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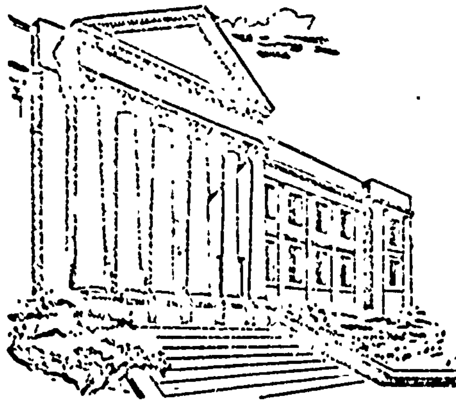

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Interim Report

I-A2132-2

RELATIONSHIP BETWEEN PROPELLANT COMPOSITION AND FLASH AND SMOKE PRODUCED BY COMBUSTION PRODUCTS

by

S.P. Carfagno
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July 14, 1958 to March 13, 1959

Prepared for

Ammunition Branch
Research and Development Division
Office, Chief of Ordnance, U.S. Army
Contract DA-36-034-501-ORD-78RD
Project TAI-3603

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ERRATA

In Final Report F-A1828, covering the period March 28, 1955 to January 10, 1958, in the fourth line from the bottom of page 6, the correct ratio is the square root of the quantity that was given; it should be:

$$[(D'/D)^2 (P'_s/P_s)]^{1/2}$$

In the Bimonthly Progress Report P-A2132-5, October 31, 1958, in the last paragraph of page 2 and in the caption for Figure 2, the numbers 30 and 70 should be interchanged.

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ABSTRACT

Part I of this report discusses progress on studies of gun muzzle flash, and Part II presents the results of work on gun smoke.

A shock tube has been used to measure the ignition limits of mixtures of air and muzzle gas (simulated by mixing gases in the proportions of calculated propellant combustion products). Limits have been obtained for mixtures of air and M17 muzzle gas at pressures between one and six atmospheres, and for mixtures of air and M2 muzzle gas at one atmosphere. Limits at one atmosphere pressure had previously been obtained for mixtures of M10 muzzle gas and air. For most compositions there is little variation of ignition limit with pressure; but for some mixtures the ignition limits increase with pressure up to 4 and 5 atmospheres pressure, then decrease with further increase in pressure. Although it is difficult to correlate the shape of the ignition boundaries with muzzle gas composition, some possible correlations are indicated.

An approximate analysis has been made of the gas dynamics outside a gun muzzle, and formulas for the temperature of the muzzle gas-air mixtures there have been derived for three cases. One case assumes that no shock waves are present; another, that the muzzle gas alone crosses a shock wave; and a third case assumes that muzzle gas and air mix and then cross a shock wave. The formulas give the temperature of the mixtures as a function of r, the mass fraction of air mixed with the muzzle gas, with the values of the coefficients being determined by gun and propellant parameters.

The above formulas enable one to estimate the temperatures that will exist outside a gun; and the ignition boundaries obtained with the shock tube determine the minimum temperatures required for ignition. Hence, the muzzle gases can be expected to ignite and cause flash under those conditions for which the calculated temperatures exceed the ignition boundary temperatures. A comparison of the ignition boundaries with the calculated temperatures for the 37mm Vigilante has been made to indicate the application of the above theory.

Studies of gun smoke have involved firing tests in which smoke density was measured with a photometer and samples of gun smoke were collected with an air sampler. A partial chemical analysis was made of the gun smoke samples. Tests have been conducted with EX5013-2 propellant, unsalted, and with up to 4% of potassium sulfate added to the charge. Five special propellants have also been tested. To some extent it has been possible to correlate results of the firing tests and chemical analyses with the propellant compositions.

Chemical analysis procedures that have been developed during the course of this work are presented in detail in the Appendix.

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INTRODUCTION

Part I of this report covers investigations of gun muzzle flash carried out at The Franklin Institute Laboratories during the eight-month period ending March 13, 1959. Muzzle flash has been a subject of continuing study at the Laboratories, and Reference (1)* provides a convenient referenced summary of earlier work.

When muzzle gases flow out of a gun, a shock wave forms normal to the direction of flow at a considerable distance from the muzzle. On passing through this shock front, the gases are compressed and heated to a temperature sufficiently high to cause luminosity in a small region beyond the front, giving rise to what is termed "intermediate" flash. The heated muzzle gases mix with the surrounding air forming a combustible mixture which may ignite and burn with a large flame called "secondary" flash. Muzzle flash is objectionable both because it reveals the location of the weapon and because its blinding brightness lowers the gunner's efficiency. Of the two types, secondary flash is by far the more objectionable because of its much greater volume and luminosity than the intermediate type.

Considerable effort has been expended in attempting to eliminate gun flash, and a certain degree of success has been achieved by both mechanical and chemical means. Mechanical techniques involve attaching to the muzzle devices such as cones and sets of bars designed to so alter the gas flow that the pressures and temperatures required for ignition do not occur. This is accomplished primarily by preventing formation of the normal shock. A suitable attachment is capable of eliminating both intermediate and secondary flash, but development of a device which is satisfactory from all standpoints is problematic. Although some progress has been made in analyzing the gas dynamics in-

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*References are indicated by underscored numerals in parentheses, and are listed at end of report.

volved, the problem is a complex one, and much remains to be learned. The highly transient nature of events at a gun muzzle makes it almost impossible to design a single device which will be completely satisfactory over the entire range of conditions; and in addition designs invariably involve compromises imposed by considerations of mechanical feasibility.

Chemical suppression of flash usually involves the addition of small amounts of potassium sulfate to the propellant charge. Various studies have indicated that this method functions by providing a chain-breaking mechanism in the scheme of reactions normally resulting in ignition of the muzzle gas. Chemical suppression is capable of eliminating secondary flash, but it does not prevent intermediate flash, which is not a combustion phenomenon. Compared with the use of mechanical devices chemical suppression has the advantage of ease of application. It usually results in the production of large quantities of smoke, however, which in some cases is considered more objectionable than the flash itself. There is also the possibility of eliminating flash by altering the basic composition of the propellant. If the internal ballistics can be so modified that the muzzle gases contain a smaller fraction of combustibles and emerge at lower temperature they will be less likely to ignite; and possibly, ignition may be prevented altogether.

In its long range study of these problems, The Franklin Institute Laboratories have been concerned with both mechanical and chemical suppression of flash(1), and more recently with the smoke problem also. Much of the work has involved empirical study of bar suppressors, chemical additives, and propellant design. Following the early work, however, it became increasingly evident that an understanding and solution of the flash problem can best be achieved through basic approaches; and we have concentrated, therefore, on the study of fundamental aspects of the problem. Thus a program of diffusion flame studies contributed toward an understanding of the mechanism of flash and its suppression by chemical additives(1) (Subsection 3.2). Theoretical studies have been concerned with the relation of ballistic efficiency to flash, with the mechanism by which air is entrained by muzzle gas and the physical consequences thereof, and with the requirements for mechanical suppressors. In each of these categories corroborative experimental work has been carried out.

During the past year our work on the flash problem has involved primarily the experimental acquisition of data on the ignition temperature of mixtures of muzzle gas and air, under various conditions of pressure and composition, and the interpretation of these data in terms of the prevention of gun muzzle flash. Our work on the smoke problem has involved the collection of data on smoke density and composition using various propellant compositions. The work on flash and smoke is presented in Parts I and II, respectively, of this report.

PART I

GUN MUZZLE FLASH STUDIES

When a gun is fired, the products of propellant combustion emerge from the muzzle and mix with the surrounding air. The composition of individual elements of gas outside the gun will range from 100% muzzle gas to 100% air, and their pressure and temperature will be governed by the internal ballistics and the external gas dynamics. If the combination of composition, pressure, temperature and their duration for one of the elements of gas satisfy the requirements for ignition we can expect a flame to be initiated. If conditions are suitable for this flame to be propagated throughout the remainder of the gas, there results the phenomenon of gun flash. There are thus two categories of information involved in a knowledge of muzzle flash: one concerns the actual physical state of the gases outside the gun, and the other concerns the requirements for ignition. Whenever these two sets of conditions overlap, we can expect the inception of flash.

In work preceding the present contract we progressed along both the above avenues of inquiry. The state of the gases outside the gun was elucidated by experimental studies of the gas flow patterns and gas mixing, with and without muzzle attachments, and by theoretical approximations of the mechanism of mixing. We began to gather information on the requirements for ignition by measuring the ignition limits and ignition delays of mixtures of muzzle gas and air with a shock tube. During the period covered by this report we have extended our efforts along both these lines, and the results of this work are presented below.

1. SHOCK TUBE STUDIES

The ignition limits of mixtures of muzzle gas and air are being measured with a shock tube. The design, construction, and operation of this apparatus have been described in earlier reports(1,2,3). Muzzle gas is simulated by a mixture of gases corresponding to the calculated combustion products of the propellants of interest; we have procured mixtures of the dry components prepared to order in commercial gas cylinders. Water vapor, dry muzzle gas, and dry air are combined to the desired proportions in a glass flask from which they are transferred to the experimental (low pressure) section of the shock tube. A shock wave is generated by bursting a diaphragm which separates the experimental section from the driver (high pressure), helium filled section of the shock tube. The shock wave propagates through the experimental gas and, upon reflection from the end of the shock tube, propagates through it a second time. Both the incident and reflected shock waves cause sudden increases in the pressure and temperature of the experimental gas. Following passage of both shock waves, the gas will remain at rest and at approximately constant pressure and temperature for an interval which lasts from a fraction of a millisecond to several milliseconds, depending primarily on the strength of the shock wave. A measurement of the speed of the incident shock wave, together with a knowledge of the initial state of the experimental gas and the aid of the usual one-dimensional theory of the shock tube, serves to determine the pressure and temperature of the experimental gas during the interval mentioned above. Possible deviations of the actual conditions from the calculated conditions have been discussed in earlier reports(1) (Subsection 6.3). Suitable instrumentation is provided to record ignition, if it occurs, and the duration of the induction period which precedes it. By performing many experiments it is possible to determine the dependence of minimum ignition temperature on the pressure and composition of the muzzle gas-air mixtures.

Prior to the present contract, the shock tube was intended to produce data that could be correlated with the theory of an "ideal" mechanical suppressor, defined as a device which confines the muzzle gases until they have expanded to atmospheric pressure so that mixing with air occurs entirely at atmospheric pressure. Hence shock tube experiments were performed almost entirely at atmospheric pressure. It has become of interest, however, to consider the situation when no mechanical devices are attached to a gun, in which case higher pressures can occur. During the course of the current project, therefore, the apparatus was modified to permit experiments at pressures up to about ten atmospheres.

In Reference (2) there is a complete account of our shock tube studies with mixtures of M10 muzzle gas and air. In this report we present the new data obtained with M2 muzzle gas at atmospheric pressure and with M17 muzzle gas at pressures in the range from 1 to 5 atmospheres.

In Table 1 appear the calculated combustion products of M2 and M17 propellant together with the actual composition of gas mixtures used to simulate the dry muzzle gas. In Table 2 are given the compositions of those mixtures, of these muzzle gases with air, that have been studied with the shock tube. Note that the percentage of water vapor in these mixtures accounts not only for that present in the muzzle gas itself, but also for that present in typically humid air, arbitrarily represented by a relative humidity of 51% at 20.5°C. The mixtures are listed in terms of the volume fraction and the mass fraction of air present, represented by the letters f and r, respectively.

Figures 1a to 1e show the ignition boundaries for several mixtures of air with M17 muzzle gas over a pressure range of 1 to 6 atmospheres. There appears to be a gradual increase of ignition limit with pressure followed by a reversal at the highest pressures. The effect is most pronounced for the mixture containing 70% air: the ignition limit increases from 980°K at atmospheric pressure to 1080°K at 4 atmospheres, dropping to approximately 900°K at 6 atmospheres.

Figure 2 shows the ignition boundaries at atmospheric pressure as a function of the mass fraction of air mixed with the muzzle gases M2, M10 and M17.

Table 1

COMBUSTION PRODUCTS OF M2 AND M17 PROPELLANT

Product	% by Volume*	Dry Basis % by Volume	Actual % by Volume**
		M2	
CO_2	23.68	30.78	29.50
CO	28.92	37.59	41.35
H_2O	23.07	-	-
H_2	10.60	13.78	13.15
N_2	13.73	17.85	16.00
		M17	
CO_2	10.13	12.81	13.85
CO	21.75	27.51	30.00
H_2O	20.95	-	-
H_2	16.92	21.40	20.30
N_2	30.25	38.27	35.85

[*] Calculated on residual solvent-free basis and assuming water gas equilibrium at 1500°K using

$$K_p = \frac{(CO)(H_2O)}{(CO_2)(H_2)} = 2.658$$

[**] Composition of mixture procured in commercial gas cylinders as determined by average of mass spectrograph analysis of two samples of each mixture.

Table 2

COMPOSITION OF MIXTURES OF MUZZLE GAS AND AIR

f*	r**	% by Volume CO_2	CO	H_2	O_2	H_2O	N_2	Rare Gases
				M2				
0	0	23.68	28.92	10.60	-	23.07	13.73	-
0.1	0.106	20.43	28.62	9.09	2.08	20.89	18.84	0.10
0.3	0.314	15.89	22.26	7.07	6.24	16.52	31.92	0.30
0.5	0.516	11.35	15.90	5.05	10.40	12.16	45.00	0.50
0.7	0.715	6.81	9.54	3.03	14.56	7.80	58.08	0.70
0.9	0.905	2.27	3.18	1.01	18.72	3.43	71.16	0.90
1.0	1.000	-	-	-	20.8	1.20	77.1	1.00
				M17				
0	0	10.13	21.75	16.92	-	20.95	30.25	-
0.1	0.119	9.81	21.33	14.40	2.08	18.97	33.27	0.10
0.3	0.343	7.63	16.59	11.20	6.24	15.01	43.01	0.30
0.5	0.549	5.45	11.85	8.00	10.40	11.05	52.75	0.50
0.7	0.740	3.27	7.11	4.80	14.56	7.09	62.49	0.70
0.8	0.829	2.18	4.74	3.20	16.64	5.11	67.36	0.80
0.9	0.916	1.09	2.37	1.60	18.72	3.13	72.23	0.90
1.0	1.000	-	-	-	20.8	1.20	77.1	1.00

* f = volume fraction of air in mixture
** r = mass fraction of air in mixture

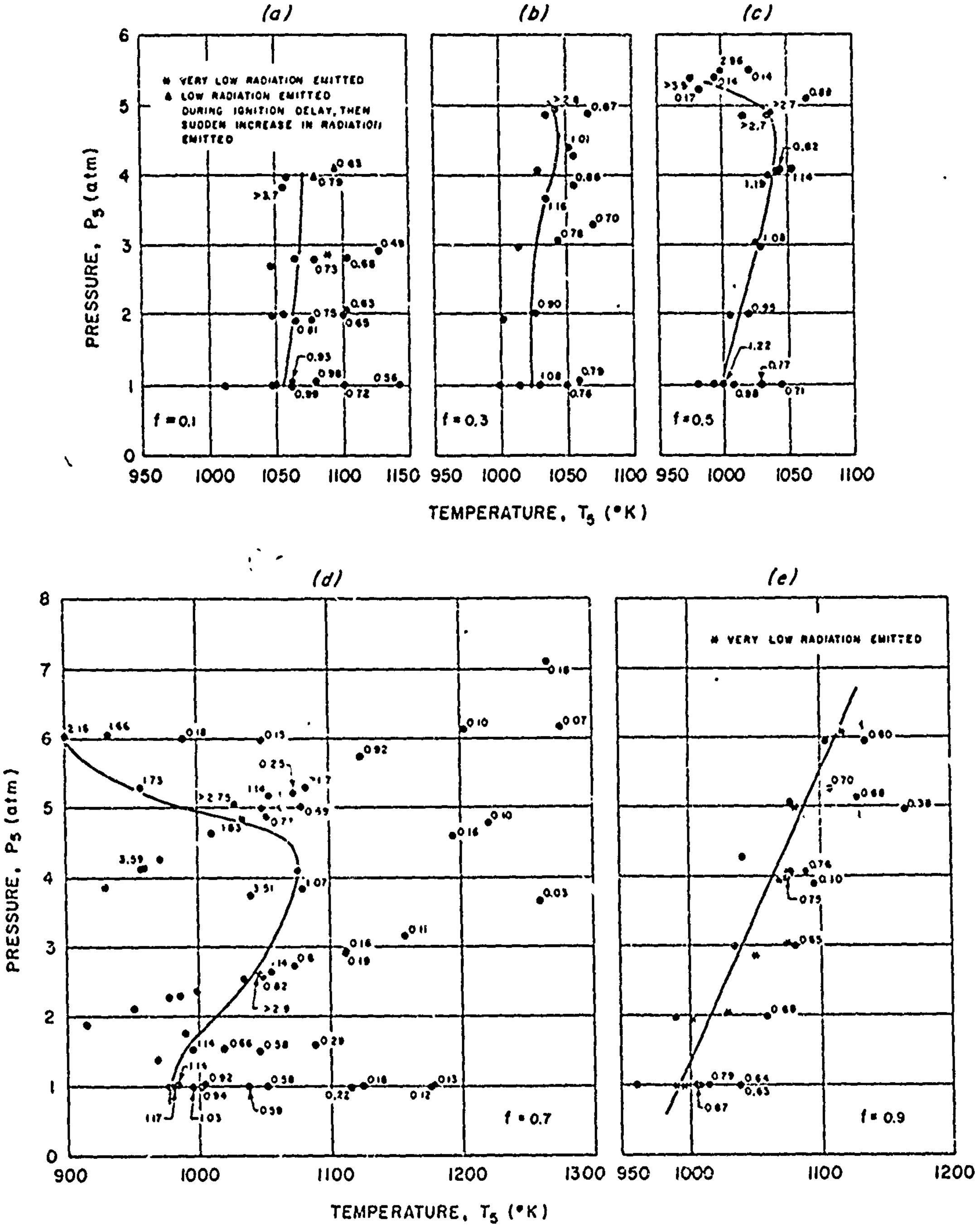


FIGURE 1 IGNITION BOUNDARIES FOR MIXTURES OF M17 MUZZLE GAS AND AIR

Numerals denote ignition delays in milliseconds. Points without numerals represent infinite delay times (no ignition)
f = volume fraction of air in mixture

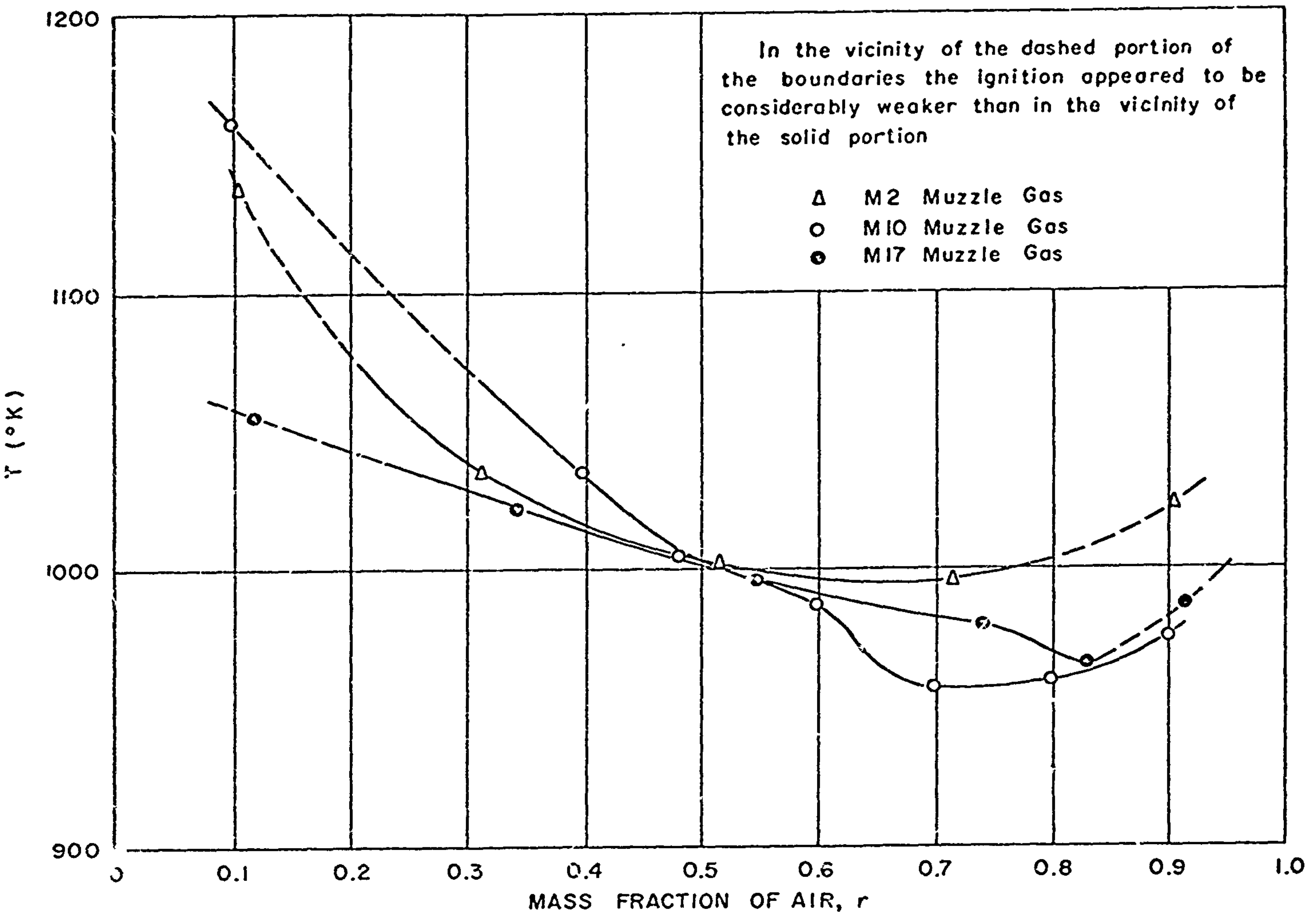


FIGURE 2. IGNITION BOUNDARIES AT ATMOSPHERIC PRESSURE FOR MIXTURES OF MUZZLE GAS AND AIR

For mixtures as complicated as our mixtures of muzzle gas and air it is very difficult to interpret the shape of the ignition boundary in terms of the gas composition. An examination of the boundaries, however, reveals a few crude correlations. The minimum ignition temperatures at atmospheric pressure have been obtained from Figure 2, and these minima have been listed in Table 3 together with the values of f, mole fraction of air, corresponding to them. We have listed in the adjacent column the values of f which result in a stoichiometric mixture, i.e., which yield a ratio of combustibles, $(CO) + (H_2)$, to oxygen of 2. A comparison of these two sets of f, one referring to the minima of the ignition boundaries and the other to stoichiometric mixtures, show a crude correlation between them. Another possible correlation concerns the concentration of water vapor, which decreases as the mole fraction of air increases, and the asymmetry of the ignition boundaries with respect to a vertical axis through the point of stoichiometry. The curves seem to be stretched toward higher temperatures where the mixtures are lean and the water concentration high and, stretched toward lower temperatures where the mixtures are rich and the water concentration low. This effect may be correlated with an inhibiting effect of water-vapor on ignition(4).

Table 3

COMPARISON OF IGNITION AND COMPOSITION DATA
FOR MIXTURES OF MUZZLE GAS AND AIR

Muzzle Gas	Minimum Ignition Temp. at Atmospheric Pressure (°K)	f* at Minimum Ignition Temp.	f where $\frac{(CO)+(H_2)}{(O_2)} = 2$
M2	995	0.64	0.50
M10	957	0.68	0.49
M17	966	0.80	0.55

* f = volume fraction of air in mixture

2. THEORETICAL INVESTIGATION OF THE MIXING OF AIR AND MUZZLE GAS

2.1 Derivation of Temperature for Three Mixing Conditions

I,II,III,etc.	Steady flow streams involved in mixing process.
1,2,3,etc.	Subscripts referring to streams I,II,III,etc., respectively.
A_1, A_2, A_3	Cross-sectional area of gas streams.
a^*	Critical sound speed.
C	Mass of powder charge.
C_p	Specific heat per unit mass, at constant pressure.
C_v	Specific heat per unit mass, at constant volume.
G	Volume of gun.
k	$= \left[S^{\frac{1}{\gamma}} \frac{(\gamma-1)S+(\gamma+1)}{(\gamma+1)S+(\gamma-1)}\right]$
M	Mach number.
n	Number of moles per unit mass of muzzle gas.
P	Pressure.
P_a	Atmospheric pressure.
P_s	Stagnation pressure.
R	Universal gas constant.
r	Mass-fraction of entrained air.
S	Pressure ratio across a shock wave.
T	Absolute temperature.
T_a	Temperature after isentropic expansion to atmospheric pressure.
T_s	Stagnation temperature.
T_v	Flame temperature of gun powder in constant volume.
U	Muzzle velocity of projectile.
u	Velocity of gas.
W	Mass of projectile.
β	Angle which oblique shock makes with direction of flow.
γ	$= C_p/C_v$.
ψ	$= nRT_v/\gamma-1 = C_vT_v$.
ρ	Density.

In order to determine whether muzzle gas-air mixtures, having the ignition properties obtained from shock tube measurements, will or will not ignite to produce muzzle flash it is necessary to estimate the actual pressure-temperature states that will be taken on by these mixtures outside the gun. If a comparison shows that there exists at least a partial overlap of those conditions which can be expected outside a gun and those conditions which are necessary for ignition, then it is likely that flash will occur. The following mathematical development is an extension of our earlier attempts to analyze the gas dynamics outside a gun and to arrive at estimates of the pressure-temperature history of the muzzle gas-air mixtures(5).

Let us consider the constant pressure mixing process indicated in Figure 3a. Streams I and II enter a mixing region from which a single stream III, emerges. The flow is one-dimensional in the same direction for all three streams, and the pressure is everywhere the same. If we let the subscripts 1, 2, and 3 refer to streams I, II, and III, respectively, we can write the following conservation equations for this system.

Conservation of mass:

$$\rho_1 A_1 u_1 + \rho_2 A_2 u_2 = \rho_3 A_3 u_3 \qquad (1)$$

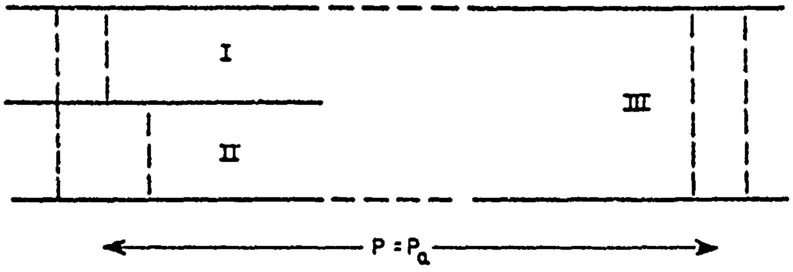
Conservation of momentum:

$$\rho_1 A_1 u_1^2 + \rho_2 A_2 u_2^2 = \rho_3 A_3 u_3^2 \qquad (2)$$

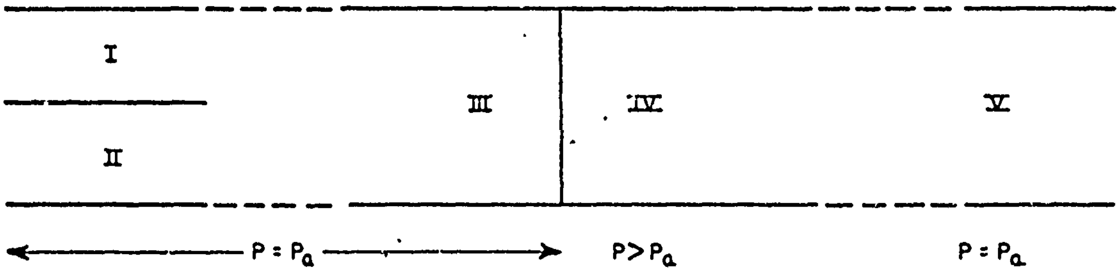
Conservation of energy:

$$\rho_1 A_1 u_1 C_{p1}\left(T_1 + \frac{u_1^2}{2C_{p1}}\right) + \rho_2 A_2 u_2 C_{p2}\left(T_2 + \frac{u_2^2}{2C_{p2}}\right) = \rho_3 A_3 u_3 C_{p3}\left(T_3 + \frac{u_3^2}{2C_{p3}}\right) \qquad (3)$$

(a) CASE A



(b) CASE B



(c) CASE C

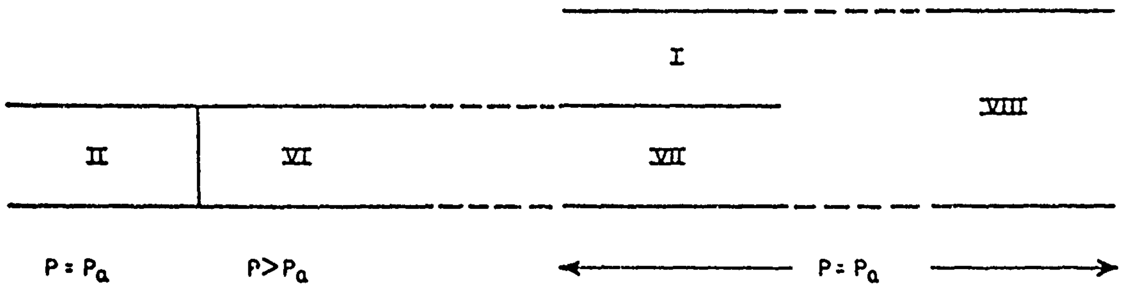


FIGURE 3. SCHEMATIC REPRESENTATION OF MIXING PROCESSES

The basis of these equations becomes more apparent if we imagine piston faces located at the left-hand dotted line of each stream in Figure 3a, moving with the speed of the stream to the position of the right-hand dotted line in unit time. It then becomes obvious, for example, that $\rho_i A_i u_i$ is the mass that in unit time passes through any cross-section of stream i.

Let us define r as the mass fraction of gas 1, in mixture 3, and write it as:

$$r = \frac{\rho_1 u_1 A_1}{\rho_3 u_3 A_3} \tag{4}$$

From Equation (1) we see that

$$1-r = \frac{\rho_2 u_2 A_2}{\rho_3 u_3 A_3} \tag{5}$$

We can now combine Equations (3), (4), and (5) to obtain the following:

$$C_{p3}\left(T_3 + \frac{u_3^2}{2C_{p3}}\right) = rC_{p1}\left(T_1 + \frac{u_1^2}{2C_{p1}}\right) + (1-r)C_{p2}\left(T_2 + \frac{u_2^2}{2C_{p2}}\right) \tag{6}$$

The quantity

$$T_s = T + \frac{u^2}{2C_p}$$

is known as the stagnation temperature. Thus, Equation (6) states that the stagnation temperature of stream III is the calorimetric average of the stagnation temperatures of streams I and II.

$$T_{s3} = r\,\frac{C_{p1}}{C_{p3}}\,T_{s1} + (1-r)\,\frac{C_{p2}}{C_{p3}}\,T_{s2} \tag{6'}$$

We can eliminate u_3 from Equation (6) by noting from Equations (2), (4), and (5), that

$$u_3 = ru_1 + (1-r)\, u_2 \tag{7}$$

Substituting this into Equation (6) and replacing the parentheses in the first and second terms on the right with T_{s1} and T_{s2}, respectively, we arrive at the following expression for the temperature in stream III:

$$T_3 = r\,\frac{C_{p1}}{C_{p3}}\,T_{s1} + (1-r)\,\frac{C_{p2}}{C_{p3}}\,T_{s2} - \frac{[ru_1 + (1-r)u_2]^2}{2C_{p3}} \tag{8}$$

When stream I is at rest we have $u_1 = 0$ and $T_{s1} = T_1$, and the following simplification results:

$$T_3 = r\,\frac{C_{p1}}{C_{p3}}\,T_1 + (1-r)\,\frac{C_{p2}}{C_{p3}}\,T_{s2} - \frac{(1-r)^2 u_2^2}{2C_{p3}} \tag{9}$$

Anticipating a later requirement let us make the following rearrangement:

$$T_3 = r\,\frac{C_{p1}}{C_{p3}}\,T_1 + r(1-r)\,\frac{C_{p2}}{C_{p3}}\,T_{s2} + (1-r)^2\,\frac{C_{p2}}{C_{p3}}\,T_{s2}\,\left(1 - \frac{u_2^2}{2C_{p2}T_{s2}}\right) \tag{10}$$

We will refer to this equation in the discussion of case C, below.

Case A

This is the case which was treated in Part I of Reference (5). It assumes that an "ideal" mechanical suppressor, attached to the gun muzzle, confines the muzzle gases until they have expanded isentropically to atmospheric pressure. The cooled and accelerated muzzle gases emerge from the suppressor in a supersonic jet which mixes with air in the boundary layer between jet and air. Since the air and jet are both at atmospheric pressure, no shock waves are formed and mixing occurs entirely at atmospheric pressure. As the muzzle gas entrains air it is decelerated and part of its kinetic energy is converted to heat; as a result, the temperature of the mixture goes through a maximum as a function of the amount of air entrained. The temperatures attained, however, are lower than those that would be caused by shock waves.

In this case, stream I refers to air and stream II to the muzzle gas. In Reference (5) the equations of interior ballistics together with the relations for isentropic expansion were used to transform T_{s2} and u_2 in Equation (9) in terms of propellant and gun parameters. The details are omitted here, and we quote only the final result:

$$T_3 = \frac{rC_{p1}T_1 + r(1-r)\gamma_2\left[\psi - \frac{U^2}{2}\left(\frac{W}{C} + \frac{1}{3} - \frac{1}{\gamma_2}\right)\right] + (1-r)^2\gamma_2\left[\psi - \frac{U^2}{2}\left(\frac{W}{C} + \frac{1}{3}\right)\right]^{\frac{1}{\gamma_2}}\left[\frac{P_aG}{(\gamma_2-1)C}\right]^{\frac{\gamma_2-1}{\gamma_2}}}{rC_{p1} + (1-r)\,C_{p2}} \tag{11}$$

Case B

This case is an approximation of the mixing conditions which hold when no mechanical devices are attached to the gun. The gas dynamics are illustrated in Figure 3b. Streams I and II mix at atmospheric pressure to produce stream III, just as in Case A. In the present case, however, the gas mixture is suddenly compressed and heated by passage through a shock wave, and this is followed with an isentropic expansion of the mixture to atmospheric pressure. We shall neglect the variation of specific heat with temperature and say that $C_{p3} = C_{p4} = C_{p5}$.

From the definition of stagnation temperature we can write the following expressions for temperature in regions III and V:

$$T_3 = T_{s3}\left(1 - \frac{u_3^2}{2C_{p3}T_{s3}}\right) \tag{12}$$

$$T_5 = T_{s5}\left(1 - \frac{u_5^2}{2C_{p3}T_{s5}}\right) = T_{s3}\left(1 - \frac{u_5^2}{2C_{p3}T_{s3}}\right) \tag{13}$$

In the preceding equation we have recognized the fact that the stagnation temperature is a constant of the flow when no mixing is involved. We shall now seek a relation between T_3 and T_5. The pressure ratio across an oblique shock is given by (see p. 86 of Ref. 6):

$$\frac{P_4}{P_3} = \frac{2\gamma_3}{\gamma_3+1}(M_3 \sin\beta)^2 - \frac{\gamma_3-1}{\gamma_3+1} \tag{14}$$

and the ratio of stagnation pressures is given by (see p. 61 of Ref. 6):

$$\frac{P_{s3}}{P_{s4}} = \left[1+\frac{2\gamma_3}{\gamma_3+1}(M_3^2 \sin^2\beta - 1)\right]^{\frac{1}{\gamma_3-1}} \left[\frac{(\gamma_3-1)M_3^2 \sin^2\beta + 2}{(\gamma_3+1)M_3^2 \sin^2\beta}\right]^{\frac{\gamma_3}{\gamma_3-1}} \tag{15}$$

Using Equation (14) to eliminate $M_3 \sin\beta$ from Equation (15), we obtain:

$$\frac{P_{s3}}{P_{s4}} = S^{\frac{1}{\gamma_3-1}} \left[\frac{(\gamma_3-1)S + (\gamma_3+1)}{(\gamma_3+1)S + (\gamma_3-1)}\right]^{\frac{\gamma_3}{\gamma_3-1}} \tag{16}$$

where $S = P_4/P_3$. We wish next to relate this ratio of stagnation pressures to the velocities in regions III and V. To do this we first write the following relations(7):

$$\frac{P_3}{P_{s3}} = \left[1 - \frac{\gamma_3-1}{\gamma_3+1}\left(\frac{u_3}{a^*}\right)^2\right]^{\frac{\gamma_3}{\gamma_3-1}} \tag{17}$$

$$\frac{P_5}{P_{s5}} = \left[1 - \frac{\gamma_3-1}{\gamma_3+1}\left(\frac{u_5}{a^*}\right)^2\right]^{\frac{\gamma_3}{\gamma_3-1}} \tag{18}$$

The parameter a* is the critical sound speed and is related to the stagnation temperature as follows:

$$a^{*2} = 2C_pT_s\frac{(\gamma-1)}{(\gamma+1)} \tag{19}$$

Combining Equations (17), (18), and (19), we arrive at the following relation.

$$\left(\frac{P_{s3}}{P_{s5}}\right)^{\frac{\gamma_3-1}{\gamma_3}}\left(1-\frac{u_3^2}{2C_{p3}T_{s3}}\right)=\left(1-\frac{u_5^2}{2C_{p3}T_{s3}}\right) \tag{20}$$

where we have made use of the facts that $P_3 = P_4$ P_5 ? under the conditions of Case B and that the stagnation temperature is a constant of the flow, i.e., $T_{s3} = T_{s5}$. Finally, noting that the stagnation pressure is the same in regions IV and V ($P_{s4} = P_{s5}$) and comparing Equations (16) and (20) we see that:

$$\left(1-\frac{u_5^2}{2C_{p3}T_{s3}}\right)=\left(1-\frac{u_3^2}{2C_{p3}T_{s3}}\right)\left[S^{\frac{1}{\gamma_3}}\frac{(\gamma_3-1)S+(\gamma_3+1)}{(\gamma_3+1)S+(\gamma_3-1)}\right] \tag{21}$$

This last equation may be regarded as a relation between the velocities in regions of the same pressure before and after a shock wave. We shall have occasion to use this result again in the development of Case C.

To complete our development it is now sufficient to combine Equations (12), (13), and (21), yielding:

$$T_5 = k_{\gamma_3} T_3 \tag{22}$$

where

$$k_{\gamma_3} = \left[S^{\frac{1}{\gamma_3}}\frac{(\gamma_3-1)S+(\gamma_3+1)}{(\gamma_3+1)S+(\gamma_3-1)}\right] \tag{23}$$

and the subscript γ_3 indicates which γ is to be used in evaluating k. This shows that in Case B, the temperature T_5 for any mixing ratio r is obtained from the corresponding temperature of Case A, T_3, by multiplication with the factor k, whose value is determined mostly by the pressure ratio across the shock wave, $S = P_4/P_3$. This pressure ratio has minimum value of unity for vanishing shock strength and a maximum value for a normal shock with $\sin\beta = 1$ in Equation (14). In this case the Mach number satisfies the following relation(8):

$$M_3^2 = \frac{2}{\gamma_3 - 1}\left(\frac{T_{s3}}{T_3} - 1\right)$$

and we find

$$S_{3max} = \frac{4\gamma_3 \frac{T_{s3}}{T_3} - (\gamma_3 + 1)^2}{\gamma_3^2 - 1}$$

This is readily calculated by using Equations (6)' and (11) to obtain the ratio T_{s3}/T_3. In Equation (6)', T_{s2}, the stagnation temperature of the muzzle gases, is given by (5, Part I):

$$T_{s2} = T_{v2}\left[1 - \frac{U^2}{2\psi}\left(\frac{W}{C} + \frac{1}{3} - \frac{1}{\gamma_2}\right)\right]$$

Case C

This is another approximation of the situation which holds when no mechanical devices are attached to the gun. In this case it is assumed that only the muzzle gas crosses the shock wave and that mixing with air occurs afterwards. The individual steps in the process are illustrated in Figure 3c. Stream II represents the muzzle gas after it has expanded to atmospheric pressure, exactly as in Cases A and B. Stream II crosses a shock wave being thereby heated and compressed (State VI); it then expands isentropically to atmospheric pressure (State VII). Finally streams I and VII, both at atmospheric pressure, mix to form stream VIII, also at atmospheric pressure. We note that this process combines steps that have already been treated in Cases A and B: the series of steps II → VI → VII corresponds to the series III → IV → V in Case B, and the mixing of streams I and VII is like the mixing of stream I and II in Case A. Hence we need only avail ourselves of relations that have been derived above in order to derive an expression for the temperature in stream VIII.

We can make Equation (21) apply to regions II and VII by making the following change in subscripts: 3 → 2, 4 → 6, 5 → 7. We obtain

$$\left(1-\frac{u_7^2}{2C_{p2}T_{s2}}\right)=\left(1-\frac{u_2^2}{2C_{p2}T_{s2}}\right)\left[S^{\frac{1}{\gamma_2}}\frac{(\gamma_2-1)S+(\gamma_2+1)}{(\gamma_2+1)S+(\gamma_2-1)}\right] \qquad (24)$$

where $S = P_6/P_2$. Equation (9), which applies to regions I, II, and III of Case A, can apply to regions I, VII, and VIII, respectively, of the present case. By appropriate change of subscripts, we get:

$$T_8 = r\frac{C_{p1}}{C_{p8}}T_1 + (1-r)\frac{C_{p7}}{C_{p8}}T_{s7} - \frac{(1-r)^2u_7^2}{2C_{p8}} \qquad (25)$$

Since we have neglected the variation of specific heat with temperature, C_{p7} is the same as C_{p2}; and C_{p8}, the specific heat of the mixture, is the same as C_{p3}. Noting this and also that $T_{s7} = T_{s2}$, we can make the following rearrangement:

$$T_8 = r\frac{C_{p1}}{C_{p3}}T_1 + r(1-r)\frac{C_{p2}}{C_{p3}}T_{s2} + (1-r)^2\frac{C_{p2}}{C_{p3}}T_{s2}\left(1-\frac{u_7^2}{2C_{p2}T_{s2}}\right) \qquad (26)$$

Using Equation (24) to eliminate u_7, yields:

$$T_8 = r\frac{C_{p1}}{C_{p3}}T_1 + r(1-r)\frac{C_{p2}}{C_{p3}}T_{s2} + (1-r)^2\frac{C_{p2}}{C_{p3}}T_{s2}\left(1-\frac{u_2^2}{2C_{p2}T_{s2}}\right)k_{\gamma_2} \qquad (27)$$

Comparing this with Equation (10), we see that the two equations are identical except for the additional factor k_{γ_2} in the last term of Equation (27). Hence, we can express T_8 in terms of the propellant and gun parameters simply by including the factor k_{γ_2} in the last term of Equation (11), giving us the final result:

$$T_8 = \frac{rC_{p1}T_1 + r(1-r)\gamma_2\left[\psi - \frac{U^2}{2}\left(\frac{W}{C} + \frac{1}{3} - \frac{1}{\gamma_2}\right)\right] + (1-r)^2\gamma_2\left[\psi - \frac{U^2}{2}\left(\frac{W}{C} + \frac{1}{3}\right)\right]^{\frac{1}{\gamma_2}}\left[\frac{P_aG}{(\gamma_2-1)C}\right]^{\frac{\gamma_2-1}{\gamma_2}} k\gamma_2}{rC_{p1} + (1-r)\,C_{p2}} \qquad (28)$$

To review our work, Equations (11), (22), and (28) give the temperature of the muzzle gas-air mixture for the three cases. Case A assumes that an ideal suppressor is used and no shock waves are present; the entire mixing process occurs at atmospheric pressure. In Cases B and C, no mechanical attachments are used so that the flow pattern at the muzzle is that of the shock bottle as shown schematically in Figure 4. In Case B, the muzzle gas and air mix at atmospheric pressure, just as in Case A; then the mixture passes through a shock wave, after which it again expands to atmospheric pressure. In Figure 4, this would correspond to air in region "a" and muzzle gas in region "b", both near

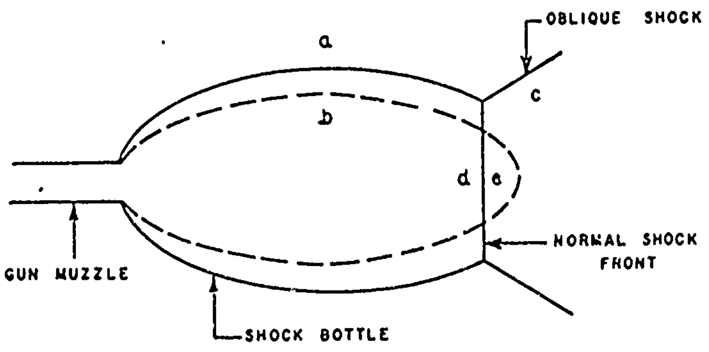


FIGURE 4. FLOW PATTERN AT A GUN MUZZLE

the boundary of the shock bottle, mixing with each other and then crossing either the oblique or the normal shock wave into region "c". In Case C, only the muzzle gas crosses the shock wave; after it expands to atmospheric pressure it mixes with air, again just as in Case A. In Figure 4 this might correspond to muzzle gas in region "d" crossing the normal shock into region "e" before mixing with air. Of the two Cases, B and C, Case B probably corresponds more nearly to reality. In one of our early studies of the mixing process(9), using a nozzle to simulate a gun in a small wind chamber, it was found that mixing does occur along the boundary of the shock bottle and that the pressure in this region does not deviate greatly from atmospheric pressure. The experiments also indicated that the region bounded by the dashed line in Figure 4, including most of the shock bottle and a small area forward of the normal shock, is occupied entirely by muzzle gas. Hence the mixture which forms around the surface of the shock bottle enters region "c" mostly by crossing the weak oblique shock, so that its pressure is not increased very much above atmospheric pressure. This part of the process appears to satisfy the conditions of Case B fairly well. The conditions of Case C are probably most nearly satisfied along the outer edge of the normal shock front. The gas which crosses this area of the shock front consists mostly of muzzle gas and has a pressure near atmospheric pressure before crossing. After crossing the shock wave it mixes with gas which has already undergone some mixing, rather than with air as specified in Case C.

2.2 Calculations for 37mm Vigilante and Comparison with Ignition Boundaries

For each of the three cases calculations have been made for the 37mm Vigilante weapon using T28 propellant. The ballistic parameters are the following:

γ = 1.24

T_v = 3081°K

$\psi = 1.495 \times 10^6 \frac{\text{ft lb}}{\text{lb}} = 1070$ cal/gm

W = 1.61 lb

C = 0.500 lb

U = 3000 ft/sec

G = 183.5 in^3

The air temperature T_1 was taken as 300°K. The factor k was calculated for the maximum S; in other words, it was assumed that all shock waves were normal shocks. The curves are shown in Figure 5 where they are labelled "physical" curves, as in previous reports, to distinguish them from the ignition boundaries which were referred to as "chemical" curves. The factor k is also plotted in Figure 5. The curve for Case C, which involves increasing one of the terms in the Equation for Case A by the factor k, lies above curve A. And the curve for Case B, which involves increasing the entire Equation for Case A by the factor k, lies above both curves A and C.

From Figure 5 we can see that, compared to the physical curves, the chemical curves - which give the minimum ignition temperatures at atmospheric pressure for mixtures of the muzzle gases M2, M10, and M17 with air - have relatively little variation both with respect to each other and also with respect to r, the mass fraction of air in the mixtures. We see that the temperatures required for ignition are exceeded, over at least part of the range of r, by the temperatures outside the gun under the conditions of all cases treated. The significance of this overlap of the "chemical" and "physical" curves is that, under the conditions they represent, ignition of the muzzle gases can be expected to occur provided only that the minimum ignition temperatures are exceeded for a time at least equal to the required induction period.

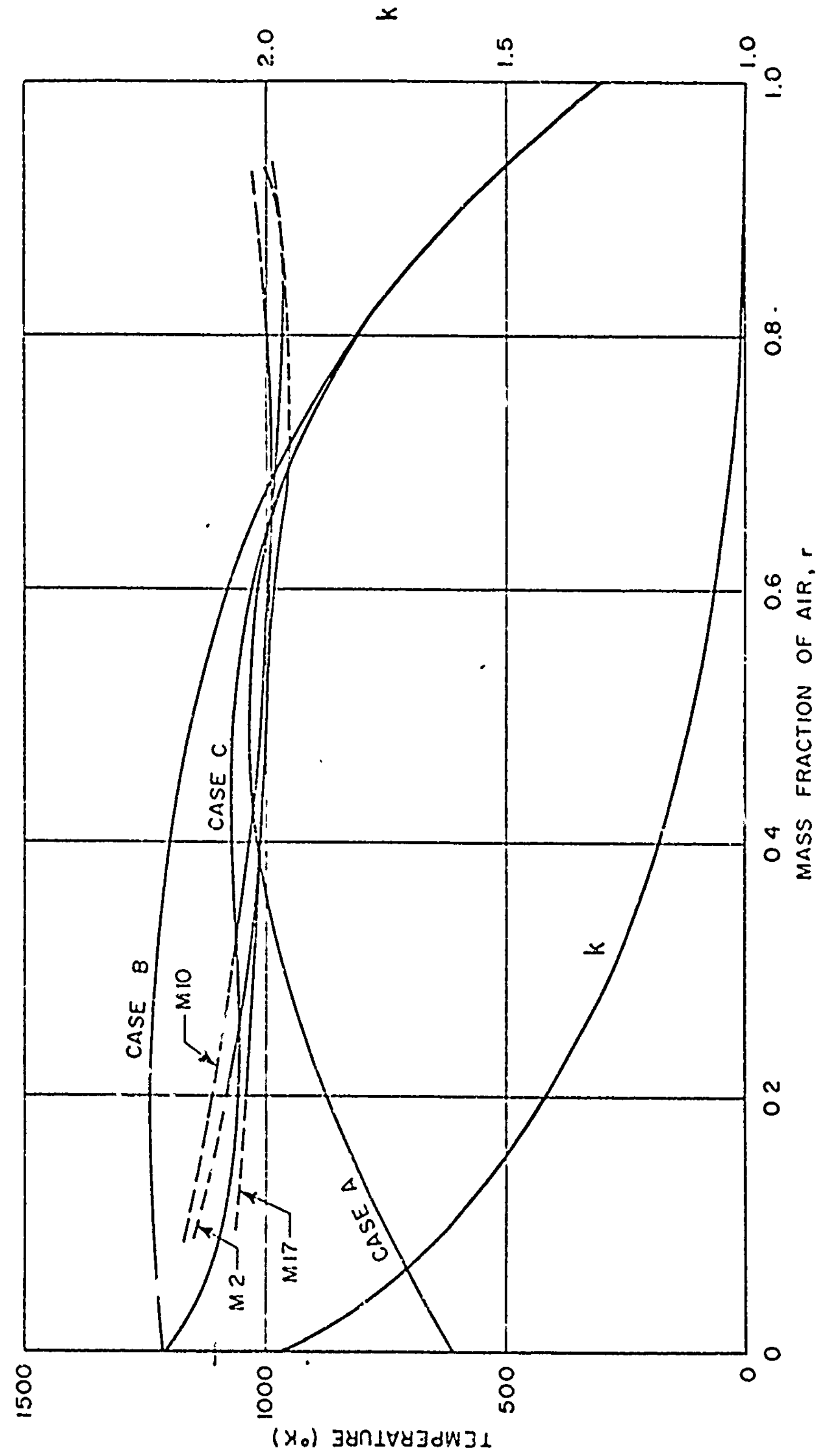


FIGURE 5. PHYSICAL CURVES FOR 37mm VIGILANTE COMPARED WITH IGNITION BOUNDARIES AT ATMOSPHERIC PRESSURE

In a continued study of this problem it would be profitable to investigate the following items:

(1) Improve and expand the mathematical treatment of the gas dynamics outside the gun.

(2) Compare calculated temperatures with measured ignition limits at pressures above atmospheric pressure.

(3) Arrive at some estimate of the times involved in the mixing process and compare with induction times.

(4) Make calculations for weapons other than the 37mm Vigilante.

(5) Acquire more accurate information on propellant gas composition and determine effect of minor components on ignition limits and delays.

Unclassified

PART II

STUDIES OF GUN SMOKE

The second phase of this project is aimed toward a better understanding of the causes and means of eliminating gun smoke. The experimental program has included measurements of the quantity and chemical composition of smoke produced by firing propellants of various compositions.

The test vehicle has been a caliber .50, M2 Browning machine gun with a 36-in. barrel. Ball M2 projectiles were used until the supply was exhausted, and then Ball M33 projectiles were used. The primers are the REM .50 type. The weight of propellant in the charge was kept constant at 226 grains. The tests were conducted in an inside range provided with apparatus for measuring projectile speed. The density of smoke which collected in a baffled area in the vicinity of the gun was measured with a smoke photometer* of our own design, described in Reference (3). Samples of the smoke were obtained by using a commercial air sampler to trap the smoke particles on a filter of Dacron blanket material. The sampling time was the same for each round fired in a given test. The total smoke collected was determined by weighing the filter before and after a test; this weight was divided by the number of rounds fired to determine the smoke collected per round. The smoke was removed from the filter by shaking and tapping the filter so that the smoke particles fell onto a sheet of clean plastic film, from which they were transferred to a small bottle. In two tests for which this method yielded insufficient sample for chemical analysis, additional smoke was removed from the filter by washing with water in a small beaker and evaporating the water.

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* Some of the light scattered out of a beam by smoke particles was allowed to fall on a photoconductive cell whose output was measured with a galvanometer.

Tests were run with the propellants listed in Table 4. In the case of the EX5013-2 propellant, additional tests were run with up to 4% of K_2SO_4 added to the basic charge. In these tests the weighed salt was poured over the propellant in the cartridge cases prior to bullet seating. All completed rounds with separately added salt were given a uniform shaking prior to firing in an attempt to attain even distribution of the salt throughout the charge. It is unlikely that an even distribution was achieved, however, because the finer salt particles had a tendency to settle out through the coarser propellant grains.

The major effort on this phase of the project was, by far, that required to work out a reliable and, at the same time, fairly routine procedure for quantitative chemical analysis of the smoke. More than once the discovery of a component of smoke which interfered with the analysis in some way required rejection or modification of a procedure that had already taken considerable time to develop.

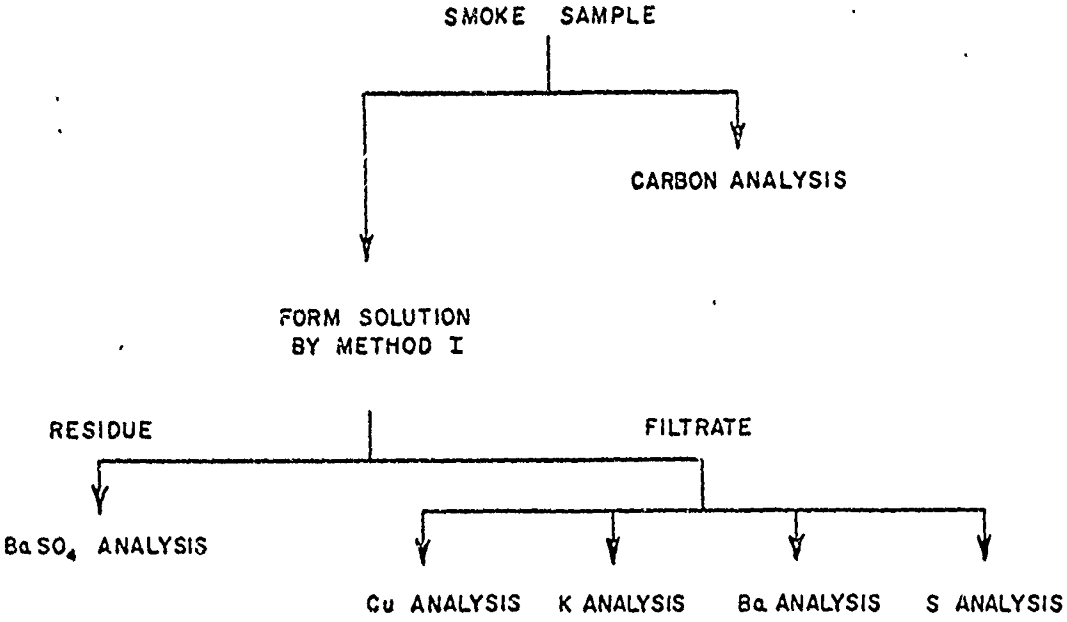
We report below our work on two groups of samples. Group A comprises samples 20 to 25 for all of which the basic charge consisted of 226 grains of EX5013-2, unsalted propellant. Samples 20 and 25 contained no additives while samples 21, 22, 23, and 24 had 1/2, 1, 2, and 4%, respectively, of K_2SO_4 added to the charge. A similar group of samples, 12 to 17, on which some work was done, as reported in Reference (3), was accidentally spoiled; we therefore repeated this series of tests and obtained the corresponding samples, 20 to 25, mentioned above. Group B comprises samples 26 to 30 obtained by firing five different propellants supplied by Picatinny Arsenal.

The chemical analysis of group A followed the outline sketched in Figure 6a. One portion of the smoke sample was analyzed for carbon by oxidizing in a tube furnace and collecting the CO_2 formed, as described in the Appendix, Section 2. A separate portion of sample was used to prepare a solution by Method I (Appendix, Subsection 1), which involves digestion in HNO_3, fuming almost to dryness, the addition first of NH_4OH

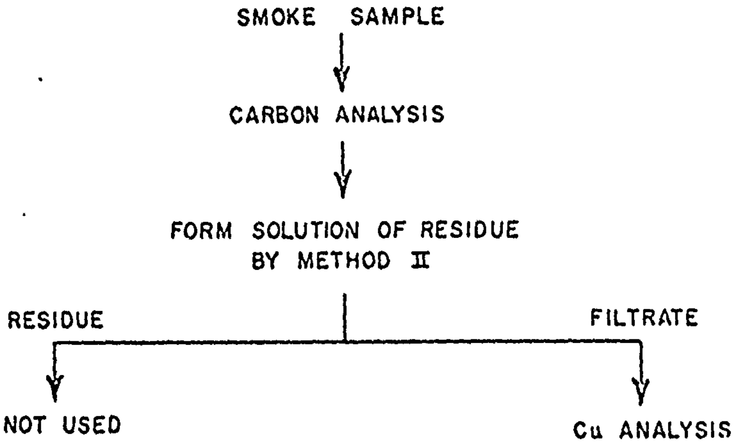
Table 4

COMPOSITION AND THERMOCHEMICAL PROPERTIES OF PROPELLANTS

	EX-5013-2 AL-29422	M2 Propellant HES-5354-3E	Unsalted IMR Propellants PA-E-26478	PA-E-26497	PA-E-26508	PA-E-26523
Nitrocellulose (%)	90.28	77.35	100.00	100.00	100.00	100.00
Nitrogen in Nitrocellulose (%)	13.15	13.25	13.15	13.15	13.15	13.15
Nitroglycerin		19.50				
Potassium Nitrate		0.80				
Barium Nitrate		1.50				
Diphenylamine	0.64					
Diphenylamine (added)			0.67	0.60	0.55	0.52
Dinitrotoluene	7.48					
Dinitrotoluene (coating)			7.44	7.74		
Graphite		0.25				
Graphite (glaze)			0.09	0.13	0.26	0.19
Ethyl Centralite		0.60				
Ethyl Centralite (coating)		4.25				
Methyl Centralite (coating)					6.14	
Ethyl Alcohol (residual)		0.60	0.20	0.38	0.57	0.66
Total Volatiles	1.60					
Moisture (residual)	0.99	0.70	0.98	0.81	0.79	0.85
Residual Solvent	0.61					
Calculated Thermochemical Properties						
Isochoric Flame Temp. (°K)	2850	3130	2959	2955	2635	3105
Force (ft-lb/lb)	311,000	352,200	341,300	341,300	319,600	347,400
Unoxidized Carbon (%)	-	0.59	1.55	1.64	5.33	-1.00
Heat of Explosion (cal/gm)	820	1003	903	900.9	786.1	970.8
Gas Volume (mole/gm)	0.0415	0.04045	0.04146	0.04150	0.04359	0.04022
Mean Heat Cap. (cal/gm/deg)	-	0.3437	0.3439	0.3437	0.3469	0.3462



(a) FIRST SEQUENCE



(b) SECOND SEQUENCE

FIGURE 6. SMOKE ANALYSIS SEQUENCES

and then of HCl, and finally dilution and filtering. The residue was analyzed for $BaSO_4$ by the method of Na_2CO_3 fusion (Appendix, Section 3). This part of the analysis was discontinued after it was performed on the three samples 23, 23X, and 24, because it was discovered that the residues contained iron and, possibly, aluminum and silicon in sufficient quantities to damage the platinum crucibles used. The presence of these ingredients was indicated by semiquantitative analyses of the residues of samples 22 and 24X (see Table 5). Since the $BaSO_4$ content of the residues checked was only 1 or 2%, it was not considered wise to exert much effort on the remaining residues to rid them of the objectionable ingredients.

The smoke solution was divided into four aliquots, one each for the analysis of the following ions: Ba^{++}, Cu^{++}, K^{+}, $SO_4^{=}$. The copper analysis was done colorimetrically by adding bis (2-hydroxyethyl) dithiocarbamate to form a color complex and measuring the absorption at 435 mμ (Appendix, Section 4). The potassium was determined by precipitation with excess of sodium tetraphenylborate, the excess being back titrated with cetyltrimethylammonium bromide (Appendix, Section 5). Barium and sulfur were both determined by the precipitation of $BaSO_4$; the former by addition of H_2SO_4, and the latter by addition of $BaCl_2$ (Appendix, Sections 6 & 7).

It was thought that the $BaSO_4$ present in the insoluble portion of the smoke would exhaust all of either the Ba^{++} or SO_4^{--} so that only one of these ions would be present in the smoke solution. In other words, of the two aliquots of smoke solution tested for Ba^{++} and SO_4^{--} content, only one was expected to yield a precipitate. In the few cases (Samples 20, 21, & 22) in which both aliquots yielded a precipitate, it is thought that the small amounts found (less than 1% for the lower of the two yields) can be accounted for by the precipitation of minor ingredients not considered in the analysis.

Table 5

RESULTS OF SPECTROSCOPIC ANALYSIS
(Performed by W.B. Coleman and Co., Philadelphia, Pa.)

Element	Sample 21 Residue After Special Treatment	Sample 22 Insoluble Residue and Filter Ash	Sample 24X Insoluble Residue and Filter Ash
Aluminum	Major	Minor	Minor (low)
Calcium	Minor	0.X	0.X
Chromium	0.0X	0.0X	0.0X
Copper	Minor	Major	Major
Iron	Minor	Minor	Minor
Lead	Minor	Minor	Minor
Magnesium	Minor	0.00X	0.00X (high)
Manganese	0.00X	**	**
Nickel	0.0X (low)	0.00X	**
Silicon	Major	Minor	Minor
Sodium	0.X	**	**
Silver	*	**	0.00X
Tin	0.0X (low)	**	**
Titanium	0.X (high)	0.0X	0.0X (high)
Antimony	0.X (high)	**	**
Molybdenum	0.0X	**	**
Vanadium	0.00X	0.0X	0.0X (low)
Zinc	*	0.0X	**
Zirconium	0.0X	**	**
Barium	Major	0.X	0.X (high)
Strontium	0.X	0.0X	0.0X
Bismuth	0.00X	**	**

* Elements checked but not found in Sample 21: Arsenic, cobalt, silver, zinc, beryllium, boron, cadmium, columbium, gallium, germanium, gold, platinum, potassium, tellurium, tungsten.

** Elements checked but not found in Samples 22 and 24X: Cobalt, manganese, nickel, sodium, tin, zinc, antimony, arsenic, beryllium, bismuth, boron, cadmium, columbium, gallium, germanium, gold, molybdenum, platimum, tellurium, tungsten, zirconium.

NOTE: Minor = 1.0 to 5.0%; Major = above 5.0% estimated; 0.X, 0.0X, 0.00X, etc. = concentration of the elements estimated to the nearest decimal place; e.g., 0.0X = 0.01 to 0.09% estimated.

The samples listed as 23X and 24X are identical to Samples 23 and 24, respectively, except that the preparation of the smoke solution for Samples 23X and 24X was done by Method III (Appendix, Section 1), which includes treatment with bromine to convert to sulfate any sulfur not initially present in that form. This was done to confirm whether it is reasonable to assume, as is done for the determination of sulfur, that sulfur is present entirely in the sulfate form. For Sample 23, the bromine treated portion had a slightly higher sulfur content; and for Sample 24 it had a slightly lower sulfur content than the non-treated portions. This would indicate that the small differences can be ascribed to experimental error and that the bromine treatment was not essential for this group of samples.

The results of the chemical analysis of the samples in Group A were reported in terms of percentages in Reference (3). The percentage figures have been converted to mass produced per round fired and are listed in Table 6. The conversion procedure will not be described in detail as it amounts simply to a straightforward accounting of the total mass of smoke collected, number of rounds fired, the fraction of total smoke represented by the sample used in any particular analysis, and the mass of each component in the sample as determined by the analysis. This procedure requires that the effective efficiency of smoke collection be constant in order that the results for different tests be comparable. By controlling the frequency of firing and the sampler running time, we tried to keep this efficiency as nearly constant as possible. The mass per round figures are preferred to percentages because the latter, alone, give no indication of the actual quantity produced.

The figures for copper listed under Method I were obtained by the analysis described above, and they correspond to the percentages reported in Reference (3). The fact that some of the numbers are much smaller than the others led us to suspect the presence of a fault somewhere in the analysis procedure because it had been expected that the copper per round would be relatively constant. We expected this because

Table 6

RESULTS OF SMOKE ANALYSIS

Sample	K_2SO_4 Added* (%)	Barium			Carbon	Copper		Potassium	Sulfur		
		In Residue	In Solution	Total		Method I	Method II		In Residue	In Solution	Total
20	0	-	4.2	-	3.02	19.4	14.8	0	-	0.041	-
21	0.5	-	3.0	-	4.08	19.0	27.9	0	-	0.36	-
22	1.0	-	0.5	-	9.52	15.9	34.2	11.80	-	0.97	-
23	2.0	3.30	0	3.30	12.53	1.2	28.6	28.4	0.77	6.80	7.57
23X	2.0	2.12	0	2.12	-	16.0	-	22.8	0.49	7.20	7.69
24	4.0	1.88	0	1.88	14.04	3.8	29.0	42.7	0.44	13.10	13.54
24X	4.0	-	0	-	-	8.7	-	44.4	-	10.06	-
25	0	-	0	-	2.47	23.0	21.1	0	-	0.39	-

* Basic charge was 226 grains of EX 5013-2 unsalted caliber .50 propellant

the sources of copper, the bullet jacket and cartridge case, were the same in all cases; and it was thought that charge variations should not heavily affect the quantity of copper in the smoke. Examination of the insoluble residue formed during preparation of the smoke solutions revealed that considerable undissolved copper was present. After repeated digestion in HNO_3 the residue still contained copper. However, when the carbon in the residue was burned off by heating in a platinum crucible, further HNO_3 digestion removed all the copper. Hence it was concluded that the presence of carbon had prevented the copper from dissolving entirely. Further experiments with the remaining residue, which was of a yellow flocculent form, showed it to be insoluble in HCl or aqua regia. It may have contained $PbSO_4$, $BaSO_4$, and possibly some silicates. A semi-quantitative analysis of this residue is given in Table 5. As a result of the above experiments it was decided that the residues from the portions of smoke sample used for carbon determination, being carbon free, would provide suitable samples for preparation of smoke solutions, which could then be analyzed not only for copper, but for the other elements of interest as well. Solutions were prepared as described in the Appendix, Section 1, and we reanalyzed for copper in Samples 20 to 25. The results are listed under Method II of Table 6. We notice that considerably higher results were obtained for those samples, 23 and 24, which had previously yielded very low values.

For a few samples the smoke solutions prepared from the carbon test residues were analyzed for potassium. The results were much lower than had been obtained with the solutions prepared from the original samples. To check this result, an artificial smoke sample containing known amounts of K_2SO_4, $BaCl_2$, Cu, and C was tested for carbon by the usual procedure with good results. A smoke solution was prepared from the residue left from the carbon test and two aliquots were checked for Cu and K. The result obtained for Cu checked very well with the known amount present. The analysis of K, however, yielded a very low result. During the carbon test it had been noticed that a substance had condensed on the cool portions of the Vycor tube containing the sample in the tube furnace. This substance was dissolved in water and HNO_3 and analyzed for Cu and K. A negligible amount of Cu, but a large amount of K was found. Evidently, under the conditions of the carbon test some potassium compounds are caused to sublime onto the cool parts of the system. To overcome this difficulty, it may be possible to burn off the carbon in a porcelain crucible at low temperature for that portion of the smoke sample from which a solution is to be prepared.

Table 7 lists the physical observations made on the Group A samples during firing tests of 10 rounds each. As expected, the smoke density increased with salt concentration. Compared to the unsalted charge, the smoke density was almost 10 times as great when 4% K_2SO_4 was added. The number of secondary flashes observed out of the 10 rounds decreased with increasing salt concentration, again as expected. We note also that, generally, the average projectile speed increased with salt concentration. This may have resulted from the higher loading density and from the additional oxygen available when more K_2SO_4 was added to the charge.

Figure 7 gives a graphical representation of the chemical analysis and some of the firing test results for the samples in Group A. We note that the potassium and carbon content of the smoke increases with K_2SO_4 added to the propellant. The contribution of barium to the smoke is small throughout. The contribution of copper is surpassed only by potassium and then only for the highest K_2SO_4 concentration. The amount of carbon increases, more rapidly at low K_2SO_4 concentrations, as more K_2SO_4 is added to the propellant. The number of secondary flashes decreases and the smoke density increases as the K_2SO_4 concentration is increased. The flash suppressant behavior of K_2SO_4 appears to be low in these tests, where it was added separately to the charge. When it is a part of the propellant composition, less than 1% is usually sufficient to eliminate secondary flash.

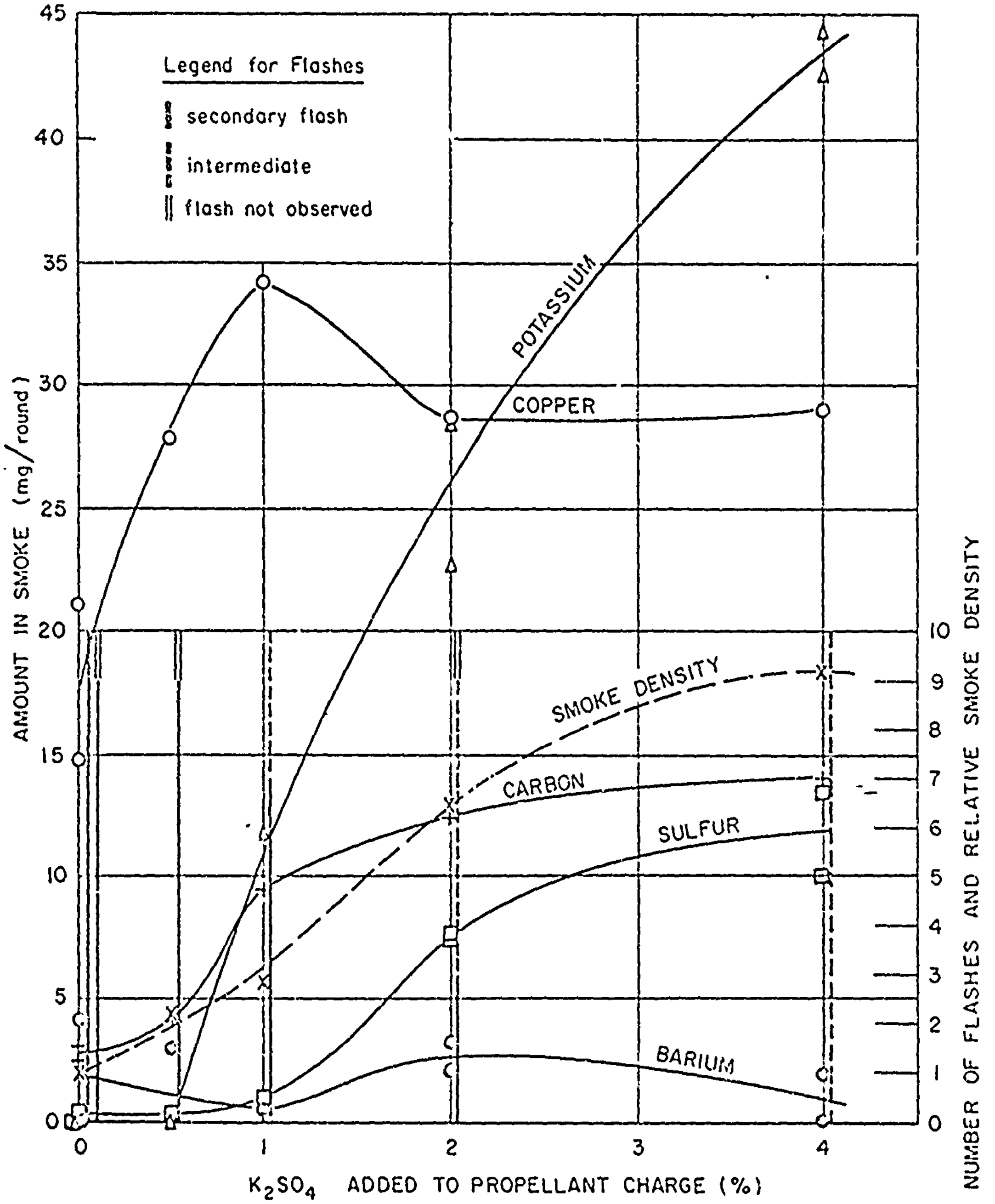


FIGURE 7 SMOKE COMPOSITION FOR SAMPLES IN GROUP A

(Basic change = 226 grains EX 5013-2)

Table 7

RESULTS OF FIRING TESTS ON SAMPLES OF GROUP A

Ambient Temperature: 26 to 27°C
Ambient Relative Humidity: 45 to 53%

		Smoke Density		Flashes		
Sample	K_2SO_4 Added* (%)	Average Photometer Reading (mm)	Relative**	Intermediate	Secondary	Average Projectile Speed (fps)
20	0	34	-	-	9	2543
21	0.5	74	2.1	-	9	2550
22	1	103	2.9	3	7	2589
23	2	226	6.5	6	3	2578
24	4	321	9.2	10	-	2625
25	0	36	-	-	10	2538

* Basic charge was 226 grains EX-5013-2 unsalted caliber .50 propellant.

** Ratio of photometer readings to average of readings for Samples 20 and 25.

We shall now proceed to a discussion of our work with the samples in Group B. In view of our experience with Group A, smoke solutions were prepared from the residues of the carbon analysis as indicated by the analysis sequence in Figure 6b. In Table 8 the results of the carbon and copper analyses are given together with the density and the projectile speed observed during the firing tests. The smoke density did not vary much among the samples of this group except for Sample 27 which produced smoke two to three times as dense as the others. This is probably due to the presence of barium nitrate and potassium nitrate in the propellant of Sample 27 (see Table 4).

All of the samples produced secondary flash in every round fired. Sample 29 produced radically more carbon than the others, and it was observed that the cartridges and the cartridge chamber of the gun became coated with a heavy layer of black residue during the firing of this

Table 8

RESULTS OF SMOKE TESTS ON SAMPLES OF GROUP B

Sample	Propellant Designation	Smoke Density		Average Projectile Speed (fps)	Carbon (mg/round)	Copper (mg/round)	Ambient Conditions	
		Average Photometer Reading (mm)	Relative*				Temperature (°C)	Relative Humidity (%)
26	PAE-26478	56	1.4	2990	2.78	31.4	24.5	37
27	HES-5354.3E	109	2.8	2444	5.48	18.5	24.0	33
28	PAE-26497	39	1.0	2630	2.84	20.6	24.9	29
29	PAE-26508	48	1.2	2248	61.1	14.5	24.0	40
30	PAE-26523	46	1.2	3080	1.77	47.1	24.5	36

* Ratio of photometer readings to that of Sample 28

particular propellant. Table 4 shows that this sample also had the largest value of calculated unoxidized carbon. Note that Sample 30 which produced the least carbon per round also has the smallest value of calculated unoxidized carbon. Except for Sample 29, the smoke of the Group B samples contained considerably more copper than carbon. The copper produced per round ranged over approximately the same values as for the Group A samples, except for Sample 30 which had about twice as much copper as the others. There was insufficient time to analyze these samples for more than carbon and copper. Percentagewise, carbon and copper accounted for 30 to 90% of the total sample.

Our smoke photometer appears to give a fairly reliable measure of smoke density. In three series of tests a comparison of the relative smoke density with the total smoke collected showed a close correlation. In view of the large discrepancy between conditions in the test range and actual field conditions, it is difficult to interpret measurements of smoke density in terms of the actual visual obstruction that the smoke can be expected to cause. The density measurements do provide a basis, however, for making a relative evaluation of propellants for obscuration. Some thought has been given to other techniques of arriving at a measure of obscuration. One possibility is to use a photographic method to measure the effect of smoke on the contrast ratio of an alternately light and dark field. When applied to inside firing tests, however, there remains the problem of interpreting the observations in terms of actual field conditions.

If the chemical analysis of smoke is to be continued an effort should be made to replace the copper jacketed projectiles with bullets that would not be expected themselves to contribute much to the smoke. This would make it easier to correlate smoke composition with propellant composition. The recommended procedure for chemical analysis would be to use one portion of sample for the carbon analysis; a separate portion should have the carbon burned off in a porcelain crucible at low temperature and the residue used to prepare a solution. It is expected that the remaining residue will be a small portion of the original sample, and the elements of interest will reside chiefly in the solution.

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REFERENCES

1. Franklin Institute Laboratories Final Report F-A1828; "Research and Development on Ignition of Propellants and Muzzle Gases", S.P. Carfagno, G.P. Wachtell; January 10, 1958.
2. Franklin Institute Laboratories Interim Report I-A1828-3; "Shock Tube Determinations of Ignition Boundary and Ignition Delays for Dry One-to-One Mixtures of Muzzle Gas and Air Near Atmospheric Pressure", S.P. Carfagno, G.P. Wachtell; June 30, 1956.
3. Franklin Institute Laboratories Interim Report I-A2132-1, "Relationship between Propellant Composition and Flash and Smoke Produced by Combustion Products", S.P. Carfagno; July 13, 1958.
4. Franklin Institute Laboratories Report Q-A1828-2, "Shock Tube Study of Ignition of Wet Mixtures of Muzzle Gas and Air", S.P. Carfagno, G.P. Wachtell; March 31, 1957.
5. Franklin Institute Laboratories Interim Report I-2364-1; "Physical Suppression of Gun Muzzle Flash; Part I. Theory of Physical suppression; Part II. Nozzle Flow Chamber", E.R. Stephens, G.P. Wachtell, S.P. Carfagno; September 1, 1953.
6. "Elements of Gas Dynamics", H.W. Liepmann, A. Roshko; John Wiley and Sons, Inc.; 1957.
7. "Introduction to Aerodynamics of a Compressible Fluid", H.W. Liepmann, A.E. Puckett; John Wiley and Sons, Inc.; 1947, p.26.
8. Same as above, p.25.
9. Franklin Institute Laboratories Interim Report I-2442-2, "Physical Suppression of Gun Muzzle Flash, and Howitzer Flash Tests", S.P. Carfagno, G.P. Wachtell, E.R. Stephens; February 1, 1955.
10. "Textbook of Quantitative Inorganic Analysis", Kalthoff and Sandell; The MacMillan Co., 3rd Ed; 1952; p. 674ff.
11. Method D715-45 for Analysis of Barium Sulfate Pigments, ASTM Standards, Part IV; p. 152.
12. "Colorimetric Determination of Metals in Sewage and Industrial Wastes", P.G. Butts, A.R. Gahler with M.G. Mellon, "Sewage and Industrial Wastes"; December 1950; p. 1552ff.
13. "Volumetric Determination of Potassium", E.P. Schall; "Analytical Chemistry", Vol. 29, No. 7; July 1957; pp. 1044-46.

APPENDIX

PROCEDURES FOR CHEMICAL ANALYSIS OF SMOKE

PROCEDURES FOR CHEMICAL ANALYSIS OF SMOKE

1. PREPARATION OF SMOKE SOLUTION

Method I

An accurately weighed portion of smoke sample (200-500 mg) was transferred to a 250-ml beaker, and 6-10 ml of 16N HNO_3 were added. This was fumed almost to dryness on a hot plate. The residue was cooled, and 40-50 ml of distilled water were added. This solution was made slightly alkaline by adding 28% NH_4OH; and it was stirred well for a few minutes. The solution was then acidified slightly with 1:1 HCl. After being diluted to 80-90 ml the solution was digested for 1-2 hours. It was then heated to 80-90°C and filtered while hot through a close-textured filter paper (Whatman No. 42). The filtrate was diluted to an exact volume of 100 ml and transferred to a 250-ml Erlenmeyer flask for storage.

Method II

The residue from the carbon analysis was scraped out of the combustion boat, and an accurately weighed portion (~ 200 mg) was placed in a 125-cc Erlenmeyer flask. Approximately 25 ml of concentrated HNO_3 were added. This was heated until a small volume remained. A yellow flocculent precipitate formed during this part of the procedure. Then approximately 25 ml of H_2O were added to dilute the HNO_3. The solution was made alkaline by adding 28% NH_4OH to a pH of 8 in an ice bath. The solution was then acidified with 1:1 HCl to a pH of 3 or 4. The solution was heated below the boiling point and filtered while hot. The filtrate was diluted to 250 ml.

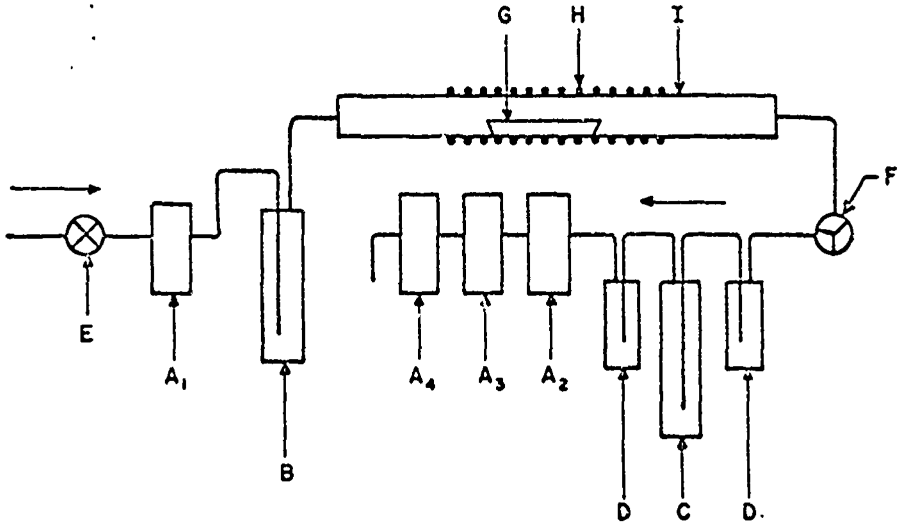
Method III

An accurately weighed portion of smoke sample (~1 gm) was placed in a beaker. Five ml of a solution consisting of 2 volumes of liquid bromine in 3 volumes of carbon tetrachloride were added. The beaker was covered and allowed to stand for 15 minutes at room temperature. Ten ml of concentrated nitric acid were added, the beaker was recovered, and digestion was continued for 15 minutes at room temperature. The beaker was then placed in a Boekel oven and heated to approximately 85°C for about 30 minutes. The cover was then raised from the beaker and the solution was evaporated to dryness. From this point the procedure of Method I was followed.

2. DETERMINATION OF CARBON

The carbon content of the smoke was determined by the "train" method, as described in Reference (10). A portion of smoke sample was oxidized in a tube furnace, and the CO_2 formed was absorbed in a bulb whose weight increase indicated the amount of carbon in the sample. The components of the train are shown in Figure 8, where the measuring absorption bulb is designated A_3. The other traps and absorption bulbs are designed to prevent the absorption in A_3 of anything except CO_2 formed by oxidation of the sample.

The actual runs were preceded by two or more blank runs to determine the blank weight of the main absorption bulb, A_3. An empty alumina combustion boat was placed in the Vycor tube; and the furnace was heated to approximately 1500°F and kept at this temperature throughout the test. The temperature was measured with a thermocouple located between the Vycor tube and the heater windings, so that its reading was higher than the temperature of the combustion boat. The train was disconnected between bulbs A_2 and A_3; and a stream of oxygen was passed through at a low rate, about 100 ml/min. After 15 minutes, the train was reconnected between A_2 and A_3, and oxygen was passed through at the same rate for an additional 5 minutes. The bulb A_3 was then closed, disconnected, and allowed to stand near the analytical balance for 10 minutes before weighing. A bulb identical to A_3 was used as a tare. Before weighing, A_3 was opened momentarily to equalize the pressure inside the bulb.



A = ABSORPTION BULBS
A_1 = ABSORPTION BULB CONTAINING ASCARITE
A_2 = ABSORPTION BULB CONTAINING $CaCl_2$
A_3 and A_4 = ABSORPTION BULB CONTAINING ASCARITE AND $CaCl_2$
B = SULFURIC ACID TRAP
C = TRAP CONTAINING MIXTURE OF SULFURIC AND CHROMIC ACIDS
D = TRAPS TO CHECK FLOW OF ACID MIXTURE THAT MIGHT OCCUR UNDER ABNORMAL CONDITIONS
E = NEEDLE VALVE FOR CONTROLLING OXYGEN FLOW RATE
F = THREE-WAY STOPCOCK
G = SAMPLE-BOAT
H = HEATER WINDING
I = VYCOR TUBE

FIGURE 8. COMBUSTION TRAIN FOR CARBON ANALYSIS

The above procedure was repeated with the oxygen flow rate increased to 200 ml/min. and the time of flow increased to 10 minutes. This was repeated as many times as necessary until the gain (or loss) in weight of the absorption bulb during the runs became nearly constant (± 1.0 mg). Usually only two blank runs were necessary.

When the blank runs were completed, the three-way stopcock F was turned so that the Vycor tube was open to the atmosphere and the rest of the train was closed. An exactly weighed portion of smoke sample (100-500 mg) was placed in the combustion boat which was then replaced in the furnace. The stopcock F was turned to reconnect the rest of the train, and the system was allowed to stand for 1/2 - 1 minute. Oxygen was then passed rapidly (300-400 ml/min.) over the sample for five minutes, after which the flow rate was reduced to 200 ml/min. and continued for an additional 5 minutes. The flow of oxygen was cut off and the absorption bulb A_3 was disconnected and weighed as in the blank runs.

The weight of carbon in the sample was calculated as follows:

$$\text{Weight of carbon} = \frac{12.01}{44.01}\left[\begin{matrix}\text{Weight increase of absorption} - \Delta W \\ \text{bottle } A_3 \text{ during carbon run}\end{matrix}\right]$$

where ΔW = average increase in weight of bulb A_3 during two successive blank runs.

3. DETERMINATION OF $BaSO_4$ BY Na_2CO_3 FUSION(<u>11</u>)

The residue left from the preparation of the smoke solution by Method I was washed well two or three times with distilled water (slightly acidified with dilute HCl). It was placed in a platinum crucible and heated 1/2 - 1 hour over a Meeker burner with free access of air to burn off the carbon present. About 3 grams of Na_2CO_3 were added, mixed thoroughly, and fuzed until the melt was clear. After cooling, the melt was leached in a dish with hot water until it was entirely disintegrated. It was then filtered with a close-textured paper and washed thoroughly with hot Na_2CO_3 (30 g per 1). The filter paper containing the insoluble carbonates was transferred to a 250 ml beaker and acidified with HCl (sp. gr. 1.18). In order not to lose any barium, the platinum crucible was also washed with HCl. The solution was boiled and filtered into a 600-ml beaker, washing well with water. Methyl red indicator was added, and the solution was made slightly alkaline with NH_4OH (sp. gr. 0.90). Then 6 ml of HCl (1:1) were added, and the solution was diluted to 300 ml. This was heated to boiling, and 5 grams of $(NH_4)_2SO_4$ dissolved in 40 ml of water were added. When a large concentration of impurities was present, the $(NH_4)_2SO_4$ solution was added dropwise from a burette to minimize inclusion. This precaution would not be necessary if the residue were rather pure (95-99% $BaSO_4$) as then the only non-volatile constituents of the solution would be barium salts.

The precipitate was allowed to digest for 4 hours or overnight, and then it was filtered through a close-textured paper. The precipitate was washed with as little cold water as possible, ignited in an oxidizing atmosphere, and weighed as $BaSO_4$.

4. DETERMINATION OF COPPER

The copper concentration was determined colorimetrically by formation of a yellow-brown water-soluble complex of cupric ion with bis-(2-hydroxyethyl)-dithiocarbamate. In solutions buffered within the pH range of 3 to 6, the color is stable for about an hour, which allows sufficient time for measuring the absorbance at 435 mμ using the Beckman Model DU spectrometer. The measured absorbances were compared with a calibration curve obtained by measurements on standard copper solutions.

The standard copper solution was prepared as described in Reference (12). An accurately weighed amount (~1 g) of mechanically cleaned copper was dissolved in 10 ml 1:1 HNO_3. This was diluted with doubly distilled water to a volume of approximately 25 ml and boiled almost to dryness in order to expel oxides of nitrogen. The remaining residue of copper salt was dissolved and diluted to an exact volume of 1000 ml.

A 2-ml aliquot of the standard copper solution was diluted to 100 ml and, in turn, 2 ml of the diluent was pipetted into an 100 ml volumetric flask. The following reagents were added in the order given: 10 ml of 1M HNO_3, 10 ml of 20% NaAc solution, and 1 ml of 10% sodium citrate solution. It proved to be essential to add the reagents in the order mentioned. The solution was diluted to approximately 50 ml and 1 ml of bis-(2-hydroxyethyl)-dithiocarbamate reagent was added. Preparation of the last reagent is discussed in the next paragraph. The solution was diluted to an exact volume of 100 ml and the absorbance was measured at 435 mμ. Other dilutions were prepared to cover the range between 0 and 50 mg Cu/100 ml. The calibration curve that was obtained is shown in Figure 9.

Because of its instability, the bis-(2-hydroxyethyl)-dithiocarbamate was prepared fresh by mixing equal volumes of a solution of 4.0 grams of diethylamine in 200 ml of methanol and a solution of 1 ml of CS_2 in 200 ml of methanol. These two solutions are fairly stable and remain effective for a long period of time when stored in a cool place.

It is important to note that this method is fairly sensitive, and rather high dilutions are preferable. In case of insufficient dilution, erroneous results may be obtained due to there being insufficient bis-(2-hydroxyethyl)-dithiocarbamate reagent to react with all the copper present in the solution.

The quantitative analysis for copper in the smoke solutions was performed as follows: From a 10-ml aliquot of the original smoke solution, dilutions were prepared to produce absorbances within the accurate portion of the calibration curve. The reagents were added to the diluent in exactly the manner described above for preparing standard dilutions for the calibration curve. Using the calibration curve, the measured absorbances were converted to copper concentrations and corrected by applying the proper dilution factor. The final result was obtained by averaging the results for at least two dilutions.

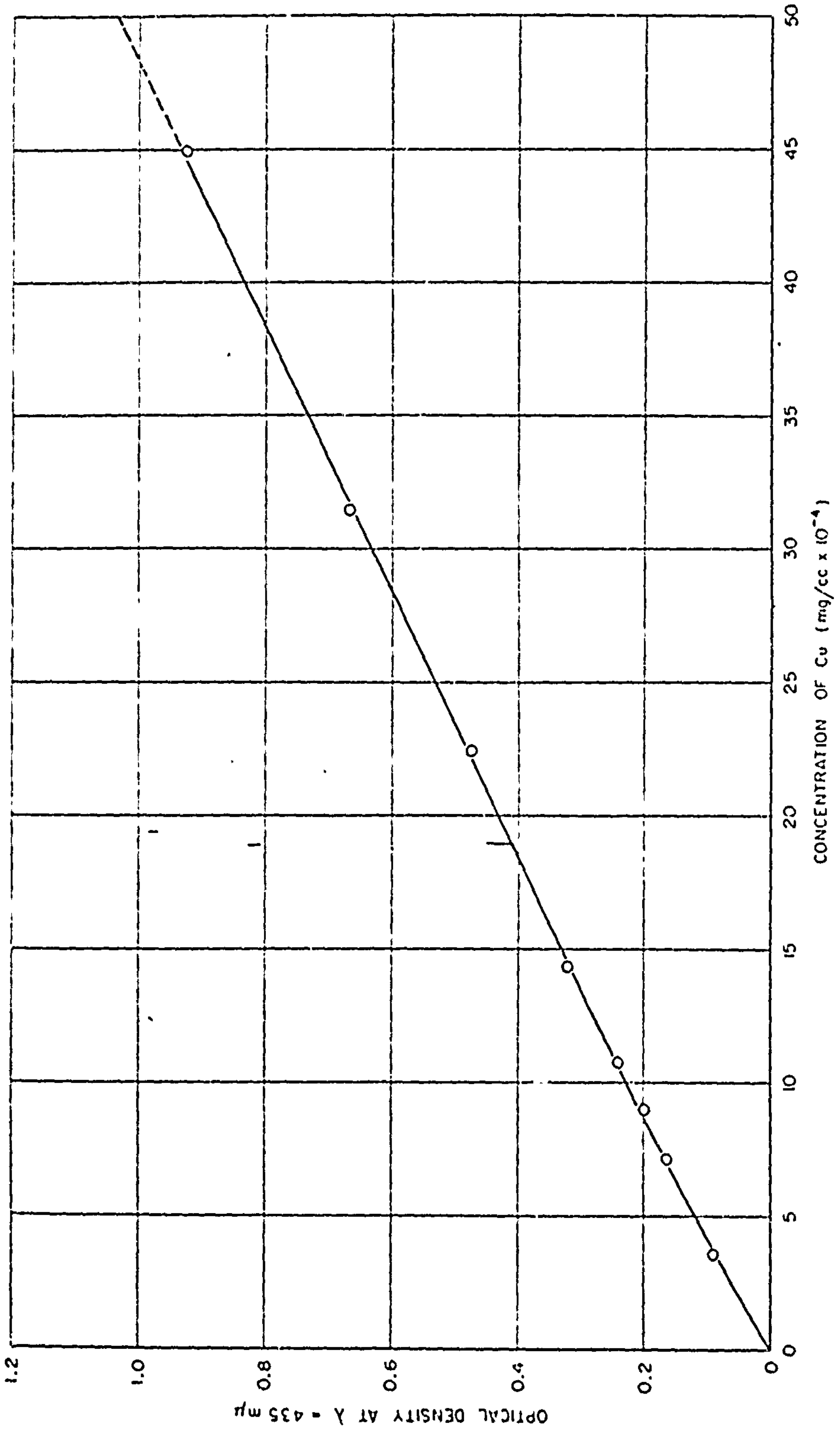


FIGURE 9 CALIBRATION CURVE FOR COPPER DETERMINATION

5. DETERMINATION OF POTASSIUM

The procedure is a slight modification of that described in Reference (13) for the determination of potassium in fertilizers. All potassium in the smoke solution was completely precipitated by addition of an excess of a standard sodium tetraphenylborate (STPB) solution, forming a salt with the tetraphenylborate ion. The excess of unreacted STPB was back titrated with a standard solution of cetyltrimethylammonium bromide (CTAB), using bromophenol blue as indicator. The only ions known to interfere with this method are ammonium, cesium, rubidium, silver, mercury (II), and the nitrogen bases, none of which are expected to be significant in the smoke solutions.

To prepare STPB solution, 23 grams of sodium tetraphenylborate was dissolved in approximately 800 ml of water. This was followed by the addition of 20-25 grams of aluminum hydroxide. After stirring for 10 minutes, the solution was filtered. A portion of 100-200 ml of the initial cloudy filtrate was collected separately and refiltered. To the clear filtrate 2 ml of 20% NaOH were added, and after dilution to 1 liter, it was stirred thoroughly.

The CTAB solution was prepared by dissolving 2.5 grams of reagent in water and diluting to a volume of 100 ml.

The STPB solution was standardized with a standard potassium solution prepared as follows: An accurately weighed amount of KCl (2.5 g) was dissolved in water in a 250 ml volumetric flask and 50 ml of 4% ammonium oxalate solution were added. This was diluted to volume and mixed. To carry out the standardization, 5 ml of the standard KCl solution was transferred to a 100 ml volumetric flask; and 2 ml of 20% NaOH, 5 ml of 37% formaldehyde, and 15 ml of STPB were added in order. The mixture was diluted to volume with water, mixed, and allowed to stand for 10 minutes. After passing through a dry filter, a 50 ml aliquot of the filtrate was transferred to a 125 ml Erlenmeyer flask, 0.5 ml of bromophenol blue indicator was added, and the excess of reagent was titrated with CTAB solution.

An additional procedure was required to standardize the CTAB solution against the STPB solution. This was done by transferring 2 ml of STPB solution, 20 ml of distilled water, 1 ml of 20% NaOH, 2.5 ml of formaldehyde, and 0.5 ml of bromophenol blue indicator to a 125-ml Erlenmeyer flask and titrating with CTAB to the blue end point. The following calculations were made:

$$\text{Molarity of KCl Solution} = \frac{\text{Weight of KCl in I liter}}{\text{Molecular Weight of KCl}}$$

$$\frac{\text{Molarity of CTAB}}{\text{Molarity of STPB}} = \frac{2(\text{ml of STPB used to standardize CTAB})}{X(\text{ml of CTAB used to back titrate the 2 ml of STPB})}$$

ml of STPB used to precipitate K^+ in standard KCl solution = ml of STPB added - ml of CTAB to back titrate x $\frac{\text{molarity of CTAB}}{\text{molarity of STPB}}$.

$$\text{Molarity of STPB} = \frac{\text{ml of KCl solution used in STPB standardization} \times \text{molarity of KCl solution}}{\text{ml of STPB used for } K^+ \text{ precipitation}}$$

Determination of the potassium content in the smoke solutions was done as follows: 25 ml of smoke solution was transferred to a 250 ml volumetric flask, and 50 ml of 4% ammonium oxalate were added. After boiling for 30 minutes, the solution was made alkaline to a pH of approximately 8 by addition of NH_4OH. The solution was cooled, diluted to volume with water, mixed, and passed through a dry filter. 15 ml of the clear filtrate were transferred to a 50-ml volumetric flask to which were added 2 ml of 20% NaOH, 5 ml of 37% formaldehyde, and 5 ml of STPB. The solution was diluted to volume with water, mixed, allowed to stand for 10 minutes, and then passed through a dry filter. 25 ml of the filtrate was transferred to a 125-ml Erlenmeyer flask, 0.5 ml of bromophenol blue indicator added, and the excess of STPB was titrated with CTAB.

The ml of STPB used to precipitate the K^+ ions in the smoke solution was calculated in the same manner indicated above for calculating the ml STPB used in precipitating K^+ in the standard KCl solution. Note that the ml of STPB "added" is 2.5 ml if one works with a 25 ml aliquot, as indicated above, from the 50-ml volumetric to which 5 ml of STPB had been added. The percent K in the sample was calculated as follows:

$$\%K = \frac{\text{ml of STPB used} \times \text{molarity of STPB} \times 39.10}{1000 \times \text{dilution of aliquot tested} \times \text{weight of sample}}$$

6. DETERMINATION OF SULPHUR IN SMOKE SOLUTION

It was assumed that sulphur was present in the solutions as SO_4^{--}, and the sulfate concentration was determined as follows: A 30 ml aliquot of smoke solution was heated to 80-90°C. A barium chloride solution, prepared by dissolving 5 grams of $BaCl_2 \cdot 2H_2O$ in 100 ml of water, was added dropwise. If a white precipitate formed, a slight excess of $BaCl_2$ solution was added, and the whole was digested for about a half hour. The precipitate was then filtered and thoroughly washed. The filter paper was burned slowly at low temperature with free access of air. The product was weighed as $BaSO_4$.

7. DETERMINATION OF BARIUM IN SMOKE SOLUTION

A 30-ml aliquot of smoke solution was heated to 80-90°C, and dilute sulfuric acid was added dropwise. If a precipitate formed, it was treated exactly as described above for the determination of sulphur.