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Part A: Studies of Organic Solvent Enhancements in Flame Photometry; Part B: Studies of the Extraction and Flame Emission of Magnesium

Jack Hudgens Knox
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To the Graduate Council:

I am submitting herewith a dissertation written by Jack Hudgens Knox entitled "Part A: Studies of Organic Solvent Enhancements in Flame Photometry; Part B: Studies of the Extraction and Flame Emission of Magnesium." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

John A. Dean, Major Professor

We have read this dissertation and recommend its acceptance:

H. Johnson, J. Robertson

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

May 27, 1960

To the Graduate Council:

I am submitting herewith a thesis written by Jack Hudgens Knox, Jr., entitled "Part A: Studies of Organic Solvent Enhancements in Flame Photometry; Part B: Studies of the Extraction and Flame Emission of Magnesium." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

John A. Dean
Major Professor

We have read this thesis and
recommend its acceptance:

Hilton A. Smith

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Accepted for the Council:

Lab. Vanthine
Dean of the Graduate School

PART A: STUDIES OF ORGANIC SOLVENT ENHANCEMENTS IN FLAME PHOTOMETRY

PART B: STUDIES OF THE EXTRACTION AND FLAME EMISSION OF MAGNESIUM

A Thesis

Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Jack Hudgens Knox, Jr.

June 1960

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PART A

STUDIES OF ORGANIC SOLVENT ENHANCEMENTS IN FLAME PHOTOMETRY

CHAPTER I

INTRODUCTION

A. Historical Introduction

Flame photometry is gradually becoming accepted as a convenient and sensitive method for the determination of a large number of elements. The method is rapid and offers good accuracy and precision in the parts-per-million range of concentration.

In many respects flame photometry is closely related to emission spectroscopy, both in theory and in practice. The development of spectroscopy began early in the Nineteenth Century, but it was not until the classic studies by Lundegardh¹ that the attention and interest of chemists were drawn to the advantages of flame excitation for quantitative analysis. In the Lundegardh method, an air-acetylene flame is employed as the excitation source and the test element solution is introduced into the flame by means of a spray-chamber type of atomizer. Conventional spectrographic techniques are used to isolate and to measure the intensity of the emitted radiation.

Direct-reading, filter flame photometers have been in use for a number of years. They are designed principally for the determination of the alkali and alkaline earth elements whose emission intensities are quite high. Conventional phototubes or photocells are suitable for the measurement of radiant energy emitted by these elements. However, until the advent of the photomultiplier tube, the flame-photometric technique could not be extended to the less strongly emitting elements in the periodic table. The use of the photomultiplier tube in conjunction with a strip chart recorder permits the direct recording of the flame spectra.

B. Fundamental Principles

The interaction of electromagnetic radiation with atoms and molecules has yielded a major portion of the present knowledge of atomic and molecular structure. Many different types of interactions are encountered. These range from the high energy changes in nuclear structure with the accompanying gamma radiation to the nuclear momentum phenomena encountered in the radio-frequency range of the spectrum. The region of the spectrum of interest in flame photometry extends from the far ultraviolet to the near infrared. In this region, the spectra arise from the energy associated with transitions among the outer valency electrons of atoms or molecules.

Two types of spectra are employed for flame-photometric determinations. Line spectra originate when an excited electron from an upper energy level of a neutral atom or a singly ionized atom falls back to a lower energy level or to the ground state. Band spectra arise from electronic transitions involving molecules, such as the alkaline earth hydroxides (e.g., CaOH). The vibrational and rotational energy change at the same time, and these cause the emitted radiation to be spread over a portion of the spectrum rather than appearing as a discrete line. Continuous radiation is also emitted from atoms and molecules in the burned flame gases. The continuum may increase considerably the flame background over a considerable range of wavelengths.

The flame-photometric process is composed of the following rapid sequence of events:

1. The solution of the test element is dispersed into a fine spray or mist and the aerosol is uniformly introduced into the flame.
2. The energy of the flame vaporizes the solvent leaving minute particles of dry salt.
3. The dry salt is vaporized and part or all of the gaseous molecules are progressively dissociated.
4. Some of the metal atoms unite with other radicals or atoms present in the flame gases.
5. The vapors of the atoms, or of the molecular species containing the metal atom, are excited by the thermal energy of the flame. Ionization may occur to some degree.
6. The excited atoms, ions, or molecules revert to lower energy levels with accompanying emission of light.

C. Use of Organic Solvents

The introduction of an organic aerosol in place of an aqueous aerosol is becoming an important technique in flame photometry. The emission intensity of the test element may be enhanced markedly and variations in the physical properties of the aspirated solutions are minimized. Beck,² Beverly,³ Fink,⁴ Lady,⁵ and Vukanovic⁶ have studied some of the factors which influence the intensification of emission readings, and Dean⁷ has summarized the present position of organic solvents in flame-photometric applications.

A number of alcohols and ketones have been used as diluents in flame photometry. Alcohols and ketones of low molecular weight are particularly effective and increase the emission sensitivity 3- to 7-fold. Concurrently,

this technique lowers the concentration of potential interferences. Typical examples of water-organic-solvent mixtures include the use of water-methanol solutions for the determination of boron by Dean and Thompson,⁸ of lanthanum by Menis, Rains, and Dean,⁹ of magnesium by Manna, Strunk, and Adams,¹⁰ and of sodium, potassium, and calcium in blood serum,^{4,11,12,13} and in water samples.¹⁴

Selective extraction methods are a powerful tool for accomplishing analytical separations,¹⁵ but only recently has this technique been exploited in flame photometry. After the partition step, the organic phase is aspirated directly into the flame. The introduction of an organic aerosol produces a flame considerably larger in size and increases the emission of metals many-fold. A selective extraction removes the test element from the matrix material and reagents that are added in the dissolution and preparation of the sample for analysis. In this laboratory, solvent-extraction methods have been developed for the determination of aluminum,¹⁶ chromium,¹⁷ copper,¹⁸ copper, manganese, and nickel successively,¹⁹ iron,²⁰ lanthanum,²¹ magnesium,²² and yttrium.²³ Gasoline samples, diluted with isooctane, are sprayed directly into a flame for the determination of lead²⁴ and of manganese.²⁵

The important role of the solvent in flame photometry is clearly emphasized by the data in Table I, a listing of the enhancements which have been reported for a number of elements. The data illustrate the striking enhancements which are achieved when organic solvents are substituted for aqueous solutions. Aluminum and chromium could not have been determined with sufficient sensitivity in aqueous solutions.

TABLE I
TABLE OF ENHANCEMENT VALUES FOR SOME ORGANIC SOLVENTS

Element	Wavelength, μ	Solvent	Enhancement	Reference
Al	396.2	MIBK ^a	100-fold	16
B	518	95% MeOH	17	8
Cr	425.4	MIBK ^a	50	17
Cu	324.7	CHCl ₃	10	5
Fe	372.0	MIBK ^a	20	3
La	560	MIBK ^a	10	21
Mg	285.2	MIBK ^a	10	22
Mn	403.4	MIBK ^a	10	3

^aMIBK = 4-methyl-2-pentanone.

D. Factors Influencing Intensification of Emission Readings

1. Flame Temperature

The temperature of the excitation source is one of the most important parameters which must be considered in any study of emission phenomena. Ionization and excitation of atoms, and the formation and dissociation of hydroxides, oxides, and other molecular species, which are often present when a quantity of metal is introduced into a flame, are all temperature dependent.

The emission intensity of a line or a band is proportional to the number of atoms or molecules which are raised to an excited state. Upon reversion to a lower energy level, energy is emitted and a line or a band appears in emission. The number of atoms in an excited energy level, N^* , is proportional to the number of atoms on the ground state, N_0 , by the relation

$$I = cN^* = aN_0 e^{\frac{-E}{kT}} \quad (1)$$

where I is the intensity of the line or band, E is the excitation energy, k is the Boltzmann constant, T is the absolute temperature, and a and c are constants of proportionality. A similar expression pertains to dissociation equilibria.

At the high temperature of the flame, a significant fraction of the metal atoms that are introduced may be ionized. For the reaction $M \rightleftharpoons M^+ + e$, the fraction of metal ionized is given by the Saha equation,²⁶

$$\log \frac{x^2 P}{1-x^2} = \frac{-5040 V_i}{T} + \frac{5}{2} \log T - B \quad (2)$$

where x is the fraction of metal ionized, P is the partial pressure of metal atoms in all forms in the burned gases, V_i is the ionization potential in

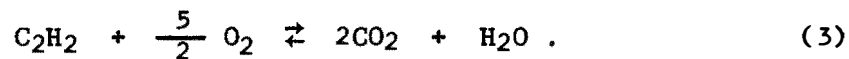
electron volts, T is the absolute temperature in degrees Kelvin, and B is a constant.

The theoretical flame temperature for various fuels range from the city gas-air flame with a temperature of 1700° Centigrade to the cyanogen-oxygen flame with a temperature of 4850° Kelvin. Lower temperature flames are useful only for strongly emitting elements such as the alkali and alkaline earth metals. For the less strongly emitting elements, hydrogen-oxygen and acetylene-oxygen flames with temperatures of 2780° and 3350° Centigrade, respectively, are commonly employed in flame photometry.

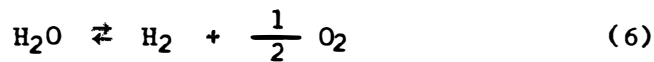
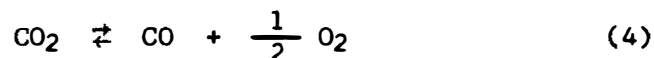
The temperatures mentioned are for "dry" flames in which the only components are the burned flame gases. The flame temperature changes when a solution of the test element is introduced; the degree of change depends upon the amount and type of solvent that is introduced. Enhancements achieved with organic solvents have been ascribed to an increase in the temperature of the flame when an organic aerosol is introduced into the flame in place of water.^{3,5,6}

2. Determination of Flame Temperatures

The stoichiometric reaction of acetylene burning in oxygen may be written as



At the high temperature of the flame, the reaction products dissociate



and molecular hydrogen and oxygen are in equilibrium with atomic hydrogen

and oxygen



Introduction of an aqueous or organic aerosol will alter the composition of the burned gases. An aqueous aerosol abstracts a significant portion of the energy liberated by the flame in order to raise the water to the temperature of the flame and to dissociate the water into its equilibrium products.

Since an organic aerosol also burns, the fuel oxygen ratio must be adjusted in order to supply additional oxygen for the combustion of the solvent. The combustion of the organic aerosol supplies some energy to the flame. However, the additional energy may not be sufficient to raise the combustion products of the aerosol to the temperature of the "dry" flame and to dissociate them into the equilibrium species. Hence, the organic aerosol may also abstract some energy from the flame but, because of the combustion of the aerosol, the amount abstracted is less than for a corresponding quantity of water.

Unfortunately, the measurement of a temperature as high as that of the flame gases does not yield the precision and accuracy which a number of physical measurements yield. Flame-temperature measurements are rendered even more difficult because of the large temperature gradients which are encountered, particularly with the small flame of an integral-aspirator burner.

Several different techniques are used for the determination of flame temperature. Among the most common are the spectrum-line reversal method, optical pyrometry, OH-intensity method, and adiabatic temperature calculations.

a. The spectrum-line reversal method. The spectrum-line reversal method employs a bright background source which is focused on a point within the flame. A small quantity of metal, generally sodium as sodium chloride, is introduced and the spectra line is observed. If the temperature of the flame is higher than the background source, the sodium line will be seen in emission. If the temperature of the background source is higher than the temperature of the flame, the line will be seen in absorption. When the line is seen neither in emission nor in absorption, the temperatures of the background source and the flame are equal. The method is not easily applied with the equipment ordinarily available in an analytical laboratory, and corrections must be made for loss of intensity as the light passes through the lenses and for self-absorption of the sodium line.

b. Optical pyrometry. A common method for the direct measurement of the temperature of flames is optical pyrometry. An optical pyrometer is an instrument which compares the brightness temperature of the flame with that of a source. The source is generally a tungsten filament lamp. When the temperatures of the filament and the flame are equal, and each is a perfect black-body radiator, each will have the same brightness. Since neither the source nor the flame is a perfect black-body radiator, corrections must be applied.

c. Calculation of flame temperature. The mathematical calculations of flame temperature have been described by Gaydon and Wolfhard²⁷ and an example has been included in Beverly's thesis.³ The method involves the calculation of the equilibrium composition of flame gases at a given

temperature. The heat content of the burned gases and the energy liberated when the reactants burn to produce the equilibrium products is also calculated. At the adiabatic flame temperature, the energy of the combustion will be equal to the energy required to heat the combustion products to the assumed temperature of the burned gases. Illustrative calculations are included in the "Experimental" section.

d. OH band intensity measurements. The burned gases from hydrocarbon fuels or from hydrogen burning in air or oxygen contain large quantities of OH radicals. This molecular specie exhibits three prominent groups of emission bands between 280 and 295, 306 and 320, and 340 to 348 μ . The OH bands constitute a severe spectral interference in the determination of any element whose emission line occurs in the same region of the spectrum. For example, the 285.2- μ line of magnesium is situated in the midst of the series of OH bands extending from 280 to 295 μ (Figure 21).

Gaydon and Wolfhard²⁷ and Gaydon²⁸ have discussed the use of intensity of the OH bands for the determination of flame temperature, and the recent work of Beck² and Foster and Hume²⁹ suggested the possibility of the measurement of the flame temperature by the OH intensity method. Beck correlated the temperatures measured with an optical pyrometer to the OH band intensity. He placed a zirconium oxide rod in the flame and measured the brightness temperature of the rod with an optical pyrometer. Both he, and Foster and Hume, showed that the OH band intensity decreased with an increase in the sample flow rate. Foster and Hume worked with aqueous solutions whereas Beck studied aqueous and organic solvents. The latter proceeded also to relate the emission intensity

of the OH band to the aspiration rate of the organic solvent.

One facet of the present investigation was to compare the enhancements of organic solvents with the emission intensity of the OH band intensity and to determine whether a relationship existed.

3. Aspiration Rate or Sample Flow Rate

The rate at which the sample solution is introduced into the flame is extremely significant. It controls the rate at which both the solvent and the test element are introduced.

In an integral-aspirator type of burner, the solution capillary is concentric with the oxygen annulus. As the oxygen flows out of the annulus and into the flame, liquid is drawn up the capillary and is dispersed into a very fine aerosol. The flow of the aspirating gas (oxygen) is the primary variable that controls the sample flow rate, except when viscosity effects are significant. The fuel flow rate has no effect in the case of acetylene gas and very little effect in the case of hydrogen gas.

The discussion of flame temperature pointed out that the introduction of the test element solution abstracts a quantity of energy from burned flame gases and a temperature lower than that of the dry flame is the result. Actually the flame temperature decreases as the sample flow rate increases.^{29,30}

If the emission intensity of the test element is plotted against the sample flow rate, a relationship that is shown in Figure 11 is observed. This relationship is the function of two temperature-dependent factors: the excitation factor and the ionization factor.

Equation (1) illustrated the relationship between the temperature and the fraction of atoms excited to emit radiant energy. At higher sample flow rates, the temperature of the flame will be decreased and, thus, a smaller fraction of the test element atoms will be elevated to an excited state. The effect of the temperature upon the fraction of atoms ionized is shown by Equation (2). Again a smaller fraction of the test element atoms will be ionized at the lower temperatures that correspond to the higher sample flow rate.

The initial increase in the emission intensity observed with larger sample flow rate is caused by a larger number of atoms of the test element passing through the area of observation per unit of time. After the maximum is reached, the decrease in emission intensity arises from the decreased flame temperature. The position of the maximum is also a function of the ionization potential of the test element. An emission line from an element which has a low ionization potential will exhibit a maximum at a higher sample flow rate.

Previous studies of the emission intensity as a function of sample flow rate have been done utilizing an aqueous aerosol and either a hydrogen-oxygen flame²⁹ or a cyanogen-oxygen flame.³¹ Lady⁵ also studied the effect of sample flow rate upon the emission intensity with different organic solvents, but he adjusted the fuel-oxygen ratio in order to introduce additional oxygen so that it would be sufficient for the stoichiometric combustion of the organic aerosol. Baker, Fuwa, Thiers, and Vallee³¹ showed that the optimum value of the sample flow rate for an aqueous solution was a smaller value for the higher-temperature cyanogen-oxygen flame than for the lower-temperature hydrogen-oxygen flame.

E. Statement of the Problem

The present investigation was designed to study the relationship of several parameters upon the flame-photometric emission of elements in an effort to elucidate the nature of the enhancements observed when an element is present in a solution of an organic solvent. Included are the calculations of flame temperature, measurement of OH band intensities, measurement of emission intensity as a function of sample flow rate, and the measurement of the emission intensities of several elements in different flames and solvent systems.

CHAPTER II

APPARATUS AND REAGENTS

A. Apparatus

1. Flame Spectrophotometer

A Beckman Model DU spectrophotometer with a Model 9200 flame attachment and Model 4304 photomultiplier attachment was used. The output of the photomultiplier was fed into a Bristol recorder by means of a Beckman Model 5800 recording adapter. The recorder had a 10 mv. full-scale response and the pen speed was $\frac{2}{3}$ of a second. The chart was driven at a speed of 4 inches per minute. A wavelength drive permitted the wavelength knob in the spectrophotometer to be rotated at a speed of approximately 0.12 revolutions per minute. A 10.5-to-1 gear reduction knob was also attached so that the wavelength knob could be more accurately positioned manually.

The excitation source for hydrogen-oxygen flames was a Model 4020 integral aspirator type burner and a Model 4030 burner was used for acetylene-oxygen. The condensing mirror was blocked.

2. Rotameters

Two Brooks Sho-Rate "150" Model 1356 rotameters were used for the measurement of the flow of the flame gases. Tube number 3-15-4 was used to monitor the oxygen flow and tube number 4-15-2 was used to monitor the fuel flow. These were calibrated by the use of a Precision Wet Test Meter.

3. Precision Wet Test Meter

The Precision Wet Test Meter was used for the calibration of the gas flow rates. The end of the burner capillary was closed off by a cork.

4. Sample Flow Rate Assembly

A weighing bottle was closed with a tight-fitting rubber stopper. The capillary of the aspirator, the microburet, outlet to the pressure system, and the syringe containing additional solution were placed in the stopper. The weighing bottle was desiccated to prevent the solution from adhering to the sides of the bottle as the level fell. A vacuum pump was used to reduce the pressure over the liquid and the increased pressure was obtained with a tank of nitrogen. A ballast tank was connected into the system in order to reduce pressure fluctuations. The pressure was measured with a U-tube manometer filled with 1,1,2,2-tetrabromoethane.

B. Reagents

1. Demineralized Water

Demineralized water was used in the preparation of all solutions. This was prepared by passing ordinary distilled water through Amberlite MB-3 resin.

2. Methanol

Reagent grade methanol was used.

3. Ethanol

Both absolute and drum grade 95 per cent ethanol were used.

4. 4-Methyl-2-pentanone

Practical grade 4-methyl-2-pentanone was used without further purification.

5. 2-Octanol

Practical grade 2-octanol was used without further purification.

6. 2-Octanone

Practical grade 2-octanone was used without further purification.

7. 2,4-Pentanedione

Practical grade 2,4-pentanedione was used without further purification.

8. Aluminum Solutions

A solution of aluminum containing 1000 $\mu\text{g.}$ of aluminum per ml. was prepared by dissolving 0.4942 g. of anhydrous aluminum chloride in 100 ml. of methanol. A solution in 4-methyl-2-pentanone containing 1000 $\mu\text{g.}$ of aluminum per ml. was prepared by dissolving 0.4942 g. of anhydrous aluminum chloride in 20 ml. of 95 per cent ethanol and diluting to 100 ml. with 4-methyl-2-pentanone.

9. Lithium Solutions

A stock solution of lithium containing 1000 $\mu\text{g.}$ of lithium per ml. was prepared by dissolving 4.6096 g. of lithium sulfate mono-hydrate in 500 ml. of water. Lithium solutions containing 100 $\mu\text{g.}$ per ml. and 10 $\mu\text{g.}$ per ml. of lithium were prepared by appropriate dilution. A lithium solution containing 100 $\mu\text{g.}$ of lithium per ml. was prepared by dissolving 0.0611 g.

of lithium chloride in 100 ml. of absolute ethanol.

10. Solution of Lithium and Cesium

A solution containing 10 $\mu\text{g.}$ per ml. of lithium and 1000 $\mu\text{g.}$ per ml. of cesium was prepared by taking 10 ml. of lithium solution containing 100 $\mu\text{g.}$ per ml. and 10 ml. of a solution containing 10,000 $\mu\text{g.}$ per ml. of cesium and diluting to 100 ml. The cesium solution was prepared by dissolving 12.668 g. of cesium chloride in 1 l. of water.

11. Copper Solutions

A solution of copper in methanol containing 1000 $\mu\text{g.}$ of copper per ml. was prepared by dissolving 0.2116 g. of cupric chloride in 100 ml. of methanol. A 100 $\mu\text{g.}$ per ml. solution of copper in methanol was prepared by diluting 10 ml. of the 1000 $\mu\text{g.}$ per ml. solution to 100 ml. with methanol. A 100 $\mu\text{g.}$ per ml. solution of copper in methanol-toluene was prepared by diluting 10 ml. of the 1000 $\mu\text{g.}$ per ml. methanol solution to 100 ml. with toluene.

12. Chromium Solutions

A chromium solution containing 1000 $\mu\text{g.}$ per ml. of chromium was prepared by dissolving 0.3054 g. of chromic chloride in 100 ml. of methanol. Ten ml. of this solution was diluted to 100 ml. with methanol to give a solution containing 100 $\mu\text{g.}$ per ml. of chromium. A 100 $\mu\text{g.}$ per ml. solution in methanol-toluene was prepared by diluting 100 ml. of the 1000 $\mu\text{g.}$ per ml. methanol solution to 100 ml. with toluene.

13. Toluene

Reagent grade toluene was used in the preparation of all solutions.

CHAPTER III

EXPERIMENTAL RESULTS

A. Calculation of Flame Temperatures

1. Method of Calculation

Equations (9) to (13) represent the equilibrium constants for the dissociations and decompositions occurring in the flame gases.

$$K_1 = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} \quad (9)$$

$$K_2 = \frac{P_{H_2} \times P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \quad (10)$$

$$K_3 = \frac{P_{OH} \times P_{H_2}^{\frac{1}{2}}}{P_{H_2O}} \quad (11)$$

$$K_4 = \frac{P_H}{P_{H_2}^{\frac{1}{2}}} \quad (12)$$

$$K_5 = \frac{P_O}{P_{O_2}^{\frac{1}{2}}} \quad (13)$$

The total pressure of the products must equal the prevailing atmospheric pressure, and the ratios of n_C/n_H and n_O/n_H must be in agreement. To obtain the equilibrium composition, the system must be solved by the method of successive approximations.

The following system is used as an example of these calculations. An aerosol of absolute ethanol was introduced into an acetylene-oxygen

flame at the rate of 1.15 milliliters per minute. The flow rates of acetylene and oxygen were 1.34 and 3.32 liters per minute, respectively. From these quantities, the number of gram atoms of carbon, hydrogen, and oxygen entering the flame each minute are 0.149, 0.228, and 0.292, respectively.

The equilibrium constants for the reactions numbered (9) to (13) are taken from Gaydon and Wolfhard²⁷ at a flame temperature of 3200°K. Values for the ratio of the partial pressure of carbon monoxide to carbon dioxide and for the partial pressure of water are assumed. The partial pressures of the components are then rewritten in terms of the assumed values for the ratio of carbon monoxide to carbon dioxide (R) and for the partial pressure of water (W):

$$P_{H_2} = 0.1267 RW \quad (14)$$

$$P_H = 0.1042 R^{\frac{1}{2}} W^{\frac{1}{2}} \quad (15)$$

$$P_{O_2} = \frac{0.420}{R^2} \quad (16)$$

$$P_O = \frac{0.162}{R} \quad (17)$$

$$P_{OH} = \frac{0.317 W^{\frac{1}{2}}}{R^{\frac{1}{2}}} \quad (18)$$

The rearranged expressions provide an insight into the manner in which the partial pressures of the other constituents in the burned gases vary with temperature. Whereas the ratio of carbon monoxide to carbon dioxide increases with temperature for the same ratios of components, the water pressure decreases.

The calculated composition of the burned gases for the example selected is given in Table II. The value assumed for the ratio of carbon

TABLE II
COMPOSITION OF BURNED GASES

Component	Partial Pressure, Atm.	Relative Number of Moles of Hydrogen	Relative Number of Moles of Oxygen
H ₂	0.0947	0.1894	
H	0.0903	0.0903	
O ₂	0.0276		0.0552
O	0.0416		0.0416
OH	0.0703	0.0703	0.0703
CO	0.3818		0.3818
CO ₂	0.0979		0.1958
H ₂ O	<u>0.1920</u>	<u>0.3840</u>	<u>0.1920</u>
	0.9962	0.7340	0.9367

monoxide to carbon dioxide was 3.90 and 0.192 atmospheres was the value assumed for the partial pressure of water.

To obtain a heat balance, the total mole number of the burned gases must be calculated. The total mole number is the apparent number of moles of burned gases that is produced in the combustion of 1 mole of acetylene. The partial pressures are proportional to the relative mole numbers of each component in the burned gases. To obtain the true mole number, the number of moles of hydrogen, carbon, or oxygen which is produced in the assumed reaction are divided by the appropriate number of moles obtained from the summation of the appropriate partial pressures of constituents containing the respective element. In the stoichiometric combustion of 1 mole of acetylene, 3 moles of gaseous products, assuming no dissociation, would be produced. The true mole number would be 3. The partial pressure of carbon dioxide would be 0.666 and of water, 0.333. The number of moles of carbon in the burned gases equals 2, the moles of hydrogen equals 2, and the moles of oxygen equals 5. The mole number calculated by the method employed is then

$$\frac{2}{P_{CO_2}} = \frac{2}{2P_{H_2O}} = \frac{5}{2P_{CO_2} + P_{H_2O}} = 3.00 \quad (19)$$

However, in the example under consideration, 1 mole of acetylene yielded 2 moles of carbon, 3.06 moles of hydrogen, and 3.92 moles of oxygen in the burned gases. When divided by the relative number of moles (calculated from the partial pressures which are shown in columns 3 and 4 of Table II), these values yield the true mole number of the burned gases for this system.

$$\frac{2}{0.4796} = \frac{3.06}{0.7340} = \frac{3.92}{0.9367} = 4.17 \quad (20)$$

The heat liberated by the combustion is calculated by multiplying the heat of formation of each product by its partial pressure, summing the heat liberated from all the products, and multiplying the sum by the mole number. Then the heat of formation of acetylene and the ratio of the number of moles of ethanol to 1 mole of acetylene multiplied by the heat of formation of ethanol are subtracted from the heat of formation of the products to obtain the net heat liberated (column 6 of Table III).

The heat required to raise the temperature of the combustion products to the assumed temperature is calculated from the total heat content of the components. Gaydon and Wolfhard²⁷ provide a list of heat contents which were obtained from several sources. These were plotted against temperature and interpolated values were obtained. The heat content of each individual component is multiplied by the partial pressure of that component and the sum is multiplied by the mole number to obtain the heat required to raise the burned gases to the assumed temperature (column 5 of Table III).

The calculations outlined are repeated at several temperatures and the flame temperature is determined from the point of intersection of the curve of heat liberated and of the curve of heat content (to raise the combustion products to the temperature) each versus temperature.

In the case of aqueous aerosols, a correction must be made in the calculation of the heat liberated by the combustion for the water added. It cannot be assumed that the heat liberated by the combustion is greater than if all the water resulted from the combustion of acetylene. If the number of moles of hydrogen present as water in the burned gases exceeds

TABLE III
ENERGY CALCULATIONS OF BURNED GASES

Component	Heat Content, 3200°K. kcal./mole	Heat of Formation, kcal./mole	Partial Pressure	Net Heat Content, kcal.	Net Heat of Formation, kcal.
H ₂	25.0		0.0947	2.37	
H	15.9	52.09	0.0903	1.49	4.70
O ₂	42.0		0.0276	1.17	
O	16.2	59.16	0.0416	0.66	2.36
OH	25.3	10	0.0703	1.78	0.70
CO	26.25	-26.42	0.3818	10.10	-10.10
CO ₂	42.0	-94.05	0.0979	4.11	-9.21
H ₂ O	35.3	-57.8	0.1920	<u>6.78</u>	<u>-11.10</u>
				28.37	-22.65

Heat required to raise the burned gases to 3200°K =

$$4.17 \times 28.37 = 118.2 \text{ kcal.}$$

Heat liberated in the combustion =

$$(4.17 \times -22.65) - (54.2 + 0.36 \times -66.2) = -125.4 \text{ kcal.}$$

TABLE IV

ILLUSTRATIVE CALCULATIONS FOR THE CORRECTION FOR ADDITIONAL WATER
FOR A FLAME FED BY A WATER AEROSOL

Component	Relative Number of Moles of Hydrogen ^a	Source	Moles of Hydrogen Added Per Minute
H ₂	0.1292	H ₂ O	0.1602
H	0.0745	C ₂ H ₂	<u>0.1096</u>
			0.2704
OH	0.1085		
H ₂ O	<u>0.4900</u>		
	0.8200		

Relative number of moles of hydrogen resulting from combustion =

$$0.8022 \times \frac{0.1096}{0.2704} = 0.325$$

From this, the net heat of formation of water in this system is

$$\frac{0.325}{2} \times -57.80 = -9.40 \text{ kcal.}$$

^aCalculated from partial pressures.

the number of moles of hydrogen that could be obtained from the acetylene, a correction is applied as illustrated in Table IV. On the other hand, if the number of moles of hydrogen present as H_2 , H, and OH in the burned gases equilibrium products is equal to or greater than the number of moles of hydrogen added as the aqueous aerosol, no correction need be applied because it may be assumed that all the water present originated from the combustion of the acetylene.

Water from all sources must be used in the calculation of the heat content since it must be raised to the temperature of the flame gases.

2. Flame Temperature Values

Flame temperature calculations have been made for several flames by the method discussed. The calculated values for the heat liberated and for the heat required to raise the combustion products to the assumed temperature have been plotted as a function of the assumed temperature. The temperature at which the heat liberated is equal to the heat required has been taken as the temperature of the burned flame gases.

The calculated values for flames of two different acetylene-oxygen ratios are shown in Figure 1. A flame composed of 1.34 l. per min. of acetylene and 3.32 l. per min. of oxygen gave a calculated flame temperature of 3317°K, whereas a temperature of 3365°K was obtained for a flame of the same oxygen flow but 1.83 l. per min. of acetylene.

The calculation of the temperature of flames composed of 1.34 l. per min. of acetylene and 3.32 l. per min. of oxygen and fed with water and ethanol aerosols has been made. The data for 1.00 ml. and 1.45 ml. of water per min. are shown in Figure 2, and 1.15 ml. of ethanol per min.

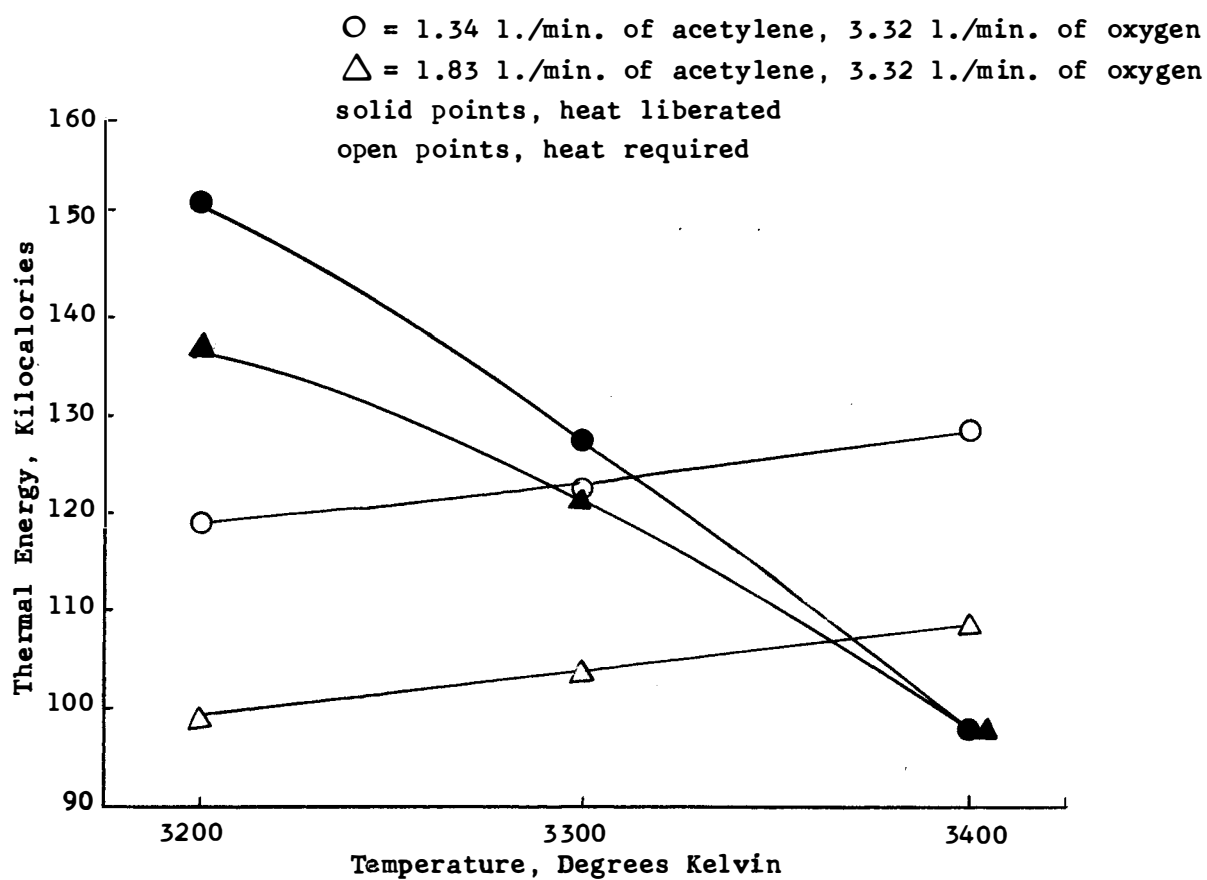


Figure 1. Heat liberated and heat required as a function of assumed temperature for dry acetylene-oxygen flames.

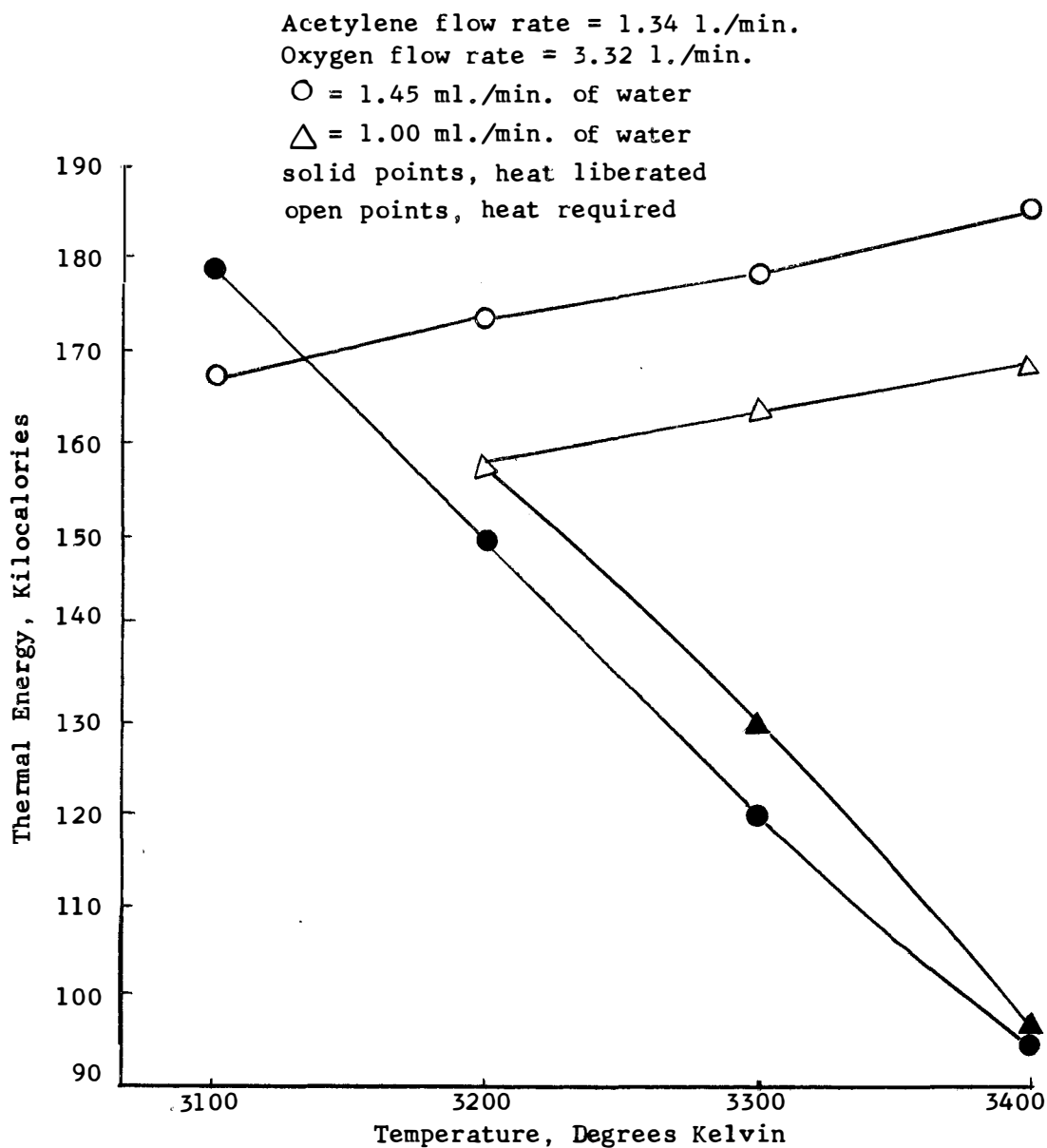


Figure 2. Heat liberated and heat required as a function of assumed temperature. Acetylene-oxygen flame plus water aerosols.

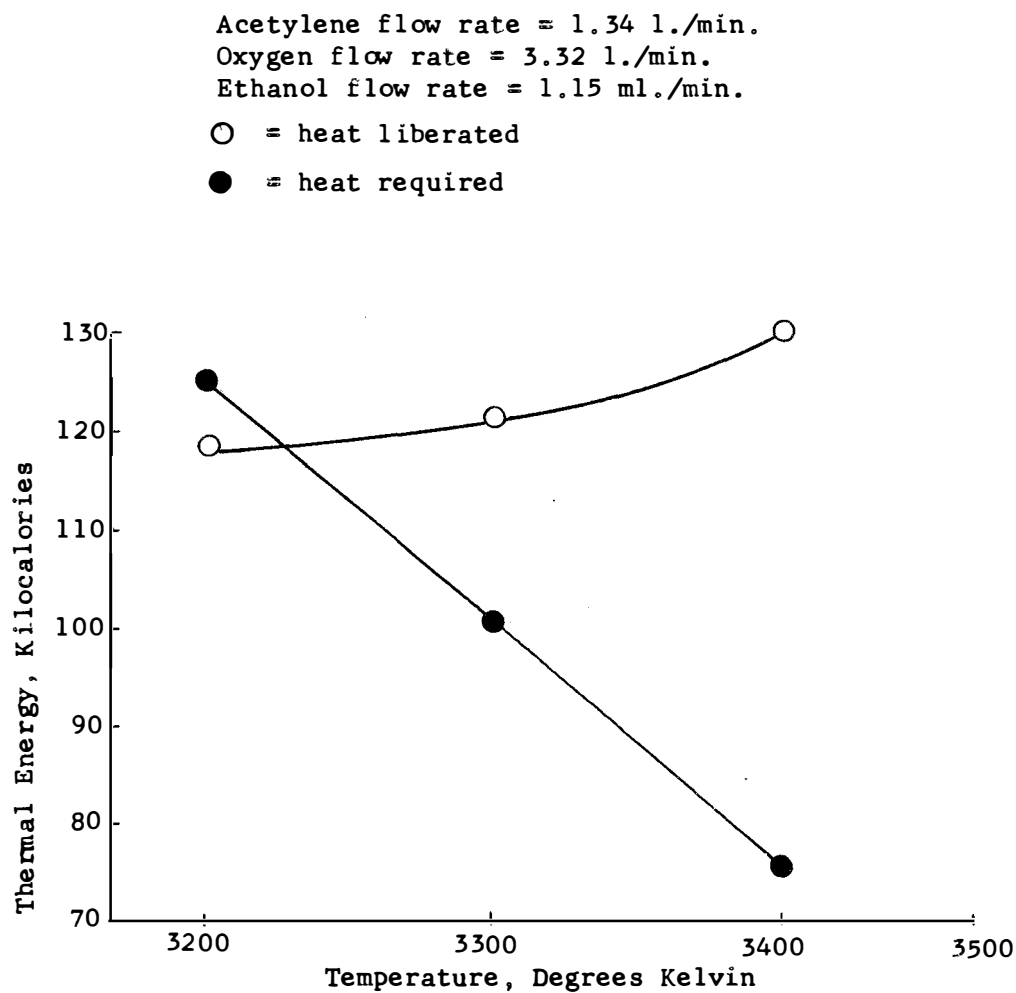


Figure 3. Plot of heat liberated and heat required as a function of assumed temperature. Acetylene-oxygen flame plus an ethanol aerosol.

is shown in Figure 3. The water-fed flames gave calculated temperatures of 3123°K for 1.45 ml. per min., and 3200°K for 1.00 ml. per min. The ethanol-fed flame gave a calculated temperature of 3223°K.

B. OH Band Intensity Measurements

1. OH Spectrum

The portion of the OH spectrum which extends from 305 to 310 μ is shown in Figure 4. The intensity measurements of the OH band, shown in Figures 5 through 9, were taken as the net reading of the peak at 306.7 μ diminished by the background reading taken at 305 μ . Although the 309.6- μ peak is slightly more intense than the 306.7- μ peak, the proximity of the 306.7- μ peak to the convenient background at 305 μ provided the reason for the choice of the 306.7- μ peak. No variation in the relative intensities of these two peaks detected as the flame conditions were varied.

2. Instrument Settings

The photomultiplier sensitivity was 52 volts per dynode for all OH band measurements. The slit width was 0.030 mm. for the intensity measurements shown in Figures 5 through 8. The burner was mounted in the normal position but the condensing mirror at the rear of the burner housing was blocked in order to eliminate any effects from the variation in the size of the flame. The "per cent adjust" knob on the recorder was set at 3.75 for the data in Figures 5, 6, and 7. A setting of 2.00 was used for the data shown in Figures 8 and 9. The data plotted in

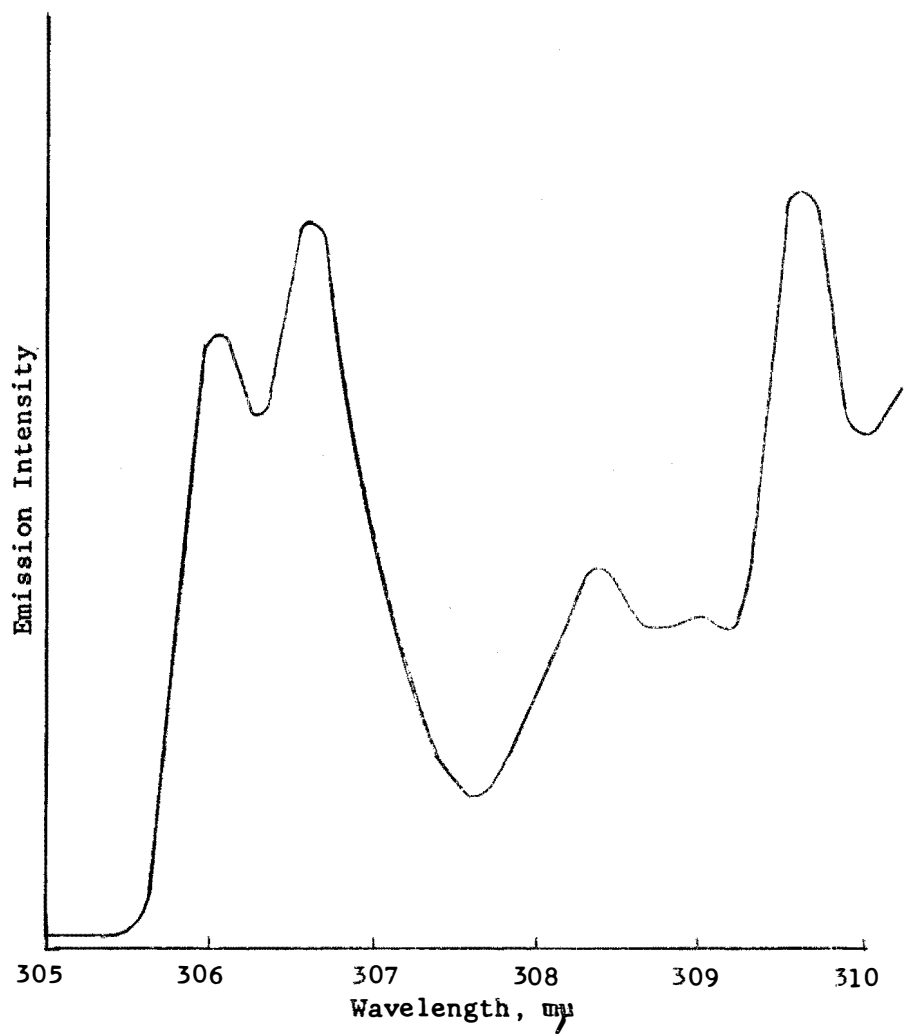


Figure 4. OH band spectrum.

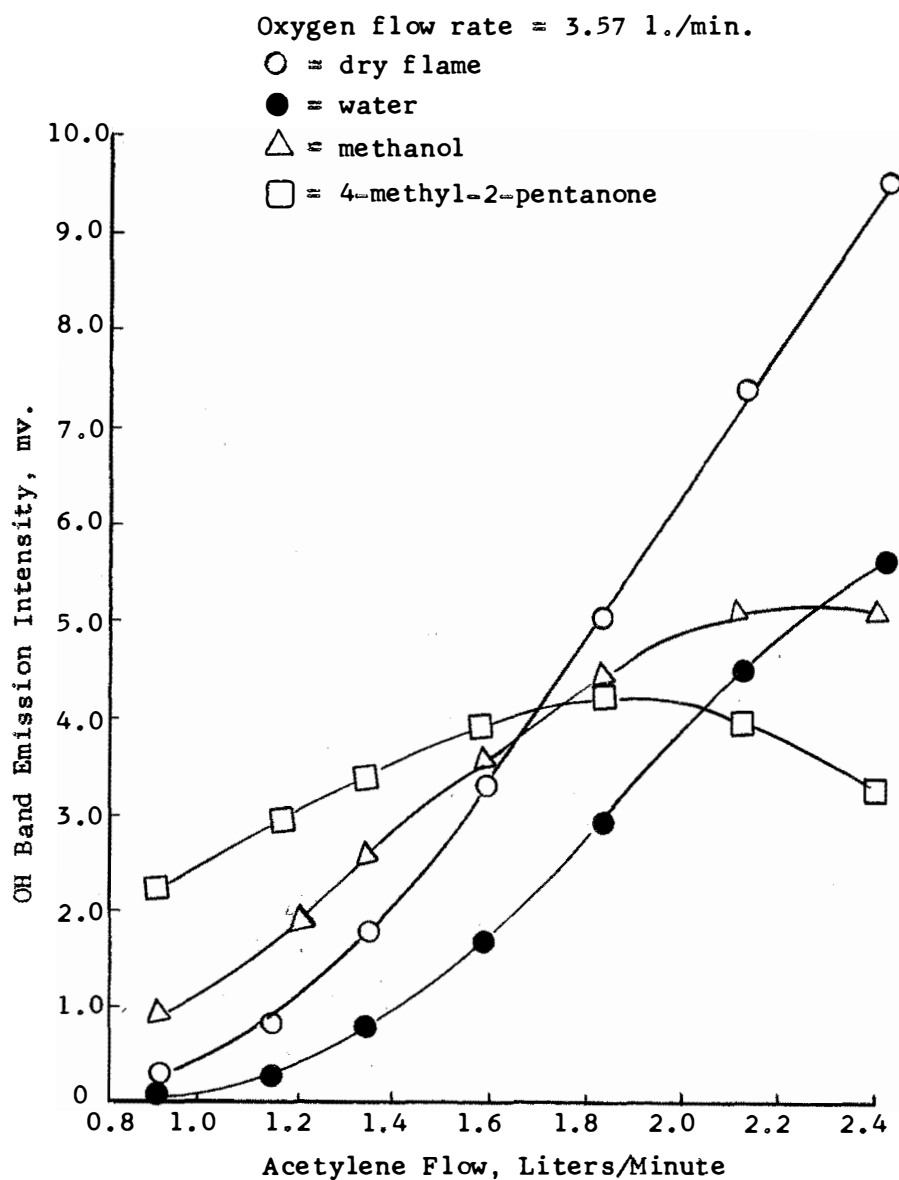


Figure 5. Emission intensity of 306.7- μ OH band as a function of acetylene flow rate.

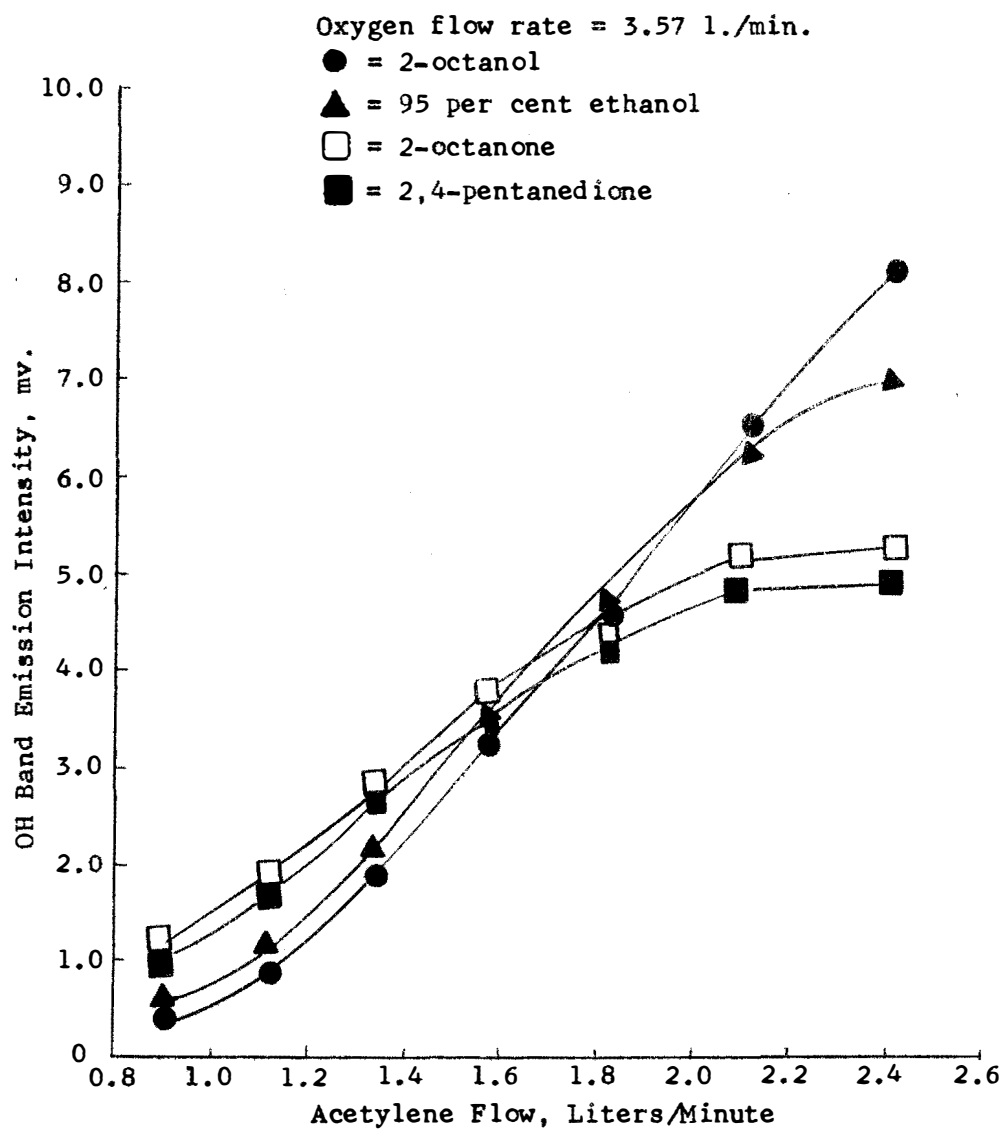


Figure 6. Emission intensity of 306.7- μ OH band as a function of acetylene flow rate.

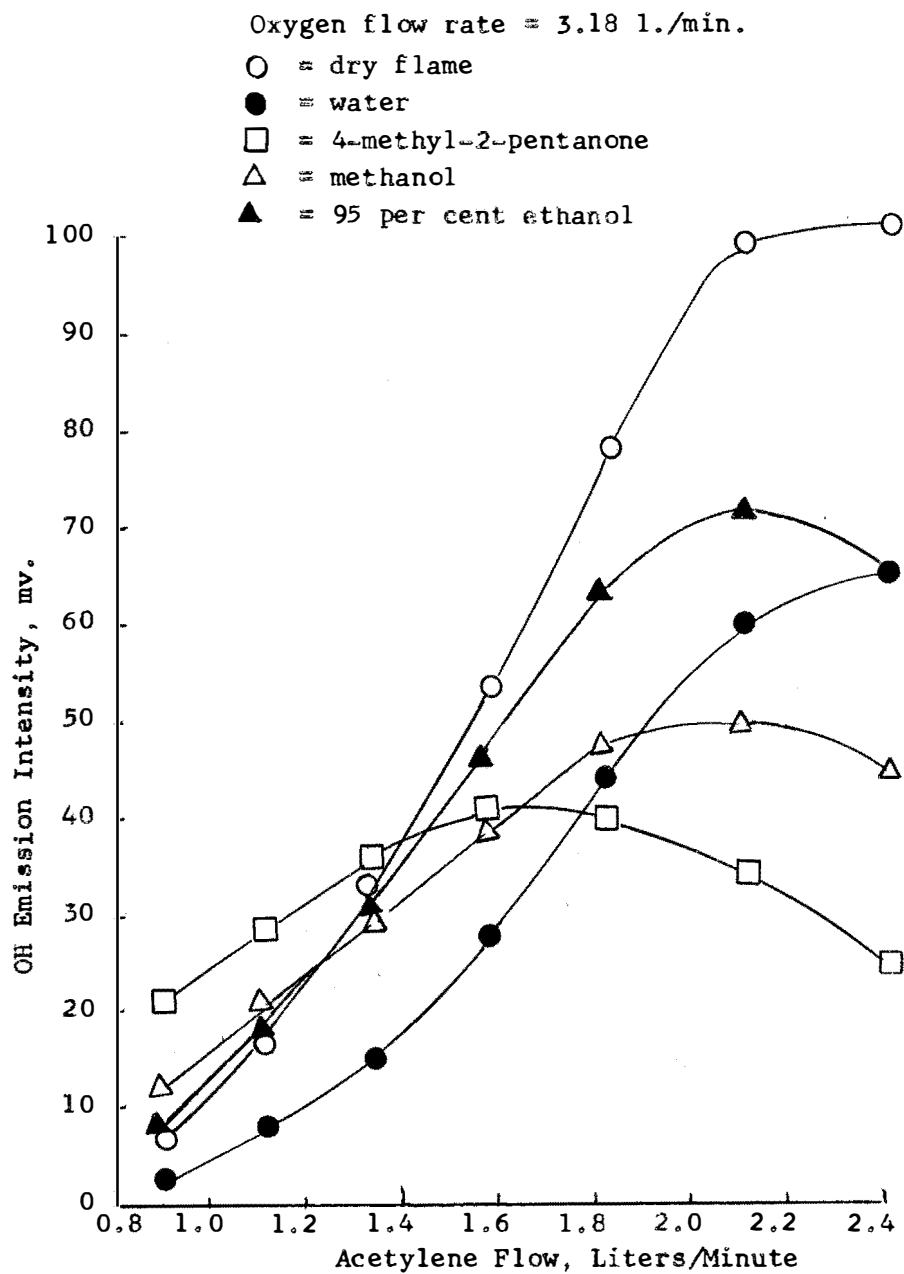


Figure 7. Emission intensity of 306.7- μ OH band as a function of acetylene flow rate.

Oxygen flow rate = 4.09 l./min.

34

○ = dry flame

● = water

□ = 4-methyl-2-pentanone

△ = methanol

▲ = 95 per cent ethanol

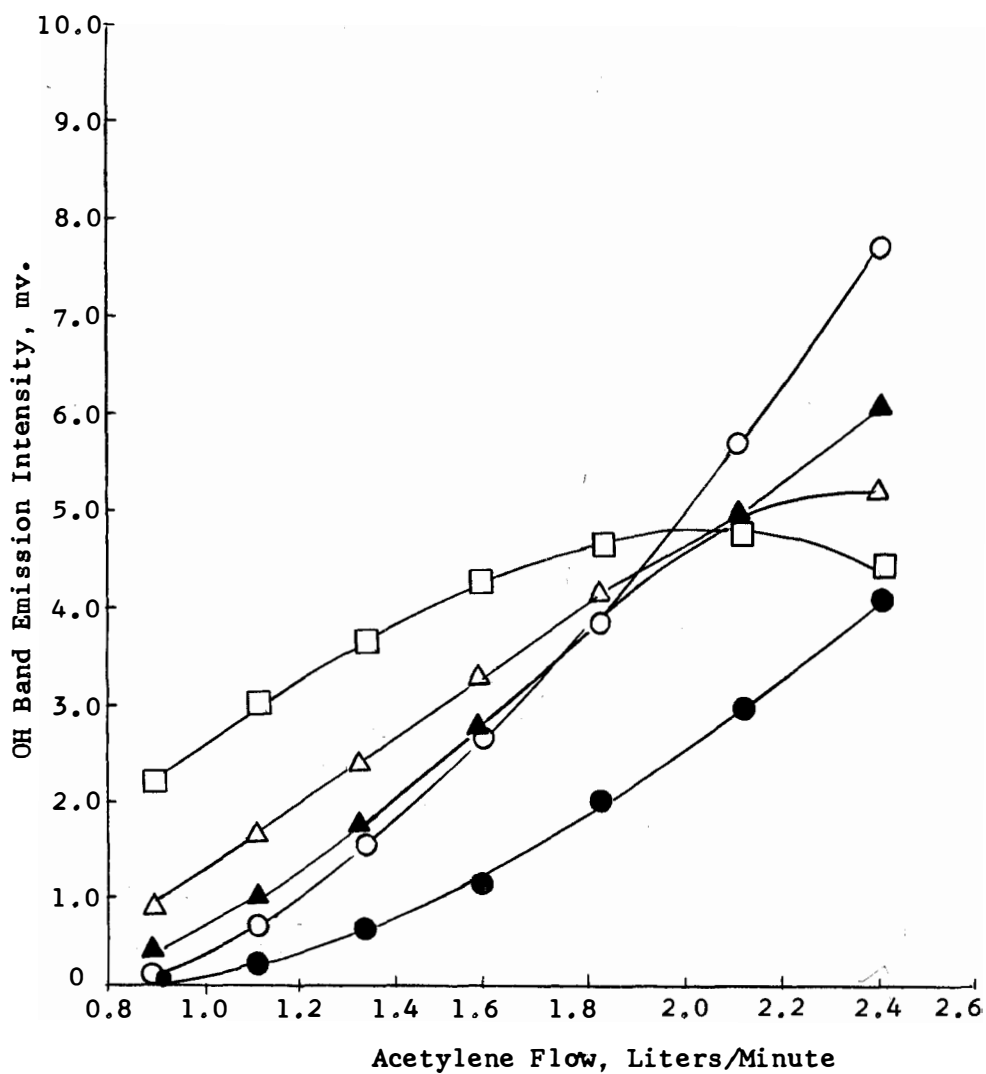


Figure 8. Emission intensity of 306.7- μ OH band as a function of acetylene flow rate.

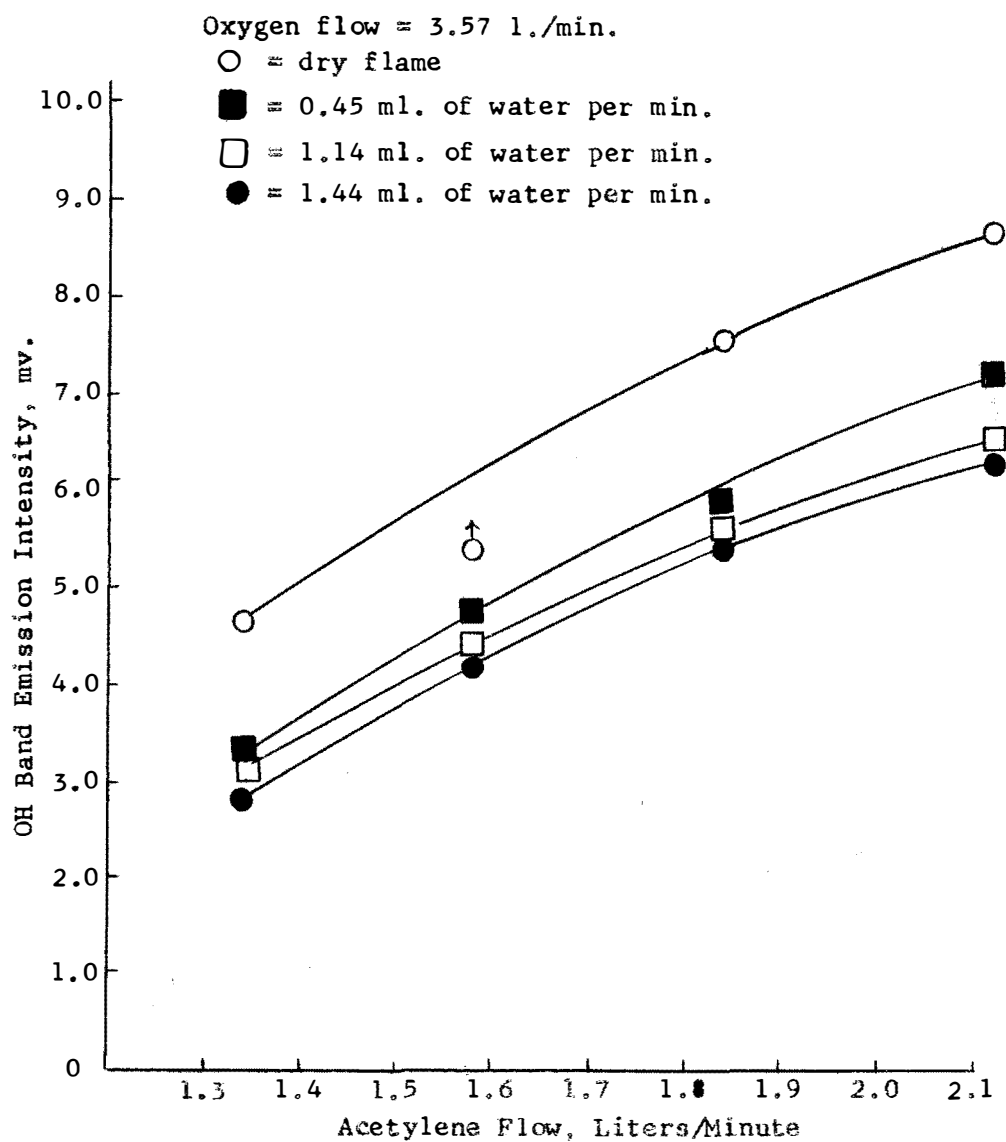


Figure 9. Emission intensity of 306.7- μ OH band as a function of acetylene flow rate at various sample flow rates of water.

Figure 8 has been adjusted so that the intensity measurements in Figures 5, 6, 7, and 8 fall on the same scale. The values plotted in Figure 9 were obtained with a slit width of 0.025 mm.

3. Systems Studied

The OH intensities which were measured in a dry flame and a flame into which water, ethanol, 4-methyl-2-pentanone, methanol, 2-octanol, 2-octanone, and 2,4-pentanedione were aspirated individually are shown in Figures 5 and 6. The acetylene flow was varied from 0.9 to 2.42 l. per min. while the oxygen flow was maintained at a constant value of 3.57 l. per min.

The OH intensities which were measured for a dry flame and a flame into which water, ethanol, 4-methyl-2-pentanone, and methanol were aspirated individually are shown in Figures 7 and 8. The acetylene flow was varied from 0.9 to 2.42 l. per min.; the oxygen flow was maintained constant at 3.18 l. per min. in Figure 7 and 4.09 l. per min. in Figure 8.

A plot of the OH band intensity as a function of acetylene flow at constant oxygen flow of 3.57 l. per min. for a dry flame and for a flame into which was aspirated 1.44, 1.14, and 0.45 ml. of water per min. is shown in Figure 9.

C. Measurement of Lithium and Cesium Intensity

1. Lithium Spectrum

The 671-~~nm~~ lithium line was used in these measurements.

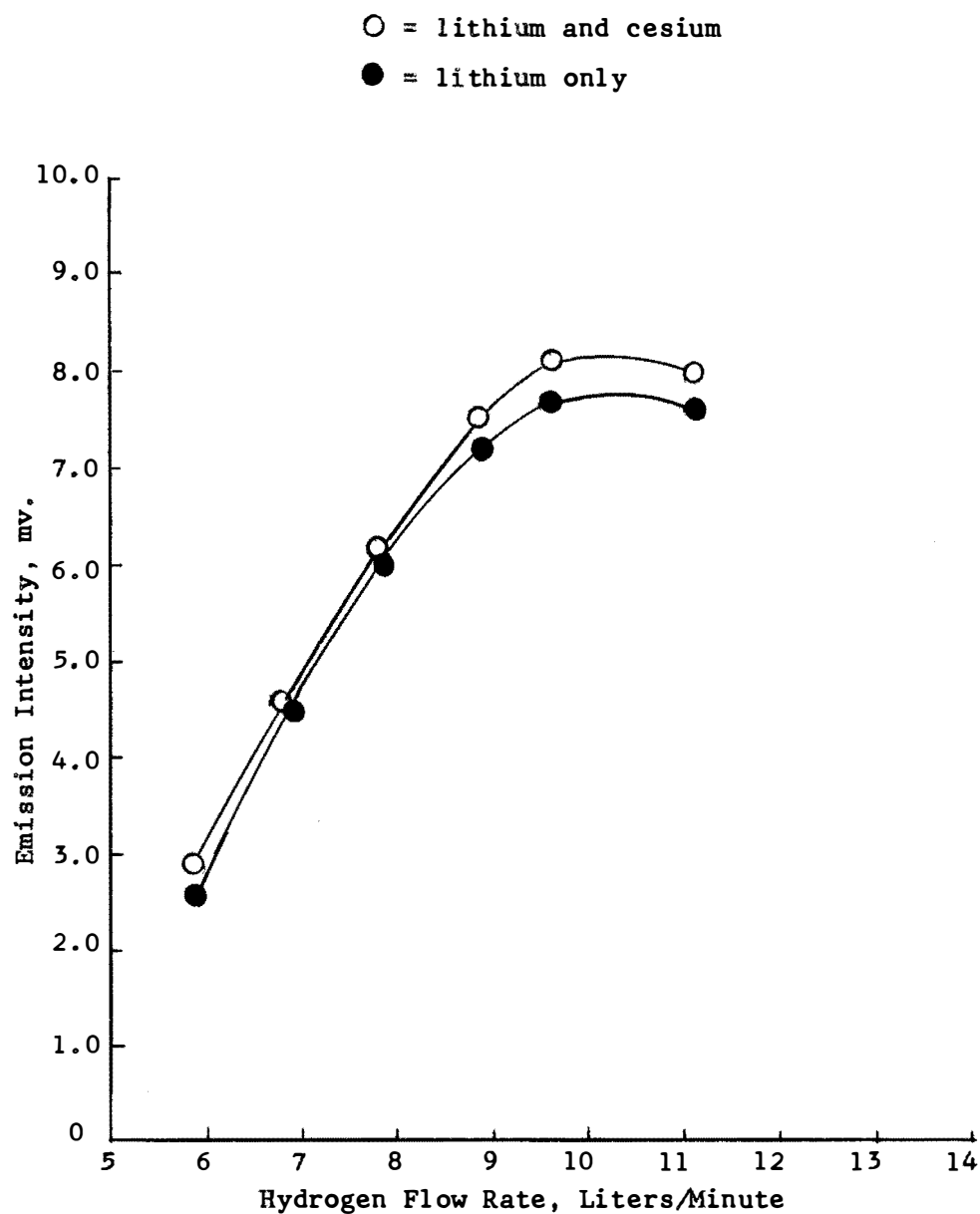


Figure 10. Emission intensity as a function of hydrogen flow rate for lithium line at 671 mμ for lithium only and lithium with cesium added.

2. Instrument Settings

The instrument settings used were as follows: photomultiplier sensitivity, 60 volts per dynode; slit width, 0.030 mm.; per cent adjust, 7.00.

3. Systems Studied

The lithium intensity of 10 $\mu\text{g.}$ per ml. of lithium and one containing 10 $\mu\text{g.}$ per ml. of lithium and 1000 $\mu\text{g.}$ per ml. of cesium was measured as a function of hydrogen flow at a constant oxygen flow rate. The hydrogen flow rate varied from 5.95 to 9.65 l. per min. and the oxygen flow was 2.53 l. per min. The results are shown in Figure 10.

D. Measurement of Lithium Intensity as a Function of Sample Flow Rate

1. Lithium Spectrum

The 671-~~m~~ μ lithium line was used.

2. Sample Flow Rates

The device used for varying the sample flow rate was described in Chapter II. The emission intensity of the lithium line was measured concurrently as the sample flow rate was being measured. This was accomplished by placing the lithium solution in the sample vessel and allowing the sample to be aspirated until cessation of aspiration. Then a known amount of the same solution was added from a microburet and the measurements made of the intensity as the time required to aspirate a fixed quantity of the solution was measured. Several deter-

minations of the emission intensity could be made as one measurement of the sample flow rate was made. Replicate measurements of sample flow rate and emission intensity were made at each particular sample flow rate.

3. Instrument Settings

The instrument settings for the water studies were: slit width, 0.020 mm.; per cent adjust, 7.00; photomultiplier sensitivity, 52 volts per dynode. Settings used for the ethanol solution were: slit width, 0.020 mm.; per cent adjust, 3.00; photomultiplier sensitivity, 52 volts per dynode.

4. Systems Studied

The emission intensity was studied as a function of sample flow rate for lithium in water and in ethanol. The lithium concentration was 100 $\mu\text{g.}$ per ml. in each case. Hydrogen and oxygen were the flame gases used. The emission intensity of the aqueous solution as a function of sample flow rate at 1.95 and 2.53 l. of oxygen per min. and the hydrogen flow at 5.95 l. per min. is shown in Figure 11. The same relationship for lithium in ethanol is shown in Figure 12. The oxygen flow rates were 1.95, 2.53, and 3.33 l. per min.; the hydrogen flow rate was 5.95 l. per min.

E. Aluminum Intensity Measurements

1. Aluminum Spectra

The emission spectrum of aluminum exhibits a doublet at 394.2 $\text{m}\mu$ and 396.2 $\text{m}\mu$ and an oxide band at 484 $\text{m}\mu$. Neither the line nor the band

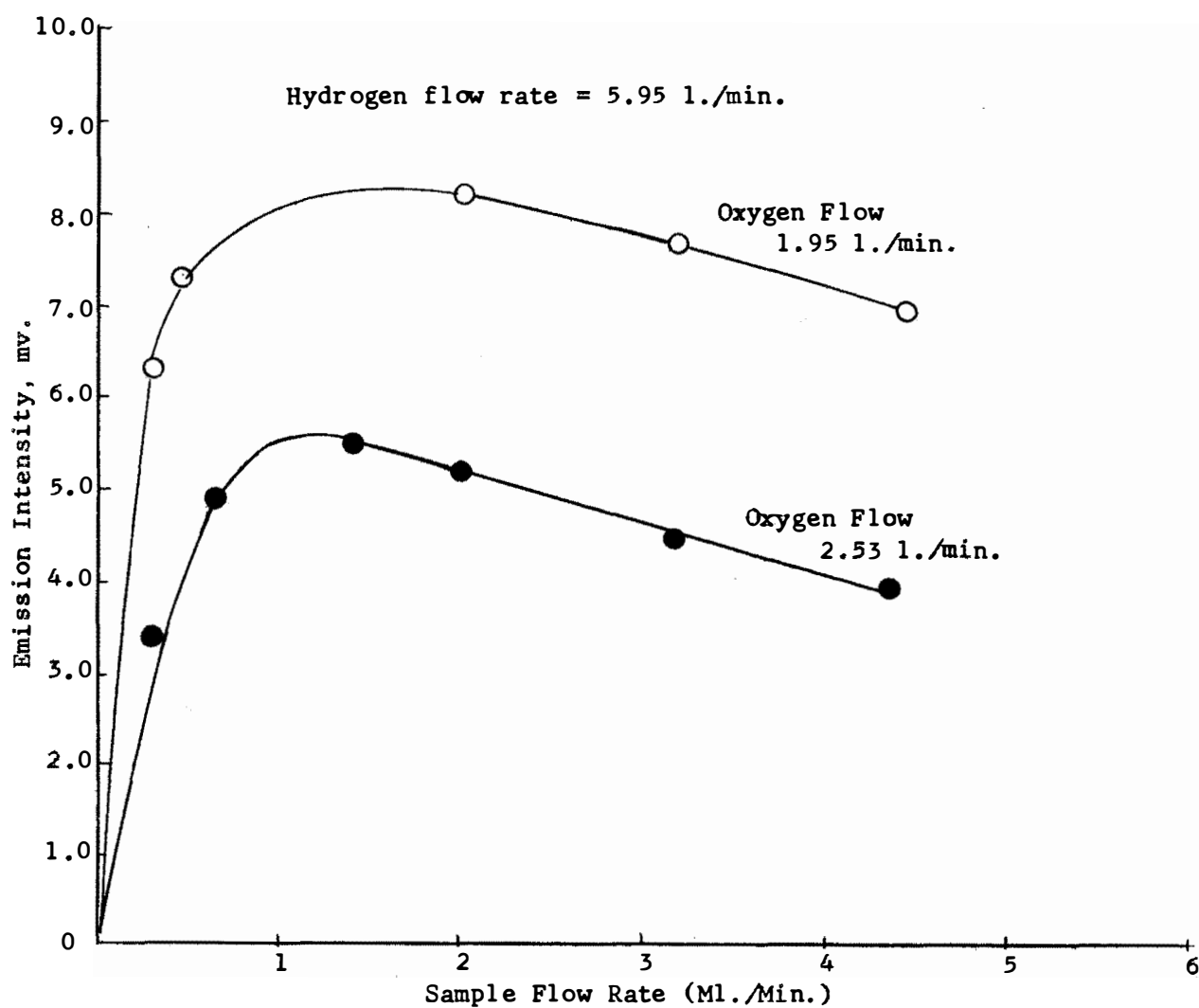


Figure 11. Emission intensity of 671-m μ lithium line as a function of sample flow rate. Solvent was water.

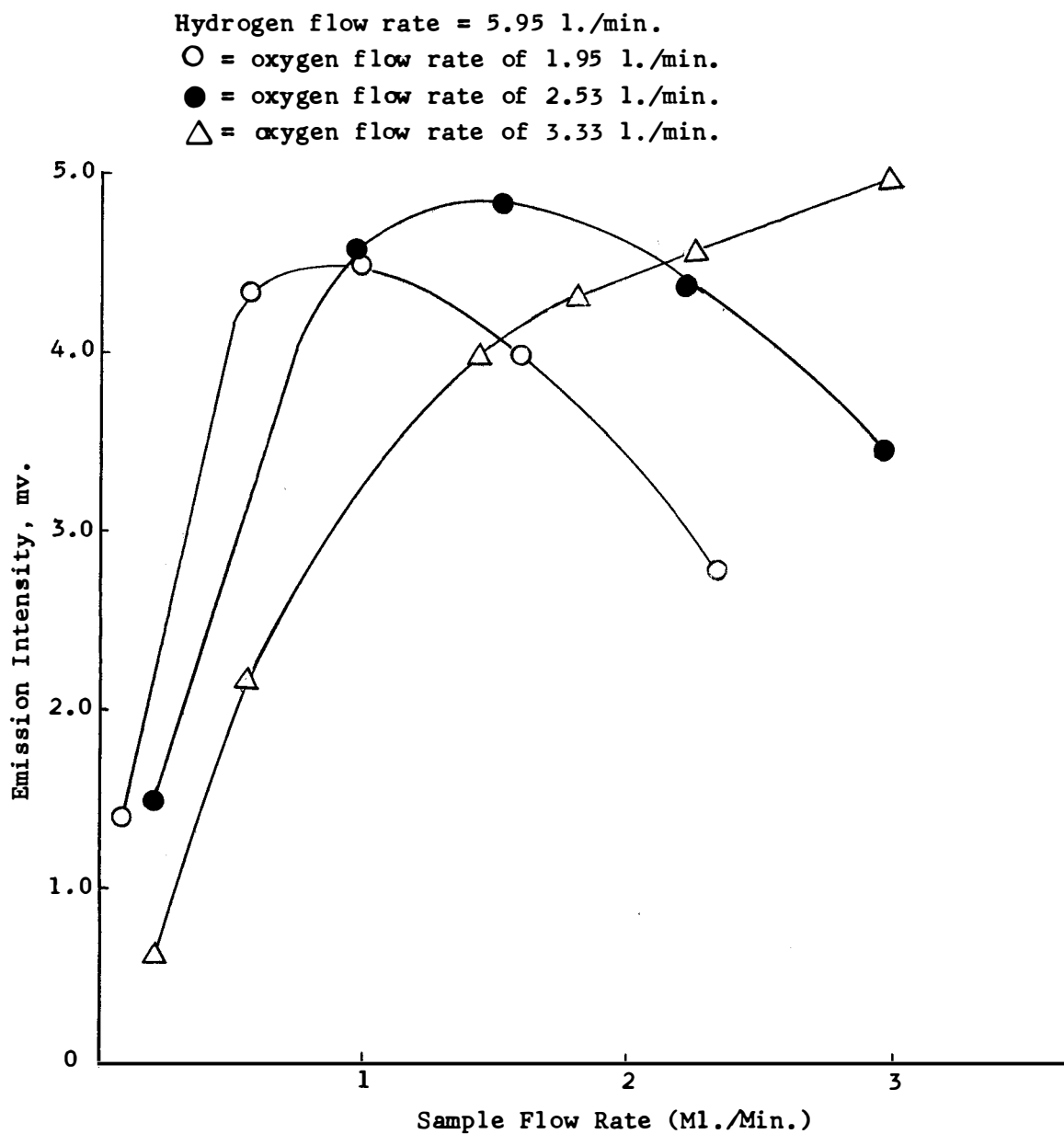


Figure 12. Emission intensity of 671- μ lithium line as a function of sample flow rate. Solvent was ethanol.

possess sufficient sensitivity to be determined by flame methods in other than organic solvents.

2. Instrument Settings

For the study of the aluminum line, the following instrument settings were employed: slit width, 0.025 mm.; per cent adjust, 3.25; photomultiplier sensitivity, 52 volts per dynode.

Settings employed for the band were: slit width, 0.030 mm.; per cent adjust, 7.0; photomultiplier sensitivity, 60 volts per dynode.

3. Systems Studied

The emission intensity of the aluminum line at 396.2 m μ and the oxide band at 484 m μ were measured as a function of acetylene flow rate at a constant oxygen flow rate for concentrations of 1000 μ g. of aluminum per ml. in methanol and in a solution containing 20 volume per cent of ethanol in 4-methyl-2-pentanone. The emission intensity of the 396.2-m μ line in these two solutions at acetylene flows from 0.9 to 2.12 l. per min. is shown in Figure 13. The oxygen flow was 3.57 l. per min. The same relationship for the 484-m μ oxide band at acetylene flows from 0.9 to 1.83 l. per min. is shown in Figure 14. The oxygen flow was 3.57 l. per min. in this case also.

F. Study of the Emission Intensity of Copper and Chromium

1. Spectra

The copper line used in this study was the line of the resonance doublet at 324.7 m μ . The chromium line was the first member of the ultra-

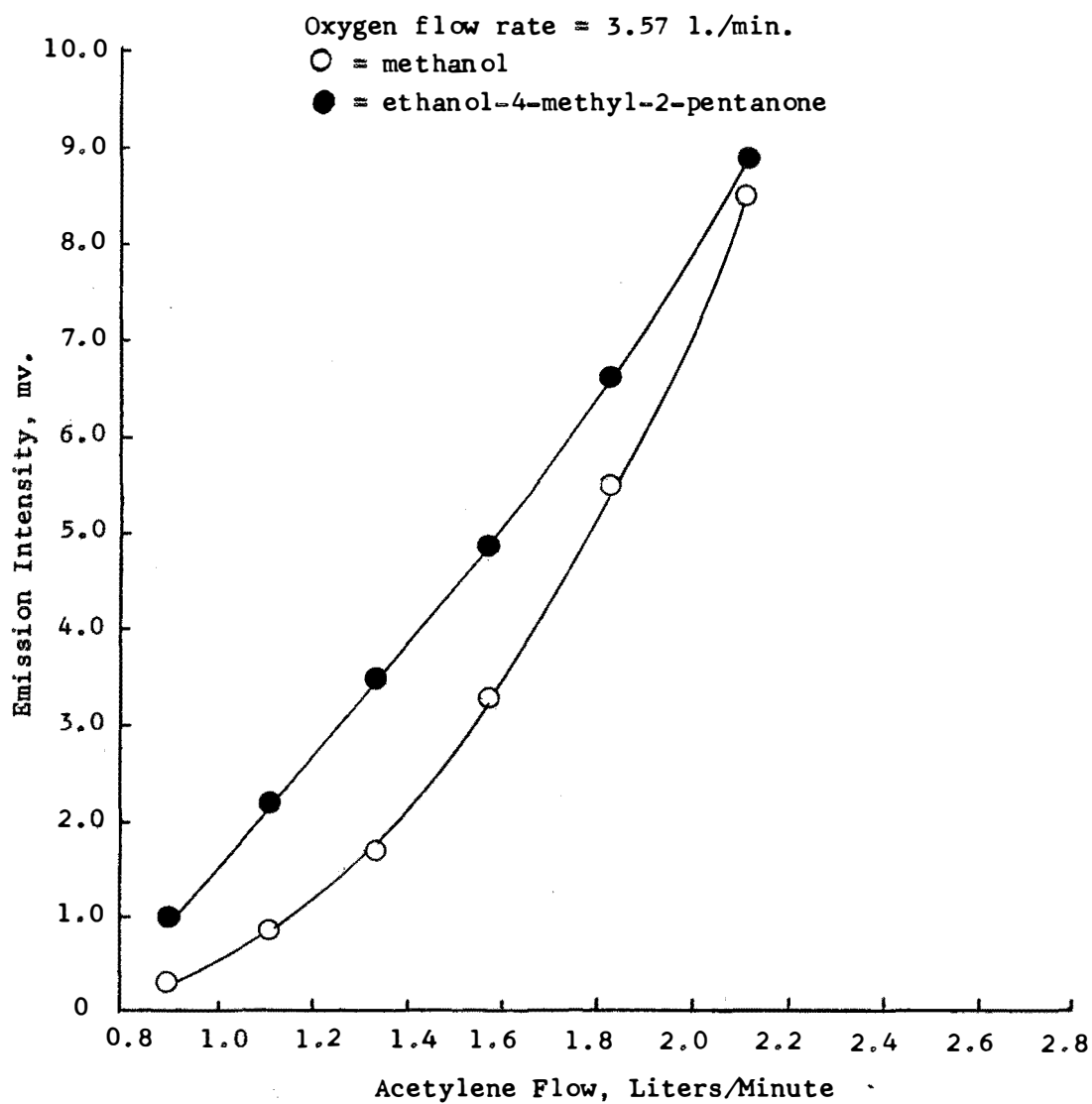


Figure 13. Emission intensity of 396.2- μ aluminum line as a function of acetylene flow rate.

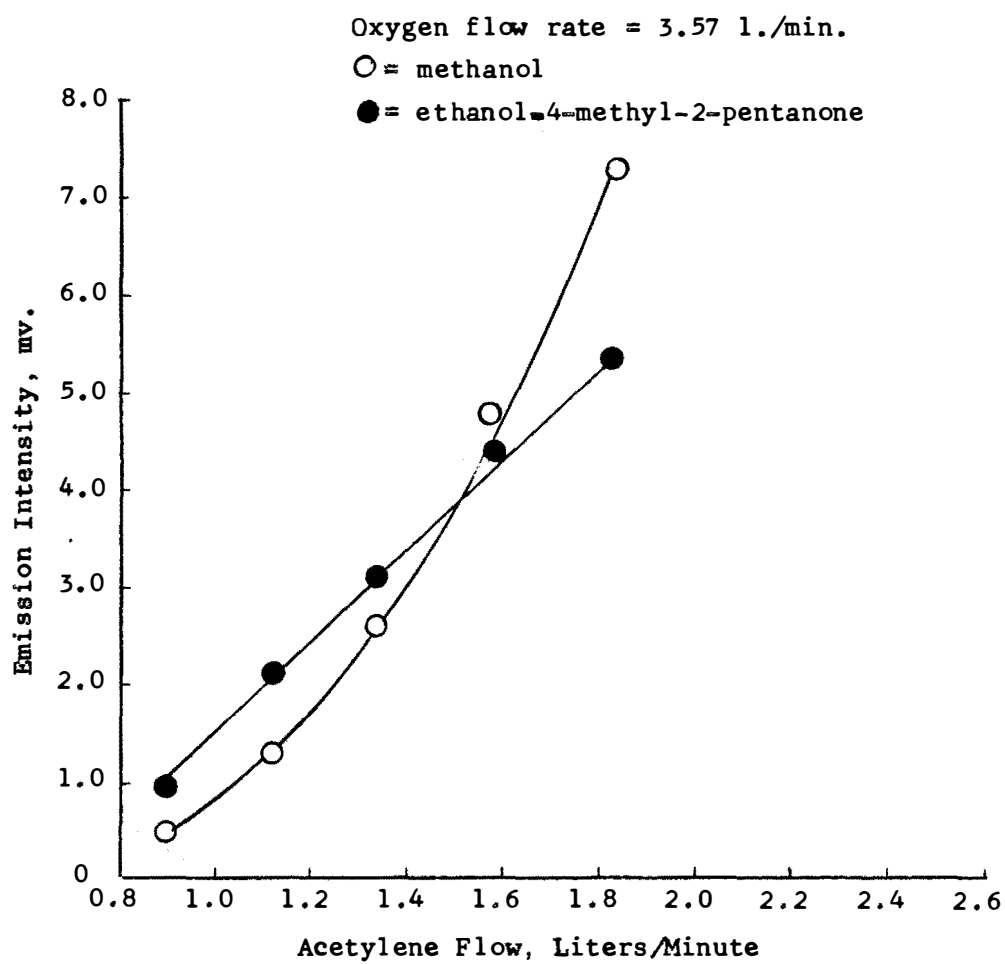


Figure 14. Emission intensity of 484-m μ aluminum oxide band as a function of acetylene flow rate.

violet triplet at 357.9 μ .

2. Instrument Settings

A slit width of 0.040 mm. was used throughout this study. All intensity measurements using acetylene were made at a photomultiplier sensitivity of 42 volts per dynode. The per cent adjust was set at 3.0. All studies done in hydrogen were carried out at a photomultiplier sensitivity of 52 volts per dynode and the per cent adjust set at 3.0 with the exception of the studies made of the emission intensity of chromium in methanol. This was done at a photomultiplier sensitivity of 60 volts per dynode and per cent adjust setting of 1.0.

3. Systems Studied

The emission intensities of copper and chromium were studied as a function of fuel flow rate in hydrogen and acetylene flames. These elements were present in concentrations of 100 μ g. per ml. in methanol and in 10 volume per cent methanol-toluene solutions.

An oxygen flow rate of 3.33 l. per min. was used for all measurements in hydrogen and an oxygen flow rate of 2.48 l. per min. was used for acetylene.

The emission intensity of copper at the 324.7- μ line as a function of hydrogen flow in these two solvents is shown in Figure 15; the same relationship for an acetylene flame is shown in Figure 16.

The plot of the emission intensity of the 357.9- μ chromium line as a function of hydrogen flow is shown in Figure 17; the same type of plot for the acetylene flame is shown in Figure 18.

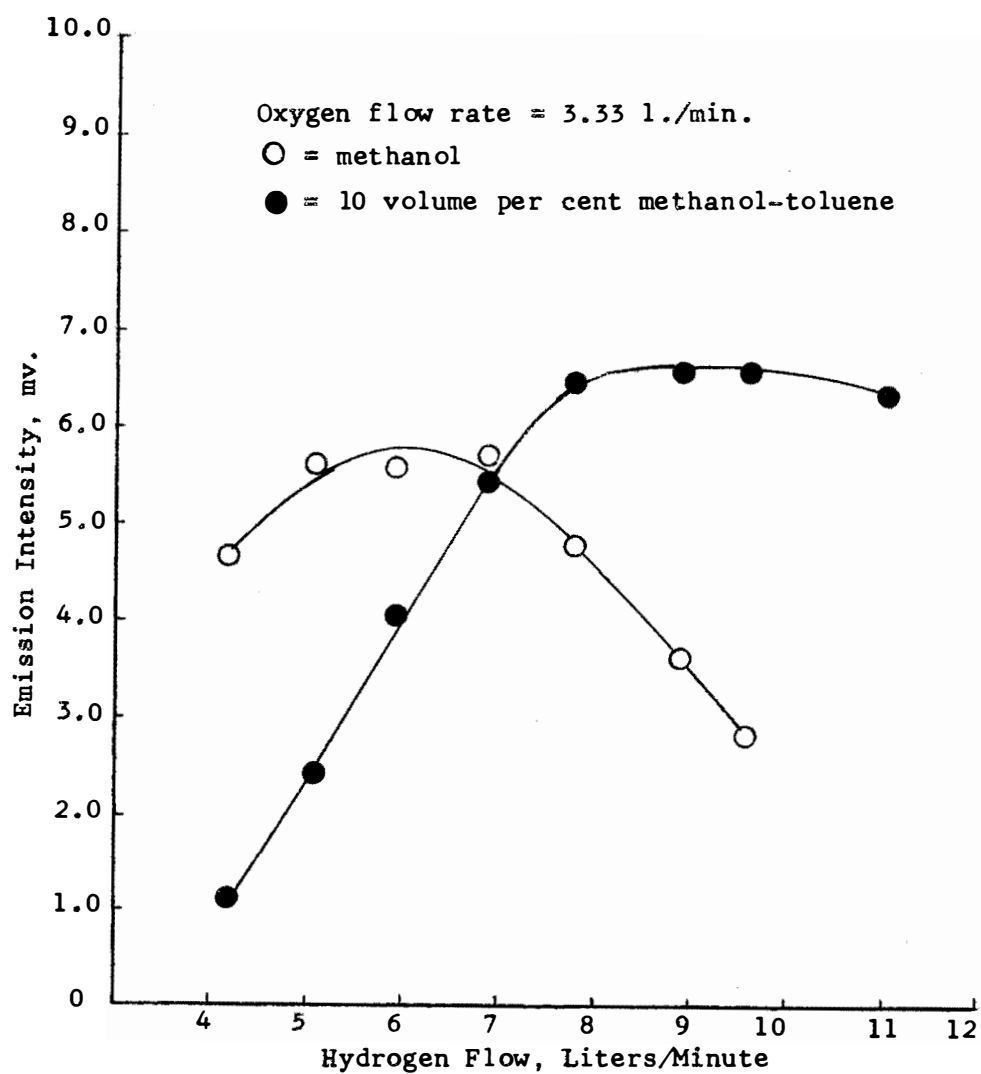


Figure 15. Emission intensity of 324.7-m μ copper line as a function of hydrogen flow rate.

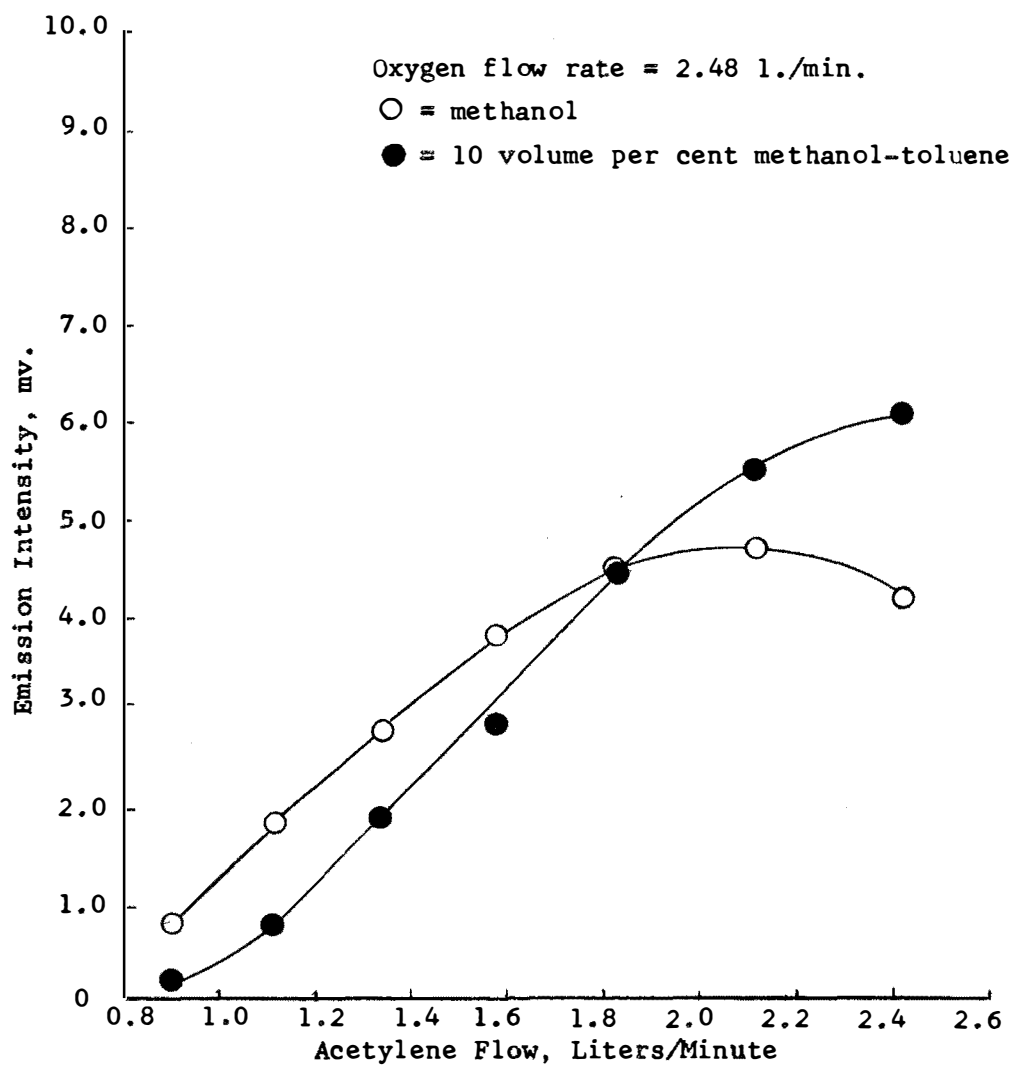


Figure 16. Emission intensity of 324.7-m μ copper line as a function of acetylene flow rate.

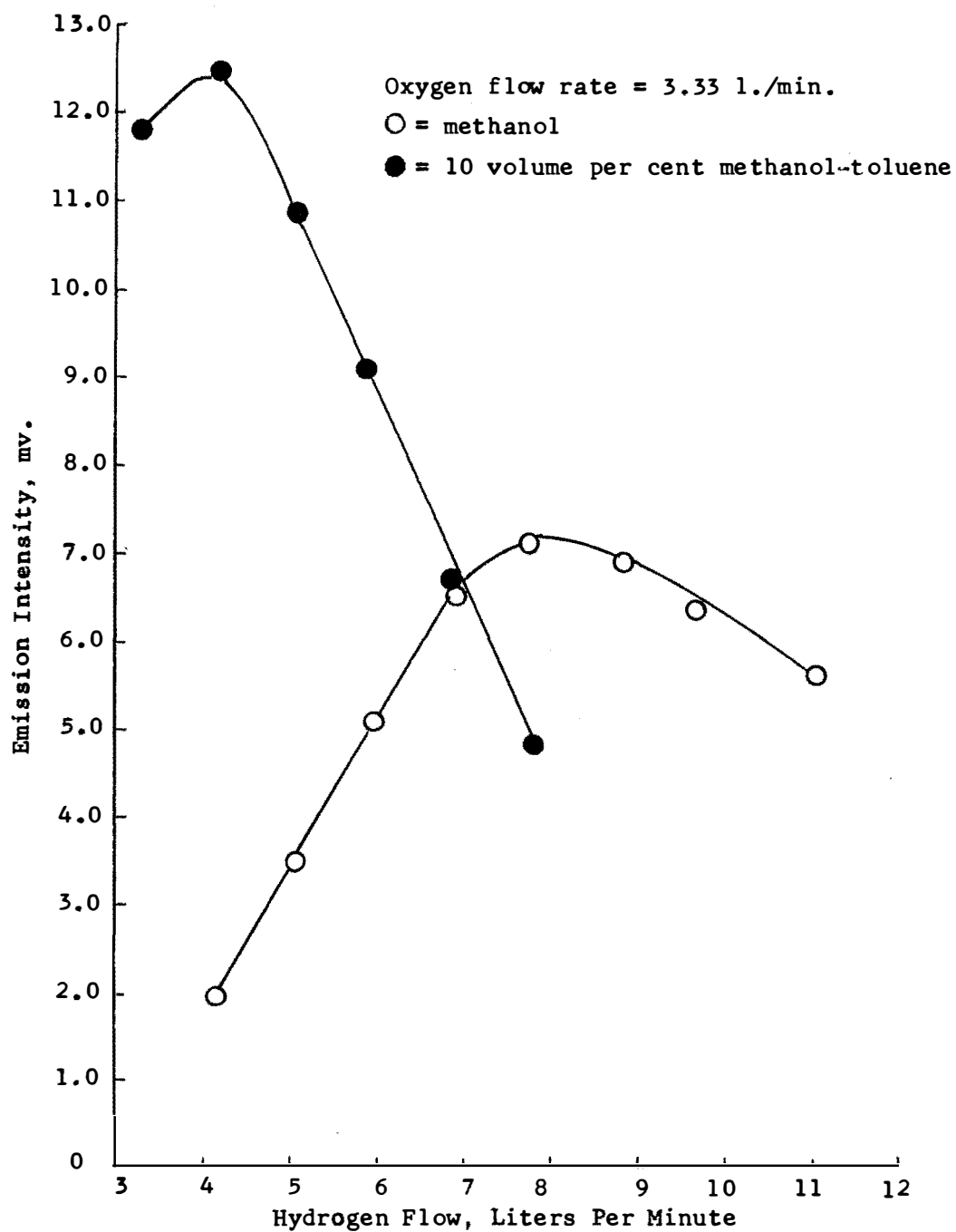


Figure 17. Emission intensity of 357.9- μ chromium line as a function of hydrogen flow rate.

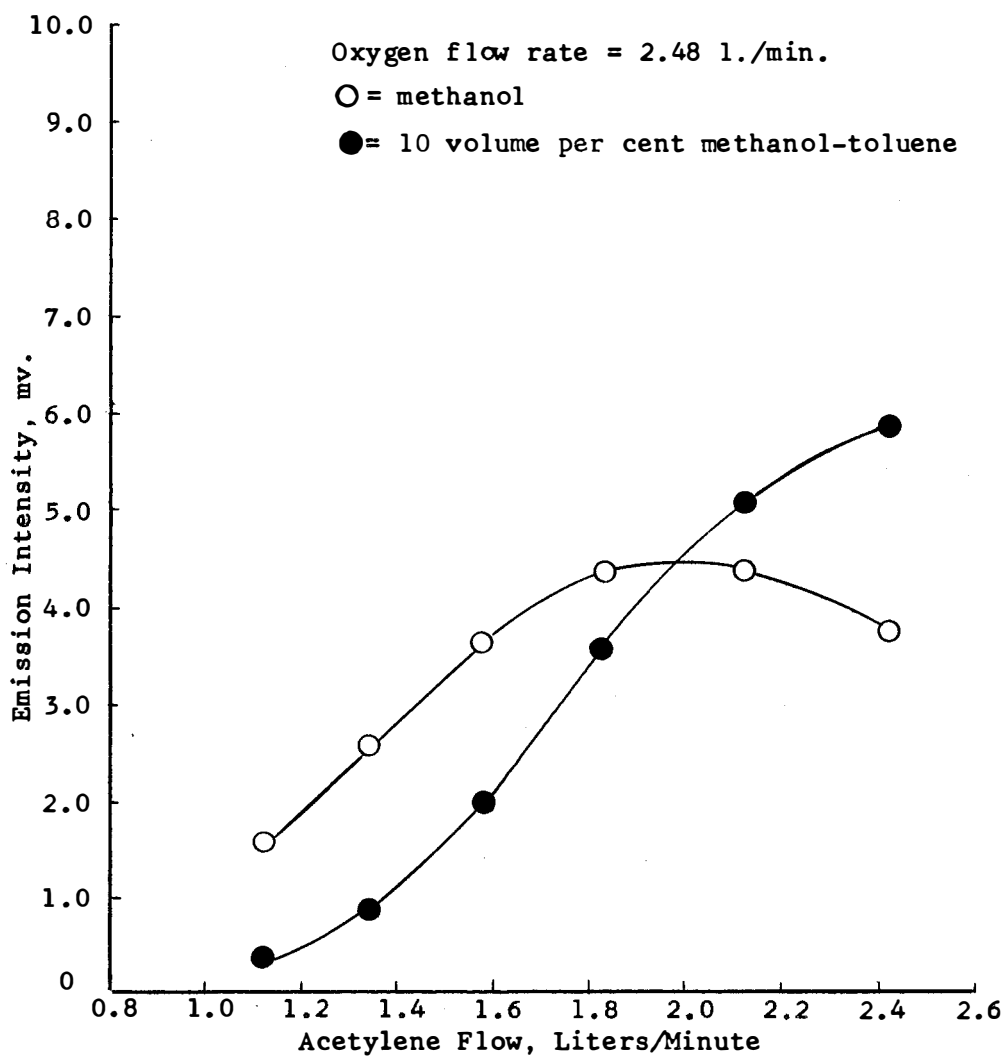


Figure 18. Emission intensity of 357.9- μ chromium line as a function of acetylene flow rate.

CHAPTER IV

DISCUSSION OF RESULTS

A. Flame Temperature Calculations

The values obtained in the temperature calculations agree with those reported by Edwards, Smith, and Brinkley.³² These workers obtained a value of 3358.5°K for an acetylene oxygen ratio of 1:2.5 and 3386.5°K for a ratio of 1:1. Values obtained in this study were 3317°K for a ratio of 1:2.48 and 3365°K for a ratio of 1:1.81. The agreement is satisfactory.

The calculated values of the flames fed by aerosols showed the expected decrease in temperature. The water-fed flame gave a lower calculated flame temperature than did the ethanol-fed flame. Both calculations were made for an acetylene oxygen ratio of 1:2.48. The flame fed by 1.15 ml. of ethanol per min. gave a calculated temperature of 3223°K. The values for a water-fed flame of the same fuel oxygen ratio were 3133°K for 1.45 ml. of water per min. and 3200°K for the flame fed by 1.00 ml. of water per min.

These values show that the temperature of the organic-fed flame is higher than that of a water-fed flame, but that temperature difference is insufficient to give the enhancements which are encountered. Assuming the temperature of a water-fed flame to be 3150°K and the temperature of the organic-fed flame to be a maximum of 100° higher, thermal enhancements of 12, 27, 44, and 62.5 per cent would be obtained for elements with excitation potentials of 1, 2, 3, and 4 electron volts.

B. Measurement of OH Band Intensities

The work of Foster and Hume²⁹ and Beck² have suggested the possibility of employing the emission intensity of the OH bands to ascertain the optimum conditions for different solvents and elements. It was felt that the emission intensities of the OH bands might elucidate the nature of the organic solvent enhancements.

The study of the OH bands to obtain the temperature of flames and the distribution of the OH intensity within the flame has been done.³³ The distribution was not done in this study because the item of interest was the relation of the OH band intensities to the intensities of elements in the same region of observation within the flame mantle. Most flame photometers do not possess the experimental means for observing different regions of the flame.

Measurements were made under a variety of conditions. The results are shown in Figures 5-9. Significant differences in molecular weight, structure, and solvent properties were considerations in the choice of the organic solvents.

At low acetylene flow rate, a greater OH band intensity is observed for the organic solvents than is observed for the dry flame. On the other hand, at high acetylene flow rates, the OH emission intensity of the organic solvents is less than that of the dry flame. A water-fed flame gives a lower OH band intensity than a dry flame throughout the range of acetylene flow rates studied. The shape of the curve of the water-fed flame parallels that of the dry flame.

The shapes of the organic solvent curves do not parallel that of the dry flame curve. For the organic solvents, the OH intensity reaches a maximum at a lower acetylene flow rate than for the dry flame or for the water-fed flame in every case.

These results show that the emission intensity of the OH band is not a measure of the optimum flame conditions for the emission of elements. At the higher acetylene flow rates, the OH band intensity of the water-fed flame is greater than that of several of the organic solvents, yet the emission intensity of the elements in the latter solvents is many fold higher. Also, the optimum flame conditions for which the OH band intensity is maximum will not yield maximum emission intensity conditions for the elements. The aluminum intensity curves for both line and molecular band emissions (Figures 13 and 14) illustrate this very strikingly.

The emission intensity of the OH band in an acetylene-oxygen flame decreases with an increase in the flow rate of the water sample, as has been reported for hydrogen-oxygen. This decrease is independent of the fuel-oxygen ratio in the regions of acetylene flow rates studied. Figure 10 shows the OH emission intensity as a function of acetylene flow rate for a dry flame and for three amounts of water being fed into the flame.

The nature of the organic solvent enhancements could not be related to the OH band intensity measurements. Beck² reported that the OH band intensity decreased with increasing sample flow rate for a hydrogen-oxygen flame. The present study shows that the relationship of the OH band intensity to the sample flow rate must be made with a consideration of the acetylene-oxygen ratio. The sample flow rate of water

is less than that of the organic solvents but the OH band intensity of the organic solvents may be greater or less than that of water depending upon the flame conditions employed.

C. Ionization

Figure 10 shows the emission intensity of the 671-m μ lithium line as a function of the hydrogen flow rate for a solution containing only lithium and for a solution which contains lithium and cesium. This study was made to investigate the effect of the presence of a large quantity of electrons arising from the ionization of cesium atoms upon the emission intensity of the lithium at different hydrogen flow rates. The optimum conditions of the emission intensity of the elements vary from solvent to solvent and the effect of ionization could contribute to this variation. Although the emission intensity of the lithium is enhanced by the cesium, the hydrogen-oxygen ratio at which the maximum emission intensity of the lithium is observed is the same both in the presence of and in the absence of cesium.

D. Sample Flow Rates

Studies of the emission intensity of the alkali metals as a function of sample flow rate have been made for an aqueous solution in a hydrogen-oxygen flame.²⁹ For the alkali metals, the optimum sample flow rate is inversely proportional to the ionization potential of the element. It was thought advisable to study the emission intensity of

an element as a function of the sample flow rate for an aqueous solution and an organic solution. Lithium was chosen because it possesses the highest ionization potential among the alkali metals. Because of the increased flame temperature, the optimum sample flow rate should be shifted to a higher value in an organic solvent than in water. The emission intensity of the 671-~~nm~~^μ lithium line in a hydrogen-oxygen flame as a function of the sample flow rate of water and of ethanol is shown in Figures 11 and 12.

The optimum sample flow rate in a water-fed flame (Figure 11) did not show a significant dependence upon the hydrogen-oxygen ratio for the two ratios employed. After the maximum intensity was attained, further increase in the sample flow rate caused a similar decline in emission intensity for the fuel ratios used. The decrease is due to diminished thermal excitation which in turn resulted from the lowering of the flame temperature through the cooling effect of the larger quantity of water aspirated. At the higher hydrogen-oxygen ratio, the maximum emission intensity is 1.5 times the maximum intensity attained in the flame of the lower ratio.

From the results obtained from the ethanol-fed flame (Figure 12), two very significant differences in the relationship of emission intensity and sample flow rate between water- and the ethanol-fed flames were observed. First, the optimum sample flow rate of the ethanol-fed flame depended more upon the flame conditions than it did for a water-fed flame. Second, the maximum intensity depended less upon the flame gas ratio than it did for the water-fed flame.

In the ethanol-fed flame, the thermal contribution of the combustion of the ethanol caused a shift to larger optimum sample flow rates with decreasing hydrogen-oxygen ratio. The presence of a quantity of oxygen in excess of the stoichiometric amount needed to burn the hydrogen yielded enough oxygen for ethanol combustion so that no decrease in the emission intensity was observed with the lowest hydrogen-oxygen ratio employed. In flames of higher hydrogen to oxygen ratio, there was less than a stoichiometric amount of oxygen present and the cooling effect of the unburned ethanol became apparent.

E. Aluminum Intensity Measurements

The emission intensities of the 396.2-m μ aluminum line and the 484-m μ aluminum oxide band are shown in Figures 13 and 14. These measurements were made in a methanol solution and a solution of 20 volume per cent of ethanol in 4-methyl-2-pentanone. In each case, the emission intensity increases as the acetylene flow rate increases.

For the 396.2-m μ line, the emission intensity in the ethanol-4-methyl-2-pentanone was greater than the emission intensity in methanol at each acetylene flow rate employed. However, the rate of increase in the intensity with increasing acetylene flow rate was greater in methanol and the emission intensities were approximately the same at the highest acetylene flow rate used.

A similar relationship was found for the emission intensity of the 484-m μ band in these two solvents. The emission intensity of the aluminum in the methanol solution was greater at the higher acetylene flow rates

and less at the lower acetylene flow rates.

From Equation (1), it is seen that a plot of the logarithm of the emission intensity versus the reciprocal of the temperature will yield a straight line whose slope is proportional to the excitation energy of the transition. Since the temperature is proportional to the acetylene flow rate, a plot of the logarithm of the emission intensity versus the reciprocal of the acetylene flow rate has been made. Fairly good straight lines resulted. These latter plots, shown in Figures 19 and 20, illustrate quite clearly the interaction of the solvent with the flame gases. The excitation energy of the band is 2.55 e. v.; of the line, 3.14 e.v.³⁴ The slopes are tabulated below:

<u>Emission System</u>	<u>Methanol</u>	<u>Ethanol-4-methyl- 2-pentanone</u>
396.2- μ line	-2.40	-1.50
484- μ line	-2.08	-1.30

These slopes indicate that the emission intensity of the system studied is more dependent upon the solvent employed than upon the excitation energy of the transition. The ratio of the slopes, line to band, is the same for each solvent. This is an indication that the solvent affects each transition in a similar manner.

F. Chromium and Copper Emission Intensity Measurements

The emission intensities of the 324.7- μ copper line and the 357.9- μ chromium line as a function of fuel flow rate are shown in Figures 15, 16, 17, and 18. Two solvents were used, pure methanol and a solution

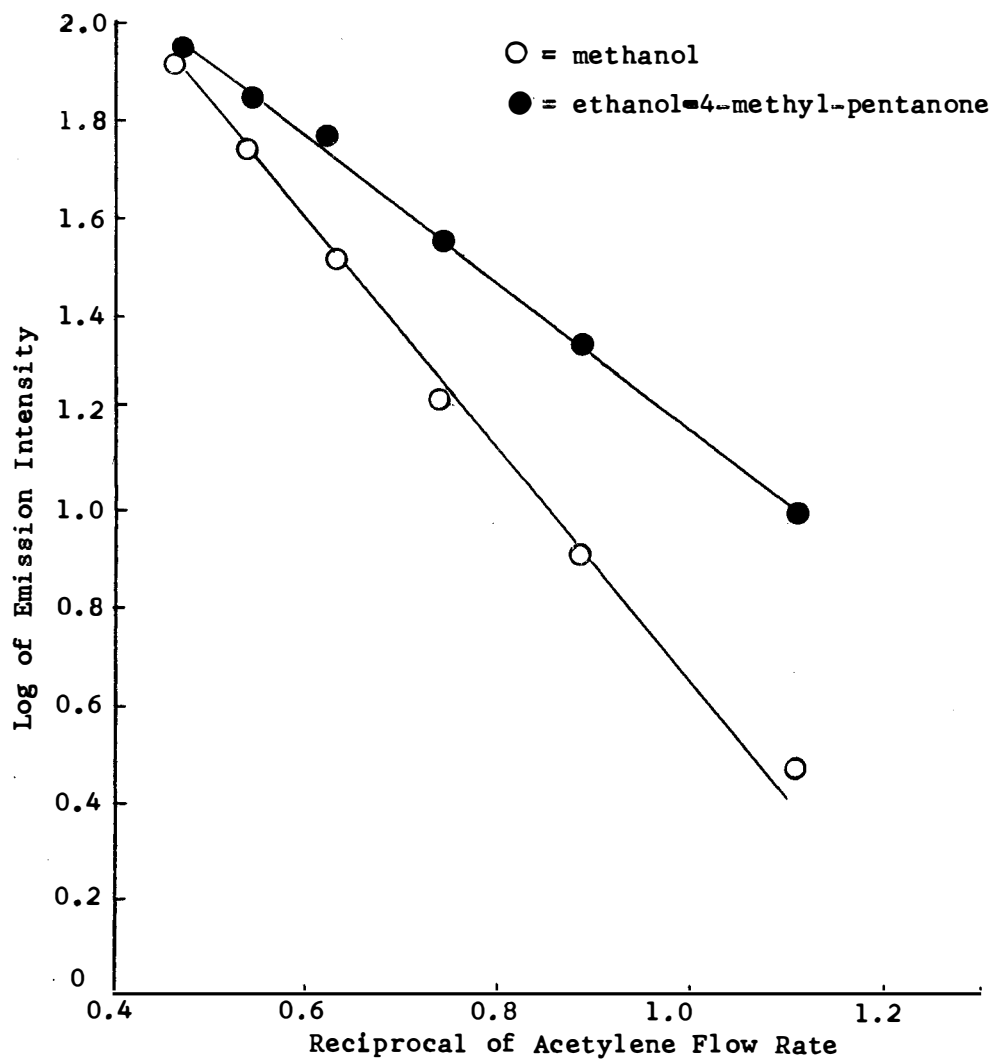


Figure 19. Log emission intensity of 396.2- μ aluminum band versus reciprocal of acetylene flow rate.

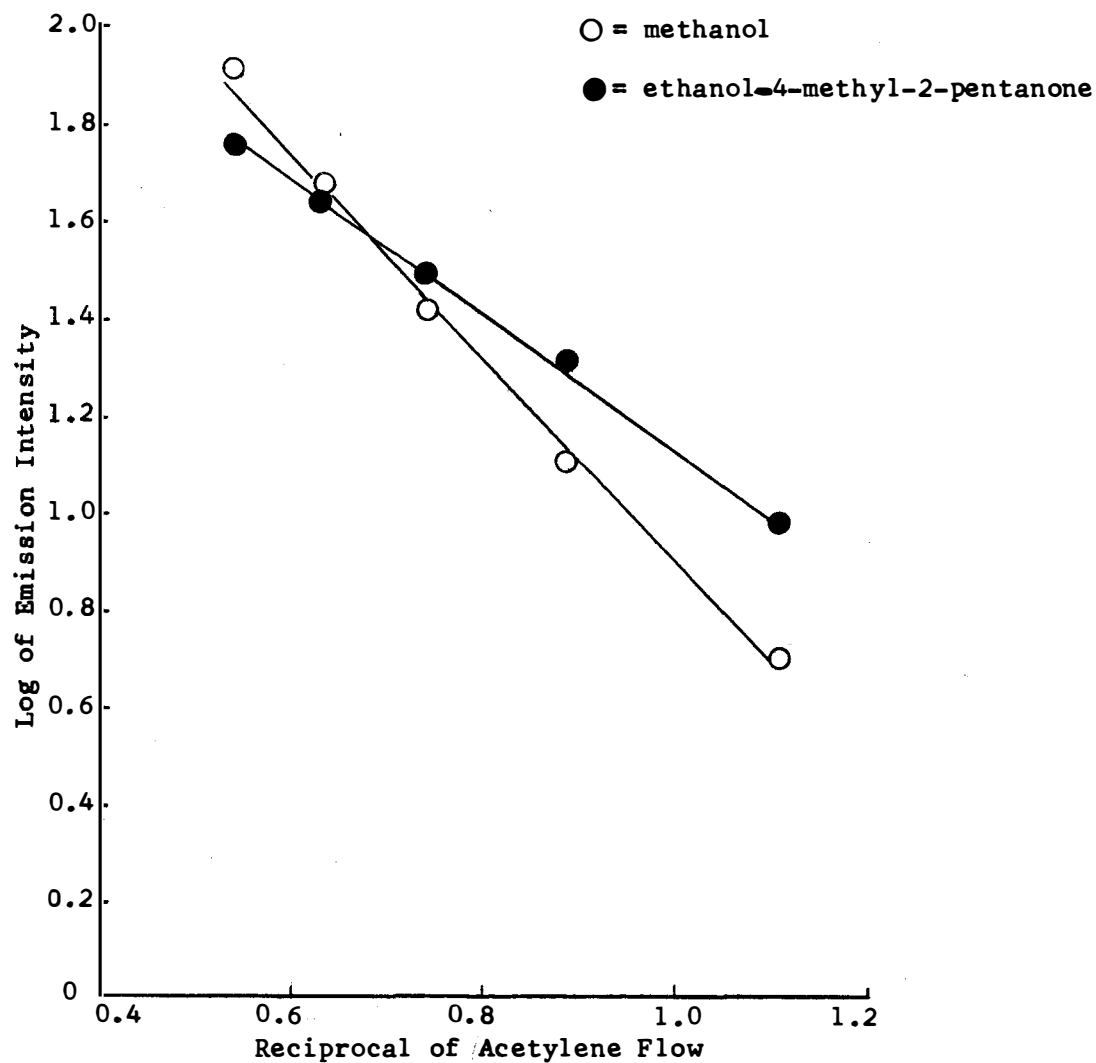


Figure 20. Log emission intensity of 484-m μ aluminum oxide band versus reciprocal of acetylene flow rate.

containing 10 volume per cent of ethanol in toluene; and two flames, hydrogen-oxygen and acetylene-oxygen. The results are summarized in Table V.

These systems were chosen for several reasons. First, the dry flame temperature of a stoichiometric hydrogen-oxygen flame is about 500° lower than that of a dry acetylene-oxygen flame. Enhancements observed with the organic solvents are due partly to the increased flame temperature of the organic-fed flame as compared with a water-fed flame. Because of the significant temperature differences provided by these flames as compared with the smaller temperature changes observed when organic solvents are employed, correlations of the emission intensities of elements in organic solvents could be attempted.

Second, the choice of solvents permitted observation of the effect of radicals containing carbon which are present in large quantities in flames fed by aromatic hydrocarbons. Significantly large background radiations originate from these radicals when aromatic solvents are burned. The solubility of the compounds from which the standard solutions were prepared necessitated the addition of a small quantity of methanol to the toluene.

Third, the elements were selected on the basis of intensifications which have been reported. These are 10-fold for copper and 50-fold for chromium. The excitation energy of the chromium line is 3.46 electron volts; for the copper line, 3.81 electron volts.³⁴

Figures 16 and 18 show the emission intensity of copper and chromium as a function of acetylene flow rate at a constant oxygen flow rate. From

TABLE V

RELATIVE EMISSION INTENSITY OF COPPER AND CHROMIUM IN ACETYLENE-OXYGEN
AND HYDROGEN-OXYGEN FLAMES INTO WHICH WERE ASPIRATED METHANOL AND
10 PER CENT METHANOL-TOLUENE SOLUTIONS

Element	Flame	Solvent	Ratio of Relative Emission Intensity
Cr	H ₂	MeOH	1.0
Cr	H ₂	MeOH-Toluene ^a	1.8
Cu	H ₂	MeOH	2.0
Cu	H ₂	MeOH-Toluene ^a	2.3
Cr	C ₂ H ₂	MeOH	6.4
Cr	C ₂ H ₂	MeOH-Toluene ^a	8.3
Cu	C ₂ H ₂	MeOH	6.6
Cu	C ₂ H ₂	MeOH-Toluene ^a	8.6

^a10 volume per cent methanol.

these figures, it is seen that the emission intensity of the elements depended more upon the solvent employed than upon the excitation energy of the element. The peak intensities of the elements occurred at approximately the same acetylene flow rate in a given solvent, and the magnitude of the emission intensities was approximately equal. In methanol the emission intensity decreased at the higher acetylene flow rates. No decrease was observed for the methanol-toluene solution, but the shapes of the curves indicated that a decrease might occur at higher acetylene flow rates.

The emission intensities of the two elements as a function of hydrogen flame rate are shown in Figures 17 and 19. The relationship between the emission and the fuel flow rate was significantly different than in an acetylene flame. In methanol-toluene, copper exhibited an emission intensity which was 1.15 times greater than that found in methanol. The difference in the fuel flow rate at which the peak emission intensity occurred for the two solvents was greater in the hydrogen flame than in the acetylene flame. The maximum intensity in methanol was observed at a hydrogen flow rate slightly greater than 6 liters per minute.

In the two solvents, the relationship between emission intensity and fuel flow rate for chromium differed markedly in the two flames. The peak emission intensity in methanol-toluene was 1.8 times the peak emission intensity in methanol. In the former solvent, the peak occurred at a much smaller hydrogen flow rate.

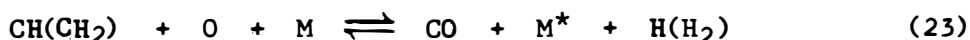
Although these results show that the flame temperature plays an important part in the excitation process, interactions among the solvent, the element, and the components in the flame gases are significant.

Abnormally high reversal temperatures have been reported for certain elements in the reaction zones of flames.³⁵ The work was done at low pressure to broaden the reaction zone. It has been suggested that these abnormal reversal temperatures resulted from chemiluminescence.

Padley and Sugden³⁶ studied the emission relationships and proposed that the actual intensity of a line is the sum of the chemical and thermal excitation. Gaydon and Wolfhard³⁵ suggested that excitation by chemiluminescence resulted from a three-body collision involving the metal atom and unspecified free radicals. A mechanism, as illustrated by Equations (21) and (22), is proposed by Padley and Sugden.³⁶



Broida and Shuler³⁸ favored a reaction of the type



where M is water, oxygen, hydrogen or acetylene and the excitation occurs by $\text{M}^* + \text{A} \rightarrow \text{M} + \text{A}^*$, where A is a metal atom.

The radically different emission intensities which were observed for copper and chromium may be caused by chemiluminescence. It is unreasonable to assume that these differences could result from thermal processes.

The proposed increase due to chemiluminescence in the reaction zone permits an interpretation of the enhancements observed with organic solvents. With organic solvents, the inner cone, which includes the reaction zone, is definitely lengthened. Also, the droplets may be observed burning even in the outer mantle. The burning of the droplets may actually yield conditions which are equivalent to many small reaction zones spread throughout the

flame mantle. By contrast, flames fed by water solutions do not have these extra reaction zones nor even an extended inner cone.

The unusual enhancement of chromium lends credence to the view that some sort of chemical process is involved. The chemiluminescence could arise if the chromium is present in a water-fed flame primarily as a molecular compound, such as the hydroxide; perhaps chemiluminescent dissociation processes render an additional number of free atoms available for thermal or chemical excitation subsequently.

G. Suggestions for Further Study

The results of the present investigation have shown that it is probably a chemical effect which gives rise to the large enhancement when an organic solvent is burned. Thermal effects alone will not provide the enhancements which have been found.

The following procedure could be applied to a flame photometric measurement to ascertain separately the effect of temperature and droplet combustion.

Alkemade and Voorhuis³⁹ have shown many concomitant effects are negligible unless the two ions are in the same solution. When phosphate was added to a flame by means of a separate atomizer, interference in the calcium emission is not encountered.

The same experimental procedure might elucidate the enhancements achieved with organic solvents. Water and the organic solvent could be introduced into the flame by means of separate atomizers. The test element would be introduced alternately in each solvent and a comparison made of

the emission intensity. If the emission intensity is higher when the test element is dissolved in the organic solvent, then the enhancement is due to the chemical reaction involving the combustion of the droplet around the test element salt.

CHAPTER V

SUMMARY

The present investigation has been concerned with the study of several parameters which influence the flame photometric emission of elements in an effort to elucidate the nature of the intensifications observed with organic solvents. Parameters such as flame temperature, OH band intensity, ionization, sample flow rate, and the emission intensities of different elements in different solvents have been studied.

Temperature calculations have shown that the temperature of an organic-fed flame is slightly higher than that of a water-fed flame but that the temperature difference is not large enough to give the intensifications found. Neither could the OH band intensity measurements be related to the intensifications. Comparison of OH intensities among the different solvents showed large variations with changes in the acetylene-oxygen ratio.

The effect of a large quantity of electrons upon the emission intensity of lithium was studied with respect to flame conditions. However, an optimal hydrogen-oxygen ratio was found to be optimum both in the presence of and the absence of the element furnishing the large quantity of electrons.

The emission intensity of lithium was studied as a function of sample flow rate in water and in ethanol. The effect of the combustion of the ethanol upon the emission intensity is shown quite clearly. The temperature contribution of the burning ethanol shifted the optimum

sample flow rate to a larger value.

Studies of the emission intensities of several elements in different solvents have shown that the emission intensity of each element depended more upon the solvent than upon the excitation energy of the transition. The intensifications are postulated as arising from chemiluminescence in the reaction zones of the burning solvent droplets. Rather than being confined to a narrow region of interconal gases, the reaction zone is enlarged and extended into the flame mantle when an organic solvent is employed.

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PART B: STUDIES OF THE EXTRACTION AND FLAME EMISSION OF MAGNESIUM

CHAPTER I

HISTORICAL

A. Introduction

Since the fundamental work on flame photometry by Lundegardh,¹ the emission of magnesium in a flame has been widely used for its quantitative determination. The determinations utilized either the line emission at 285.2 mμ or the band emissions at 371 and 383 mμ. The line has a detection limit of 0.15 p.p.m. and the bands have detection limits of 3 p.p.m. in a water-fed oxygen-acetylene flame.²

The line possesses the advantage of being situated in a portion of the spectrum in which there are no spectral interferences from other elements. It does, however, have the disadvantages of being strongly self absorbed and being in a region of the spectrum in which there are a series of relatively strong OH bands (Figure 21). Base-line background corrections are made with difficulty and it is quite advantageous to employ a recording flame spectrophotometer.

Magnesium emission is plagued by many serious radiation interferences and many of these are present in samples in which it is desirable to determine the magnesium content. These have been extensively investigated.^{3,4,5}

The use of organic solvents in flame photometry for the purpose of increasing the emission sensitivity is well known. Several procedures have been applied to magnesium. Ikeda⁶ studied the use of 50 per cent methanol solutions and found that he was able to determine as little as 1 μg. of

magnesium per ml. Manna, Strunk and Adams⁷ used 80 per cent acetone solutions and determined magnesium in the range of 1 to 6 $\mu\text{g.}$ per ml.

Organic extraction techniques have been extensively used in this laboratory for the flame-photometric determination of elements. This technique offers the advantage of removing the test element from the matrix material containing possible interferants and at the same time greatly increasing the emission sensitivity.

Luke and Campbell⁸ and Luke⁹ have employed an extraction system of 8-quinolinol-chloroform for the colorimetric determination of magnesium in electronic nickel. The same type of procedure was to be employed for the flame photometric determination of magnesium.

B. Statement of the Problem

The present investigation was undertaken to investigate certain emission characteristics of the 285.2- $\text{m}\mu$ magnesium line in water and in 4-methyl-2-pentanone. An extraction procedure for the determination of magnesium was to be investigated.

CHAPTER II

APPARATUS AND REAGENTS

A. Apparatus

1. Flame Spectrophotometer

The flame spectrophotometer has been described in Part A. In this portion, the burner height was varied by means of a rack and pinion type of arrangement. A setting of 10 mm. is equal to the normal height and higher portions of the flame are observed with increasing setting in mm.

2. Gas Flow Rates

The measurement of gas flow rates has been described in Part A.

3. pH Meter

A Beckman Model H-2 pH meter was used for all pH measurements.

B. Reagents

1. Demineralized Water

Demineralized water was prepared by passing ordinary distilled water through Amberlite MB-3 resin.

2. 4-Methyl-2-pentanone

Practical grade 4-methyl-2-pentanone was used without further purification.

3. Standard Magnesium Solutions in Water

A standard magnesium solution containing 1000 μg . of magnesium per ml. was prepared by dissolving 1.6579 g. of reagent grade magnesium oxide in a minimum amount of glacial acetic acid and diluting to one liter with water. Other standards were prepared by appropriate dilution.

4. Standard Magnesium Solutions in 4-Methyl-2-pentanone

A standard magnesium solution containing 1000 μg . of magnesium per ml. was prepared by dissolving 0.1658 g. of reagent grade magnesium oxide in a minimum amount of glacial acetic acid and diluting to 100 ml. with 4-methyl-2-pentanone. Other standards were prepared by appropriate dilution.

5. Ammonium Hydroxide-Ammonium Chloride

A solution of 2 N with respect to both ammonium chloride and ammonium hydroxide was prepared by dissolving 77 g. of ammonium chloride and 133 ml. of concentrated ammonium hydroxide in one liter of water.

6. 8-Quinolinol Solution

A 5 per cent (w/v) solution of 8-quinolinol was prepared by dissolving 5 g. of 8-quinolinol in 11.5 ml. of glacial acetic acid and diluting to 100 ml.

7. Extraction Solution

The extraction solution was prepared by dissolving 0.6 g. of 8-quinolinol in 4-methyl-2-pentanone, adding 20 ml. of tri(iso-octyl)amine, and diluting to 100 ml. with 4-methyl-2-pentanone.

8. Extraction Solvent

The extraction solvent was prepared by diluting 20 ml. of tri(iso-octyl)amine to 100 ml. with 4-methyl-2-pentanone.

9. Tri(iso-octyl)amine

The tri(iso-octyl)amine used was obtained from Union Carbide Chemicals Company and was used without further purification.

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

A. Flame Spectrum

The flame spectrum of the 285.2-m μ magnesium line is shown in Figure 21. This spectrum was run with 100 μ g. of magnesium present per ml. of water. The severity of the OH band interference upon the magnesium emission is clearly shown in Figure 21. The magnesium line is situated between two OH peaks and at sufficiently high magnesium concentrations, the OH peaks are practically masked by the magnesium line. At low concentrations, the magnesium line appeared as a widening of one of the OH peaks. With these changes in the appearance of the spectrum, the choice of a base line was difficult. The solid line drawn and labeled background in Figure 21 was found most satisfactory for background correction. For quantitative measurements, it is desirable to employ a base line correction which will yield a calibration curve that passes through the origin. The base line employed did not give a calibration curve that passed through the origin but it remained constant with respect to the magnesium emission as conditions varied. In some measurements of the emission characteristics of magnesium, only magnesium was present and a solvent blank provided a satisfactory background correction.

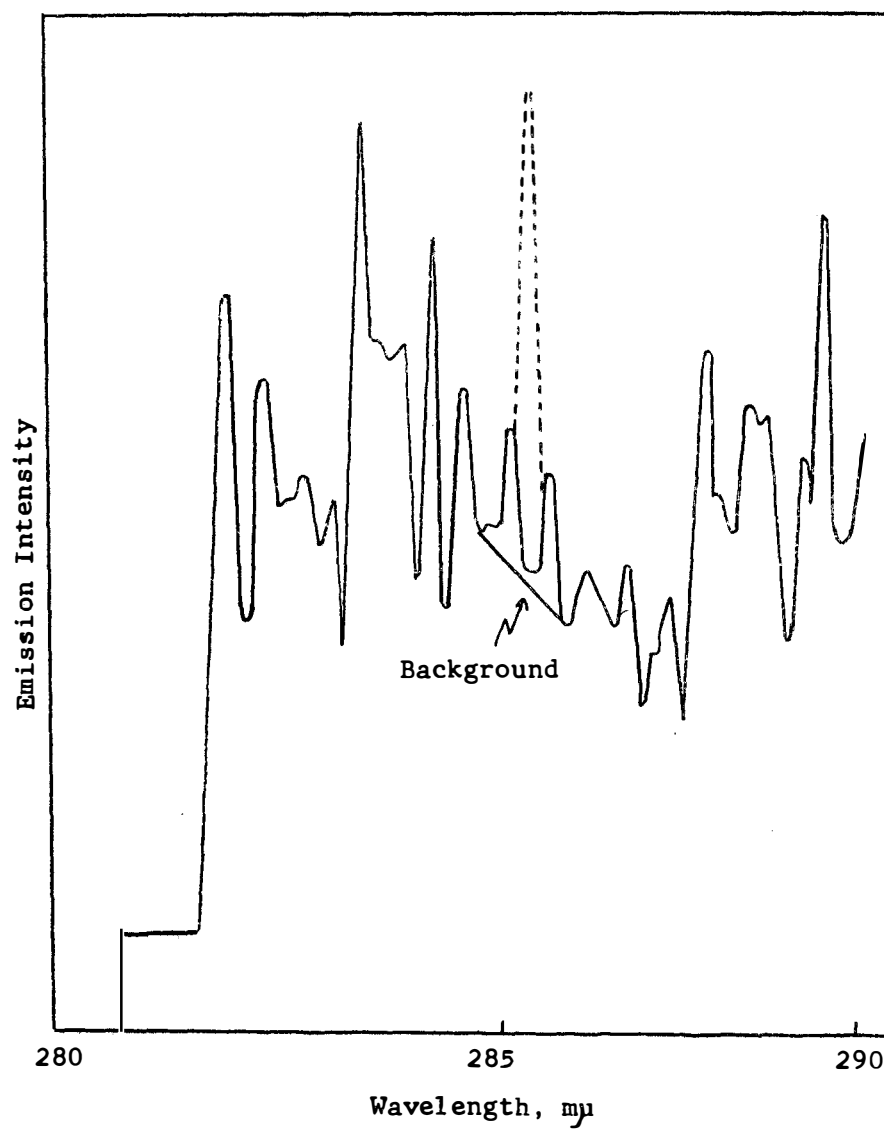


Figure 21. Flame spectrum of magnesium.

B. Emission Intensity of Magnesium in Water Solution as a Function of
Acetylene Flow Rate at Various Burner Heights

In Figure 22, the emission intensity of magnesium is shown as a function of the acetylene flow rate at different burner heights. The oxygen flow rate was 2.16 l. per min. and the acetylene flow rate was varied from 0.9 to 2.60 l. per min. Instrument settings were as follows: per cent adjust, 3.00; slit width, 0.04 mm. The magnesium concentration was 100 μg . per ml. A fixed wavelength of 285.2 $\text{m}\mu$ was used and the background correction was made with water.

Magnesium emission was found to vary significantly with acetylene flow rate and with the portion of the flame viewed by the entrance slit of the spectrophotometer. As the region of observation was changed to higher portions of the flame, the acetylene flow rate yielding the maximum emission intensity increased. At the burner heights which corresponded to the highest portions of the flame being in the region of observation, the emission intensity did not reach a maximum at the highest acetylene flow rate studied. Presumably, maxima would also be reached at these heights with sufficiently high acetylene flow rates. The values of the maximum emission intensities reached for the systems exhibiting maxima were approximately the same. This series of measurements illustrated the fact that some of the variables in flame photometry are very closely interrelated and the effect on the emission intensity of a change in one may well be compensated for by a change in another.

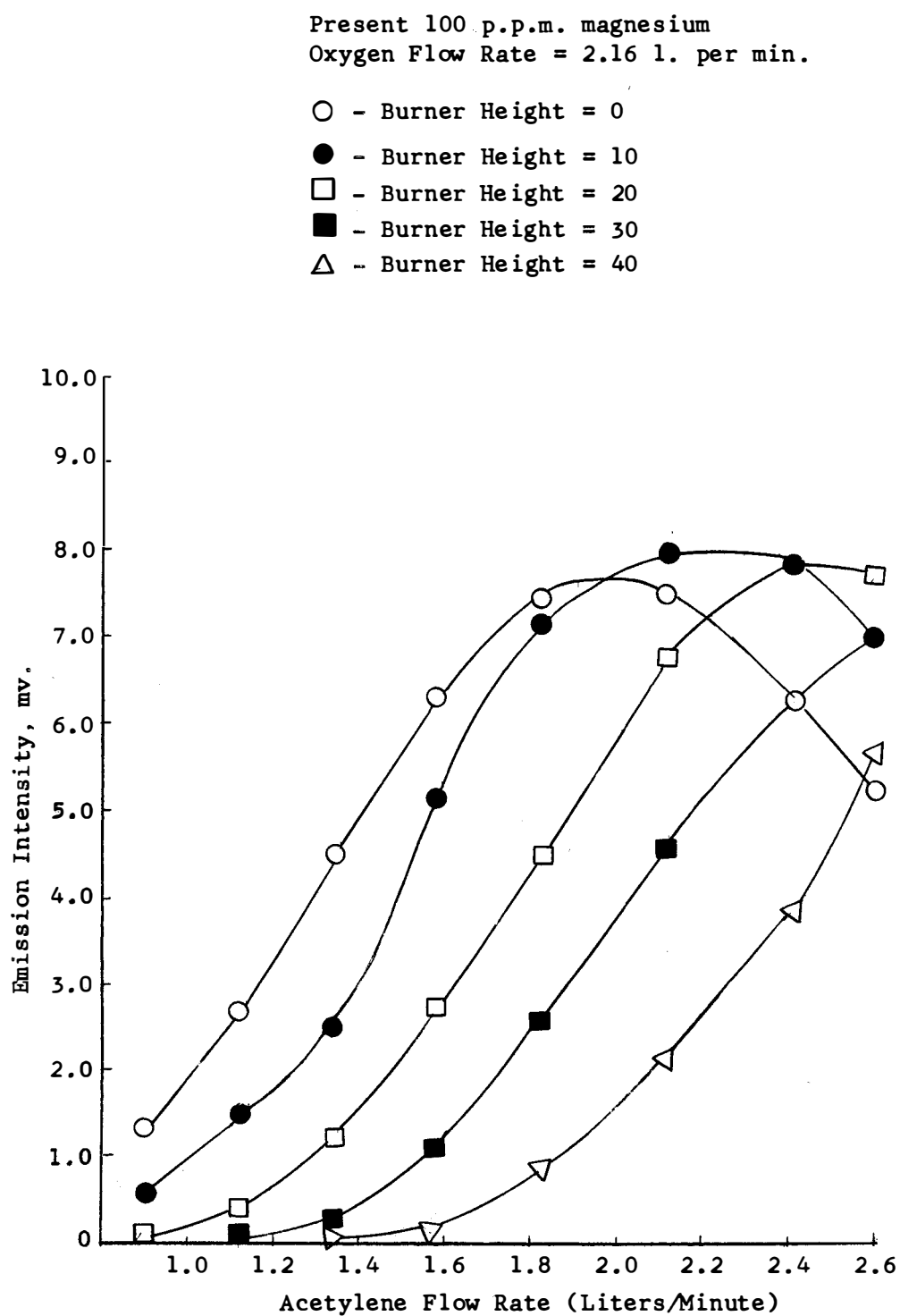


Figure 22 Emission intensity of 285.2-m μ magnesium line as a function of acetylene flow rate at various burner heights.

C. Variation in the Emission Intensity of Magnesium in 4-Methyl-
2-pentanone Solvent with Acetylene Flow Rate

The emission intensity of magnesium in 4-methyl-2-pentanone is shown in Figure 23. The solution contained 10 $\mu\text{g.}$ of magnesium per ml. The instrument operating conditions were as follows: per cent adjust, 3.00; slit width, 0.05 mm.; burner height, 10 mm. The oxygen flow rate was 2.16 l. per min. A fixed wavelength of 285.2 $\text{m}\mu$ was used and the background correction was made with 4-methyl-2-pentanone aspirated into the flame.

In 4-methyl-2-pentanone, the acetylene flow rate at which the maximum emission intensity of magnesium was observed was less than the acetylene flow rate for maximum emission in water at the same oxygen flow rate. 4-Methyl-2-pentanone enhances the emission intensity approximately 10-fold. The fuel-oxygen ratio at which the maximum magnesium emission was observed was the same as the ratio observed for the maximum emission intensity of the 306.7- $\text{m}\mu$ OH band (Figure 5). This indicates that the OH bands (flame background emission) are varying in the same manner as the magnesium emission and that a change in flame conditions will not bring about a more favorable OH to magnesium emission intensity ratio.

D. Effect of Burner Height Upon the Calibration Curve of Magnesium

The emission intensity of magnesium solutions containing 25, 50, 75 and 100 $\mu\text{g.}$ of magnesium per ml. have been measured at burner heights of 10, 20, 30, and 40 mm. The oxygen flow rate was 2.16 l. per min. and the

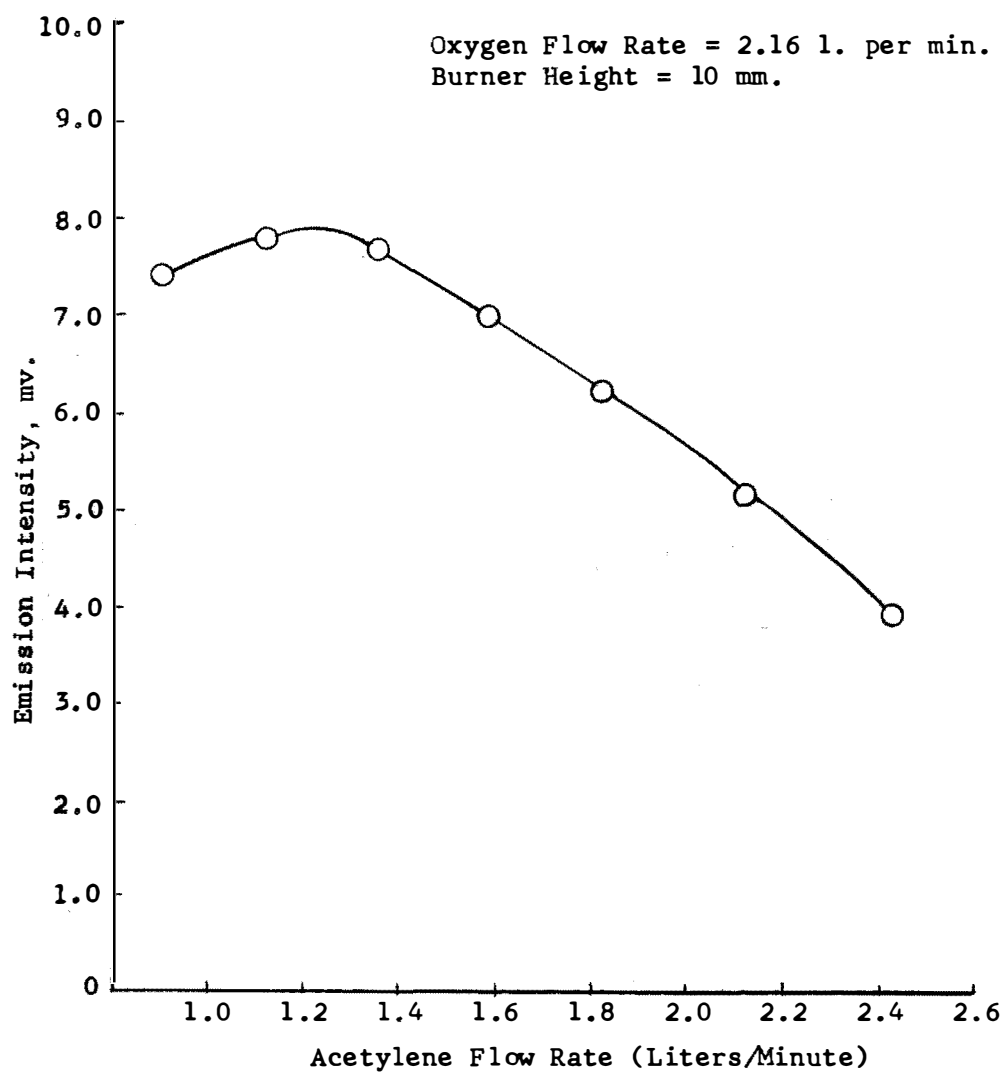


Figure 23. Emission intensity of magnesium as a function of acetylene flow rate in 4-methyl-2-pentanone.

acetylene flow rate was 1.58 l. per min. The instrument settings employed are tabulated below:

Burner Height, mm.	Slit Width, mm.	Per Cent Adjust
10	0.03	6.5
20	0.04	6.5
30	0.05	6.5
40	0.06	8.0

The results are shown in Figure 24. Background corrections were made by the use of a base line. Different base lines were employed at each burner height because the spectral emission of the background changed with burner height. The OH bands were less intense with respect to the magnesium intensity as the higher portions of the flame were observed. Thus background interference from the OH bands could be minimized but only at the loss of magnesium sensitivity.

Self-absorption appeared to influence the emission intensity quite markedly. A plot of the logarithm of the emission intensity versus the logarithm of the concentration gave slopes of 0.394 for burner heights of 10 and 20 mm., 0.490 for a height of 30 mm., and 0.552 for a height of 40 mm. There is a region of constant self-absorption down to 25 $\mu\text{g.}$ per ml.

E. Extraction of Magnesium

The use of an extraction system which extracted magnesium from an aqueous solution into 4-methyl-2-pentanone has been studied. The extraction may be carried out by either of two procedures.

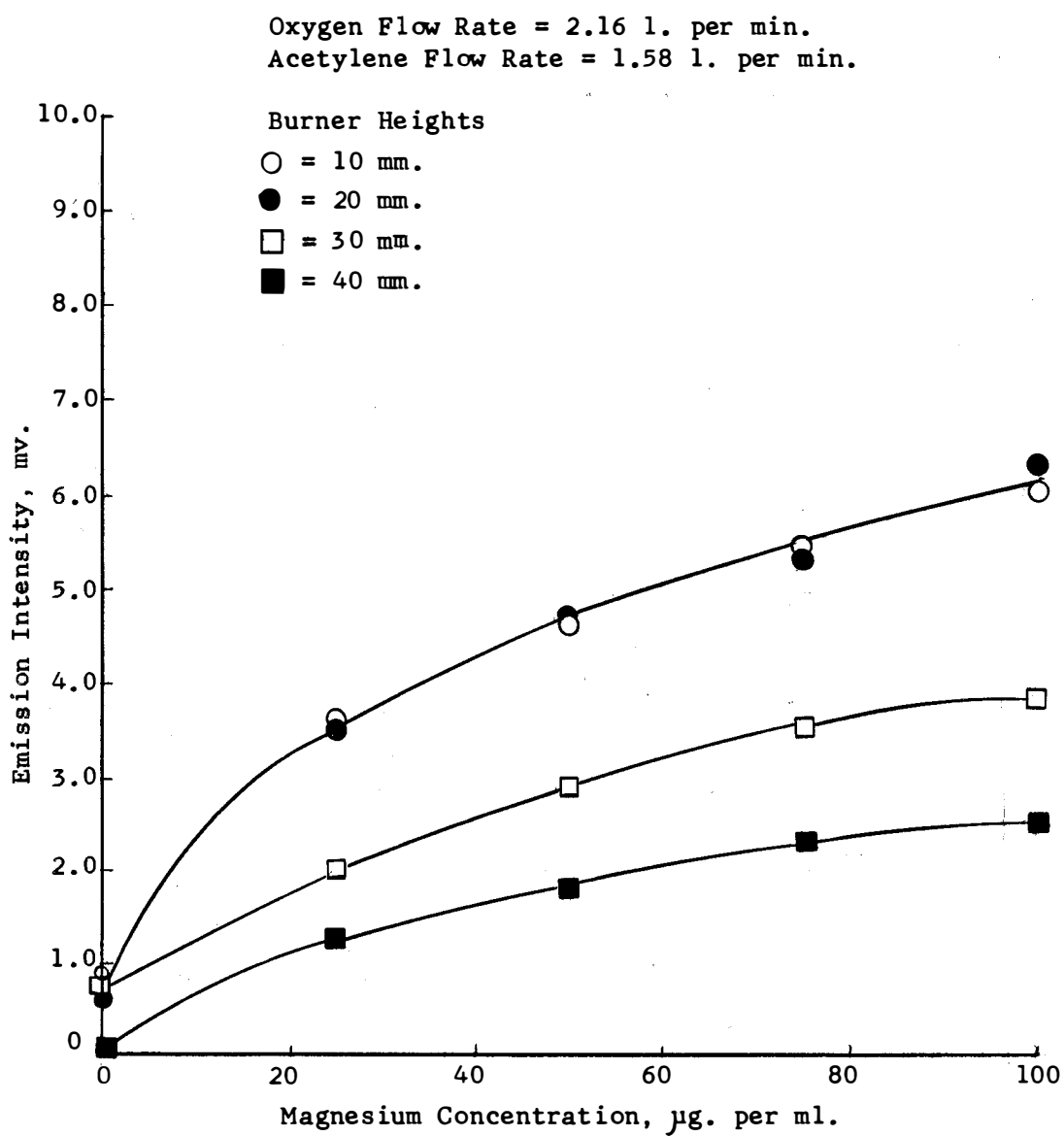


Figure 24. Emission intensity as a function of concentration at various burner heights.

Five milliliters of a solution 2 N with respect to both ammonium hydroxide and ammonium chloride was added to 10 ml. of a solution containing 10 $\mu\text{g.}$ of magnesium per ml. The pH of the solution was adjusted to 10 with concentrated ammonium hydroxide and the solution transferred to a separatory funnel. Ten milliliters of the extraction solution was added and the phases equilibrated. After separation of the phases, the 4-methyl-2-pentanone layer was aspirated directly into the flame. The emission intensity of the magnesium line at 285.2 $\text{m}\mu$ was compared to a standard solution of magnesium in 4-methyl-2-pentanone. This standard contained 10 $\mu\text{g.}$ of magnesium per ml. Results indicated extraction to be complete in one equilibration.

Phosphate prevented the extraction of the magnesium by the above procedure but an alteration in the extraction procedure circumvented this difficulty. When phosphate was present, 2 ml. of a 5 per cent solution of 8-quinolinol was added to the test solution. Concentrated ammonium hydroxide was added until the excess 8-quinolinol dissolved. The solution and the precipitate were transferred to a separatory funnel and equilibrated with 10 ml. of the extraction solvent. In this manner, 10,000 $\mu\text{g.}$ per ml. of phosphorus (as phosphate) can be tolerated when 10 $\mu\text{g.}$ per ml. of magnesium are present.

Calcium was coextracted and enhanced slightly the magnesium readings, approximately 3.5 per cent for 500 $\mu\text{g.}$ of calcium per ml. in presence of 5 $\mu\text{g.}$ of magnesium per ml.

The results of the method are precise even though complete extraction may not be achieved. Anion interferences are virtually eliminated.

The extraction method limits the interference from other metals to those which coextract and affect the emission intensity of the magnesium or those which inhibit the extraction of the magnesium. This is an advantage which the usual colorimetric 8-quinolinol method does not possess. In the colorimetric method, any of the numerous metals which form coextractable quinolates interfere severely. Furthermore, interference from calcium in the flame-photometric extraction method is less severe than in the titan yellow method. Aluminum must be absent because aluminum quinolate precipitated and tended to clog the capillary of the atomizer.

Extraction techniques employing eriochrome black T and p-nitrobenzazo- α -naphthol were investigated briefly but found unsatisfactory.

CHAPTER IV

SUMMARY

The emission intensity of the 285.2-m μ magnesium line has been measured as a function of the acetylene flow rate under a variety of conditions. A higher acetylene flow rate was required to give the maximum emission intensity as higher portions of the flame were observed. As a result of solvent combustion, magnesium solutions in 4-methyl-2-pentanone required less acetylene to give maximum emission intensity than did aqueous solutions of magnesium.

A study of the calibration curve of magnesium showed self absorption to be severe in the different regions of the flame. A plot of the logarithm of the emission intensity versus the logarithm of the concentration was linear down to at least 25 μ g. per ml.

An extraction procedure for magnesium showed that some of the interferences which hinder flame-photometric methods could be eliminated or minimized.

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VITA

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