

AD-773 337

UPPER ATMOSPHERIC CHEMICAL RELEASE  
TECHNIQUES

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AeroChem Research Laboratories,  
Incorporated

Prepared for:

Rome Air Development Center  
Defense Advanced Research Projects Agency

October 1973

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AD 773337

RADC-TR-73-375  
Final Technical Report  
October 1973



UPPER ATMOSPHERIC CHEMICAL RELEASE TECHNIQUES

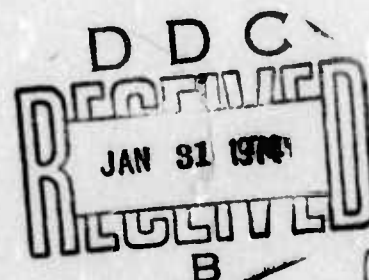
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AD 773337

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-73-375	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Upper Atmospheric Chemical Release Techniques		5. TYPE OF REPORT & PERIOD COVERED Final, 1 January 1973 to 30 August 1973
7. AUTHOR(s) Dr. W. Felder Mr. H.S. Pergament		6. PERFORMING ORG. REPORT NUMBER TP-298
9. PERFORMING ORGANIZATION NAME AND ADDRESS AeroChem Research Laboratories, Inc. P.O. Box 12 Princeton, NJ 08540		8. CONTRACT OR GRANT NUMBER(s) F30602-72-C-0420
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advanced Research Projects Agency 1400 Wilson Blvd. Arlington, VA 22209		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PEC-62301E PROJ-1649 TASK-02 WUN-03
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Rome Air Development Center (RADC) Griffiss AFB, NY 13441		12. REPORT DATE October 1973
		13. NUMBER OF PAGES 36
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		16. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Commerce Springfield VA 22151		
18. SUPPLEMENTARY NOTES Monitored by Joseph J. Simons/OCSE RADC Griffiss AFB, NY 13441		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Upper Atmospheric Chemical Releases Nucleation, Condensation Aluminum Vapor		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The goal of this work was to develop preliminary designs of upper atmospheric payload packages for the release of atomic Al and Fe vapors. For this purpose, we have emphasized the development of a combustion process, 'Flashbulb', which has been shown (on theoretical grounds) in previous AeroChem reports <sup>1</sup> to be capable of depositing large amounts of atomic Al and Fe vapors in the upper atmosphere. The results of the present experimental		



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The mixtures used give large Al vapor yields and differ from previously tested mixtures (which gave negligibly small yields<sup>1</sup>) by inclusion of a binder (laminac resin) and by reduction of the metal particle sizes. From tests on these mixtures a composition (15% Al, 47.3% Zr, 27.7%  $\text{NH}_4\text{ClO}_4$ , 10% laminac by weight) has been identified which gives the optimum atomic Al vapor yields (15% of the Al initially present) when burned at a combustion pressure of about 75 psia. Tests were made to demonstrate effects of variations in combustion temperature and pressure, Al loading, and burning rate on Al vapor yields.

Further preflight testing of both the Flashbulb mixture and release hardware is recommended, including the measurement of burning rates as a function of pressure and the determination of optimum orifice sizes, configurations, and materials. It is also recommended that flight scale release packages and hardware be ground-tested to test the effects of scaling-up on burning characteristics and hardware durability.

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UPPER ATMOSPHERIC CHEMICAL RELEASE TECHNIQUES

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Contractor: AeroChem Research Laboratories, Inc.  
Contract Number: F30602-72-C-0420  
Effective Date of Contract: 15 May 1972  
Contract Expiration Date: 30 September 1973  
Amount of Contract: \$138,450.00  
Program Code Number: 3E20

Principal Investigator: Harold S. Pergament  
Phone: 609 921-7070

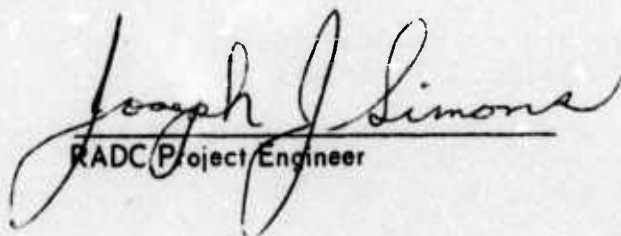
Project Engineer: Joseph J. Simons  
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This research was supported by the  
Defense Advanced Research Projects  
Agency of the Department of Defense  
and was monitored by Joseph J. Simons  
RADC (OCSE), GAFB, NY 13441 under  
Contract F30602-72-C-0420.

# PUBLICATION REVIEW

This technical report has been reviewed and is approved.

  
RADC Project Engineer

### SUMMARY

The goal of this work was to develop preliminary designs of upper atmospheric payload packages for the release of atomic Al and Fe vapors. For this purpose, we have emphasized the development of a combustion process, 'Flashbulb', which has been shown (on theoretical grounds) in previous AeroChem reports<sup>1</sup> to be capable of depositing large amounts of atomic Al and Fe vapors in the upper atmosphere. The results of the present experimental program demonstrate that these large calculated yields can be practically achieved for Al: absorption spectroscopic measurements of atomic Al vapor produced by Flashbulb prototypes show that when a small scale ( $\approx 100$  g) sample is burned in a canister with an orifice, about 15% of the Al initially present (i.e. about 2% of the total chemical mass) can be released as the atomic vapor. Thus, full scale packages of this mixture<sup>2</sup> should be suitable for the purposes of IVY OWL.

The mixtures used give large Al vapor yields and differ from previously tested mixtures (which gave negligibly small yields<sup>1</sup>) by inclusion of a binder (laminac resin) and by reduction of the metal particle sizes. From tests on these mixtures a composition (15% Al, 47.3% Zr, 27.7%  $\text{NH}_4\text{ClO}_4$ , 10% laminac by weight) has been identified which gives the optimum atomic Al vapor yields (15% of the Al initially present) when burned at a combustion pressure of about 75 psia. Tests were made to demonstrate effects of variations in combustion temperature and pressure, Al loading, and burning rate on Al vapor yields.

Further preflight testing of both the Flashbulb mixture and release hardware is recommended, including the measurement of burning rates as a function of pressure and the determination of optimum orifice sizes, configurations, and materials. It is also recommended that flight scale release packages and hardware be ground-tested to test the effects of scaling-up on burning characteristics and hardware durability.

FOREWORD

This is the final report on Contract F30602-72-C-0420, covering the period 1 January to 31 August, 1973. It is a pleasure to acknowledge the contributions of R.F. Burkert to the experimental program. Helpful discussions with Drs. H.F. Calcote and A. Fontijn and Mr. A.J. Sabadell of Aero-Chem are also appreciated. We also acknowledge useful consultations with Dr. I. Glassman (Princeton Univ.), Dr. D. Rosner (Yale Univ.), Drs. B. Werbel and A. Beardell, and Mr. S. Kaye (Picatinny Arsenal).



TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	iii
FOREWORD	v
LIST OF FIGURES	viii
I. INTRODUCTION	1
II. MECHANISMS OF Al VAPOR PRODUCTION	2
A. Granular Diffusion Flame Mechanism	2
B. Liquid Drop Mechanism	3
III. FLASHBULB FORMULATIONS	4
A. Compositions	4
B. Size and Ballistic Considerations	5
IV. EXPERIMENTAL	6
A. Facilities	6
1. Atmospheric Pressure Tank	6
2. Operational Description of Spectroscopic Measurements	6
3. Combustion Chamber and Samples	7
B. Method of Measurement	8
V. RESULTS AND DISCUSSION	9
A. Yield Measurements	9
1. "Standard Mix" (Composition A)	9
2. Other Compositions	10
B. Consistency Checks	11
C. Explosions	12
D. Mechanism of Al Vapor Production	12
VI. CONCLUSIONS AND RECOMMENDATIONS	13
VII. REFERENCES	15

	<u>Page</u>
APPENDIX A: METHOD OF PREPARATION AND SAFETY TESTS OF PROTOTYPE SAMPLES	A-1
APPENDIX B: DATA HANDLING	B-1
APPENDIX C: ALTERNATE RELEASE TECHNIQUES	C-1

### LIST OF FIGURES

#### Figure

1	Effect of Binder on Atomic Al Vapor Yields at a Combustion Pressure of 1 atm	19
2	Effect of Binder on Equilibrium Combustion Temperature at a Combustion Pressure of 1 atm	20
3	Effect of Combustion Pressure on Atomic Al Vapor Yields	21
4	Schematic of AeroChem Atmospheric Pressure Test Facility	22
5	Combustion Chamber Prepared for Loading	23
6	Cover Flange (inner Face) and 0.64 cm Graphite Orifice	24
7	0.64 cm Graphite Orifices	25
8	100 g Flashbulb Samples	26
9	Combustion Chamber Loaded for Firing	27
10	Experimental Atomic Al Vapor Yield Measurement (Run 70)	28
11	Experimental Chamber Pressure Measurement (Run 70)	29
12	Slag Buildup on 0.64 cm Orifices	30
13	Slag Buildup on 1.25 cm Orifice	31
14	Effect of Atomic Al Density on Attenuation of a Continuum Source near 396.2 nm	32

## I. INTRODUCTION

The goal of this work was to develop preliminary designs (in terms of composition, method of burning and size) of payload packages to release atomic Al and Fe vapors (emphasizing Al) in the upper atmosphere. The major effort was expended in demonstrating the feasibility of the Flashbulb technique<sup>1</sup> for releasing significantly large amounts of atomic Al vapor. Feasibility has been demonstrated by showing experimentally that approximately 1% by weight of the Flashbulb composition\* (payload) is converted to Al vapor in small scale tests (i. e. a yield<sup>†</sup> of 1%). Such a conversion efficiency is necessary to release a significantly large amount of Al vapor ( $\approx 1$  mole) from a full scale ( $\approx 3$  kg) payload. Specific amounts required for an actual release will, of course, be determined by the detection methods used and the purposes of the user.

Measurements of atomic Al vapor yield from small scale (up to 100 g) samples were performed in the atmospheric pressure test facility at AeroChem using atomic absorption spectroscopy. The measurement technique and data reduction procedures have been described in detail previously<sup>1</sup> (the test facility is discussed in Section II. A). Samples were formulated and tested with three purposes:

1. Optimize Al vapor yields.
2. Obtain smooth and reproducible burning.
3. Identify mixtures which are reasonably simple and safe to formulate and handle.

Previous experimental work on the development of Flashbulb mixtures was described in Ref. 1. Spectroscopic yield measurements on a number of unconfined strand firings of Flashbulb mixtures containing no binder showed Al vapor yields which were too small ( $\leq 10^{-4}$  %) to be useful. These tests indicated the need for changes in composition (e. g. to include a binder), metal particle sizes, method of burning (from unconfined to confined) and mass of samples.

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\* A typical Flashbulb mixture contains 15% Al, 47.3% Zr, 27.7%  $\text{NH}_4\text{ClO}_4$  (AP), and 10% binder by weight. Metal particles are about  $10\mu$  diam and AP particles are  $50\mu$  diam.

† Throughout this report, yield will be given as a percentage of the total payload mass, i. e.

$$\% \text{ yield} = \frac{\text{mass of Al vapor}}{\text{mass of payload}} \times 100.$$

In addition, a number of experimental problems were identified in these tests: overloading of the discrimination capability of the tuned amplifier and/or saturation of the detector photomultiplier tubes due to the high luminosity of the burning Flashbulb composition; 100% attenuation of the analyzing light beam due to particulates in the release plume; and a number of ignition failures. The present facility and test procedures incorporate changes which have virtually eliminated these problems.

Theoretical work performed under the present contract was also described in Ref. 1 which gives the results of thermochemical equilibrium calculations which demonstrate that Flashbulb compositions are capable of producing large yields of Al and Fe vapors.\* Other preliminary design calculations reported<sup>1</sup> included a series of pressure-time history calculations comparing steady-burning and explosive type releases (the testing of explosive type releases in the present facility was ruled out by safety considerations) in terms of release cloud size and payload hardware. Finally, estimates were made which showed that condensation losses of metal vapor (specifically Fe, but the results should be comparable for Al) due to homogeneous nucleation were negligible for combustion pressures up to 20 atm. Arguments were presented to show that, for Al, heterogeneous nucleation via ions was about 10 times less effective as a vapor loss process than homogeneous nucleation. These results will not be discussed further in this report.

## II. MECHANISMS OF Al VAPOR PRODUCTION

Our last report<sup>1</sup> indicates that the development of successful Flashbulb release formulations would require optimizing both thermochemical and ballistic parameters. However the combustion mechanism is unknown, and knowledge of it is essential to such optimization. We have therefore considered two extreme cases:

### A. Granular Diffusion Flame Mechanism

This mechanism is based on the Granular Diffusion Flame (GDF) model for composite solid propellant combustion of Summerfield et al.<sup>2</sup> The release grain is assumed to burn by pyrolysis of the solid followed by diffusion-limited reaction between fuel particles and pyrolyzed oxidizer. Heat transfer by radiation and conduction from the reaction zone to the grain surface supports the pyrolysis. The region of maximum reaction is just downstream (at a distance determined by the combustion chamber pressure) of the solid surface. The grain composition includes a binder which (i) provides a gas efflux from its pyrolysis to carry metal particles away from the surface, (ii) is the source of gas to raise the chamber pressure and

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\* Appendix C discusses some alternate combustion techniques to release atomic Al vapor.



(iii) can be chosen to give a range of values for the burning rate exponent<sup>3</sup> of the mixture. The mechanistic picture is as follows:

Decomposition products from the surface and ejected metal particles enter the zone of maximum reaction. Zr reacts preferentially (over Al) with the oxidizer and a large heat release ensues. (The oxide coat on Al particles aids this preferential reaction.) Al particles passing through this zone and the hot gases further downstream are vaporized. The vapor and combustion product gases (poor in oxidizer) are then expelled from the chamber orifice. From this picture, we conclude that:

- (i) The maximum obtainable yield<sup>a</sup> will be the thermochemical equilibrium yields in the combustion chamber (see Fig. 1).
- (ii) Burning rates must be sufficiently large to give high enough chamber pressures to keep the zone of maximum heat release close to the surface of the grain.
- (iii) Burning rates must be sufficiently small to allow maximum residence time within the combustion chamber, i.e., to allow the combustion to come to equilibrium.
- (iv) The highest possible combustion temperatures must be sought in order to compensate for the effects of heat loss and residence times too small to achieve equilibrium.
- (v) Al particles must be small enough to vaporize during their residence time in the chamber.

#### B. Liquid Drop Mechanism

This mechanism for Al vapor production is similar to that proposed and tested by workers at the Max Planck Institut (MPI)<sup>4-6</sup> for Ba vapor production from thermite-type releases. In this picture, hot liquid (multicomponent in the MPI case) droplets containing the metal of interest are formed in a very high pressure, high temperature combustion chamber and fragment when expelled into ambient (vacuum in the MPI case) due to aerodynamic forces. Evaporation from the smaller droplets thus formed accounts for the presence of metal vapor. It follows from this mechanism that:

- (i) The maximum obtainable yields can exceed the calculated thermochemical equilibrium vapor yield in the chamber because the bulk of the metal remains in liquid form at the very high chamber pressure. The actual yield will depend upon the rate of evaporation of Al from the liquid droplets at the ambient pressure.<sup>7,8</sup>

- (ii) The mixture should burn as rapidly as possible in order to create very high combustion pressures. Ideally, the burning time should be much less than the time required for the products to be expelled from the canister. The combustion chamber pressure can be increased by the addition of a gasifying substance, e.g., binder,  $\text{NaN}_3$ .
- (iii) The chamber residence time should be short enough so that heat loss by droplets contacting cooler chamber walls is minimized.
- (iv) The chamber temperature should be as high as possible.

There is little a priori reason to favor one or the other of these mechanisms as more effective in producing Al vapor via the Flashbulb technique. Consequently, during this development program, we attempted to vary compositions and conditions to conform as much as possible to the common requirements of both mechanisms.

### III. FLASHBULB FORMULATIONS

#### A. Compositions

All mixtures were prepared using the (fuel-rich) fuel/oxidizer mole ratio, 1.1 Zr/0.5  $\text{Al}$ . They differed from mixtures tested previously<sup>1</sup> in the following aspects:

- (i) A binder (e.g. laminac resin; vinyl alcohol acetate resin, VAAR; or polybutadiene acrylic acid, PBAA) was used in order to:
  - a. give the mixture a reproducible burning rate exponent<sup>3</sup> of less than unity
  - b. enable the mixtures to be pressed or cast as integral grains
  - c. provide a source of gaseous combustion products.
- (ii) Al particle sizes were reduced from the 10-50  $\mu$  to the 5-25  $\mu$  range to increase the probability of particle vaporization. (The vaporization rate of a spherical particle is inversely proportional to the square of the particle diameter.<sup>9</sup>)
- (iii) A combustion modifier was used to increase the burning rate.

- (iv) Zr particle sizes were reduced\* from the 10-25 $\mu$  to the 2-10 $\mu$  range to increase the burning rate.

The results of a series of thermochemical equilibrium calculations for mixtures used in the present tests are shown in Figs. 1-3. Figure 1 shows the calculated % yield of atomic Al vapor as a function of the % Al in the mixture for practical levels of some binders, at a combustion pressure of 1 atm. Also indicated in Fig. 1 are the calculated % yields required to release 1 mole of atomic Al vapor from chemical payloads of 5, 10, and 20 kg. 1 mole of Al vapor is easily observed in fluorescence from a sunlit cloud 2 km in diam at a height of  $\approx 100$  km.<sup>10,11</sup> If it is assumed that 1 mole of AlO vapor is formed from Al by reaction at this altitude, there is good evidence that it too could be observed in fluorescence.<sup>10-13</sup> Figure 1 shows that the 1 mole requirement is in principal exceeded by a factor of  $\approx 10$  for the 5 kg payload, leaving a large margin for simple ground based measurements of emission. Figure 2 shows the effect of the binder on the equilibrium combustion temperature at 1 atm and Fig. 3 shows the effect of pressure on the % yield of atomic Al vapor for mixtures containing 15% Al.

#### B. Size and Ballistic Considerations

From the above discussion of mechanisms, it is clear that a successful release (i.e. one which gives significant amounts of Al vapor) will be one which approaches thermochemical equilibrium in a confined (combustion chamber) environment. To accomplish this, it is necessary to make trade-offs among the requirements of rapid burning (minimum heat loss to ambient), long residence time (maximum time to heat/evaporate/react), and chamber pressures  $>$  a few atmospheres<sup>†</sup> (optimum size of reaction/evaporation regions).

The test sample size chosen was 100 g--this being the largest size which could be safely tested in the present facility. Large samples minimize the effects of heat losses and are necessary to obtain controllable combustion conditions in a canister. Smaller samples would require use of smaller orifices, resulting in a long lead time to develop a suitable canister-orifice system.

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\* This proved to be the most difficult change to effect in practice. Prototype mixtures using 2 $\mu$  diam Zr particles were extremely difficult to prepare and handle and one mixture exploded during pressing. Mixtures were therefore prepared using (nominal) 10 $\mu$  diam Zr, although variations among lots received from the supplier (Varlacoid Chemical, Elizabeth, NJ) ranged from 9.2 to 14 $\mu$  diam.

† In these tests we have used a binder as a source of gas to pressurize the combustion chamber. The use of smaller chamber orifices (than the 0.635 cm diam used here) was ruled out by the large fraction of liquid/solid combustion products from Flashbulb which will clog small orifices.



Small (10-50 g) samples were prepared and tested at AeroChem to gain familiarity in handling and firing the modified mixtures.\* 100 g samples were supplied by Picatinny Arsenal where more adequate preparative facilities are available. Compositions to be tested experimentally were selected from those mixtures which gave calculated yields  $\geq 1\%$  (cf. Fig. 1). Within this range of Al concentrations, variations to alter the ballistic properties (e.g., charges in particle sizes and binder levels) were attempted in order to optimize atomic Al vapor yields. Table I contains a summary of mixtures prepared both at Picatinny Arsenal and at AeroChem.

#### IV. EXPERIMENTAL

##### A. Facilities

##### 1. Atmospheric Pressure Tank

Figure 4 is a schematic of the open-ended atmospheric pressure tank (see also Figs. 5 and 9) which is 0.6 m in diam, 2.4 m long, with the observation axis on a diameter 0.5 m from the open end. The release package, on its support plate, can be placed at various distances from the observation axis which is defined by opposing quartz windows (3.8 cm diam) and a light and smoke shield. The shield consists of two pieces of 2.5 cm diam pipe protruding from the inner walls of the tank through which the analyzing light beam passes. The pipes define an 11 cm zone, perpendicular to and symmetric about the tank axis, through which the release plume passes. The tank was flushed with  $N_2$  to exclude atmospheric  $O_2$  from the measurement region. The shield, which is also flushed with  $N_2$ , eliminates the problems of overloading and smoke attenuation which interfered in our first test series.

The optical system has been described in detail previously.<sup>1</sup> In the present facility, however, a number of high quality, front surface mirrors have been added to the light path, allowing the light source and monochromators to be set up more compactly next to and beneath the tank, respectively.

##### 2. Operational Description of Spectroscopic Measurements

(Designations given in the text refer to Fig. 4.) The technique used here for measuring absolute atom densities in a release plume is absorption spectroscopy. For this purpose, a light beam for a suitable source<sup>①</sup> (e.g. high pressure arc or hollow cathode lamp) is directed perpendicular to the

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\* Appendix A discusses the methods used and safety tests made on these mixtures.



release plume<sup>(2)</sup>. After passing through the plume, the attenuated beam is split<sup>(3)</sup> and focused<sup>(4)</sup> onto the slits of two monochromators<sup>(5)(6)</sup>. One monochromator<sup>(5)</sup> is set at an absorption maximum of the species to be measured and the other<sup>(6)</sup> is set at a nearby wavelength. Thus the first monochromator<sup>(5)</sup> passes light attenuated by the release vapor and particulates and the second passes light attenuated by particulates alone. The difference in the two signals, obtained electronically relative to zero attenuation (obtained in a calibration before each test), is the net absorption due to the species of interest. From this value a relatively straightforward transformation yields the total number of atoms released.<sup>1</sup>

Three features of this particular spectroscopic measurement system are noteworthy in the context of measuring atom concentrations in release vapors:

- a. Real-time differential detection (using lock-in detectors<sup>(7)(8)</sup>) allows immediate interpretation of data without laborious post-experiment subtraction of particulate attenuation. This capability is particularly important when the release produces a great deal of 'smoke'.
- b. The combination of phase-sensitive detection with the light and smoke shield<sup>(10)</sup> allows effective discrimination against the effects of unmodulated plume emission from very hot releases (e.g. Flashbulb).
- c. By using either resonance line or continuum light sources<sup>(1)</sup> we are able to measure a large range of release vapor densities. For Al, for example, vapor densities from as low as  $10^9$  to as high as  $10^{16}$  ml<sup>-1</sup> can be conveniently measured across a 10 cm path.<sup>1</sup>

The nominal time resolution of the measurement system is  $\approx 0.001$  sec, determined by the modulation frequency (2 kHz). However, the output filter time constant necessary for reasonable signal stability was found in practice to be between 0.03 and 0.1 sec for the highly luminous Flashbulb composition. A release producing its major yields in times comparable to or less than this (e.g. an 'explosive' release) could not be fairly tested under the present conditions. Thus, the present facility is most effective for measuring yields from steady-burning (trail type) mixtures.

### 3. Combustion Chamber and Samples

Figure 5 is a photograph of the brass combustion chamber (hereafter, canister) prepared for loading. It is a 10 cm diam, 14 cm long brass cylinder mounted on a heavy-duty Uni-strut support and bolted to the 1.25 cm thick aluminum baseplate. The sample is loaded into the bored-out (3.8 cm diam  $\times$  10 cm deep) hole in the center. The samples are  $\leq 7.6$  cm long, thus there is  $\approx 3.0$  cm between the face of the release and the open end of the canister.

Orifices for the pressure transducer (Teledyne Taber 176, 0-1000 psia, periodically calibrated against a high pressure gas regulator) and safety head (Black, Sivalls & Bryson, Inc., 500 psi) are drilled into this part of the canister. The safety head orifice (2.5 cm diam) is packed with fullers' earth to protect the blowout disc from combustion gases. Figure 6 shows the inner face of the cover flange and a graphite orifice (inserted in the step seen in the flange) used for these experiments. Figure 7 shows the 0.635 cm diam graphite orifices in the three configurations used:

1. Recessed orifice: depth of recess, 1.25 cm; diameter of recess 1.9 cm; wall thickness 0.32 cm. Recess faces sample.
2. Same as 1, but inverted so that recess faces ambient.
3. Flat disc: 0.64 cm thick, 3.8 cm diam to fit flange step and canister bore.

Figure 8 shows the release sample as received (a) and as prepared for loading (b). The mixtures were received from Picatinny Arsenal as 2.5 cm diam,  $\approx 8.0$  cm long grains pressed into waxed kraft paper tubes. The tubes are held in the canister by molding them in Plexiglas collars (3.8 cm o.d., 3.2 cm i.d.) with silica loaded (10-20% by weight) epoxy. In this way, the canister is protected from the burning mixture and insulated to minimize heat transfer.

A reliable igniter (Fig. 8c) ( $\sim 0.1$  g of a mixture of  $\approx 70\%$   $10\mu$  diam Zr,  $\approx 25\%$   $50\mu$  diam AP,  $\approx 5\%$  binder) developed at AeroChem is taped to the front surface of the sample. Leads for electrical ignition are led out through the orifice (these leads are blown out immediately upon ignition and do not interfere with the sample burning). The loaded canister in firing position is shown in Fig. 9.

#### B. Method of Measurement

(Designations given in the text refer to Fig. 10.) The measurement procedures are described in detail in Ref. 1 and will only be summarized here. Typical raw data are given in Fig. 10 which shows tracings of the oscilloscope photographs obtained in run 70 (see Table II). The calibration traces (a) for the metal atom (bottom trace) and smoke (top trace) attenuation measurement lines give the range of observable absorption. The various sections of the calibration traces are obtained as follows: (1) no absorption in either metal line or smoke attenuation line; (2) total absorption of the metal line (monochromator slits closed--note that the smoke attenuation line trace is unaffected); (3) total absorption of both the metal line and the smoke attenuation line (both monochromator slits closed). After these traces are obtained, the monochromator slits are re-opened and the release is ignited. The experimental traces (b) are begun  $\approx 5$  sec before ignition and show zero absorption (4).

The observed deflection of the metal resonance line in trace (b) is then compared with maximum observable deflection from trace (a) and the fractional transmission  $I/I_0$  is obtained, where  $I_0$  is the maximum deflection obtained from trace (a) and  $I$  is the deflection (measured from 100% absorption) obtained from trace (b). From this value, the total number of atoms released is calculated by the procedures given in Ref. 1 and outlined in Appendix B.

## V. RESULTS AND DISCUSSION

### A. Yield Measurements

#### 1. "Standard Mix" (Composition A)

The compositions chosen for testing are listed in Part 2 of Table I and the results of the yield measurements are given in Table II. By a fortunate choice, composition A, which had the best handling and preparation characteristics, consistently gave the largest yields of Al vapor observed in these tests. This mixture became a standard against which other compositions were compared for yield.

- a. Yields of Al Vapor - Run numbers 39-42, 44-48, and 66-74 were made using the "standard mix" with changes only in particle sizes or additives to alter the ballistic properties. Valid data were collected in 10 of the 17 runs. (Runs 39, 45, 68, and 69, were unsuccessful for various reasons; Runs 44 and 66 were made with 1.25 cm diam nozzle and no nozzle respectively; and run 48 was a consistency check\*--see Table II.) The average yield from this composition is 2.3% with a precision (standard deviation) of  $\pm 1.1\%$ . The estimated accuracy of the yield is  $\pm$  a factor of 10 due to:
  - (1) A factor of  $\approx 1.5$  uncertainty in the diameter of the release plume (optical path length).
  - (2) A factor of  $\approx 2$  uncertainty in the calculated average release gas velocity.
  - (3) A factor of  $\approx 1.5$  instrument uncertainty in the measured % absorption.
  - (4) An estimated 50% uncertainty in the calculation of  $N_{inst}$  (cf. Ref. 1) from the observed absorption due to approximations made in the derivation of the absorption coefficient<sup>14,15</sup> and the use of an idealized slit function.

---

\* Discussed in Section V.B.



- b. Burning Characteristics - For the "standard mix" using the 0.64 cm diam orifices, the combustion pressures were  $90 \pm 40$  psi. Figure 11 shows a trace of the chamber pressure for release No. 70. It is typical of the pressure traces obtained, showing an initial rise and smooth climb to the ultimate chamber pressure and then a sustained, slowly rising chamber pressure until burnout.

This behavior is consistent with the buildup of slag observed on both the inside (facing release) and outside of the orifices. After ignition liquid/solid particles are deposited on the orifice walls, gradually decreasing its diameter and consequently increasing chamber pressure. As the run continues, a steady state is achieved in which the hot combustion gases keep a  $\approx 0.3$  cm diam channel open in the continuously depositing slag. Thus, it is apparently the rate and amount of slag buildup that is responsible for the rate and ultimate magnitude of the chamber pressure rise. Figure 12 shows these deposits on the three orifice configurations used (cf. Fig. 4). The slag deposits can become quite spectacular--Fig. 13 shows the deposit obtained in run 53 in which a 1.25 cm diam orifice was used. Because of the large orifice, the chamber pressure is not as high as with the 0.63 cm orifice. Particles are thus ejected with less velocity and the resulting accretion can grow quite large. The deposit shows a wavelike surface structure, consistent with a liquid surface over which hot, relatively high velocity gases pass.

## 2. Other Compositions

- a. "High Al Loading" (Composition B)

In runs 49-52, the Al loading was increased from 15 to 25 % by weight. Al vapor yields are less than those observed from the standard mix. These samples are also somewhat undependable in their burning characteristics: in one run (51), 'chugging'; and in others, (49, 50, and 52) giving very long, smooth burns. As a result of the low yields, highly loaded compositions were not tested further.

- b. "High Temperature" (Compositions C, D, E, F)

Figure 2 shows that the combustion temperature can be increased by decreasing the Al and binder levels in the mixture. Compositions C, D, E, and F were prepared to test the effects of an increase in combustion chamber temperature on Al vapor yields. Runs using these mixtures (53, 59-65) showed very low Al vapor



yields. As can be seen from Table II, many of the samples caused the orifices to blow out and, in two cases, rather forceful explosions occurred. Attempts to strengthen the orifice by using configurations (2) and (3) (cf. Fig. 7) were not successful in increasing the Al vapor yields. The valid data on these mixtures is insufficient to evaluate their effectiveness in producing Al vapor. It appears, however, that the risk of orifice failure or explosion is high enough to warrant their exclusion from further development.

c. "High Burning Rate" (Composition G, A)

In runs 54, 56, 58 the size of the oxidizer (AP) particles was reduced to  $\approx 15\mu$ , and in runs 66 and 74 (Composition A) copper chromite was added, in an attempt to increase the burning rate of the mixture. However, no significant increase in burning rate is observed from either of these changes, and the Al vapor yields are below measurable limits.

d. "Small Al Particle Size" (Composition B)

Only one attempt at decreasing the Al particle size (run 43) was made. Firing resulted in a violent explosion. No further testing in this direction was undertaken. (See Appendix A.)

## B. Consistency Checks

Because of the duration of the sample burns, the density of Al vapor in the measuring zone at any instant of the burn is a factor of 2 to 5 less than the optimum for measurement resulting in observed attenuations of less than 10% of the continuum intensity at 396.2 nm.\* Some consistency checks were therefore made to insure that the observed small attenuations resulted from Al absorption and not from experimental artifacts.

The major concern was that large particulate attenuations could affect the Al channel by improper tracking in the electronic subtraction (cf. Ref. 1). There is good experimental evidence that this is not the case, e.g.

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\* It was possible neither to use a low f-number resonance line from the hollow cathode source (the emission intensities of the 265.2 nm,  $f = 0.014$ , and 237.2 nm,  $f = 0.004$  lines<sup>16</sup> were too small to be useful in the present system), nor to decrease the slit width of the Al atom monochromator while using the continuum source (i.e. to increase the sensitivity of the detection system for Al atoms).

runs 44, 46, 54-59, 61-62, and 64 in which particulate attenuations as high as 60% were observed with no detectable Al absorption. In addition, when a CO<sub>2</sub> fire extinguisher was emptied through the observation path, large particulate attenuation was observed with no measurable effect on the Al absorption signal. As a final, and most convincing check, the Al-detecting monochromator was set ~ 10 nm off the 396.2 nm Al line (at 386.0 nm) and a release was fired (run 48). Again, no significant Al absorption was observed, although some excursions of the order of  $\pm 2\%$  absorption were seen for short periods during the burn.

These checks and observations add up to a rather convincing picture of the validity of the present measurement technique. Although small, the observed signals are quite real, and represent the release of significantly large amounts of Al vapor by Flashbulb formulations.

### C. Explosions

Three explosions occurred in the course of this work. All resulted from mixtures deliberately ignited for yield measurements. The first occurred in run 43, when Al particle size was decreased. The greater surface area of the smaller particles required the use of a less viscous binder with better wetting properties than laminac resin. VAAR was used because it is chemically similar to laminac and has these other properties. However, it also polymerizes to a less dense structure. This resulted in a more porous, less uniform grain which exploded rather violently immediately upon ignition. At the time, it was not known whether the explosion was a result of the porosity, Al particle size, or an inadvertent change in Zr particle size (cf. footnote page 5). However, two subsequent explosions (runs 60 and 65) shared the characteristic of porosity with run 43, and it is felt that this is the most important contributing factor to the unstable combustion observed. As an aside, and a caution to others who might work with similar highly-loaded mixtures, we note that these explosions were quite forceful, shearing the orifice holder plate from the canister and displacing the canister and test tank itself over large distances. The explosion in run 43 actually destroyed the canister by blowing out the rear wall (1.25 cm thick brass) like a cork.

### D. Mechanism of Al Vapor Production

On the basis of the above observations it is useful to speculate on the mechanism of Al-vapor production from Flashbulb packages. A comparison between Figs. 10 and 11 shows that the shapes of the smoke attenuation trace and the pressure trace are quite similar. However, the Al yield shows two maxima: at the beginning and end of the burn. This behavior is typical of the successful releases and is consistent with the formation of Al vapor in the combustion chamber at pressures lower than the ultimate combustion pressure. As the pressure rises, the rate of vapor production decreases slightly

and remains constant over the region of relatively constant chamber pressure. This behavior is consistent with the predictions of Fig. 3 which show decreasing Al vapor yield with increasing chamber pressure. Finally, at burnout, the chamber pressure again falls, and an increase in Al vapor yield is observed.

It is thus suggested that a GDF-type mechanism is operating in these experiments. If the combustion pressure rises too high, the region of maximum heat release is compressed and the amount of evaporation is correspondingly decreased. On the other hand, the region of maximum heat release is apparently too diffuse to be effective in evaporating Al in unconfined (strand burning) samples.

However, the fact that the observed yields approach the theoretical limits (cf. Table II and Figs. 1, 2) despite the loss processes which must be operating suggests that another source may be contributing to Al vapor production. An analysis\* of the slag deposits in the orifices showed an Al content a factor of 5 to 10 less than that of the unburned release mixture. On the basis of this, it is not unreasonable to speculate that the passage of hot combustion gases over the slag deposits can generate Al vapor and/or entrain small Al droplets which subsequently evaporate.

## VI. CONCLUSIONS AND RECOMMENDATIONS

On the basis of the results presented above, we conclude that the Flashbulb technique is a feasible method for producing large amounts of atomic Al vapor. The present results indicate that the most likely candidate for flight use is Composition A, which should be burned in a combustion chamber at a pressure of 50-100 psi. However, the preparation of a sample for flight testing will require more detailed ballistic tests such as the determination of the burning rate exponent<sup>3</sup> of the mixture. When combined with the experimental requirements of the flight test (i.e. trail or point release), this measurement will enable determination of the proper combinations of orifice size and burning surface area.

During the present work, only the simplest orifice configuration was employed and only graphite was used as a construction material. Other materials and configurations should be investigated for strength and ability to withstand clogging. As indicated above, the amount of orifice clogging was apparently a determining factor in the combustion chamber pressure during the present work. It is clear that a more dependable and reproducible method

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\* Quantitative analyses for total Al and Zr in the slag were performed for runs 66-70 and 72-73 by SpectroChem Laboratories, Inc., Franklin Lakes, NJ.

for attaining the recommended chamber pressure is needed. One avenue of approach might be a nozzle constructed of a material to which the slag produced in these burns would not adhere or from which it would be easily ablated.

Flight-scale samples should be ground fired to test the effects of scaling-up on burning characteristics. The flight hardware (canister and orifice) should also be tested in ground firings for their ability to withstand the high temperatures and large particulate yields of Flashbulb mixtures.



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TABLE I. PROPERTIES OF FLASHBULB MIXTURES

Preliminary Tests--AcroChem Preparation - Part 1									
Al			Zr		AP				
Composition	Wt %	Particle size (μ)	Wt %	Particle size (μ)	Wt %	Particle size (μ)	Wt %	Particle size (μ)	
1	15	18	47.3	18	27.7	50	10	glyptal, butyrate dope	
2	15	18	47.3	18	27.7	50	10	glyptal, butyrate dope	
3	14	18	47.3	18	27.7	50	10	glyptal, butyrate dope	
4	15	18	47.3	18	27.7	50	7	monomethyl methacrylate (MMM)	
5	15	6.7	47.3	18	27.7	50	7	MMM	
6	15	18	41.4	18	23.6	50	20	PBAA/epon	
100 g Samples--Picatinny Arsenal Preparation - Part 2									
A	15	16	47.3	9.2-18.5	27.7	50	10	laminac	
B	25	16	41	14	24	50	10	laminac	
C	15	16	50.5	14	29.5	50	5	laminac	
D	10	16	53.6	13.2	31.4	50	5	laminac	
E	20	16	47.3	13.2	27.7	50	5	laminac	
F	15	16	51.7	13.2	30.5	50	3	laminac	
G	15	16	47.3	13.2	27.7	15	10	laminac	
H	15	6.7	49.8	9.2	29.2	50	6	Vinyl alcohol acetate resin (VAAR)	

Additive		Binder		Method of Preparation		Purpose	
Wt %	Identity	Wt %	Identity				
3	MMM polymerizer (Mt-MP)	10	glyptal, butyrate dope	Coat metal particles with glyptal and dry; break up and mix with AP, press at 8000 psi for 3 min.		Test glyptal binder.	
3	MMM	10	glyptal, butyrate dope	Coat either Al or Zr with binder; then prepare as 1.		Test effect on burning characteristics of coating only one of metal particles.	
3	MMMP	10	glyptal, butyrate dope	Make a slurry by adding acetone, cast in tubes and dry.		Find a simpler way to prepare samples by casting.	
3	MMMP	7	monomethyl methacrylate (MMM)	Make a slurry and cast in tubes, allow to polymerize.		Test polymethylmethacrylate as a binder.	
3	MMMP	7	MMMP	Same as 4.		Test effect of varying Al particle size on burning.	
20	PBAA/epon	20	PBAA/epon	Same as 4.		Test PBAA binder.	
Mixture with best handling and preparation characteristics for first runs. Mixture A with 2 μ Zr exploded in the press (see test).							
Dry AP 4 hrs @ 105°C. Wet Zr with laminac, add Al to mixture and stir. Add dried AP to mix and stir. Air dry. Press at 4 ton dead load on 20 ton press into 1" i.d. waxed case. Press each 100 g batch in 4 equal increments of ~25 g.							
Same as A.							
Same as A.							
Same as A.							
Same as A.							
Same as A.							
Same as A.							
Same as A.							
Same as A but store air-dried mixture overnight at 80°C before pressing.							

TABLE II. ATOMIC AL VAPOR YIELD MEASUREMENTS<sup>b</sup>

Run No.	Mass of Sample (g)	Length of Sample (cm)	Burn Time (sec)	Average Combustion Pressure (psia)	Orifice (cm)	Optical Path Length (cm)	Average Absorption (%)	Atoms Released	% Al Released as Vapor	Yield (%)	Comments
<b>Composition A</b>											
"Standard Mix"											
39	91.5	6.2	14	100	(1)	6.6	f	•	•	•	*No data--trace overexposed.
40	94	6.6	8*	•	(1)	6.6	8	9.5 × 10 <sup>22</sup> †	30†	4.6†	*Orifice blew out after 8 sec; †Calculated assuming t <sub>b</sub> of 15 sec; **No pressure trace obtained.*
41	90.5	6.4	15	100	(1)	6.6	6	5.4 × 10 <sup>22</sup>	17	2.6	*1.25 cm orifice.
42	92.5	6.6	15	100	(1)	11	5	5.4 × 10 <sup>22</sup>	17	2.5	*Ignition failure--no valid data.
44	94	6.4	30	•	(1)*	11	•	•	•	•	
45	80	5.4	•	•	(1)	11	•	•	•	•	
46	87	4.9	15	50	(1)	11	•	•	•	•	
47	100	7.0	15	80	(1)	11	4	4.3 × 10 <sup>22</sup>	9	1.4	
48	92	6.5	15	50	(1)	11	•	•	•	•	
66**	99	6.8	30	15*	•	11	80*	2 × 10 <sup>19</sup>	6 × 10 <sup>-5</sup>	10 <sup>-5</sup>	Consistency check--see text.
68	93.4	6.4	8	50	(1)	11	•	•	•	•	*1% copper chromite additive; *No orifice--resonance line measurement.
69	92	6.5	12	80	(1)	11	•	•	•	•	*Improper wavelength setting--no valid data.
70	95.4	6.4	12	80	(1)	11	6	5.3 × 10 <sup>22</sup>	17	2.5	*Improper wavelength setting--no valid data.
71	92	6.4	13	80*	(1)	11	8	9 × 10 <sup>22</sup>	29	4.3	*Slow pressure buildup.
72	95.7	7.0	11	120	(3)	11	5	4 × 10 <sup>22</sup>	12	1.8	
73	94	6.4	12	100	(3)	11	6	5.3 × 10 <sup>22</sup>	18	2.7	
74**	95.5	6.5	3*	175	(1)	11	5	4.3 × 10 <sup>22</sup> †	13†	2.0†	*1% copper chromite additive; *Orifice blew out after 3 sec; †Calculated assuming t <sub>b</sub> = 12 sec.
<b>Composition B</b>											
"High Al Loading"											
49	88.6	6.5	>30	•	(1)	11	•	•	•	•	*No pressure trace, large deposit left in canister.
50	94.3	6.8	19	120	(1)	11	3	1.4 × 10 <sup>22</sup>	2	0.6	
51	93.2	6.8	12	100*	(1)	11	†	†	†	†	*8 sharp pressure 'chugs' = 100 psia; †Zero drift in amplifier--no valid data.
52	92.9	6.8	25	•	(1)	11	2	1.4 × 10 <sup>22</sup>	3	0.7	*No pressure trace.
<b>Compositions C, D, E, F</b>											
"High Temperature"											
53(C)	97	7.0	28	<45	(1)*	11	~1	~10 <sup>22</sup>	~2	~0.5	*1.25 cm orifice.
55(C)	97	7.5	4*	175*	(1)	11	•	•	•	•	*Orifice blew out after 6 sec.
57(C)	99	7.3	16	50	(2)	11	•	•	•	•	
59(D)	98	6.2	12	15	(3)	11	•	•	•	•	
60(E)	99	6.8	•	•	(3)	11	•	•	•	•	
61(E)	98	7.0	25	15*	•	11	•	•	•	•	*Violent explosion after 5 sec.
62(F)	98	7.1	25	15*	•	11	•	•	•	•	*No orifice--burned open at 1 atm.
63(D)	100	6.4	15	50	(3)	11	•	•	•	•	*No orifice--burned open at 1 atm.
64(F)	100	6.4	12	75	(3)	11	•	•	•	•	*No data obtained--operator error.
65(D)	100	7.0	~1*	•	(3)	11	•	•	•	•	*Violent explosion after 1 sec.
67(F)	98	5.6	15	88	(1)	11	•	•	•	•	*Resonance line measurement--electronics overload, no valid data.
<b>Composition G</b>											
"High Burning Rate"											
54	92.5	6.2	20	<25	(1)*	11	•	•	•	•	*1.25 cm orifice.
56	94	6.8	5*	150*	(1)	11	•	•	•	•	*Orifice blew out after 5 sec.
58	93.5	6.5	12	75	(2)	11	•	•	•	•	
<b>Composition H</b>											
"Small Al Particle Size"											
43	96.4	7.3	•	•	(1)	11	•	•	•	•	*Violent explosion immediately on ignition.

<sup>a</sup> below measurable limits.<sup>b</sup> In all experiments, the distance from the release to the optic axis was 17 cm.<sup>c</sup> Letters in parentheses indicate composition (see Table I).<sup>d</sup> See Fig. 7.<sup>e</sup> % yield =  $\frac{\text{mass Al released as vapor}}{\text{mass of sample}} \times 100$ <sup>f</sup> •, ••, † indicate comment follows.



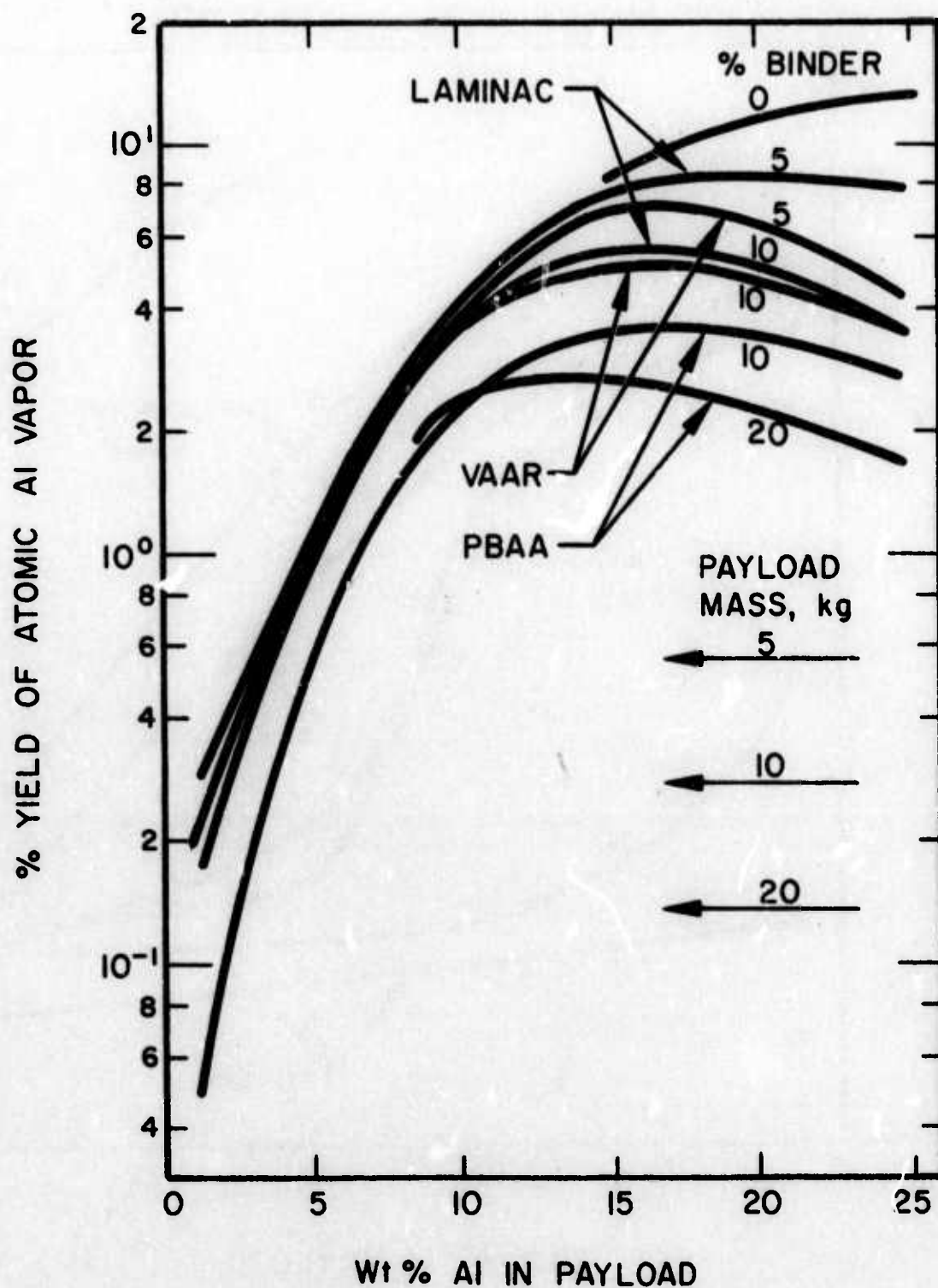


Fig. 1 Effect of Binder on Atomic Al Vapor Yields at a Combustion Pressure of 1 atm. Arrows indicate yields required to release 1 mole of Al vapor from the indicated chemical payload mass; fuel/oxidizer mole ratio fixed at 1.1 Zr/0.5 AP.

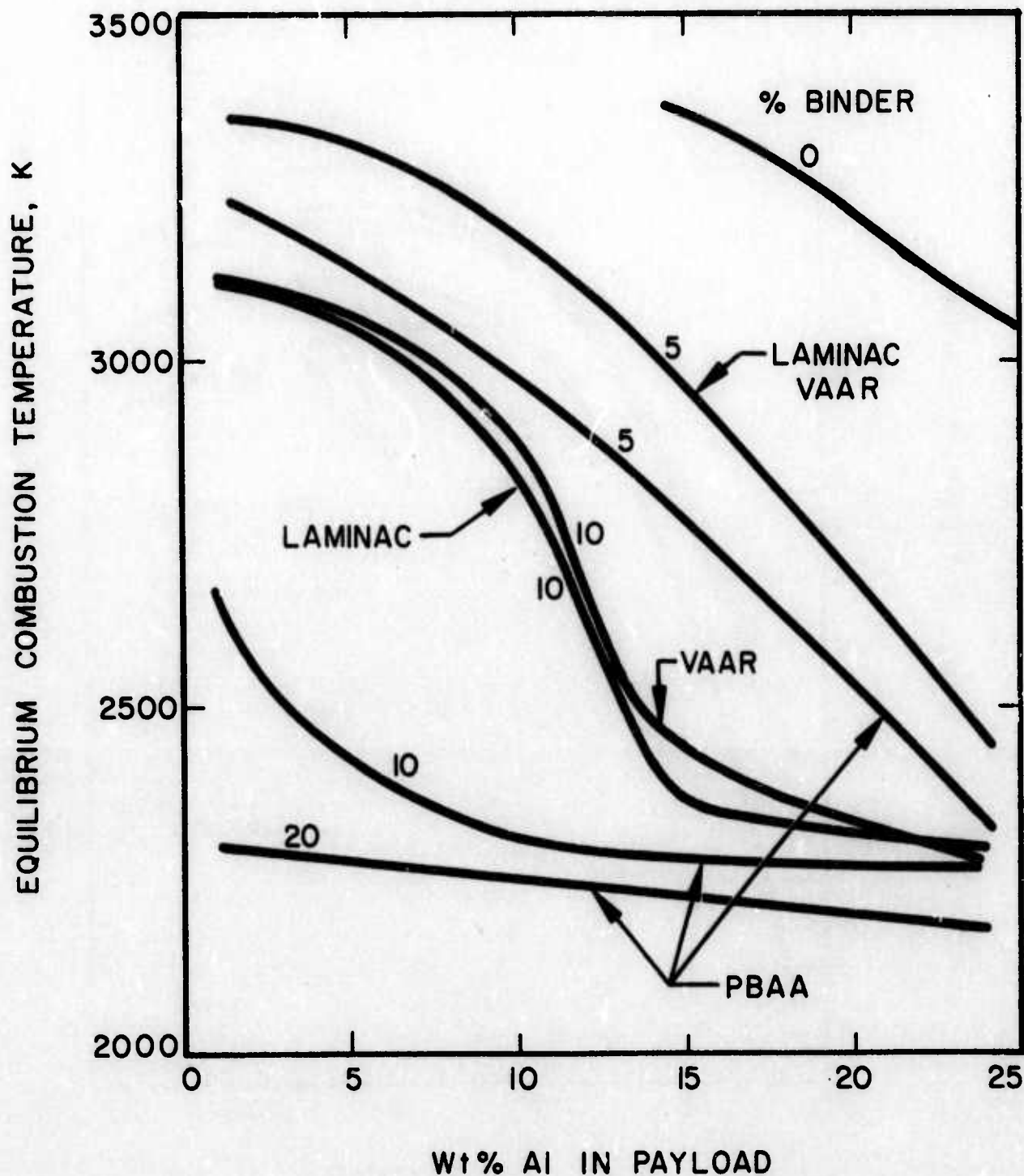


Fig. 2 Effect of Binder on Equilibrium Combustion Temperature at a Combustion Pressure of 1 atm. Fuel/oxidizer mole ratio fixed at 1.1 Zr/0.5 AP.

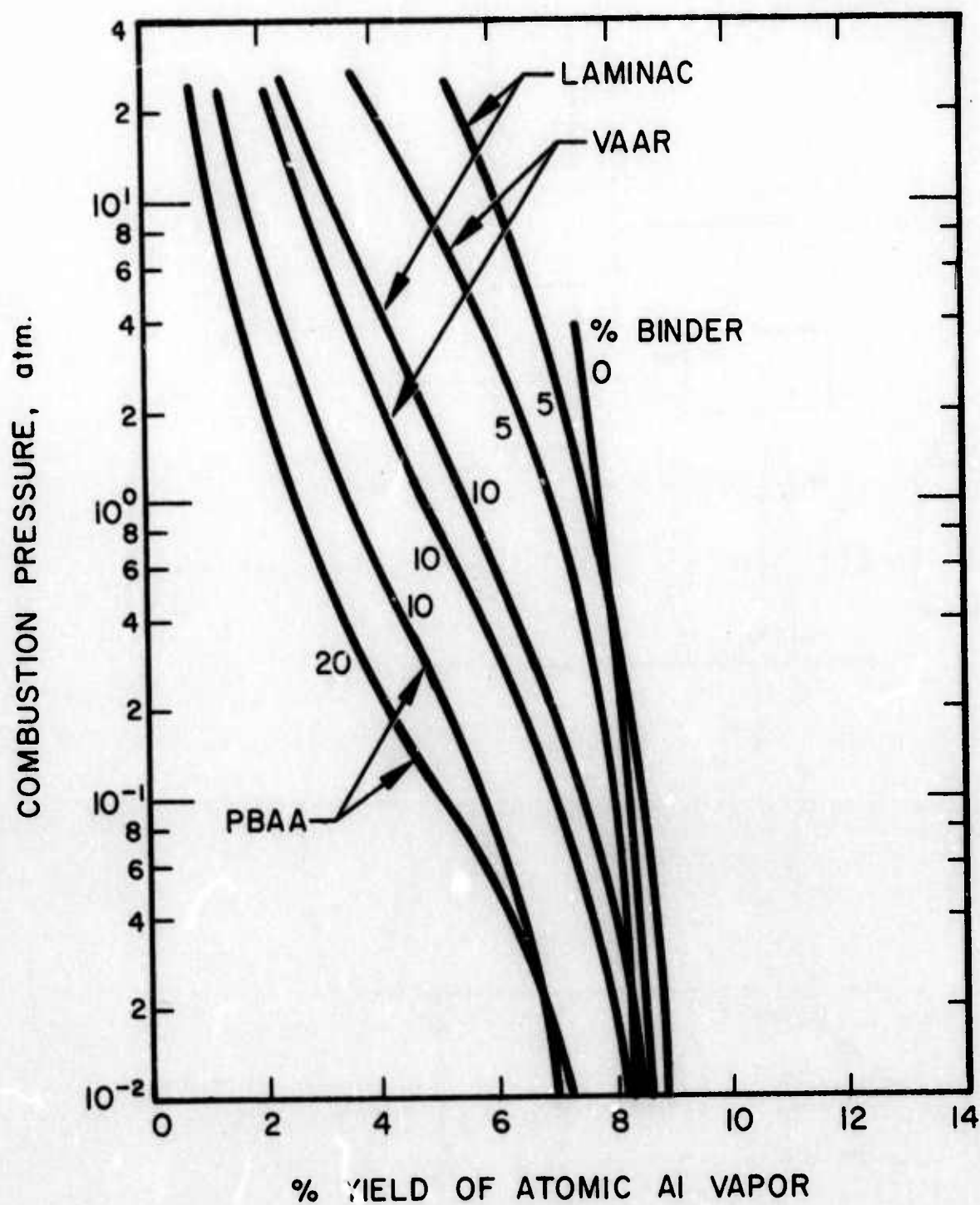


Fig. 3 Effect of Combustion Pressure on Atomic Al Vapor Yields.  
Fuel/oxidizer mole ratio fixed at 1.1 Zr/0.5 AP.

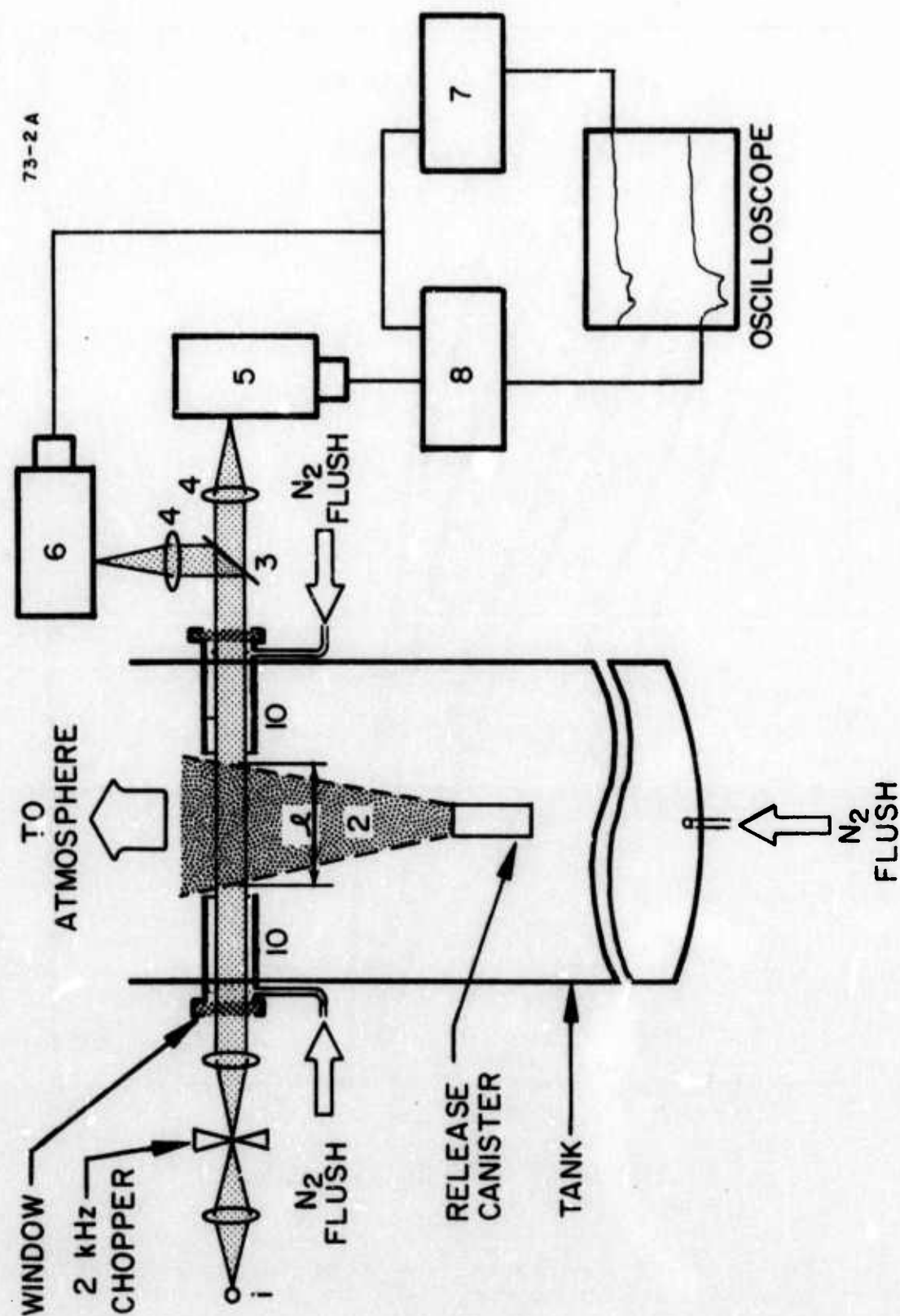


Fig. 4 Schematic of AeroChem Atmospheric Pressure Test Facility.  
Numbers referred to in Section IV.4.2.



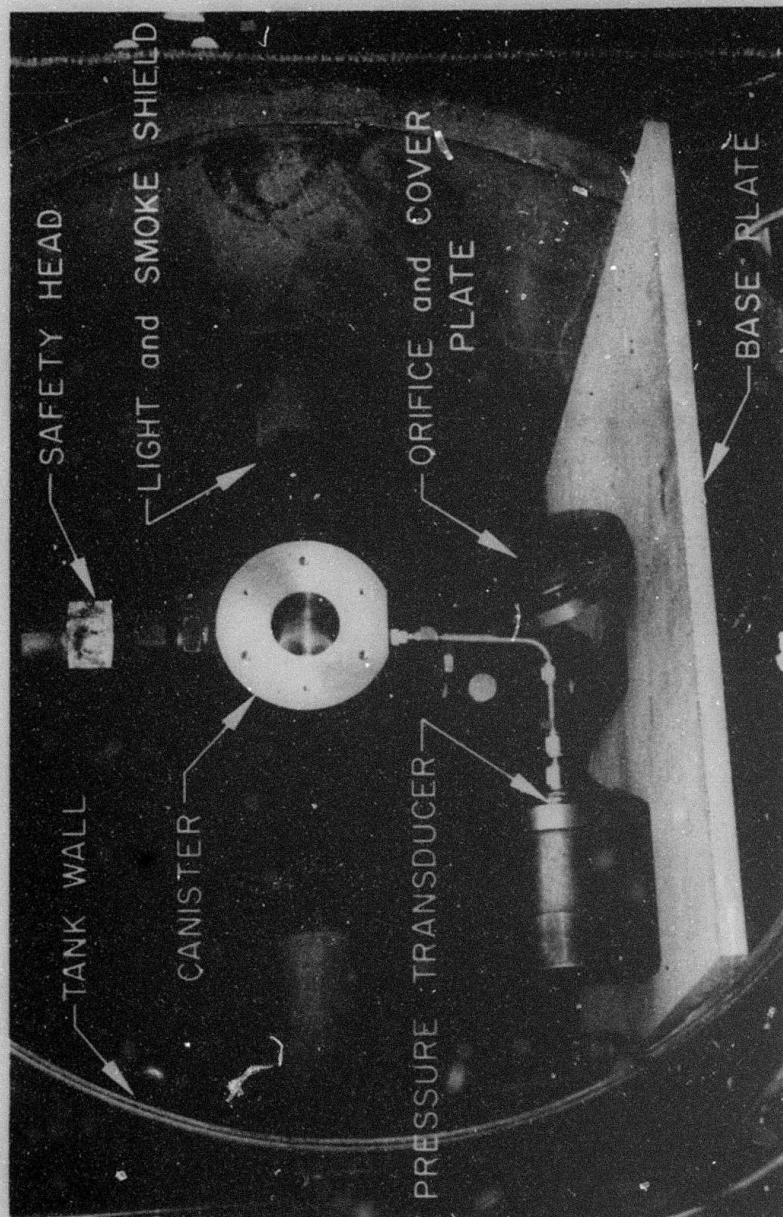


Fig. 5 Combustion Chamber Prepared for Loading.

73-137

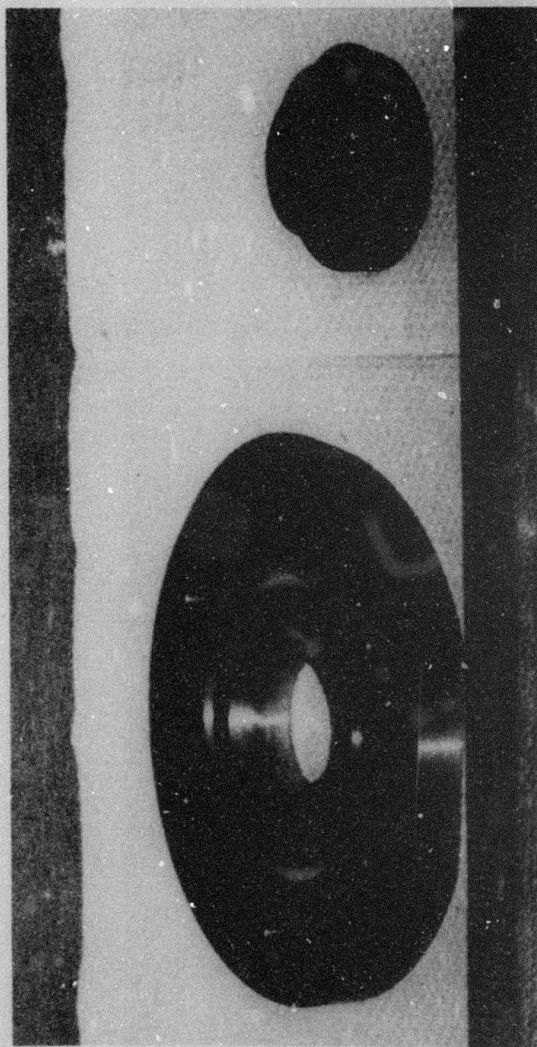


Fig. 6 Cover Flange (Inner Face) and 0.64 cm Graphite Orifice.



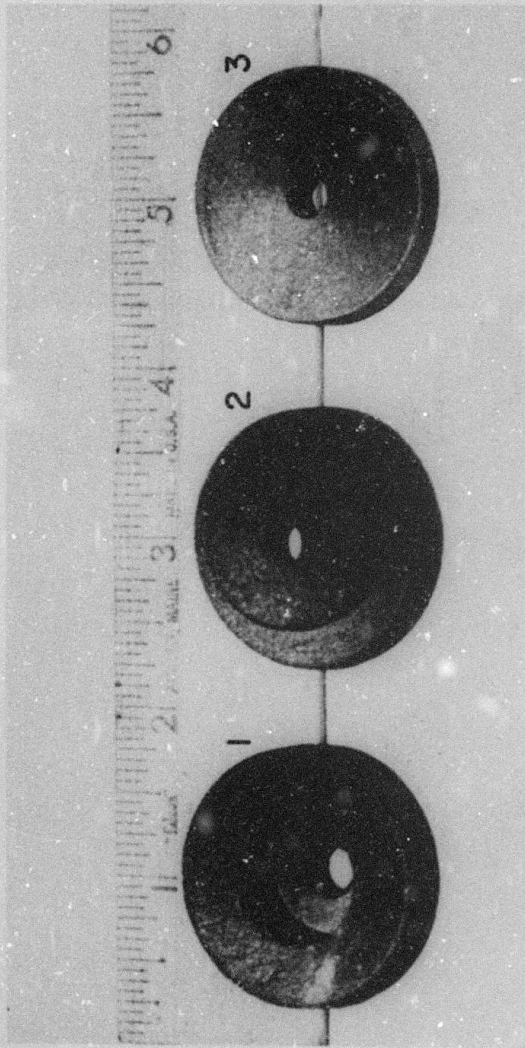


Fig. 7 0.64 cm Graphite Orifices. Numbers referred to in Section IV. A. 3 and Table II.

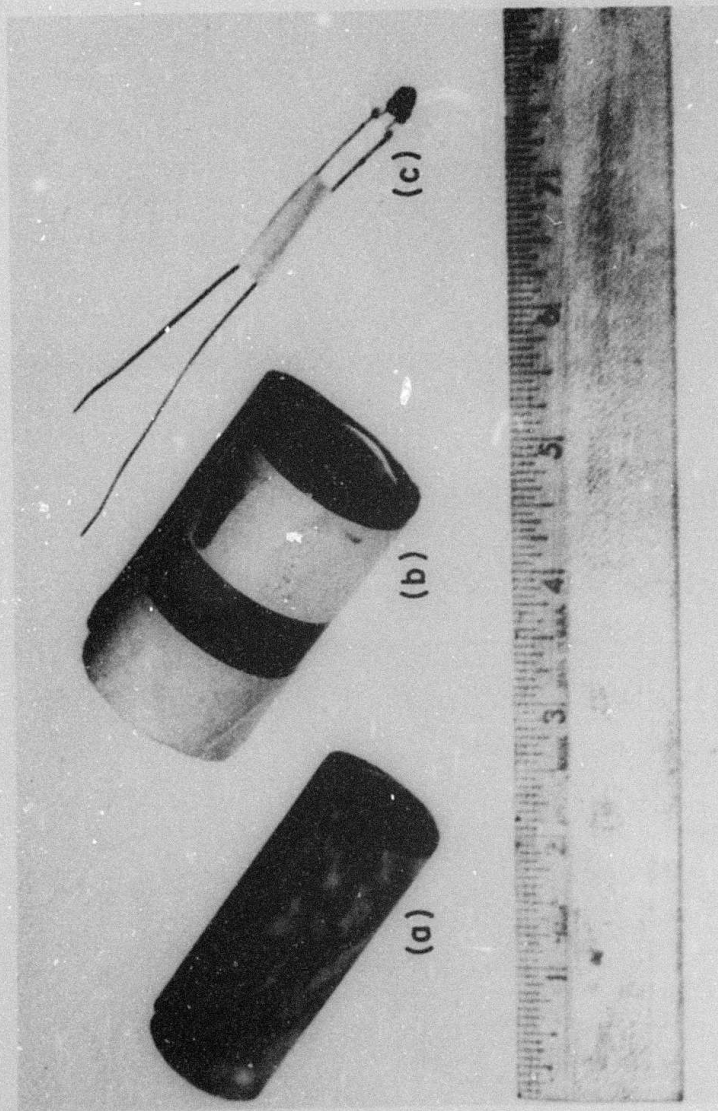


Fig. 8 100 g Flashbulb Samples  
(a) As received from Picatinny Arsenal  
(b) Prepared for firing  
(c) Igniter



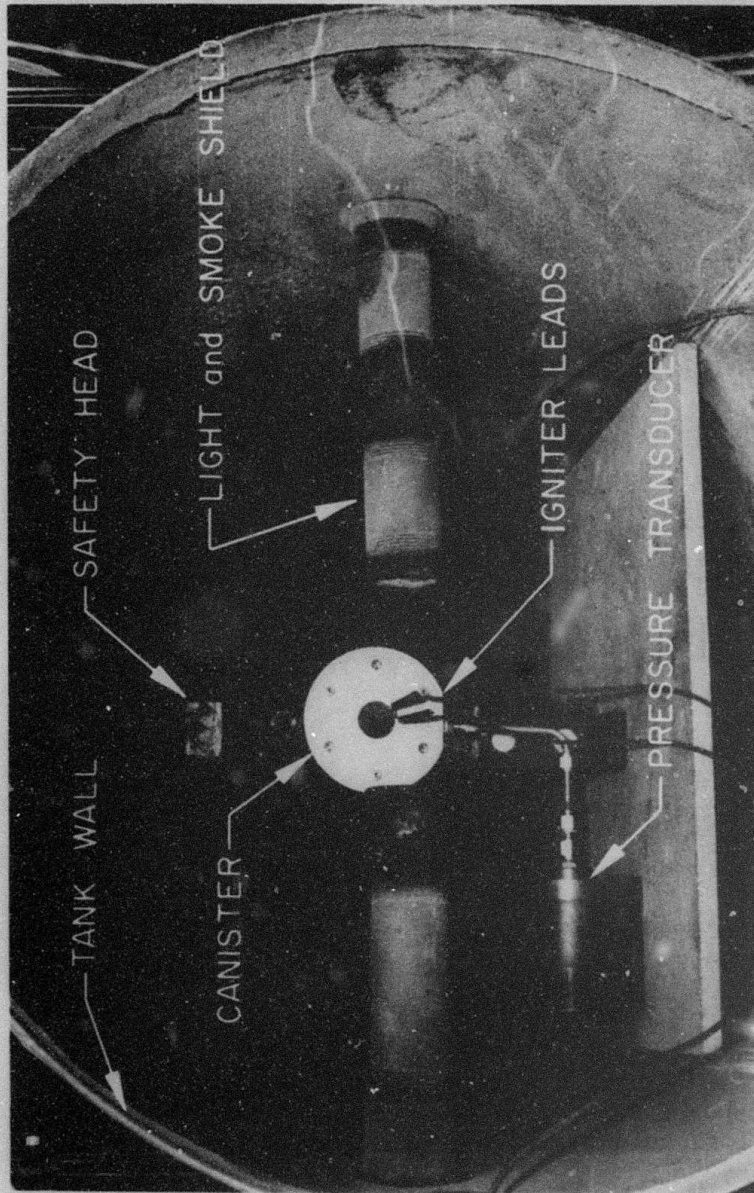


Fig. 9 Combustion Chamber Loaded for Firing  
(tank diameter, 0.6 m).

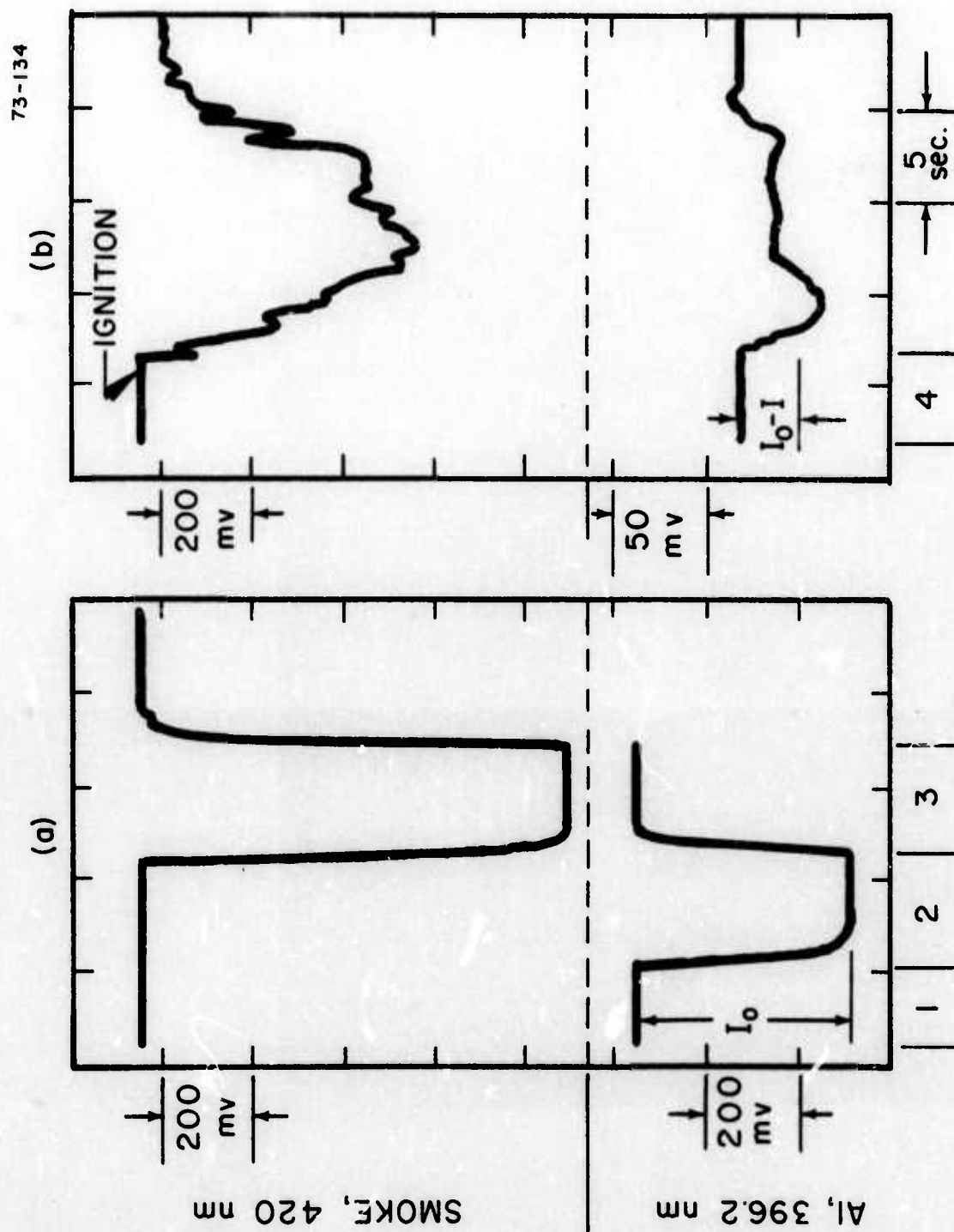


Fig. 10 Experimental Atomic Al Vapor Yield Measurement (Run 70)

(a) Calibration trace

(b) Experimental trace (note scale change in metal atom line)  
Numbers referred to in Section IV.B.

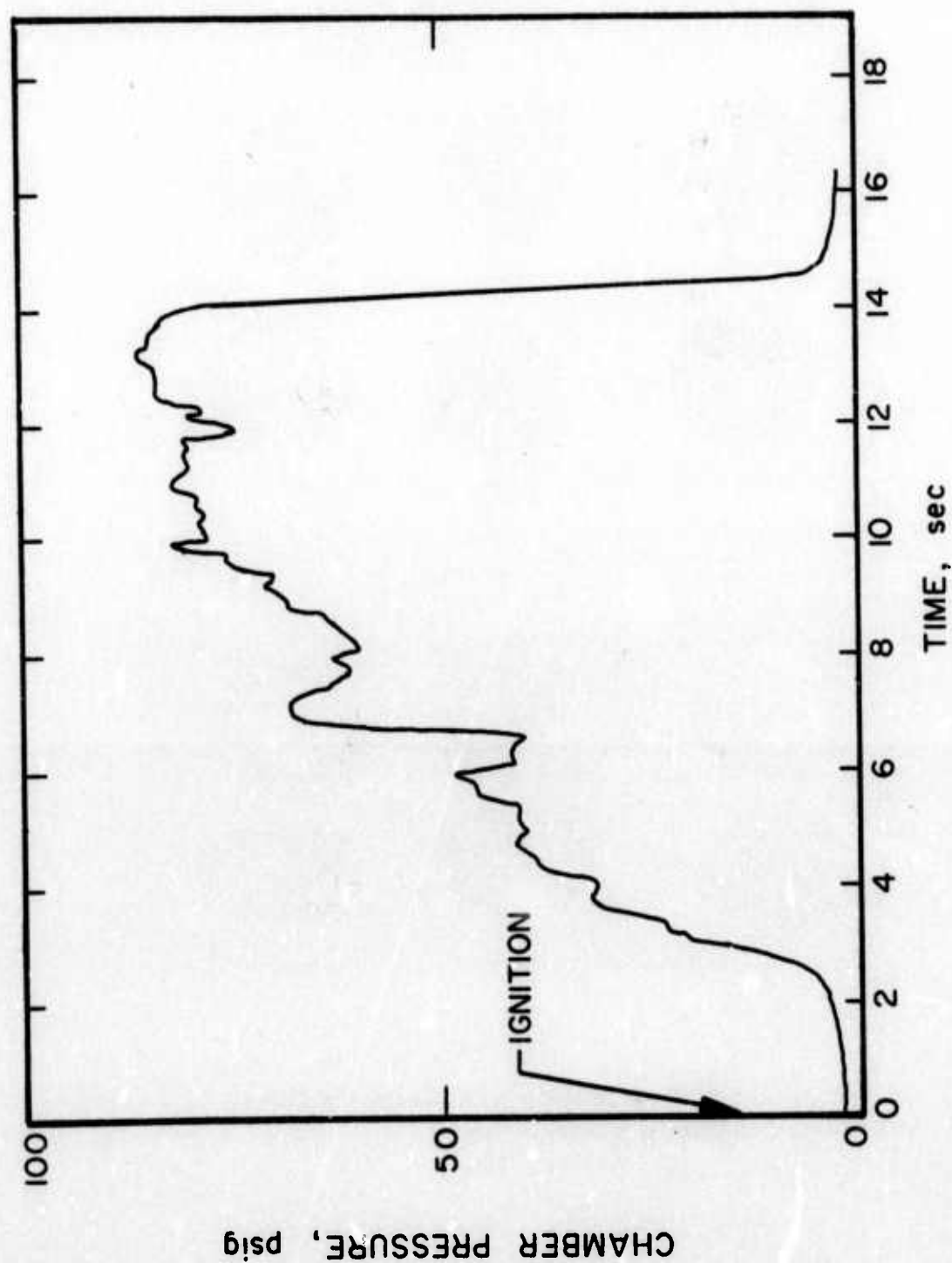


Fig. 11 Experimental Chamber Pressure Measurement (Run 70).



73-136

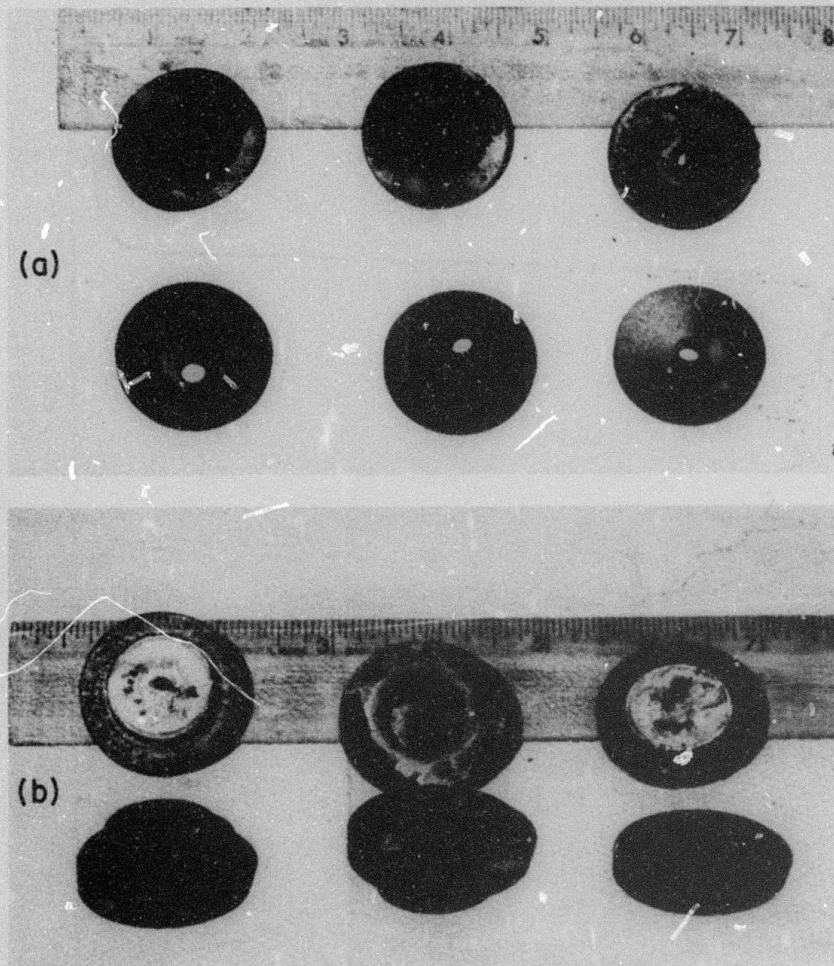


Fig. 12 Slag Buildup on 0.64 cm Orifices.

(a) Facing release

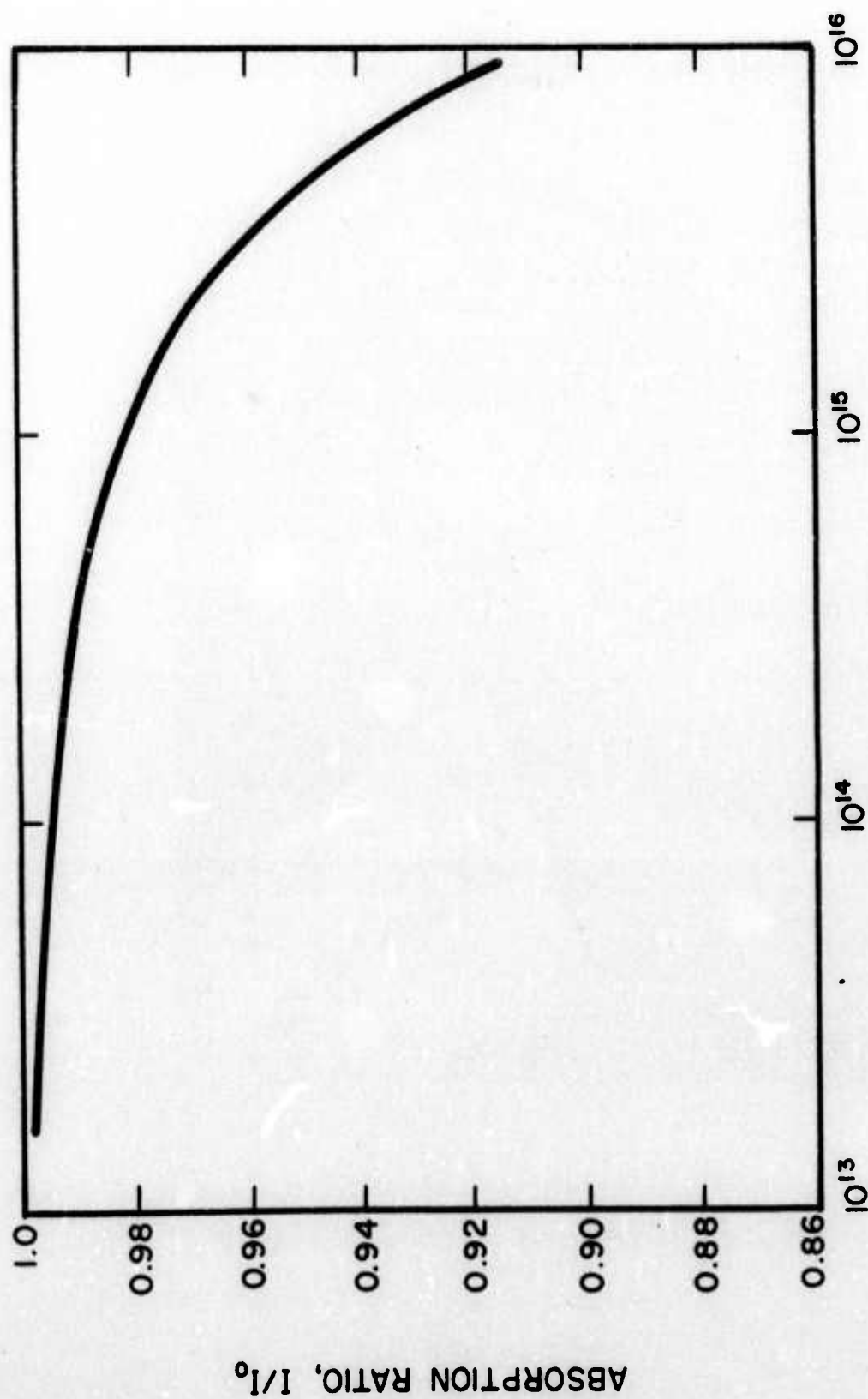
(b) Facing ambient



73-140



Fig. 13 Slag Buildup on 1.25 cm Orifice.



INSTANTANEOUS ATOMIC Al DENSITY,  $\text{cm}^{-3}$

Fig. 14 Effect of Atomic Al Density on Attenuation of a Continuum Source near 396.2 nm. The path length is 11 cm and the half bandwidth is 0.5 nm.

## APPENDIX A

METHOD OF PREPARATION AND SAFETY TESTS  
OF PROTOTYPE SAMPLES

Preliminary tests of burning characteristics, methods of formulation, pressing, and safety were made on about 35 strand-type samples prepared at AeroChem. These samples ranged from ~ 10 to 50 g in mass and ~ 1-3 cm in diameter. The purposes of these tests were:

1. To identify difficulties in handling or firing.
2. To identify a convenient type of binder and range of compositions for formulating larger samples.
3. To test the effects of variations in Zr and Al particle sizes on the burning characteristics.
4. To establish a procedure for preparation of larger samples.
5. To identify compositions which were simple to handle, easily prepared, smooth-burning and which gave large, reproducible Al vapor yields.

As a result of these tests, it was found that:

- (i) Binder levels of  $\gtrsim 10$  by weight were easiest to handle.
- (ii) Al particle sizes of  $8\mu$  resulted in uneven burning and explosions during combustion. This was probably due to voids and/or incomplete coating of the metal particles by the binder.
- (iii) Binders which gave denser samples (e.g., glyptal, polymethylmethacrylate, and butyrate dope) allowed smoother, slower sample burning than did those which gave less dense samples (e.g. PBAA/Epon 828).
- (iv) Smoothest burning samples were those which were prepared by first coating both Al and Zr particles with binder, drying, breaking up the mass with a mortar and pestle, and mixing thoroughly with the oxidizer. This mixture was pressed into tubes (press for 1-3 min at 4000-10000 psi) 1.25 cm diam and ~ 5 cm long.

- (v) Samples prepared in pourable form (e.g. PBAA binder or with excess solvent added to glyptal) were simplest to prepare and handle. However, grain sizes were too large to allow complete drying or curing in a reasonable time. This resulted in 'wet' samples which gave erratic burning and which often fell apart during testing.
- (vi) Safety tests indicated that Flashbulb mixtures of 10 $\mu$  diam Zr, 8 $\mu$  Al, and 50 $\mu$  AP gave no action to impact of a 1 kg weight dropped 10 times from a height of 1 m. These samples gave no action to a stainless steel shoe friction test for 20 sec of continuous rubbing. Samples ignited after  $\sim$  5 sec of electrostatic stimulation from a tesla coil (this may have been due simply to heating).

One mixture of 10% glyptal binder (see Table I) exploded during pressing as a free-standing strand. It was determined that particles had wedged between the die and ram and were probably ignited by friction. Thereafter, all samples were pressed in cardboard tubes.

- (vii) Facilities at AeroChem were inadequate for the safe and rapid preparation of the large numbers of 100 g samples we wished to test. For this purpose, Picatinny Arsenal was engaged to fabricate such samples according to our specifications.



## APPENDIX B

DATA HANDLING

The total number of Al atoms,  $n_{TOT}$ , released in a firing is calculated from<sup>1</sup>

$$n_{TOT} \approx N l^2 v_g t_b \quad (B-1)$$

where  $l$  is the optical path length through the release plume;  $v_g$  is the release gas velocity, calculated from a gas dynamic analysis of the plume;  $t_b$  is the burn time, estimated from the experimental oscilloscope trace (cf. trace 2, Fig. 10); and  $N$  is the instantaneous Al number density in the optical path, obtained from the observed attenuation. The relationship between  $I/I_0$ , the observed ratio in these experiments, and  $N$  was given in Ref. 1. Figure 14 is the plot of  $I/I_0$  against  $N$  from which values of  $n_{TOT}$  appearing in Table II were obtained (via Eq. B-1).

## APPENDIX C

ALTERNATE RELEASE TECHNIQUES

The feasibility of releasing significantly large amounts of atomic Al vapor in the upper atmosphere using combustion techniques other than Flashbulb was investigated. Thermochemical equilibrium calculations of atomic Al vapor yield as a function of composition and chamber pressure were carried out for chemical systems containing TMA (trimethyl aluminum) as an Al source (either by its pyrolysis or its combustion) and for the Al/Teflon system. However, on the basis of arguments presented below, the now proven Flashbulb technique appears more suitable for the purposes of IVY OWL than the alternate release techniques investigated.

1. C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub>/TMA - The pyrolysis of TMA in a cyanogen-oxygen flame results in equilibrium atomic Al vapor yields of 4 to 7 % (cf. calculated Flashbulb yields of 5.5 % for composition A) over the 0.1 to 25 atm pressure range. Optimum yields are obtained from the composition 15 % TMA/53 % C<sub>2</sub>N<sub>2</sub>/32 % O<sub>2</sub> by weight at combustion pressures of from 1 to 10 atm. If payload packaging of the liquids (or high pressure gases) in this mixture could be worked out, this could be a suitable method for the release of atomic Al vapor.

2. UDMH/N<sub>2</sub>O<sub>4</sub>/TMA - The pyrolysis of TMA in an unsymmetrical dimethyl hydrazine (UDMH)/N<sub>2</sub>O<sub>4</sub> flame is much less efficient than in a C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub> flame in releasing atomic Al vapor. The maximum Al vapor yield calculated is 0.6 % for the mixture 24 % TMA/25 % N<sub>2</sub>O<sub>4</sub>/51 % UDMH by weight at a combustion pressure of 25 atm. Space and weight limitations preclude carrying enough payload on a reasonably sized booster for this mixture to be suitable for the purposes of IVY OWL.

3. TMA/LF<sub>2</sub> - The combustion of TMA with liquid fluorine (LF<sub>2</sub>) is an attractive alternate release mechanism because AlO is not produced in the combustion. Unfortunately, only small amounts of atomic Al vapor can be obtained from this system because practically all the Al is tied up as fluorides. The maximum calculated Al vapor yield was 0.4 % at a combustion chamber pressure of 1 atm from a mixture of 49 % TMA/51 % LF<sub>2</sub> by weight. This mixture would therefore be unsuitable for the purposes of IVY OWL.

4. Al/Teflon - The combustion of Al by the pyrolysis products of Teflon also gives calculated Al vapor yields below those required for IVY OWL. The maximum yield calculated (0.5 %) was at a combustion pressure 1 atm for a 45 % Al/55 % Teflon mixture.