NASA CONTRACTOR
REPORT

NASA CR-141

NASA CR-1415

DEVELOPMENT OF A BARIUM CHEMICAL RELEASE SYSTEM

by C. S. Stokes, E. W. Smith, and W. J. Murphy

Prepared by
TEMPLE UNIVERSITY
Philadelphia, Pa.
for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1969

NASA CR-1415

DEVELOPMENT OF A BARIUM CHEMICAL RELEASE SYSTEM

By C. S. Stokes, E. W. Smith, and W. J. Murphy

Prepared under Contract Nos. NAS 1-6199 and NAS 1-7070 by
THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY
Philadelphia, Pa.

for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – CFSTI price $3.00

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to James L. Jones, Jr., Hal T. Baber, Jr. and Beverley W. Lewis of Langley Research Center, NASA, for their helpful suggestions and encouragement in carrying out this study. The authors are grateful to the National Aeronautics and Space Administration for their support of this research under NASA Contracts NAS1-6199 and NAS1-7070.

The assistance of William J. Liddell, Ralph W. Segletes and Leon A. Streng of the Research Institute staff is gratefully acknowledged.

ABSTRACT

A method for producing Ba° and Ba^+ in a gaseous medium was developed utilizing a liquid propulsion system. The fuel consisted of $BaCl_2$ and $Ba(NO_3)_2$ salts dissolved in hydrazine. The oxidizers tested were OF_2, ClF_3 and F_2. The Ba° and Ba^+ yield for all systems at varying oxidizer/fuel ratios was measured using spectroscopic techniques. The chemical system producing the highest yield of Ba° and Ba^+ consisted of a 17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4 fuel mixture tested with fluorine.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

DEVELOPMENT OF A BARIUM CHEMICAL RELEASE SYSTEM

by

C. S. Stokes, E. W. Smith and W. J. Murphy

Research Institute of Temple University
Philadelphia, Pa.

SUMMARY

The objective of this work was to develop a chemical system suitable for the point releases in good yield of free barium (Ba^o) atoms and barium ions (Ba^+), at an altitude on the order of several earth radii. This effort was accomplished by dissolving barium salts (barium chloride and/or barium nitrate) in a fuel (hydrazine or ammonia) and reacting this mixture with various oxidizers in a liquid rocket motor combustion chamber. Photometric intensity measurements of the Ba^o 5535Å and Ba^+ 4554Å spectral lines were made for those systems to determine the relative yield of Ba^o and Ba^+ species in the exhaust plume. This method then enabled selection of the chemical system providing the highest yield of free barium (Ba^o) atoms and barium ions.

The following fuel/oxidizer systems were evaluated:

1. 50% $Ba(NO3)_2$ - 50% $NH3/ClF3$
2. 42.9% $Ba(NO3)_2$ - 57.1% $N_2H_4/ClF3$
3. 16.7% $BaCl_2$ - 83.3% N_2H_4/F_2
4. 26% $BaCl_2$ - 74% N_2H_4/F_2
5. 21% $BaCl_2$ - 9% $Ba(NO3)_2$ - 70% N_2H_4/F_2
6. 17% $BaCl_2$ - 16% $Ba(NO_3)_2$ - 67% N_2H_4/F_2
7. 13% $BaCl_2$ - 21.5% $Ba(NO3)_2$ - 65.5% N_2H_4/F_2
8. 9% $BaCl_2$ - 30% $Ba(NO_3)_2$ - 61% N_2H_4/F_2
9. 42.9% $Ba(NO3)_2$ - 57.1% N_2H_4/F_2
10. 42.9% $Ba(NO_3)_2$ - 57.1% N_2H_4/OF_2

Note: Fuel compositions are given in weight percent

Two systems, 26% $BaCl_2$ - 74% N_2H_4/F_2 and 13% $BaCl_2$ - 21.5% $Ba(NO_3)_2$ - 65.5% N_2H_4/F_2, were run in a 42.4 cubic meter vacuum tank at pressures ranging from 0.05 to 0.50 torr. The system having the highest yield of Ba^o and Ba^+, as determined by photometric measurements, was the 17% $BaCl_2$ - 16% $Ba(NO_3)_2$ - 67% N_2H_4/F_2 mixture.

Solubility studies of barium salts in hydrazine (N_2H_4) and ammonia (NH_3) were performed. The barium salt/hydrazine solutions were investigated to determine shock sensitivity.

INTRODUCTION

It has been proposed to create ion clouds in the upper atmosphere and interplanetary space for the study of geophysical properties of the medium. For example: the physics of comet tails, the magnetic field of the earth, solar winds, and electric fields in the ionosphere can be investigated using data generated from observation of artifically produced ion clouds. Several elements have been suggested as having suitable optical properties for the generation of an ion cloud; such as calcium, strontium, barium, europium, ytterbium.

In reference 1 Föppl developed a barium solid chemical release system using copper oxide with Ba in excess of that stoichiometrically required and utilizing the heat of formation of BaO to vaporize the remaining Ba. The vaporized Ba^o would be photo-ionized to Ba^+ by sunlight action. The same investigator has estimated that from 2.4 to 4.8 kg of free Ba would be required in order to produce sufficient mass for measurement at 5 earth radii.

A degree of disparity exists between various observers in regard to the time scale for photo-ionization. An increase in the time scale required for photo-ionization would require greater amounts of vaporized Ba than previously estimated. Since the barium-copper oxide system produced a relatively low yield, less than 15%, of free barium (Ba^o) and barium ions (Ba^+), it appeared desirable to develop a system having a higher yield of Ba^o and Ba^+.

After consideration of the above parameters, the Research Institute of Temple University proposed the development of a system which would readily lend itself to scale-up and provide a higher temperature (3800°K) than the barium-copper oxide system (approximately 2200°K). The higher temperature should result in a more efficient yield of Ba^o and Ba^+. The proposed system consisted of a liquid fuel containing Ba in conjunction with an extremely energetic liquid oxidizer.

This report covers the experimental development and evaluation of systems using barium salts dissolved in hydrazine and ammonia with several fluorine containing oxidizers. Previous and concurrent investigations using barium chloride and barium nitrate dissolved in hydrazine with nitrogen tetroxide and chlorine trifluoride oxidizers were carried out by the Research Institute of Temple University for the Air Force Cambridge Research Laboratories, reference 2.

APPARATUS AND PROCEDURES

At the start of the investigation it was decided to evaluate the various systems by measuring photometrically the light intensity of the 5535Å Ba^{o} and 4554Å Ba^{+} lines. By monitoring this light intensity, it was expected that the relative amounts of Ba^{o} and Ba^{+} produced (as well as efficiency) could be estimated. The first test set-up consisted of two interference filters, used to measure the above spectral lines, mounted on a rotating disc and placed in front of a 931A photomultiplier tube. This device was focused on the exhaust plume of the system being tested. The input to the photomultiplier consisted of alternate pulses of Ba^{o} and Ba^{+} light and was fed into an oscillograph. After several runs, it was realized that this system was producing unrealistic values. Due to the wide band widths of the filters, approximately 14 mμ, the photocell was seeing more than the 5535Å and 4554Å lines. This was particularly true in systems where considerable band spectra was produced. To overcome this problem it was decided to use a 1.5 meter stigmatic grating spectrograph coupled with two 931A photomultiplier tubes mounted to the film holder at the point where the 5535Å Ba and 4554Å Ba^{+} line appeared. Each photomultiplier tube was placed in an aluminum holder with a 0.25 mm slit. This slit then accepted a 4Å increment of wave length since the spectrograph had a 15Å/mm first order dispersion. By use of a barium hollow cathode discharge tube and the two previously mentioned interference filters, the photomultiplier was alined in the proper position on the spectrograph to monitor the Ba^{o} (5535Å) and Ba^{+} (4554Å) lines in the exhaust plume. The signals from the photomultipliers were fed into an oscillograph. This system gave a repeatable, reliable method for accurately measuring the Ba^{o} and Ba^{+} values.

Spectra of all the systems were taken with the above spectrograph. Figure 1 shows the optics for tests conducted at ambient conditions. The flame was reflected from a front surface mirror through a focusing lens to the spectrograph slit. The slit was arranged to have the spectrograph grating rulings parallel to flame axis. This, in turn, assured filling of the slit and photomultiplier tube openings. The average flame length ranged from 0.6 to 0.9 meters. Photocells were mounted as in a typical Wadsworth mounting at the 4554Å and 5535Å position, as shown in Fig. 2.

Figure 3 shows a schematic of the combustion system. The optics for tests conducted at vacuum conditions are shown in Fig. 2. The burner was mounted inside a 42.4 cubic meter vacuum tank. Two optical paths are shown. The film spectrograph viewed the flame from the side. The optical path consisted of a tank sight glass and a focusing lens. The spectrograph used to measure line intensity viewed the flame from a head-on position; it saw the core or flame center. The optics consisted of a sight glass and focusing lens.

The propellant flow rates were measured with turbine-type flowmeters and recorded on oscillographs.

The combustion unit consisted of a stainless steel pipe closed at one end, 5.7 cm long and 3.5 cm inside diameter, see Fig. 1. The unit contained injector orifices mounted at 90° to each other and sized for pressure drops of 5.24 to 10.2 x 10^5 Newtons/meter^2 across the orifice. Fuel and oxidizer flows generally ranged from 22.5 to 68.2 gm/sec. each. A pressure tap was placed in the back of the combustion unit and pressure was monitored for the initial runs. This was done to determine the net pressure drop across injector orifices. The chamber pressure of the combustion unit ranged from 1.02 to 3.45 x 10^5 Newtons/meter^2 absolute.

Fuel, containing the dissolved barium salt, was poured into the fuel tank using a funnel. The usual charge was from 340 to 454 gm., which provided several runs of 3 seconds duration.

Cryogenic oxidizers such as OF_2 and F_2 were condensed from gases in the closed oxidizer system enclosed in a liquid nitrogen bath. The oxidizer flow meter and feed line to the combustion unit were also maintained at liquid nitrogen temperature with a liquid nitrogen jacket.

The ClF_3 (non-cryogenic) was pressurized into the closed oxidizer system from a supply bottle with super dry nitrogen.

The system was pressurized with helium by means of dome regulators remotely operated. Propellant tank pressures ranged from 6.89 to 20.06 x 10^5 Newtons/meter^2. Figure 3 shows a schematic of the equipment.

The experimental temperatures given in Table I for the various systems were deduced from the emission spectra as follows, using the standard technique described by Corliss and Bozman, reference 3.

$$I = \frac{N}{U} \frac{8\pi^2 e^2 h}{m} \frac{gf}{\lambda^3} e^{-\frac{E}{kT}} \qquad 1$$

Using subscripts for the two spectral lines

$$I_1 = \frac{N}{U} \frac{8\pi^2 e^2 h}{m} \frac{g_1 f_1}{\lambda_1^3} e^{-\frac{E_1}{kT}} \qquad 2$$

and

$$I_2 = \frac{N}{U} \frac{8\pi^2 e^2 h}{m} \frac{g_2 f_2}{\lambda_2^3} e^{-\frac{E_2}{kT}} \qquad 3$$

for a given spectrum $\frac{N}{U} \frac{8\pi^2 e^2 h}{m}$ can be considered constant

that is,

$$\frac{N}{U} \frac{8\pi^2 e^2 h}{m} = C \qquad \text{(constant)} \qquad 4$$

Then

$$I_1 = C \frac{g_1 f_1}{\lambda_1^3} e^{-\frac{E_1}{kT}} \qquad 5$$

and

$$I_2 = C \frac{g_2 f_2}{\lambda_2^3} e^{-\frac{E_2}{kT}} \qquad 6$$

Various spectral lines may be plotted by taking the logarithm of Eq. 6 and plotting

$$\ln \frac{gf}{I\lambda^3} \text{ versus } \frac{E}{kT} .$$

These points will yield a straight line if the source has a Boltzmann distribution. Using equations 5 and 6, taking logs and subtracting,

$$\frac{E_2}{kT} - \frac{E_1}{kT} = 2.3026 \left(\log \frac{g_2 f_2}{I_2 \lambda_2^3} - \log \frac{g_1 f_1}{I_1 \lambda_1^3}\right) \qquad 7$$

By plotting $gf/I\lambda^3$ vs. E on semi-logarithmic paper, the temperature is obtained from the slope of the line

$$\frac{1}{T} = \frac{2.3026 \text{ K} \left(\log \frac{g_2 f_2}{I_2 \lambda_2^3} - \log \frac{g_1 f_1}{I_1 \lambda_1^3}\right)}{E_2 - E_1} \qquad 8$$

Taking two points from the Ba° curve on Fig. 2, E_2 and E_1 respectively are 32,000 and 24,000, and $\frac{g_2 f_2}{I_2 \lambda_2^3}$ and $\frac{g_1 f_1}{I_1 \lambda_1^3}$ respectively are 20.8×10^{12} and 1.26×10^{12}.

Therefore $$\frac{1}{T} = \frac{2.3026\ (0.69502)(\log 20.8 \times 10^{12} - \log 1.26 \times 10^{12})}{32{,}000 - 24{,}000}$$

$$T = 4085^\circ K$$

The theoretical N_2H_4/F_2 flame temperature is 4687°K. Comparison of the experimental spectral temperatures with other calculated thermodynamic flame temperatures are given in Table I.

The gf and E values were obtained from Corliss and Bozmann, reference 3. For those lines available, gf values as determined by Penkin, reference 4, were used. The latter gave better distribution while also resulting in slightly lower temperatures (200 to 300°K) less.

Intensities of the spectrograms were measured with a densitometer modified to include a photocell pickup. The signal was amplified and a trace was made with an oscillograph to provide a continuous measurement of film intensity. Tri-X film was used for the ambient tests. Kodak Type I with F film sensitization was used for the vacuum test spectra.

The degree of ionization may be calculated by writing equation 1 for the Ba^+ species and for the Ba° species, eg.

$$I^+ = \frac{N^+}{U^+} \frac{8\pi^2 e^2 h}{m} \frac{gf}{\lambda^3}^+ e^{-\frac{E^+}{kT}} \tag{9}$$

and

$$I^\circ = \frac{N^\circ}{U^\circ} \frac{8\pi^2 e^2 h}{m} \frac{gf}{\lambda^3}^\circ e^{-\frac{E^\circ}{kT}} \tag{10}$$

Therefore

$$\frac{I^+}{I^\circ} = \frac{\frac{N^+}{U^+} \frac{gf}{\lambda^3}^+ e^{-\frac{E^+}{kT}}}{\frac{N^\circ}{U^\circ} \frac{gf}{\lambda^3}^\circ e^{-\frac{E^\circ}{kT}}} \tag{11}$$

or

$$\frac{N^+}{N^\circ} = \frac{I^+}{I^\circ} \frac{U^+}{U^\circ} \frac{\frac{gf}{\lambda^3}^\circ}{\frac{gf}{\lambda^3}^+} e^{\frac{E^+ - E^\circ}{kT}} \tag{12}$$

Values of the partition coefficients (U^+ and U^o) were calculated and plotted vs. temperature using the method as described by Corliss and Bozmann, reference 3. The temperature was calculated by the Boltzmann plot as previously described.

Assume the temperature using the Boltzmann plot was found to be 4085°K, then the partition coefficients would be: $U^+ = 3.4$ and $U^o = 1.58$. The best literature values for gf/λ^3 and E for the 4554Å and 5535Å lines would be obtained. Using values of relative intensity from the photomultiplier, $I^o = 27{,}600$ mv and $I^+ = 11{,}800$ mv found in Table II and substituting in equation 12

$$\frac{N^+}{N^o} = \frac{11{,}800}{27{,}600} \; \frac{3.4}{1.58} \; \frac{8.25 \times 10^{12}}{14.0 \times 10^{12}} \; e \; \frac{21{,}952 - 18{,}060}{0.6950(4085)}$$

$$= 2.13$$

and % ionization

$$\frac{N^+(100)}{N^o + N^+} = \frac{2.13(100)}{1 + 2.13} = 68.1\%$$

This provided a means of estimating the % ionization using relative line intensity values and not relying on film spectra.

PROPERTIES OF CHEMICAL SYSTEMS

MATERIALS

The chemical suppliers and manufacturers stated purity is as follows:

Chemical	Supplier	Purity
N_2H_4	Olin Matheson Chemical Co. Lake Charles, La.	Technical Grade 97 to 98% N_2H_4 (2 to 3% H_2O)
NH_3	Air Products and Chemicals Allentown, Pa.	Technical Grade 99.99% NH_3
$BaCl_2$	J, T. Baker & Co. Phillipsburg, N. J.	Reagent Grade
$Ba(NO_3)_2$	J. T. Baker & Co. Phillipsburg, N. J.	Reagent Grade
F_2	Air Products and Chemicals Allentown, Pa.	98%
ClF_3	Allied Chemical Co. Baton Rouge, La.	99.5%
OF_2	Allied Chemical Co. Baton Rouge, La.	98%

SOLUBILITY STUDIES

The solubilities of $Ba(NO_3)_2$ and $BaCl_2$ in NH_3 and N_2H_4 as given by various investigators are as follows:

Salt	Solvent	Solubility in gm/100 gm mixture	Temp. °C	Investigator
$Ba(NO_3)_2$	NH_3	50.0	25	Reference 5
$BaCl_2$	N_2H_4	23.7	25	Reference 6
		26.0	25	RITU
$Ba(NO_3)_2$	N_2H_4	2.9	25	Reference 6
		43.0	25	RITU

The solubility of $Ba(NO_3)_2$ in NH_3 was verified as that given in the literature. The solubility of $BaCl_2$ in N_2H_4 was approximately 10% greater than the literature showed. This might possibly be attributed to the small amount of water present in the commercial grade "anhydrous" hydrazine used. The hydrazine water content ranged from one to two percent.

The significant difference between the literature value for the $Ba(NO_3)_2$ solubility in N_2H_4 and the value determined by this laboratory has not been explained. A difference of several percent could be attributed to the presence of water in the solvent. The reason for this disparity has not been investigated.

A solubility study of various mixtures containing $Ba(NO_3)_2$, $BaCl_2$ and N_2H_4 was made at room temperature and is shown as a triangular plot in Fig. 5. Seven solutions that were used in tests are indicated on the figure. A mixture below the saturation line (toward the $Ba(NO_3)_2$ or $BaCl_2$ corners) contained two phases (a solution and solid phase), whereas the salts were in complete solution above the saturation line. Figure 5 also shows a line of stoichiometric mixtures (a chemical equivalent of hydrazine per equivalent of salt). As a point of interest, a stoichiometric mixture of $Ba(NO_3)_2$ and N_2H_4 was prepared, i.e. three moles of N_2H_4 per mole of $Ba(NO_3)_2$. This mixture was a slush at room temperatures and when heated to 50°C became gel-like in appearance.

The temperature at which solids began precipitating in the hydrazine salt solution were studied. It was found that the solutions became cloudy below -1°C. The cloudiness was attributed to occluded air bubbles. As temperatures were lowered, they were more viscous and appeared to form a gel. The point at which small crystals were observed is noted in the following table as the freezing point. The table also shows the solution density.

Solution	Density @ 77°F gm/cc	Solids Formation Temperature °C
1. 16.7% $BaCl_2$-83.3% N_2H_4	1.167	-5.6
2. 26% $BaCl_2$-74% N_2H_4	1.260	2.2 to -6.6
3. 21% $BaCl_2$-9% $Ba(NO_3)_2$-70% N_2H_4	1.322	-11.7 to -12.8
4. 17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4	1.358	-6.7 to -10
5. 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4	1.361	-11.1 to -12.2
6. 9% $BaCl_2$-30% $Ba(NO_3)_2$-61% N_2H_4	1.400	-11 to -12.7
7. 42.9% $Ba(NO_3)_2$-57.1% N_2H_4	1.477	-2.8
8. 50% $Ba(NO_3)_2$-50% NH_3	0.905	25

SHOCK SENSITIVITY

Two approaches were used to determine the shock sensitivity of mixtures used. The preliminary method consisted of placing 50 ml of fuel mixture in a test tube and supporting the tube in a clean, open quart can. Fifteen cm. of primacord was placed in a 6.3 mm diameter tube and sealed at one end. The primacord tube was in turn placed in the test tube and a blasting cap attached to the primacord tube. The assembly was then detonated. All solutions were tested in this qualitative manner and in addition a blank of pure hydrazine was also tested. None of the systems showed any significant difference in shock sensitivity. All cans appeared to be torn and fragmented to the same degree.

Semi-quantitative comparisons and impact sensitivities were determined by the apparatus and procedures described in Liquid Propellant Test Method Number 4, "Drop-Weight Test", as recommended by the JANAF Panel on Liquid Propellant Test Methods and published by the Chemical Propulsion Information Agency. This data is shown in the next table.

Hydrazine, 12.3% $Ba(NO_3)_2$-20% $BaCl_2$-67.7% N_2H_4, 17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4, and 26% $BaCl_2$-74% N_2H_4 gave negative results in five consecutive tests at 100 kgcm. This indicates a very low sensitivity which is not measureable on the Drop-Weight Tester. The mixture 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4 gave only one positive test in nine tests at 100kgcm. This material also shows a very low sensitivity.

The 42.9% $Ba(NO_3)_2$-57.1% N_2H_4 gave positive tests, but the rupture diaphragm was not perforated. The positive tests were reactions which left a solid residue and produced gas. This result indicates that high order detonation did not occur, but that the impact produced low order detonation or ignition of the samples. The energy required for a 50% probability of reaction (E_{50}) was 79 kgcm.

For reference purposes, typical impact sensitivites are listed for several liquid propellants and explosives. These data were taken from the operation manual for the Drop-Weight Tester furnished by the manufacturer.

IMPACT SENSITIVITY OF HYDRAZINE MIXTURES

Sample Designation	Impact Sensitivity	E_{50}
Hydrazine	No shots in 5 trials @ 100 kgcm	Neg.
12.3% $Ba(NO_3)_2$-20% $BaCl_2$-67.7% N_2H_4	No shots in 5 trials @ 100 kgcm	Neg.
26% $BaCl_2$-74% N_2H_4	No shots in 5 trials @ 100 kgcm.	Neg.
13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4	1 shot in 9 trials @ 100 kgcm. (no shots in last 5 consecutive trials)	Neg.
42.9% $Ba(NO_3)_2$-57.1% N_2H_4	No high order shots in 23 trials	79 kgcm
17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4	No shots in 5 trials @ 100 kgcm	Neg.

TYPICAL IMPACT SENSITIVITY VALUES OF LIQUID PROPELLANTS AND EXPLOSIVES*

Sample	E_{50} (kgcm)
Hydrazine	Neg.
Hydrazine/Hydrazine Nitrate (40/60)	89.7
Nitromethane	67.4
n-Propyl Nitrate	15.6
Nitroglycerine	1.6

---

*Data from operating manual, Technoproducts, Div. of Quantic Industries, Inc., San Carlos, Calif.

RESULTS AND DISCUSSION

A. Evaluation at Ambient Conditions

Data for all systems tested is listed in Table II and shown graphically in Figs. 6, 7a, 7b, 7c and 8.

The test parameters given in Table II are: fuel, oxidizer, O/F (oxidizer to fuel weight ratio), fuel flow and relative light intensity of the 5535Å (Ba^o) and 4554Å (Ba^+) spectral lines.

Figures 6, 7a, 7b, 7c and 8 show the relative intensity of the 5535Å (Ba^o) and 4554Å (Ba^+) spectral lines vs. O/F.

All fuel systems were easily handled except the 50% $Ba(NO_3)_2$-50% NH_3 system. This system caused clogging of feed valves. As the fuel expanded, immediately following the propellant valve opening, $Ba(NO_3)_2$ precipitated on the valve seat causing clogging. The light values obtained using this system were low.

Figure 6 shows the two systems tested using ClF_3 as the oxidizer. Figures 7a, 7b, and 7c show the seven systems tested using F_2 as the oxidizer. Figure 8 shows the two systems tested using OF_2 as the oxidizer. For comparison Figs. 6 through 8 have the same horizontal scale. The light intensity measurements are given in millivolts as recorded and corrected for photomultiplier response at the particular wavelength. Neutral density filters and a small spectrograph entrance slit width (10 µ) were used to keep the photomultiplier tubes within their linear range.

The 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4/F_2 system was used as a comparative standard. The relative light output from this chemical mixture at a given O/F was compared to the light output obtained in previous tests using the same chemical mixtures. This provided a means of regularly checking the optical system and comparing various chemical mixtures.

The Ba^o light was greater than the Ba^+ light for a given O/F in any system. The maximum light occured in all systems at a point located between the stoichiometric O/F and 3% less than the stoichiometric O/F. The stoichiometric O/F is defined as being equivalent to the oxidizer to fuel weight ratio in a balanced equation assuming the salt is converted to free Ba, F to HF, Cl to HCl and O to H_2O.

As an example, one system tested had an O/F ratio of 142 grams oxidizer per 100 grams fuel or 1.42/1.00. If the barium is assumed to be converted to BaF_2, then the stoichiometric O/F is 1.47. Since the greatest light output in all cases occurred with O/F less than stoichiometric, it is apparent that little of the Ba was combined as BaF_2 or $BaCl_2$. This was confirmed by spectrographic analysis.

Table III lists the systems in order of decreasing light output (relative light intensity) with respect to Ba^o, thereby indicating the relative barium yield.

Figure 9 shows a plot of intensity ratio versus weight % of oxygen, chlorine and fluorine. Review of the data (shown in Table I) indicates a dependence of Ba^o/Ba^+ ratio on the percentage oxygen and fluorine. As the oxygen content increases, the Ba^o/Ba^+ ratio increases. As the fluorine content increases, the Ba^o/Ba^+ decreases. This means that more barium ion is formed using increasing amounts of fluorine; that is, up to pure fluorine. The effect of chlorine is not clear.

Film spectra showed some BaO bands present in all systems containing O_2. Quantitative measurements of band spectra were not taken; however, it appeared that the lower temperature systems had considerably more BaO. Some $BaCl_2$ and BaF_2 band spectra was noted in the systems without O_2. No BaO bands were noted in those systems without O_2. Since mixtures containing no oxygen showed no BaO bands, it was considered that the oxygen in the atmosphere had little significant effect on ambient tests.

B. Evaluations at Vacuum Conditions

Two systems were run in a 42.5 cubic meter vacuum tank:

1. 26% $BaCl_2$-74% N_2H_4/F_2
2. 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4/F_2

The same combustion unit was used for the vacuum tests as for the ambient tests. The feed rates were also the same: 22.5 to 68 gm/sec. each of fuel and oxidizer. The vacuum at ignition corresponded to an altitude of 70 km (5.8 Newtons/meter^2) and after 3 sec. burning the equivalent altitude was 35 km (613 Newtons/meter^2).

Initially the photomultiplier-spectrograph was set up to view the flame at a right angle to the axis of the flame propogation path. In this position the photomultipliers were not sensitive enough to pick up the 4554Å Ba^+ and 5535Å Ba^o light. The spectrograph was then placed to view the motor from a head-on position with respect to the flame (see Fig. 2). The rapidly expanding flame caused a lowering of particle density and in turn the relative light intensity diminished to approximately 1/40 of the intensity measured at one atmosphere in air.

An additional spectrograph was placed at right angle to the axis of the flame propagation path to obtain spectrograms.

The data for the vacuum tests is given in Table IV and shown in Fig. 10.

The light intensity curves for the vacuum tests have the same form as the curves for the ambient pressure tests. The optimum O/F ratio of the 26% $BaCl_2$-74% N_2H_4/F_2 and 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4/F_2 systems are the same under vacuum and ambient conditions.

CONCLUDING REMARKS

An optical system was developed to measure the intensity of the 4554Å Ba^+ and 5535Å Ba^o lines of several chemical mixtures and gave reproducible and repeatable results.

It was determined that the 17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4/F_2 system gave the greatest amount of light intensity of the 4554Å Ba^+ and 5535Å Ba^o spectral lines. Ambient tests showed that the optimum oxidizer to fuel weight ratio of this system was 1.32 to 1. This system containing 7.52 weight % barium was estimated to be 68.1% ionized. Since the relative light intensity of this system was the largest of all the systems tested, it would be expected to give the greatest amount of free Ba^o and Ba^+. For this reason, it was selected to be used in a barium payload release. It was also found for all systems that the relative light reached a maximum at the O/F corresponding to the stoichiometric equation yielding Ba as one of the reaction products. The relative light output was sensitive to the O/F. Moving to either side of the optimum O/F caused a sharp decrease in relative light.

In vacuum tests the ignition was smooth and took place within the combustion chamber. The rapid expansion in vacuum caused a decreased atom and ion density in the luminous flame which caused the light intensity to be about 1/37 to 1/50 the intensity measured in ambient tests. The % ionization was approximately the same for vacuum and ambient tests.

It is recommended that the system $Ba(NH_3)_6/F_2$ be investigated as to its suitability for Ba release experiments. This system is a very promising candidate for producing a high yield of Ba^o and Ba^+ because: (1) the system has a high percentage of barium, 23%, assuming the same type reaction with F_2 as the barium salts had with F_2; (2) the system would yield a flame temperature comparable to present systems evaluated (4000°K); (3) the barium ammonia solution has a low freezing point, about -89°C; and (4) the system does not contain any oxygen or chlorine to possibly lower the yield.

This work indicates that additional studies to determine the absolute concentration of Ba^o and Ba^+ at ambient and vacuum conditions would be desirable in order that reasonable predictions could be made concerning quantities of barium released in space.

APPENDIX - SYMBOLS

I	intensity, joules/meter^3-second
N	particle density, number/meter^3
U	partition function
e	electronic charge, esu
m	electron mass, 9.1091 x 10^{-31} kg
h	Planck's constant, 6.62 x 10^{-34} joule-seconds
g	statistical weight of upper level
f	Ladenburg's oscillator strength for the emitted line
λ	wavelength of the line, meters
E	energy of level, kaysers
k	Boltzmann's constant, .69502 kaysers/°K
T	temperature, °K

REFERENCES

1. Föppl, H., et al: Preliminary Experiments for the Study of the Interplanetary Medium by the Release of Metal Vapour in the Upper Atmosphere. Planetary & Space Sciences 1965, Vol. 13, No. 3, pp 95-114.

2. Stokes, C. S. and Smith, E. W.: Development of a Barium Payload, Research Institute of Temple University, Contract No. AF19(628)-5710, June 30, 1967, RITU 1967-28.

3. Corliss, C. H. and Bozman, W. R.: Experimental Probabilities for Spectral Lines of Seventy Elements-NBS Monograph 53, U. S. Government Printing Office, 1962.

4. Penkin, N. P.: Determination of Oscillator Strength in Spectral Atmos. J. Quant. Spectrosc. Radiat. Transfer, Vol. 4, pp 41-94, 1964.

5. Hunt, Herschel and Boncyk, L.: Liquid Ammonia As A Solvent, III. The Solubility of Inorganic Salts at 25°. J. Am. Chem. Soc. Vol. 55, 1963, pp 3528-3530.

6. Welsh, T. W. B. and Broderson, H. J.: Anhydrous Hydrazine. III. Anhydrous Hydrazine as a Solvent. J. Am. Chem. Soc. Vol. 37, 1915, pp 816-824.

TABLE I

SYSTEMS COMPARISON

System	Optm. O/F	% Ba	% O	% Cl	% F	Theor.(1) Temp. °K	Experimental Results			
							Temp. °K(2)	Relative Intensity Ratio Ba°-Ba$^+$	% Ion(3)	Condition
16.7% $BaCl_2$- 83.3% N_2H_4/N_2O_4(4)	1.18	5.00	26.0	3.60	0	3225	3080	12.7	37.9	Ambient
43% $Ba(NO_3)_2$- 57% N_2H_4/N_2O_4(4)	0.595	14.10	35.8	0	0	3225	3250	8.0	37.8	Ambient
16.7% $BaCl_2$- 83.3% N_2H_4/ClF_3(4)	2.36	3.25	0	28.0	43.5	3683	3300	3.4	68.0	Ambient
26% $BaCl_2$- 74% N_2H_4/ClF_3(4)	2.08	5.57	0	25.8	41.6	3683	3220	3.23	70.0	Ambient
50% $Ba(NO_3)_2$- 50% NH_3/ClF_3	1.52	10.43	7.3	23.1	37.2	3600	----	5.02	----	Ambient
42.9% $Ba(NO_3)_2$- 57.1% N_2H_4/ClF_3	1.19	10.04	7.3	20.7	33.5	3683	3300(5)	7.4	50.0	Ambient
16.7% $BaCl_2$- 83.3% N_2H_4/F_2	1.95	3.75	0	1.92	66.2	4687	4250	2.17	68.8	Ambient
26% $BaCl_2$- 74% N_2H_4/F_2	1.71	6.32	0	3.28	63.0	4687	3860	2.22	70.6	Ambient
							4370	2.53	61	Vacuum
21% $BaCl_2$- 9% $Ba(NO_3)_2$- 70% N_2H_4/F_2	1.57	7.23	1.29	2.78	61.2	4687	4000(5)	2.26	68.5	Ambient

TABLE I (continued)

SYSTEMS COMPARISON

System	Optm. O/F	% Ba	% O	% Cl	% F	Theor.(1) Temp. °K	Experimental Results Temp. °K(2)	Relative Intensity Ratio Ba°-Ba+	% Ion(3)	Condition
17% $BaCl_2$- 16% $Ba(NO_3)_2$- 67% N_2H_4/F_2	1.31	7.52	2.25	5.77	56.6	4687	4085	2.33	68.1	Ambient
13% $BaCl_2$- 21.5% $Ba(NO_3)_2$- 65.5% N_2H_4/F_2	1.34	8.49	3.4	1.90	57.3	4687	4150	2.80	63.7	Ambient
							4340	2.46	62	Vacuum
9% $BaCl_2$- 30% $Ba(NO_3)_2$- 61% N_2H_4/F_2	1.04	10.62	5.41	1.50	51.0	4687	4000(5)	2.78	63.7	Ambient
42.9% $Ba(NO_3)_2$- 57.1% N_2H_4/F_2	0.976	11.45	8.0	0	49.5	4687	4540	4.4	43.0	Ambient
42.9% $Ba(NO_3)_2$- 57.1% N_2H_4/OF_2	0.694	13.35	21.5	0	28.9	4036	3710	5.8	46.9	Ambient
26% $BaCl_2$- 74% N_2H_4/OF_2	1.22	7.70	16.2	4.0	38.5	4036	3600	5.5	52.8	Ambient

(1) Theoretical temperature of salt free systems at 69.3 x 10^5 Newtons/meter^2
(2) Temperature calculated as noted on pp 6, 7
(3) % ionization calculated as noted on pp 7, 8
(4) Included for comparison; systems studied on AFCRL Contract No. AF19(628)-5710
(5) Estimated temperature

TABLE II

SUMMARY OF AMBIENT TEST RESULTS

System			Fuel Flow	Relative Intensity mv	
Fuel	Oxidizer	O/F	Gm/Sec	Ba° 5535Å	Ba+ 4554Å
1. 50% $Ba(NO_3)_2$-50% NH_3	ClF_3	4.70	13.5	177	17
		3.51	12.7	118	11
		2.87	14.2	191	33
		1.65	15.9	177	33
		1.52	16.9	221	44
		1.42	18.4	191	44
2. 42.9% $Ba(NO_3)_2$-57.1% N_2H_4	ClF_3	2.03	21.6	604	78
		1.34	27.5	604	78
		1.22	31.0	632	78
		1.04	34.0	663	83
		0.96	33.6	663	94
		0.89	34.9	617	72
3. 16.7% $BaCl_2$-83.3% N_2H_4	F_2	3.60	20.0	4240	1270
		3.10	17.9	5000	1465
		2.72	20.6	6820	2000
		2.67	20.5	5000	1465
		2.65	19.0	5300	1600
		2.43	29.9	8800	3300
		2.34	25.9	7060	2840
		2.34	25.9	8800	3670
		2.34	12.6	1125	1100
		2.30	22.7	6000	1870
		1.98	27.9	9100	3350
		1.97	25.2	6200	3700
		1.95	14.2	7260	6650
		1.93	28.4	2050	3000
		1.86	24.3	9200	5010
		1.74	26.1	8350	4000
		1.52	29.9	7950	3300
		1.48	20.1	16000	5850
		1.35	23.3	11400	4170
		1.18	27.0	6920	2330
		1.14	25.9	7300	6200
		1.06	----	12400	4180
		1.05	22.8	6550	7000

TABLE II (continued)

SUMMARY OF AMBIENT TEST RESULTS

System			Fuel Flow	Relative Intensity mv	
Fuel	Oxidizer	O/F	Gm/Sec	Ba° 5535Å	Ba^+ 4554Å
4. 26% $BaCl_2$-74% N_2H_4	F_2	3.20	22.7	12250	5350
		2.91	23.4	13600	6500
		2.79	26.3	10900	4200
		2.71	23.5	11800	5660
		2.54	32.0	12200	4500
		2.48	29.5	12200	5000
		2.24	32.3	14500	5700
		1.75	38.8	16000	6520
		1.70	37.5	14100	6350
		1.56	40.6	14500	7000
		1.50	42.8	14100	6500
		1.32	35.1	7300	2700
5. 21% $BaCl_2$-9% $Ba(NO_3)_2$-70% N_2H_4	F_2	1.87	27.1	12200	5370
		1.64	31.2	15850	6400
		1.57	34.7	20600	9100
		1.52	31.8	15350	7400
		1.44	34.7	10600	5370
		1.40	34.6	9150	4020
		1.35	35.1	8300	3610
		1.29	35.1	6900	3110
6. 17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4	F_2	1.63	28.2	11500	4960
		1.49	29.0	17800	7800
		1.41	28.2	22500	10200
		1.38	28.9	24800	----
		1.37	28.2	24400	10800
		1.35	29.3	25100	11400
		1.32	30.4	27000	11400
		1.32	30.4	27600	11800
		1.25	29.3	25100	10200
		1.17	29.1	23300	9100
		1.11	32.0	23100	8500
		1.08	29.1	21800	8500
7. 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4	F_2	2.51	34.8	15000	4350
		2.16	39.1	16300	4700
		1.74	35.5	19100	5900
		1.54	36.2	21800	6700
		1.26	43.2	22700	7700
		1.04	43.2	23600	8340
		0.895	50.3	10000	3200

TABLE II (continued)

SUMMARY OF AMBIENT TEST RESULTS

System			Fuel Flow	Relative Intensity mv	
Fuel	Oxidizer	O/F	Gm/Sec	Ba° 5535Å	Ba^+ 4554Å
8. 9% $BaCl_2$-30% $Ba(NO_3)_2$-61% N_2H_4	F_2	1.72	23.4	9700	3450
		1.46	28.0	11300	4200
		1.29	36.4	13700	5120
		1.20	36.4	14600	5550
		1.04	35.7	16600	5970
		1.03	35.1	16000	5970
		0.97	41.8	14100	5620
		0.92	39.7	12700	4870
		0.90	37.7	11600	5120
9. 42.9% $Ba(NO_3)_2$-57.1% N_2H_4	F_2	2.01	21.5	3880	660
		1.49	22.0	5640	1320
		1.09	22.0	8810	1980
		0.955	43.1	9000	1800
		0.95	22.2	7050	1850
		0.72	22.5	3530	540
10. 42.9% $Ba(NO_3)_2$ 57.1% N_2H_4	OF_2	1.12	44.3	5450	1000
		0.915	44.3	6200	940
		0.869	44.3	6550	1200
		0.775	44.3	7300	1330
11. 26% $BaCl_2$-74% N_2H_4	OF_2	1.58	32.8	10550	1870
		1.45	35.2	10900	2000
		1.15	38.6	11800	2100
		1.12	38.6	10700	1660
		1.11	37.7	11200	2080
		1.07	40.0	10300	1720
		1.03	41.7	9100	1600
		0.99	39.5	10300	1870
		0.91	41.7	8300	1400

TABLE III

SYSTEMS RELATIVE BARIUM YIELD

System	Maximum Relative Intensity mv	
	Ba° 5535Å	Ba^{+} 4554Å
17% $BaCl_2$-16% $Ba(NO_3)_2$-67% N_2H_4/F_2	27600	11800
13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4/F_2	23600	8340
21% $BaCl_2$-9% $Ba(NO_3)_2$-70% N_2H_4/F_2	20600	9100
9% $BaCl_2$-30% $Ba(NO_3)_2$-61% N_2H_4/F_2	16600	5970
26% $BaCl_2$-74% N_2H_4/F_2	16600	6520
26% $BaCl_2$-74% N_2H_4/OF_2	11800	2100
16.7% $BaCl_2$-83.3% N_2H_4/F_2	9100	3350
42.9% $Ba(NO_3)_2$-57.1% N_2H_4/F_2	9000	1800
42.9% $Ba(NO_3)_2$-57.1% N_2H_4/OF_2	7300	1330
42.9% $Ba(NO_3)_2$-57.1% N_2H_4/ClF_3	663	94
50% $Ba(NO_3)_2$-50% NH_3/ClF_3	221	44

TABLE IV

SUMMARY OF VACUUM TEST RESULTS

System			Fuel Flow	Relative Intensity mv	
Fuel	Oxidizer	O/F	Gm/Sec	Ba^{o} 5535Å	Ba^{+} 4554Å
1. 26% $BaCl_2$-74% N_2H_4	F_2	2.19	28.7	253	116
		1.74	34.7	450	175
		1.00	40.2	223	116
2. 13% $BaCl_2$-21.5% $Ba(NO_3)_2$-65.5% N_2H_4	F_2	2.03	24.1	250	97
		1.54	36.5	283	107
		1.31	36.8	352	116
		1.08	39.5	478	194
		0.99	39.1	392	175
		0.96	38.7	231	98
		0.70	42.6	140	78

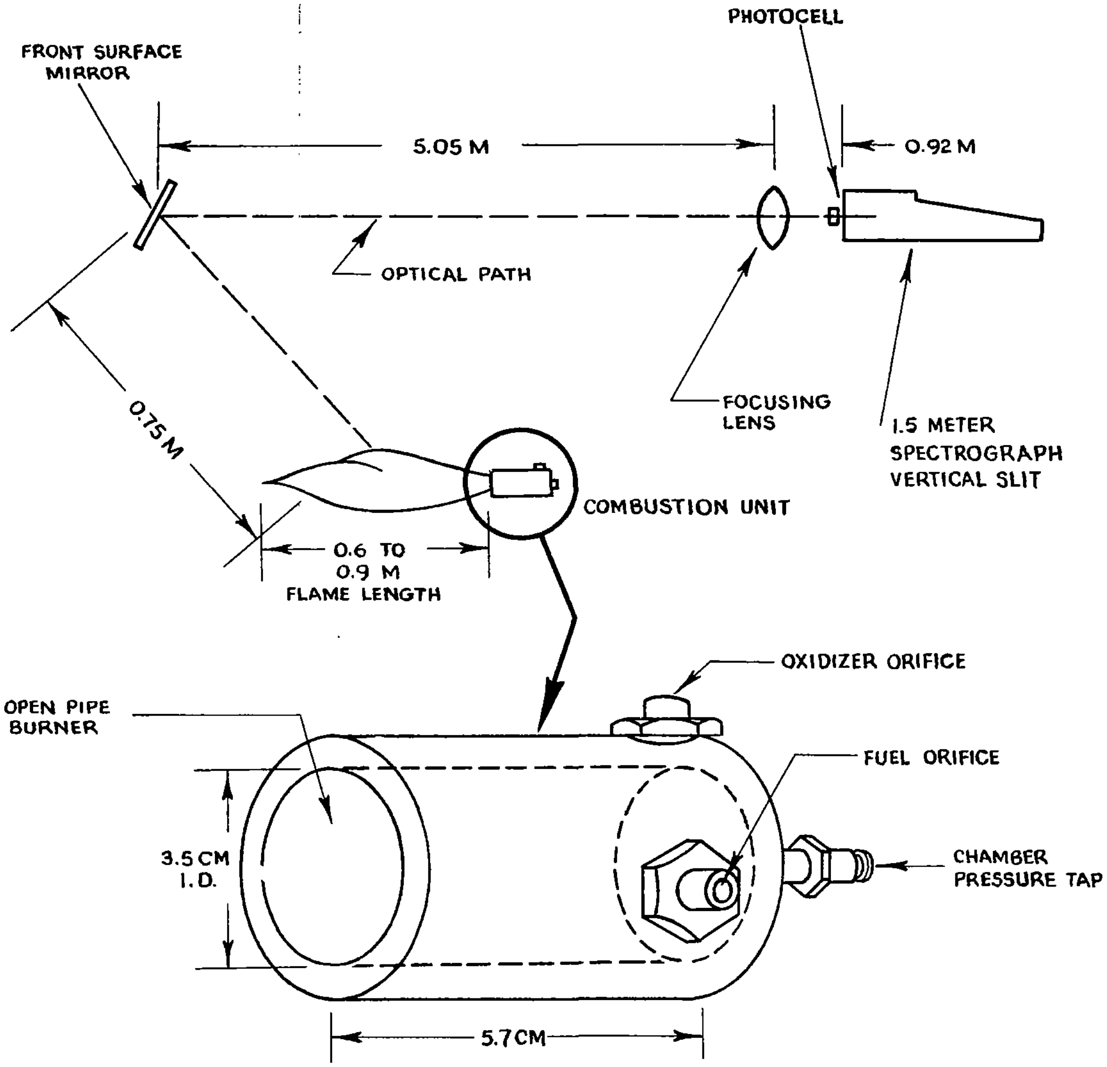

FIGURE 1

OPTICS FOR TESTS CONDUCTED AT AMBIENT CONDITIONS

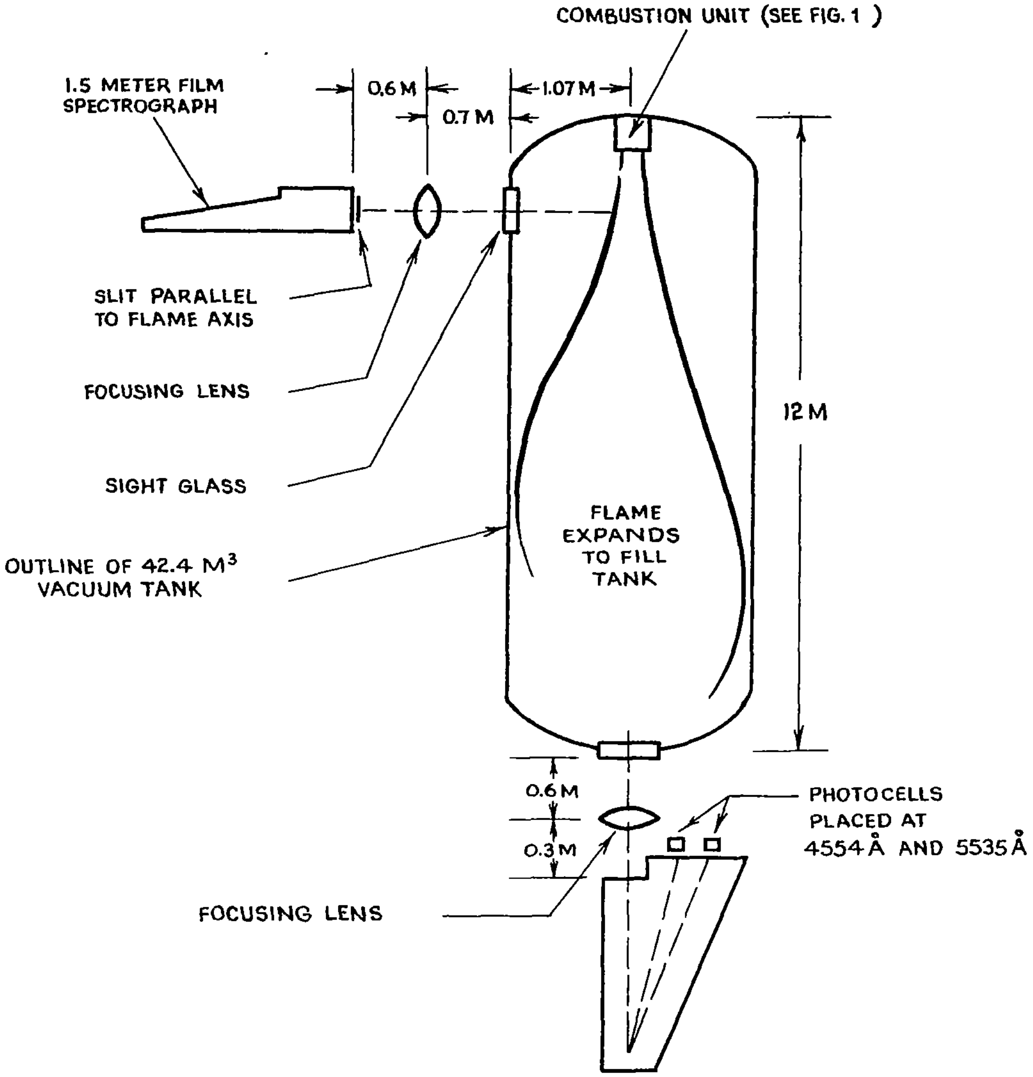

FIGURE 2

OPTICS FOR TESTS CONDUCTED AT VACUUM CONDITIONS

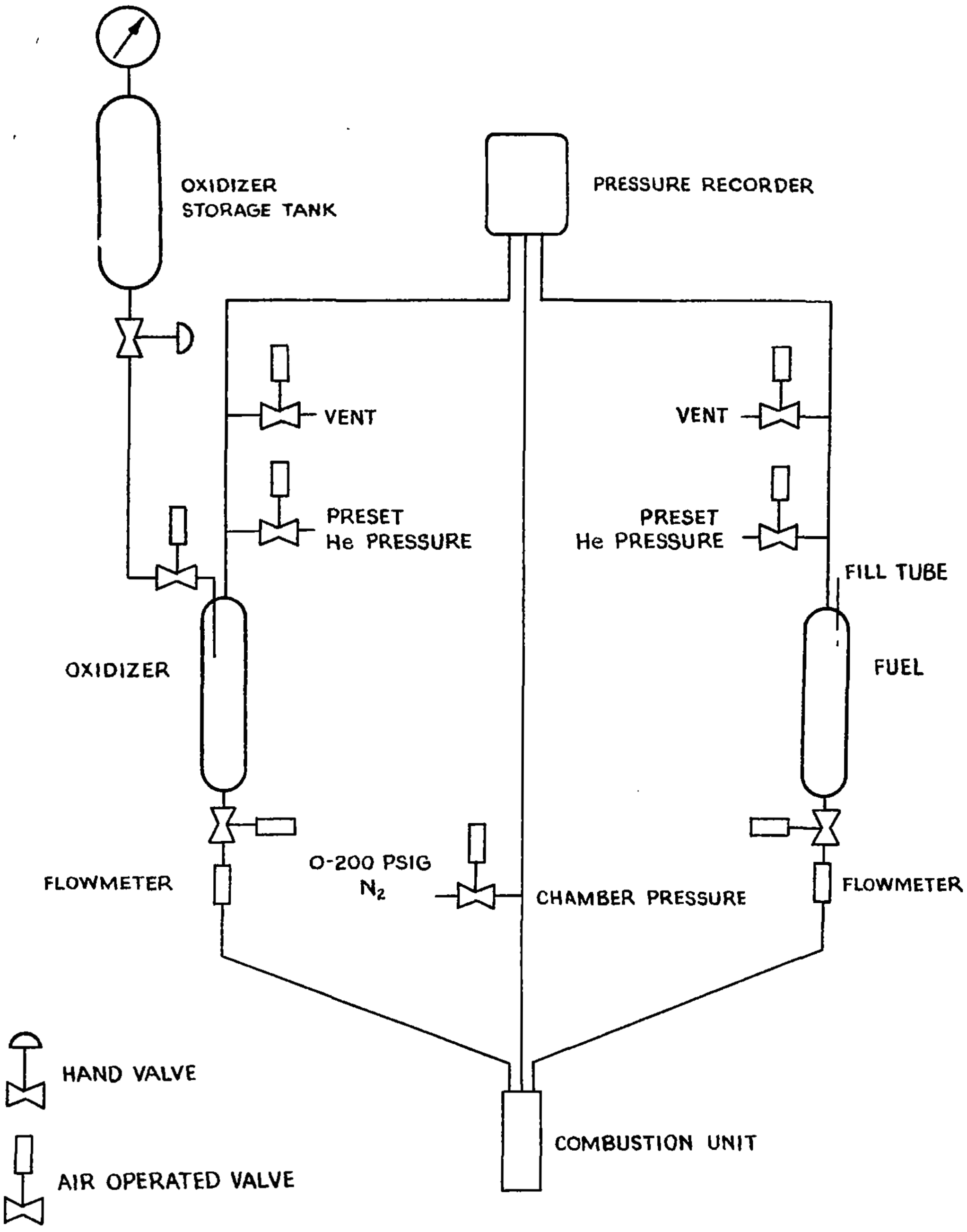

FIGURE 3
COMBUSTION SYSTEM PIPING SCHEMATIC

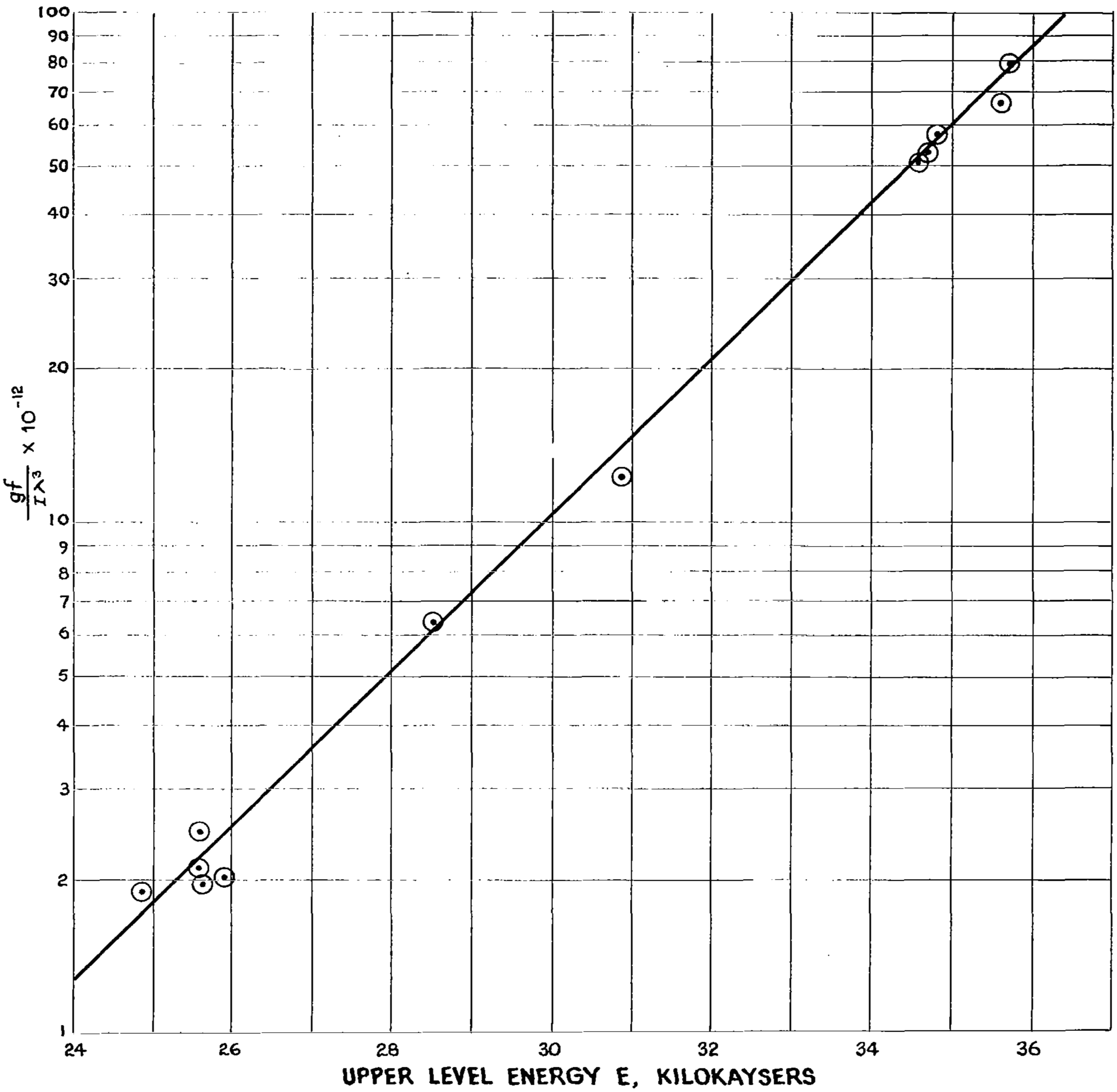

FIGURE 4

LOG RATIO OF gf-VALUE TO INTENSITY TIMES λ^3 FOR MULTIPLETS OF Ba IN THE BURNER FLAME PLOTTED VERSUS UPPER LEVEL

SOLUTION

1) 16.7% $BaCl_2$ - 83.3% N_2H_4
2) 26.% $BaCl_2$ - 74.% N_2H_4
3) 21.% $BaCl_2$ - 9.% $Ba(NO_3)_2$ - 70% N_2H_4
4) 17.% $BaCl_2$ - 16.% $Ba(NO_3)_2$ - 67% N_2H_4
5) 13.% $BaCl_2$ - 21.5% $Ba(NO_3)_2$ - 65.5% N_2H_4
6) 9.% $BaCl_2$ - 30.% $Ba(NO_3)_2$ - 61.% N_2H_4
7) 42.9% $Ba(NO_3)_2$ - 57.1% N_2H_4

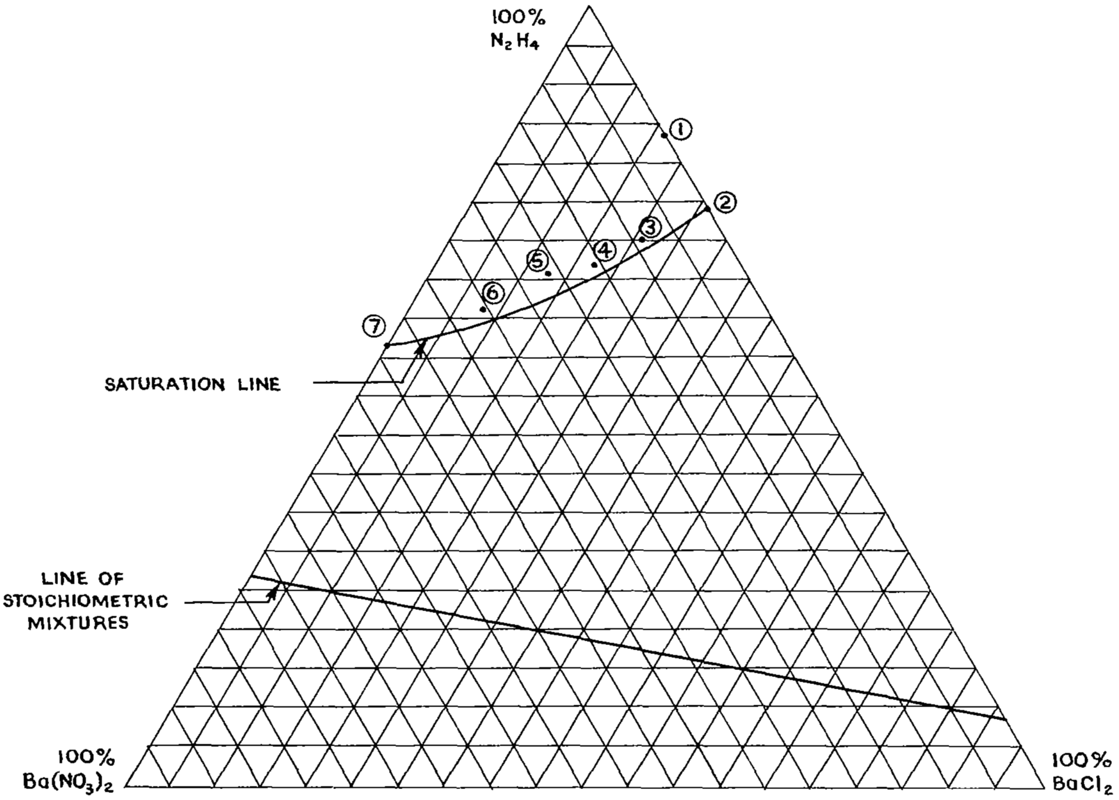

FIGURE 5

$Ba(NO_3)_2$-$BaCl_2$-N_2H_4 **WEIGHT %**

SOLUBILITY DIAGRAM

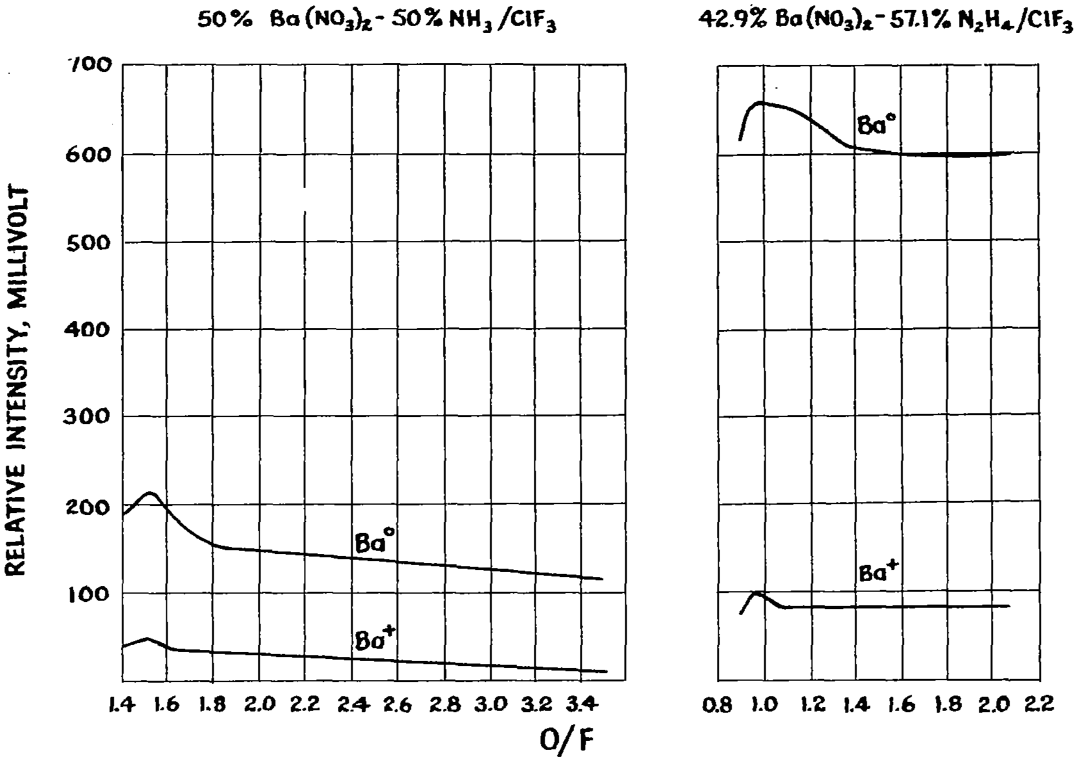

FIGURE 6

RELATIVE INTENSITY VS O/F USING ClF_3 AS OXIDIZER

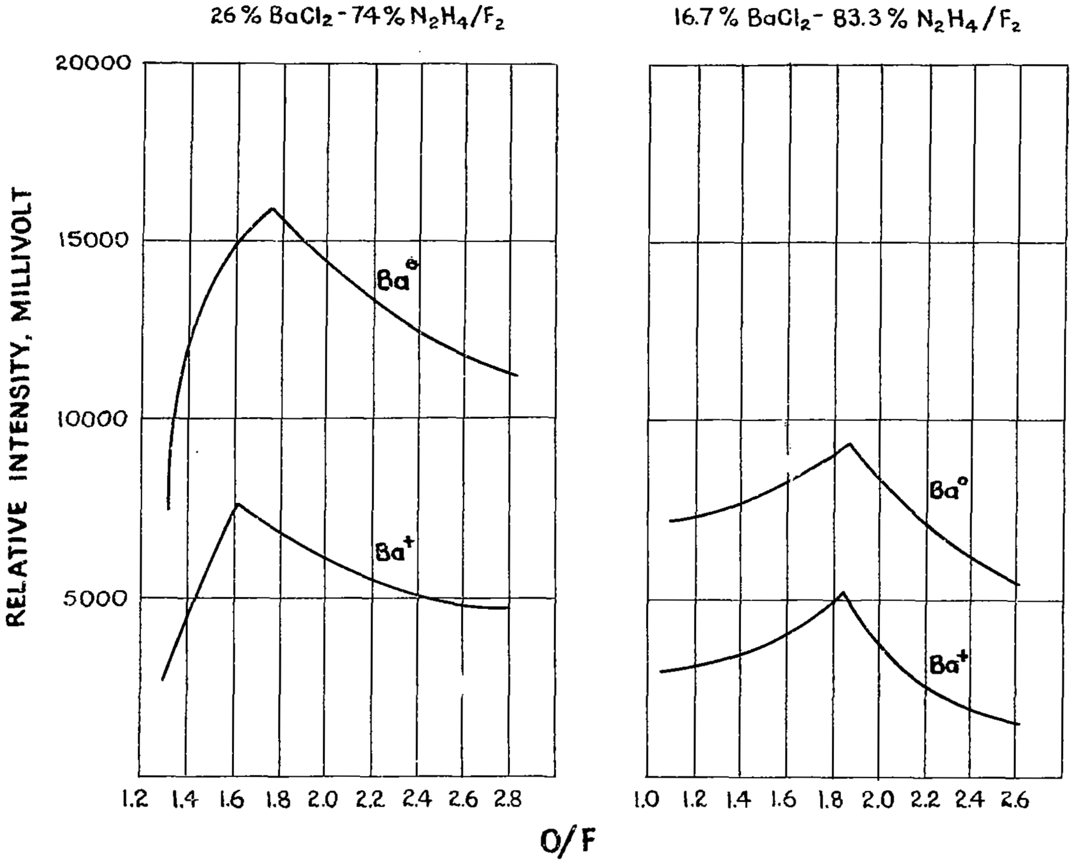

FIGURE 7a

RELATIVE INTENSITY VS O/F USING F_2 AS OXIDIZER

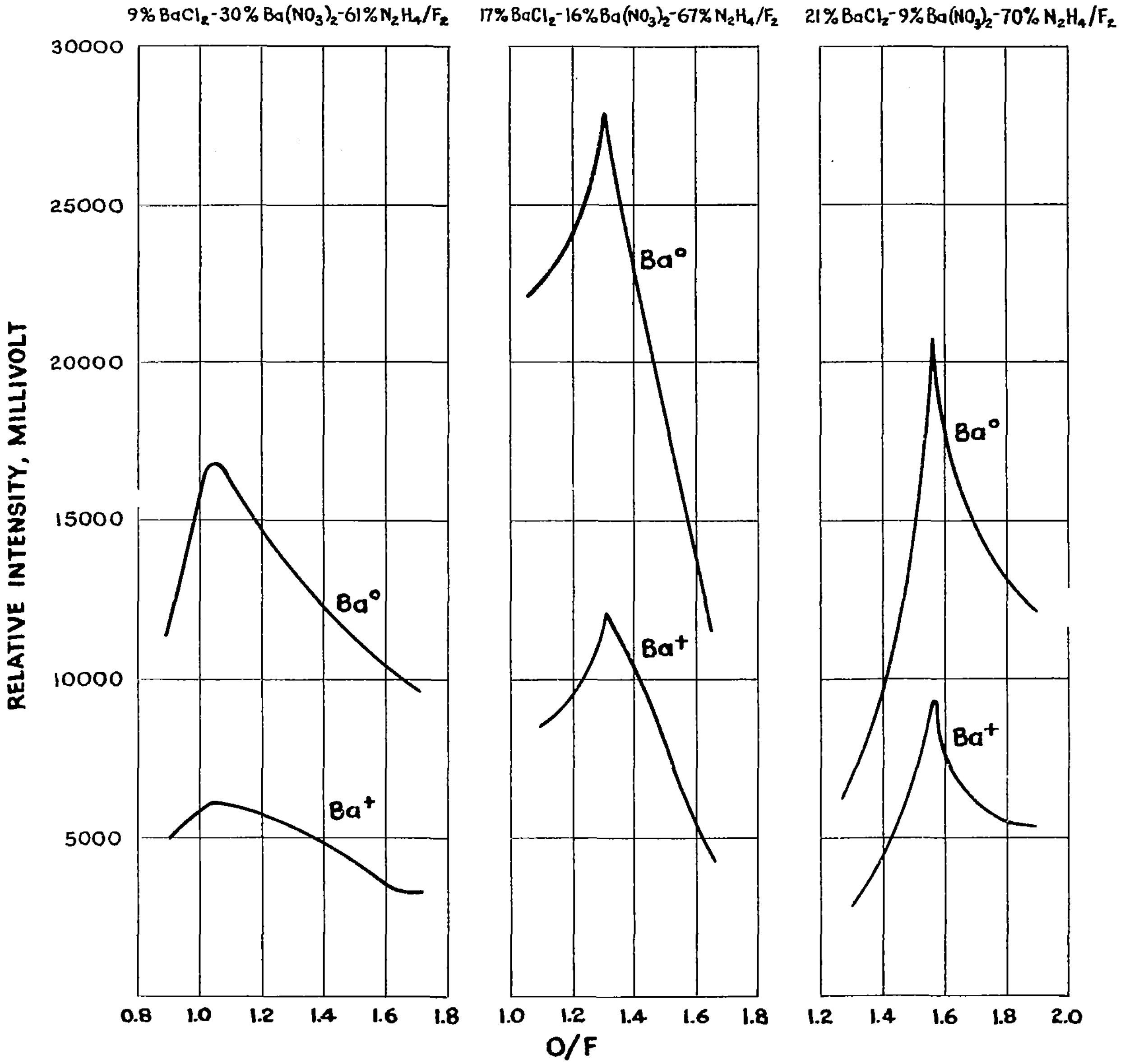

FIGURE 7b

RELATIVE INTENSITY VS O/F USING F_2 AS OXIDIZER

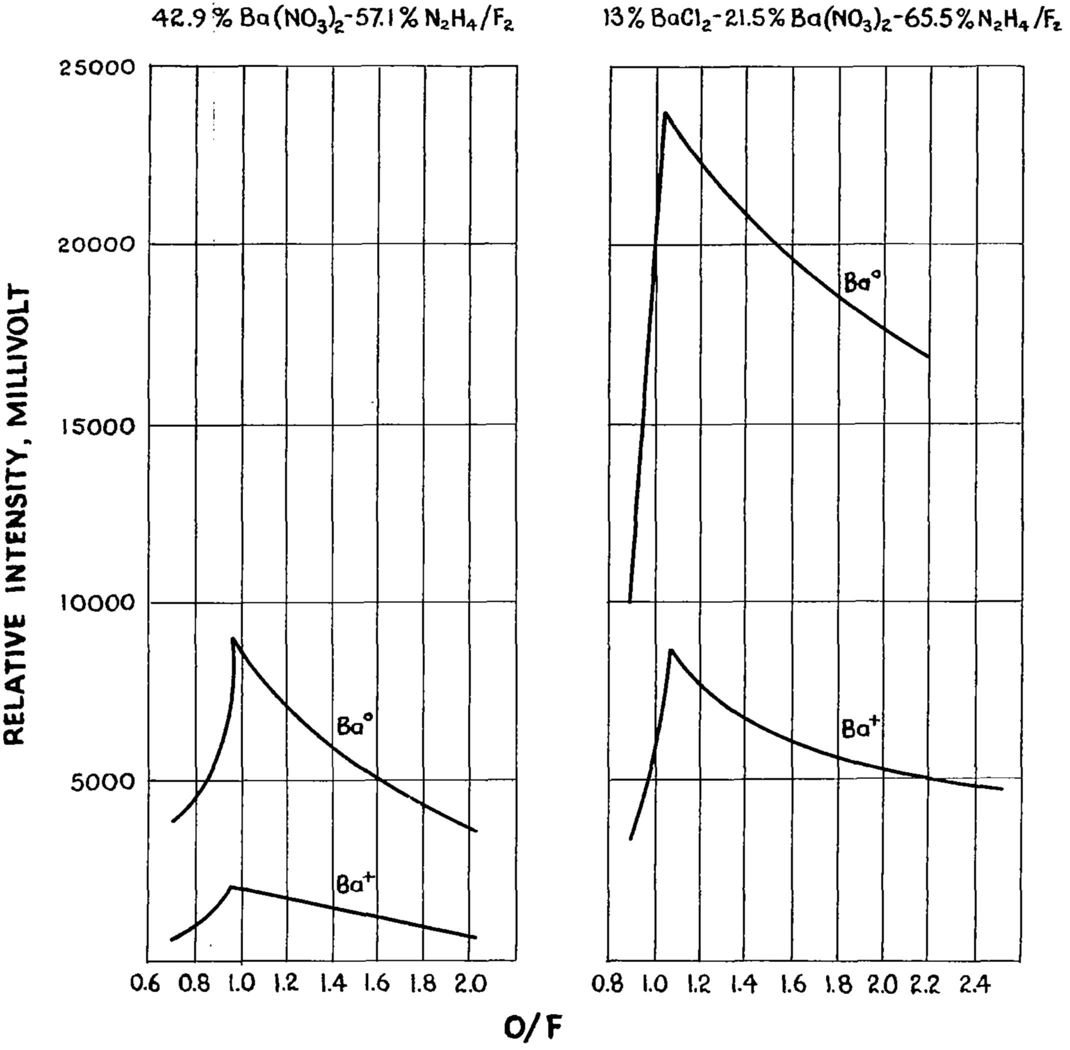

FIGURE 7c

RELATIVE INTENSITY VS O/F USING F_2 AS OXIDIZER

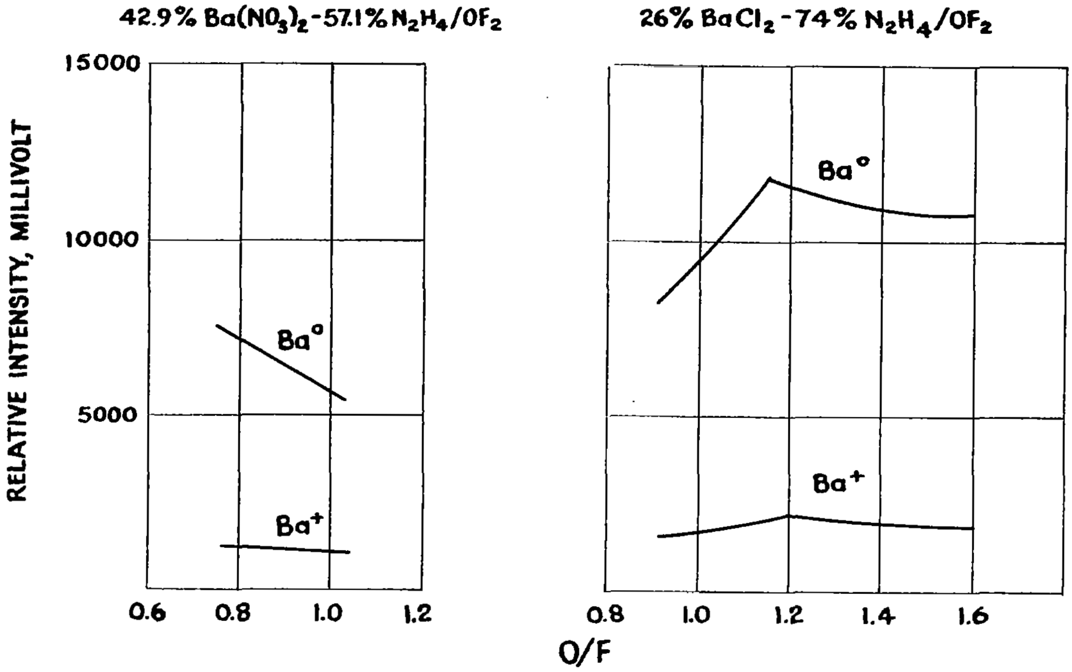

FIGURE 8
RELATIVE INTENSITY VS O/F USING OF_2 AS OXIDIZER

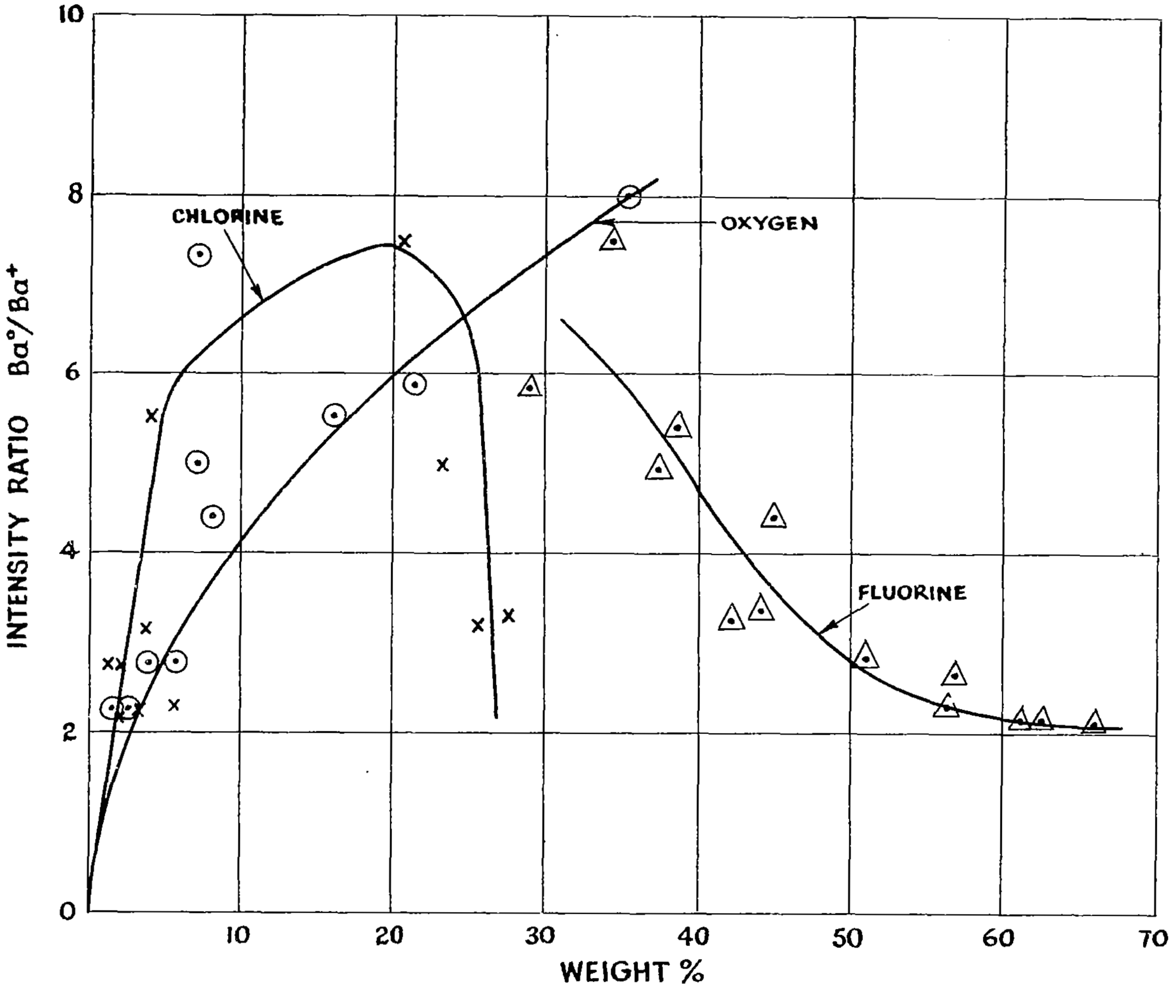

FIGURE 9

OPTIMUM Ba°/Ba⁺ INTENSITY RATIO VS WEIGHT % OXYGEN, CHLORINE & FLUORINE

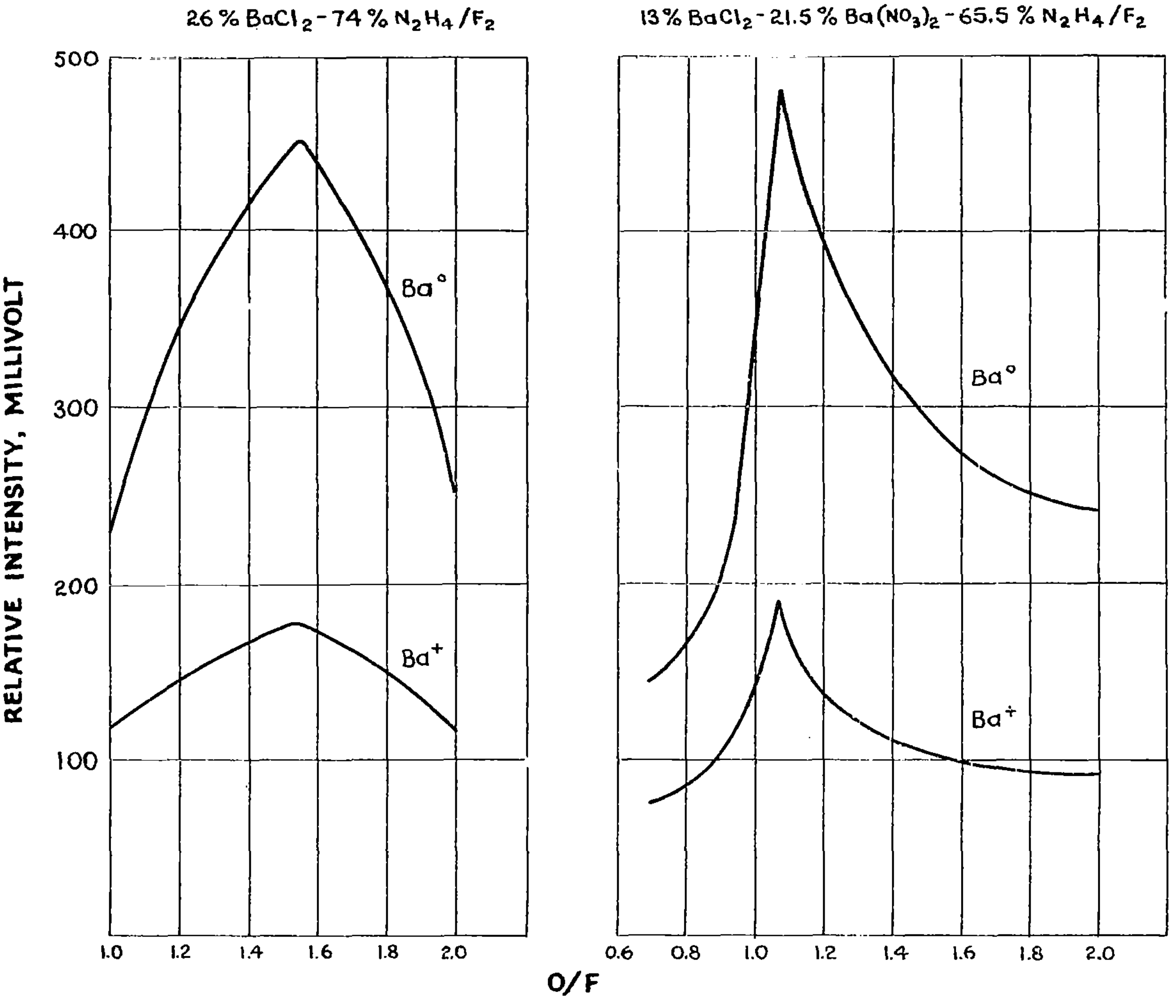

FIGURE 10

RELATIVE INTENSITY VS O/F FOR VACUUM TESTS