 0.474 | 10 | 0.891 | 0.382 |
| 12 | 90.0 | 0.455 | 12 | 0.834 | 0.371 |
| 14 | 72.3 | 0.474 | 14 | 0.781 | 0.382 |
| 22 | 72.6 | 0.492 | -- | -- | -- |
| 24 | 90.3 | 0.470 | -- | -- | -- |
| 26 | 81.6 | 0.458 | 25 | 0.849 | 0.424 |
| 28 | 77.3 | 0.499 | 27 | 0.803 | 0.420 |
| 30 | 86.3 | 0.466 | 29 | 0.727 | 0.421 |

Table A12

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 22

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 23.3 | 0.324 | 2 | 0.803 | 0.289 |
| 4 | 48.8 | 0.386 | 4 | 1.607 | 0.324 |
| 6 | 117.9 | 0.381 | 6 | 1.565 | 0.290 |
| 8 | 111.2 | 0.400 | 8 | 1.724 | 0.321 |
| 10 | 140.9 | 0.390 | 10 | 1.626 | 0.330 |
| 12 | 132.4 | 0.414 | 12 | 1.615 | 0.341 |
| 14 | 164.4 | 0.428 | 14 | 1.453 | 0.342 |
| 20 | 158.8 | 0.443 | 20 | 1.228 | 0.372 |
| 25 | 131.5 | 0.451 | 25 | 0.963 | 0.387 |
| 30 | 118.5 | 0.450 | 30 | 0.811 | 0.406 |

Table A13

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 23

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|---|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] (x10 ⁶ /cm ³) | d_{av} , μm |
| 2 | 22.7 | 0.377 | 2 | 2.255 | 0.321 |
| 4 | 132.2 | 0.414 | 4 | 2.144 | 0.333 |
| 6 | 150.5 | 0.428 | 6 | 2.070 | 0.343 |
| 8 | 163.8 | 0.411 | 8 | 1.808 | 0.359 |
| 10 | 131.0 | 0.422 | 10 | 1.746 | 0.371 |
| 12 | 137.7 | 0.386 | 12 | 1.594 | 0.381 |
| 14 | 113.0 | 0.395 | 14 | 1.532 | 0.385 |
| 16 | 109.2 | 0.387 | -- | -- | -- |
| 18 | 103.4 | 0.386 | -- | -- | -- |
| 20 | 96.8 | 0.326 | 20 | 1.221 | 0.424 |
| 22 | 71.8 | 0.300 | -- | -- | -- |
| 24 | 62.5 | 0.282 | 24 | 1.122 | 0.424 |

Table A14

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 24

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 38.5 | 0.242 | 2 | 2.217 | 0.306 |
| 4 | 31.7 | 0.274 | 4 | 2.093 | 0.315 |
| 6 | 37.5 | 0.228 | 6 | 1.882 | 0.329 |
| 8 | 42.8 | 0.242 | 8 | 1.881 | 0.342 |
| 10 | 31.7 | 0.274 | 10 | 1.711 | 0.349 |
| 12 | 28.5 | 0.242 | 12 | 1.554 | 0.348 |
| 14 | 25.6 | 0.235 | 14 | 1.545 | 0.361 |
| 16 | 15.3 | 0.264 | -- | -- | -- |
| 18 | 16.1 | 0.231 | -- | -- | -- |
| 20 | 9.5 | 0.242 | 20 | 1.303 | 0.385 |
| 22 | 19.0 | 0.242 | -- | -- | -- |
| -- | -- | -- | 24 | 1.129 | 0.391 |

Table A15

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 25

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 8 | 69.5 | 0.361 | 8 | 2.019 | 0.253 |
| 10 | 142.2 | 0.323 | 10 | 2.068 | 0.260 |
| 12 | 125.9 | 0.409 | 12 | 1.944 | 0.260 |
| 14 | 120.0 | 0.387 | 14 | 1.876 | 0.264 |
| 16 | 125.9 | 0.367 | 16 | 1.550 | 0.276 |
| 18 | 99.2 | 0.382 | 18 | 1.465 | 0.287 |
| 20 | 102.9 | 0.391 | 20 | 1.438 | 0.285 |
| 22 | 99.2 | 0.358 | 22 | 1.279 | 0.291 |
| 24 | 84.3 | 0.403 | 24 | 1.256 | 0.293 |

Table A16

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 26

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 73.2 | 0.412 | 2 | 0.938 | 0.311 |
| 4 | 113.2 | 0.360 | 4 | 1.085 | 0.301 |
| 6 | 118.6 | 0.416 | 6 | 1.036 | 0.337 |
| 8 | 111.2 | 0.410 | 8 | 0.780 | 0.318 |
| 10 | 111.2 | 0.431 | 10 | 0.767 | 0.319 |
| 12 | 100.8 | 0.415 | 12 | 0.788 | 0.334 |
| 14 | 123.6 | 0.421 | 14 | 0.763 | 0.326 |
| 16 | 117.8 | 0.455 | -- | -- | -- |
| 18 | 105.8 | 0.455 | -- | -- | -- |
| 20 | 112.0 | 0.434 | 20 | 0.622 | 0.347 |
| 22 | 98.4 | 0.478 | -- | -- | -- |
| 24 | 105.8 | 0.455 | -- | -- | -- |
| 26 | 98.4 | 0.478 | 25 | 0.474 | 0.349 |
| 28 | 105.0 | 0.471 | -- | -- | -- |

Table A17

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 27

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 48.4 | 0.316 | 2 | 4.593 | 0.235 |
| 4 | 114.2 | 0.463 | 4 | 4.356 | 0.238 |
| 6 | 181.4 | 0.385 | 6 | 4.291 | 0.244 |
| 8 | 145.2 | 0.492 | 8 | 3.515 | 0.263 |
| 10 | 188.0 | 0.419 | 10 | 3.438 | 0.262 |
| 12 | 166.2 | 0.477 | 12 | 3.222 | 0.272 |
| 14 | 166.6 | 0.477 | 14 | 2.781 | 0.280 |
| 16 | 165.4 | 0.476 | -- | -- | -- |
| 18 | 143.6 | 0.512 | -- | -- | -- |
| 20 | 153.4 | 0.478 | 20 | 1.826 | 0.342 |
| 22 | 140.2 | 0.526 | -- | -- | -- |
| 24 | 134.6 | 0.488 | 25 | 1.361 | 0.370 |

Table A18

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 28

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2 | 56.2 | 0.479 | 2 | 0.871 | 0.314 |
| 4 | 69.8 | 0.455 | 4 | 0.816 | 0.322 |
| 6 | 64.4 | 0.314 | 6 | 0.750 | 0.328 |
| 8 | 93.8 | 0.455 | 8 | 0.803 | 0.324 |
| 10 | 50.8 | 0.435 | 10 | 0.743 | 0.355 |
| 13 | 38.3 | 0.368 | 12 | 0.705 | 0.334 |
| 15 | 34.5 | 0.290 | 14 | 0.635 | 0.342 |
| 18 | +1.1 | 0.373 | -- | -- | -- |
| 21 | 47.5 | 0.422 | 20 | 0.575 | 0.337 |
| 24 | 49.8 | 0.446 | 25 | 0.520 | 0.353 |

Table A19

SIZE AND CONCENTRATION HISTORY, HC FOG EXPERIMENT 29

| P/Z Cascade Impactor | | | Aerosol Spectrometer | | |
|----------------------|--------------------------|--------------------------------|----------------------|--|-----------------------------|
| Time, min:sec | TSP mg/m ³ | \bar{d}_m , μm | Time, min | conc. [n] ($\times 10^6/\text{cm}^3$) | d_{av} , μm |
| 2:00 | 37.5 | 0.464 | -- | -- | -- |
| 4:00 | 56.4 | 0.419 | 4 | 0.755 | 0.339 |
| 6:00 | 61.1 | 0.433 | 6 | 0.723 | 0.350 |
| 8:00 | 62.0 | 0.395 | 8 | 0.676 | 0.349 |
| 10:00 | 51.8 | 0.440 | 10 | 0.641 | 0.360 |
| 12:15 | 60.9 | 0.450 | 12 | 0.660 | 0.361 |
| 14:30 | 58.4 | 0.415 | 14 | 0.566 | 0.359 |
| 16:45 | 54.9 | 0.449 | -- | -- | -- |
| 19:00 | 48.9 | 0.448 | -- | -- | -- |
| 21:15 | 55.1 | 0.436 | 20 | 0.529 | 0.371 |
| 23:30 | 54.9 | 0.449 | -- | -- | -- |
| -- | -- | -- | 25 | 0.464 | 0.376 |

APPENDIX B

LEAD AND CADMIUM CONCENTRATIONS IN HC SMOKE POTS

Flame ionization was used in the determination of the lead and cadmium levels in the PC canisters. Following the usual procedure, the analytical samples were placed in solution at suitable concentrations and four to six determinations were made on each sample. The reported results are the averages of these individual determinations.

Two canisters were sampled from each of Lots 1, 2, 4 and 5 and one was sampled from Lot 3. Each canister was sampled at two positions at three levels. The results are listed in Table B-1.

The mean concentrations and their standard deviations are given in Table B-2.

TABLE B-1. LEAD AND CADMIUM CONCENTRATIONS IN HC SMOKE POTS

| Sample | Lead, ppm by weight | | Cadmium, ppm by weight | |
|--------|---------------------|-----|------------------------|------|
| | 1st | 2nd | 1st | 2nd |
| 1.1.1 | 844 | 805 | 52 | 47 |
| 1.1.2 | 842 | 805 | 55 | 52 |
| 1.1.3 | 916 | 937 | 59 | 55 |
| 1.2.1 | 799 | 827 | 61 | 54 |
| 1.2.2 | 711 | 748 | 55 | 59 |
| 1.2.3 | 848 | 835 | 55 | 55 |
| 2.1.1 | 49 | 44 | 1480 | 1510 |
| 2.1.2 | 44 | 49 | 1550 | 1538 |
| 2.1.3 | 57 | 61 | 1530 | 1530 |
| 2.2.1 | 42 | 47 | 1404 | 1410 |
| 2.2.2 | 43 | 45 | 1220 | 1241 |
| 2.2.3 | 41 | 41 | 1274 | 1263 |
| 3.2.1 | 649 | 639 | 287 | 284 |
| 3.2.2 | 642 | 650 | 335 | 338 |
| 3.2.3 | 612 | 598 | 274 | 277 |
| 4.1.1 | 608 | 606 | 297 | 296 |
| 4.1.2 | 664 | 658 | 298 | 293 |
| 4.1.3 | 786 | 750 | 296 | 300 |
| 4.2.1 | 797 | 785 | 280 | 278 |
| 4.2.2 | 698 | 725 | 302 | 296 |
| 4.2.3 | 719 | 749 | 307 | 304 |
| 5.1.1 | 75 | 78 | 800 | 793 |
| 5.1.2 | 35 | 34 | 802 | 808 |
| 5.1.2 | 40 | 39 | 813 | 818 |
| 5.2.1 | 34 | 29 | 887 | 862 |
| 5.2.2 | 27 | 25 | 906 | 897 |
| 5.2.3 | 33 | 35 | 934 | 937 |

TABLE B-2. MEAN CONCENTRATIONS AND STANDARD DEVIATIONS OF LEAD AND CADMIUM IN EACH LOT

| Lot No. | Lead, ppm by weight | | Cadmium, ppm by weight | |
|---------|---------------------|----------|------------------------|----------|
| | mean | σ | mean | σ |
| 1-1 | 858.17 | 56.0 | 53.33 | 4.03 |
| 1-2 | 794.67 | 54.25 | 56.50 | 2.81 |
| 2-1 | 50.67 | 6.95 | 1523.0 | 24.78 |
| 2-2 | 43.17 | 2.40 | 1302.0 | 83.45 |
| 3-2 | 631.67 | 21.53 | 299.17 | 29.31 |
| 4-1 | 678.67 | 74.20 | 296.67 | 2.34 |
| 4-2 | 745.5 | 39.0 | 294.5 | 12.55 |
| 5-1 | 50.17 | 20.55 | 805.67 | 9.14 |
| 5-2 | 30.50 | 4.09 | 870.50 | 89.62 |

The data of Table B-2 were used to derive the correlation:

$$\text{Pb} = -0.632 \text{ Cd} + 817.98$$

with the correlation coefficient of 0.914. A plot of the correlation is shown in Figure B-1.

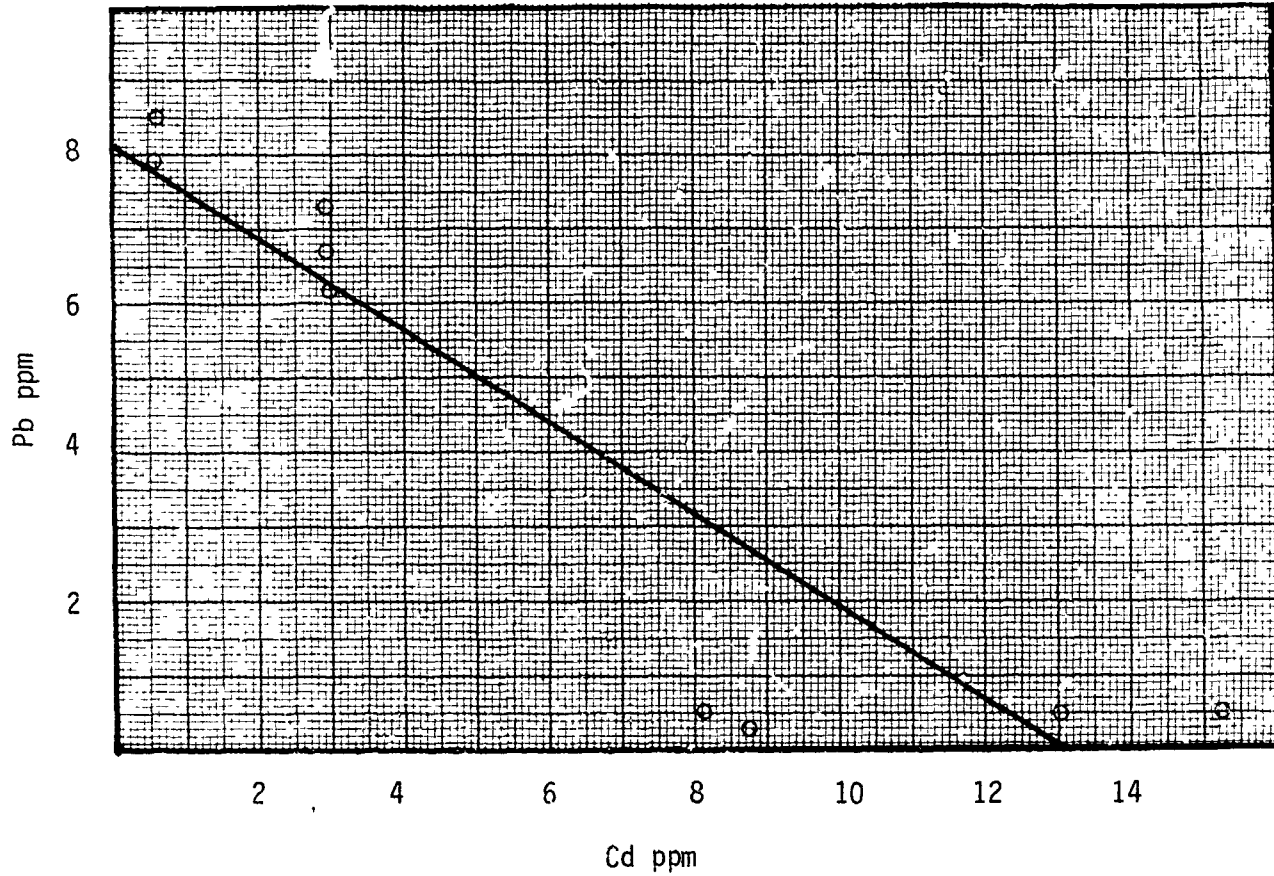


Figure B-1. Lead-cadmium concentration correlation.

$$Pb = -0.632 Cd + 817.98$$

APPENDIX C

THE M5-HC SMOKE POT

The M5-HC canister is a cylindrical metal container 22 cm (8 3/4 in) in diameter and 24.0 cm (9 1/2 in) in external length and weighing approximately 15.85 kg (35 lb) when fully loaded. A canister is shown in Figure C-1. The description of the canister and the sequence of events in disarming and opening it are described here.

The top of the can is permanently affixed. The firing mechanism was exposed by peeling back a tearable circular opening approximately 4 inches in diameter. Upon removing this central cover (Figure C-2) a felt "horse-shoe" was observed protecting the igniter squibs and the button of friction match material. A small envelope contained a friction striker for mechanical ignition. The striker and felt washer were discarded. A permanent metal inner cover about 1/2" below the outer cover was found. Two electric igniter squibs were clipped to a cardboard cover in the center of the can (Figure C-3). The starter mix is contained in a plastic cup below this cover. The clips were bent back, (Figure C-4) the squibs freed, the wires cut and the squibs removed for disposal. The metal ring retaining the cup of starter mix and its cardboard cover were cut and removed using a pair of diagonal cutting pliers shown in Figure C-5. The cup of igniter mix was then removed (Figure C-6) and disposed of in a safe manner.



Figure C-1. M5-HC 30-1b smoke pot.



Figure C-2. 30-1b HC smoke pot; top opened.

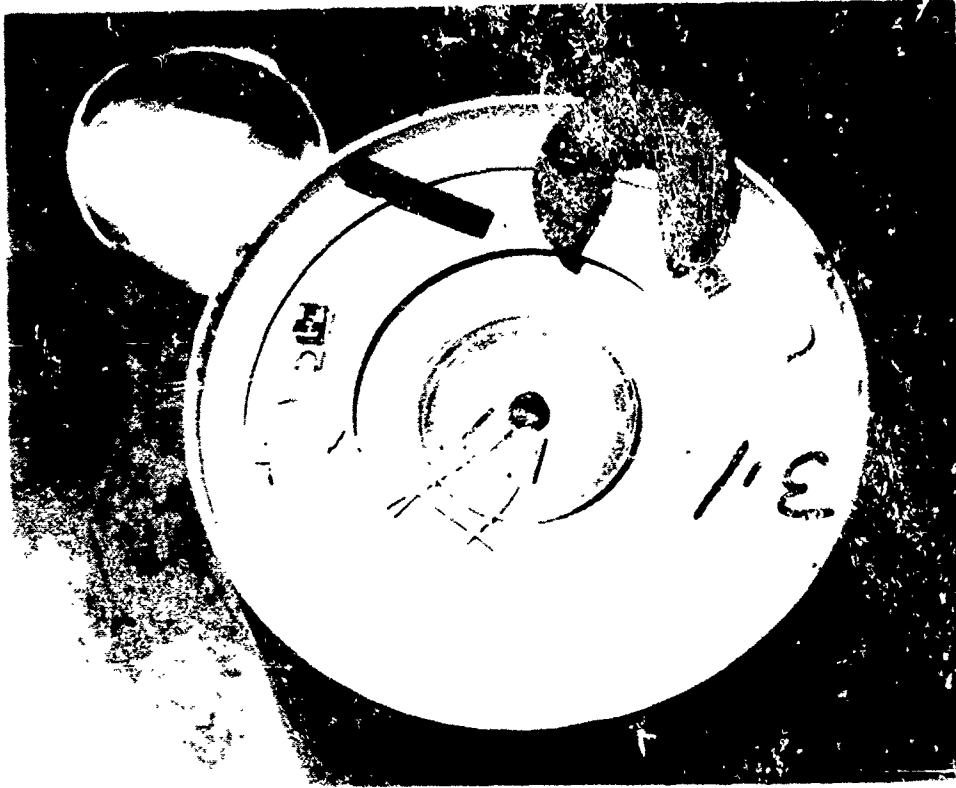


Figure C-3. 30-1b HC smoke pot; electric squibs exposed.

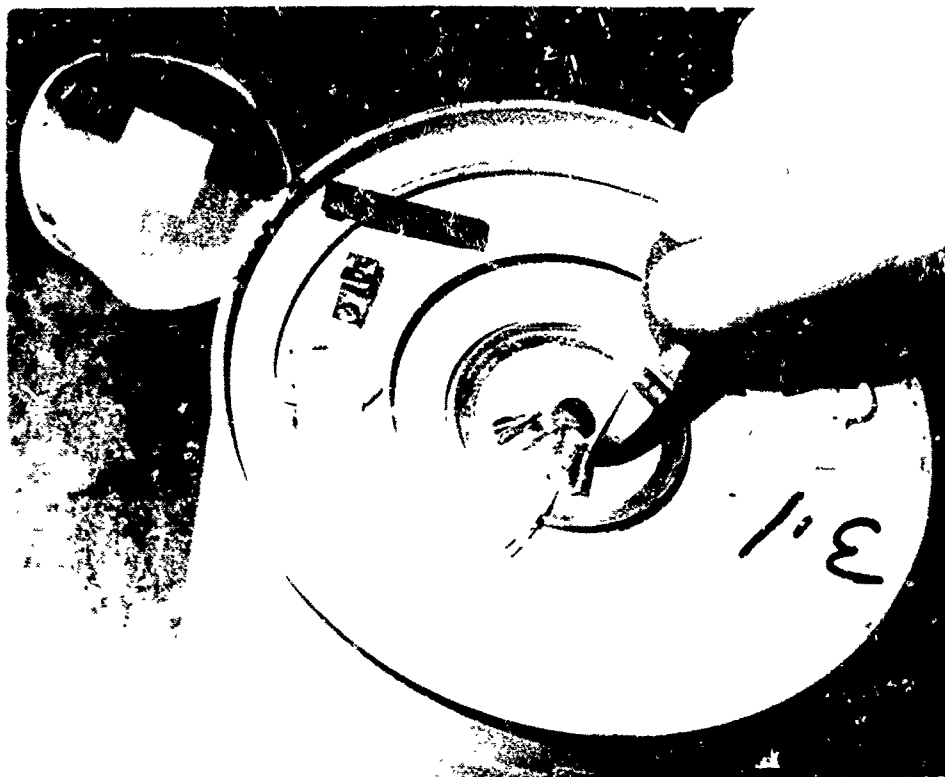


Figure C-4. 30-lb HC smoke pot; removing igniter squibs.

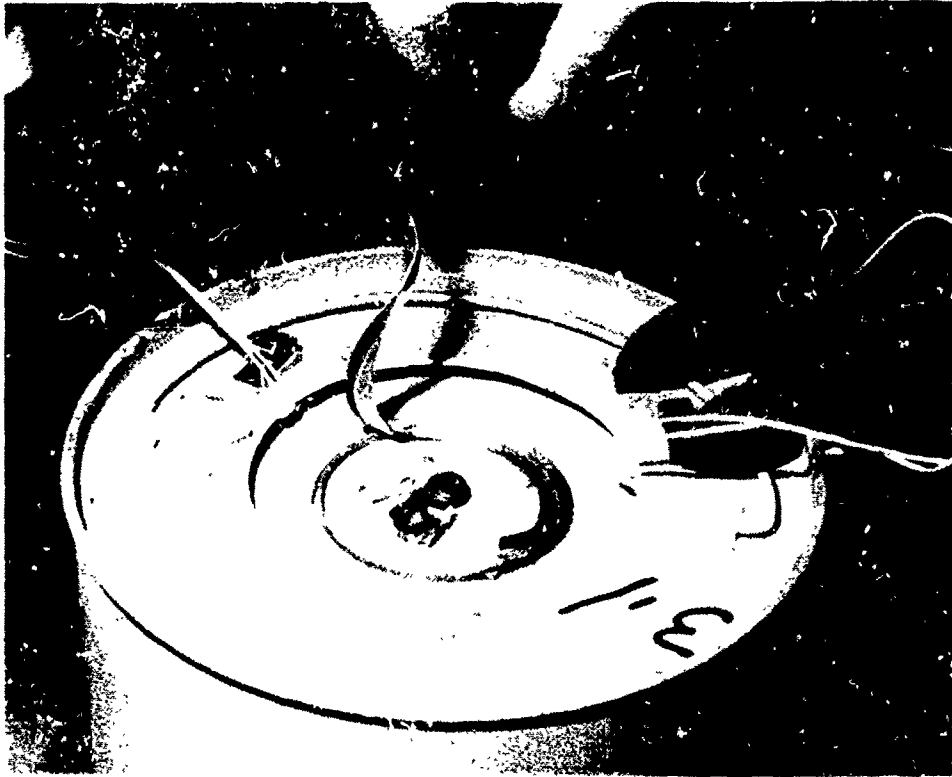


Figure C-5. 30-7b smoke pot; removing cup retaining ring.

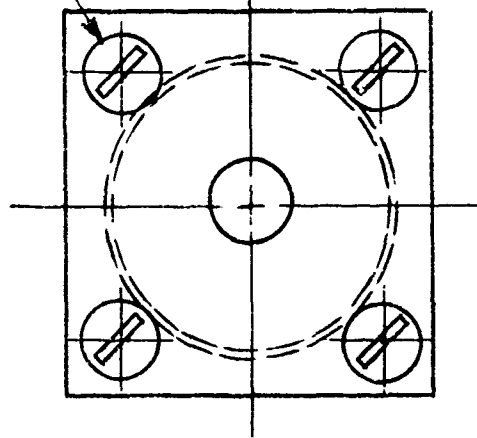


Figure C-6. 30-1b smoke pot; starter mix cup.

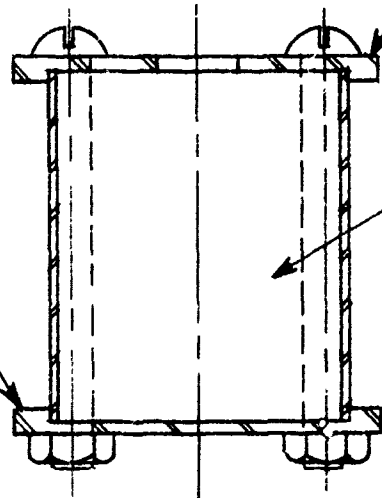
APPENDIX D
MINIPOT DESIGN

-A-

#12-28UNF-2, STEEL MACHINE
SCREW & NUTS IN APPROP. LENGTHS.
4 REQ'D EACH ASSY



ORIFICE PLATE
SP-A-2




BODY
SP-A-3

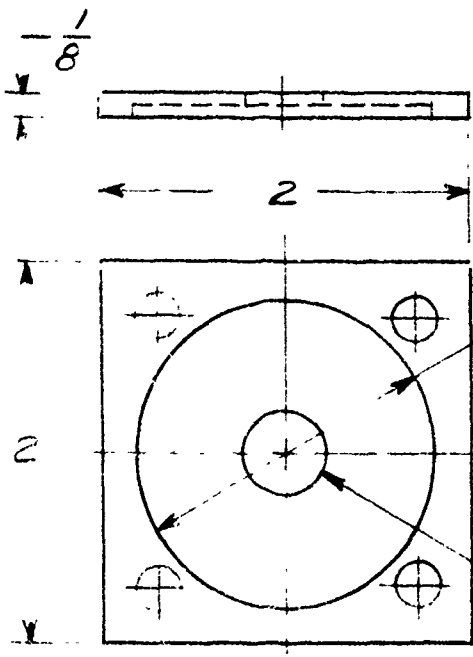
BOTTOM PLATE
SP-A-2

NOTE:

3 ASSEMBLIES REQ'D
1 EACH OF SIZE 100, 50 & 10

| | | | | | | |
|---|---|--------------|-------------------------|--------------------------------------|---------|----------|
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| | IIT RESEARCH INSTITUTE TECHNOLOGY CENTER CHICAGO, ILLINOIS 60616 | | | | | |
| MATERIAL | MODEL SMOKE POT ASSY C6437 | | | | | |
| HEAT TREA. | | | | | | |
| TOLERANCES UNLESS OTHERWISE SPECIFIED FRACTIONS $\pm 1/64$ DECIMALS $\pm .005$ THDS CLASS 2 FIT ANGULAR $\pm 1^\circ$ | FINISH  UNLESS OTHERWISE NOTED | QUANTITY PER | DESIGNED | DRAWN | CHECKED | APPROVED |
| | | NAME | RR | J.N. | | |
| DO NOT SCALE - REPORT ERRORS BREAK ALL SHARP CORNERS C'SINK ALL TAPPED HOLES $1/32 \times 45^\circ$ REMOVE BURRS | UNLESS OTHERWISE NOTED | SUB-ASSEMBLY | DATE | 1/2/79 | 6/18/79 | |
| | | SCALE | NEXT ASSEMBLY NO. | PROJECT DRAWING NO. SP-A-1 | | |

-A-

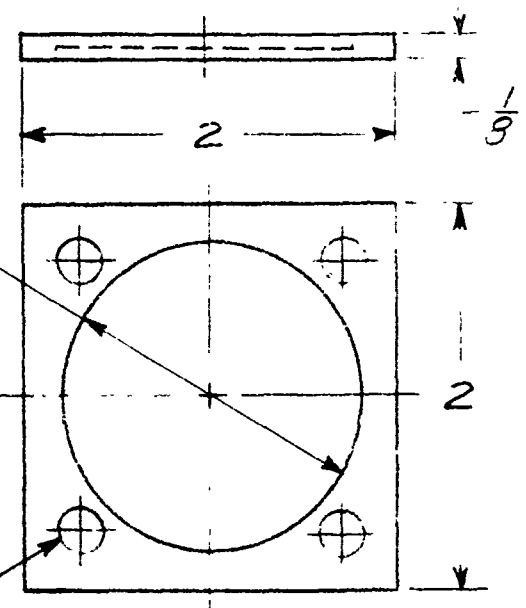


ORIFICE PLATE

"D" DIA.
SEE NOTE A

"D" DIA.
SEE NOTE A

"d" DIA.



BOTTOM PLATE

LOCATE & DRILL FOR #12-28 UNF MACHINE SCREWS, 4 HOLES TO JUST CLEAR "D" DIA. AND HOLES IN BOTH PLATES TO BE IN LINE

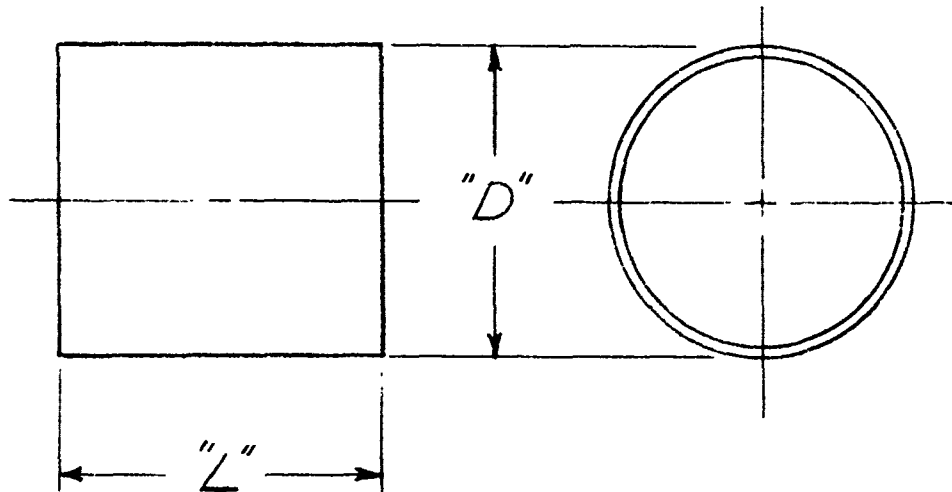
NOTES:

A. SPOTFACE 1/16 DEEP x "D" DIA., MAKE TO FIT APPROP BODY DIA.
PART NO. SP-A-3

| SIZE | REQ'D | "D" DIA. | "d" DIA. |
|------|-------|----------|------------|
| 100 | 1 | 1 5/8 | 7/16 DRILL |
| 50 | 1 | 1 1/4 | "Q" DRILL |
| 10 | 1 | 7/8 | #7 DRILL |

| | | | | | | |
|---|--------------------------------------|--|-------------|-------------------------|-------------------------------|----------|
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| MATERIAL STAIN. STL. | | IIT RESEARCH INSTITUTE TECHNOLOGY CENTER CHICAGO, ILLINOIS 60616 | | | | |
| HEAT TREAT | | ORIFICE AND BOTTOM PLATES C6437 | | | | |
| TOLERANCES UNLESS OTHERWISE SPECIFIED FRACTIONS ± 1/64 DECIMALS ± .005 THDS CLASS 2 FIT ANGULAR ± 1° | FINISH UNLESS OTHERWISE NOTED | QUANTITY PER | DESIGNED | DRAWN | CHECKED | APPROVED |
| | | SUB-ASSEMBLY | NAME R.R. | J.N. | | |
| DO NOT SCALE - REPORT ERRORS BREAK ALL SHARP CORNERS C/SINK ALL TAPPED HOLES 1/32 x 45° REMOVE BURRS | | SCALE 1:1 | DATE 1/2/79 | 6/18/79 | PROJECT DRAWING NO. SP-A-2 | |

-A-



| SIZE | REQ'D | "D" O.D. | WALL | "L" |
|------|-------|----------|--------|-----|
| 100 | 1 | 1 5/8 | 20 GA. | 1.7 |
| 50 | 1 | 1 1/4 | 20 GA. | 1.3 |
| 10 | 1 | 7/8 | 18 GA. | .8 |

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| SYM. | DATE | DESCRIPTION OF REVISION | NAME |
|--|------|-------------------------|------|
| IIT RESEARCH INSTITUTE TECHNOLOGY CENTER CHICAGO, ILLINOIS 60616 | | | |

MATERIAL *STAIN. STL. TUBING*

HEAT TREAT

BODY
C6437

TOLERANCES
UNLESS OTHERWISE SPECIFIED
FRACTIONS ± 1/64 DECIMALS ± .005
THDS CLASS 2 FIT ANGULAR ± 1°

FINISH

UNLESS OTHERWISE NOTED

QUANTITY PER

SUB-ASSEMBLY

SCALE
1:1

| DESIGNED | DRAWN | CHECKED | APPROVED |
|------------|-------------|---------|----------|
| <i>ICK</i> | <i>J.N.</i> | | |

| NAME | DATE |
|------------|---------------|
| <i>ICK</i> | <i>1/2/79</i> |

| DATE |
|----------------|
| <i>6/18/79</i> |

NEXT ASSEMBLY NO.

PROJECT DRAWING NO.

SP-A-3

DO NOT SCALE - REPORT ERRORS
BREAK ALL SHARP CORNERS
C/SINK ALL TAPPED HOLES 1/32 x 45°
REMOVE BURRS

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SUPPLEMENTARY

INFORMATION

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IIT Research Institute
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312/567-4000

February 22, 1980

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Command Contract DAMD17-78-C-8085
Final Report on Hexachloroethane Smoke

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At the request of the Contractor's Technical Review Group, I enclose
with this letter replacement sheets for the front cover and title page.
Would you please use them to replace the corresponding pages in your
copies of the report.

Sincerely,

A handwritten signature in black ink, appearing to read 'Sidney Katz', with a stylized flourish at the end.

Sidney Katz
Senior Science Advisor

SK:im
Enclosures (12)

PHYSICAL AND CHEMICAL CHARACTERIZATION OF
FOG OIL SMOKE AND HEXACHLOROETHANE SMOKE

Final Report On
Hexachloroethane Smoke

By

Sidrey Katz
Alan Snelson
Raleigh Farlow
Roger Welker
Stephen Mainer

January 1980

Supported by

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