THE ANALYTICAL APPLICATIONS OF A PREMIXED FUEL RICH NITROUS OXIDE - HYDROGEN FLAME

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A Thesis Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1967

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ACKNOWLEDGMENT

The author wishes to thank Dr. Louis Ramaley for his interest and guidance throughout the course of this research.

The author also gratefully acknowledges partial financial support from a National Science Foundation Institutional Grant.

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ABSTRACT

The hydrogen-nitrous oxide premixed laminar flame was studied to determine the optimum conditions for its use in analysis. The flame background was compared to the turbulent hydrogen-oxygen and acetylene-oxygen flames. Emission sensitivity was studied as a function of the flow rate ratio of hydrogen to nitrous oxide. The flame emission profile was also studied. The alkaline earth elements were chosen for this study because of their desirable properties. The detection limits for the flame were compared to those reported for turbulent flames.

INTRODUCTION

In flame photometry, a solution to be analyzed is introduced into a flame. The light from the flame enters a monochromator to isolate the desired region of the spectrum. A photocell and amplifier system measure the intensity of radiation emitted. Through knowledge of the wavelength and the intensity of light emitted, the type of element present in a sample and its amount can be determined.

The following events take place when a solution is sprayed into a flame.

1. The solvent evaporates leaving particles of salt, or other decomposition products.

2. The salts or other products are vaporized and may dissociate into atoms, molecules, or radicals.

3. The vapors of the metal atoms, or the molecules, or radicals containing the metal atom, may then be excited by the energy of the flame.

4. If the temperature of the flame is high enough, enough energy may be present to ionize some of the atoms and these ions may be excited.

5. In the process of emission the excited atoms, ions, or molecules fall back to their ground state and emit radiation. The radiation emitted will consist of lines for atoms or ions and bands for molecules.

Flame photometry has several advantages over other forms of analysis. It is a very fast method of analysis, because it does not generally require a prior chemical separation or other chemical treatment. Small amounts of samples are used and only about 1 ml of a sample is needed per element determined. It is useful in trace analysis, especially with the alkali and alkaline earth metals for which few good methods of analysis exist.

In the past 30 years over a thousand articles and books have been published demonstrating the usefullness of flame photometry in analytical chemistry. Mavrodineanu's book "Flame Spectroscopy"[1] is probably the most complete book on the subject to date. Dean's book "Flame Photometry"[2] and also the "Treatis on Analytical Chemistry" Part 1, Volume 6[3] contain a large amount of information on the subject. A few of the more recent reviews can be found in refrences 4, 5, and 6.

The temperature of the flame is one of the most important factors in the excitation of elements. The hotter the flame, the greater the number of atoms in the excited state. A good example is calcium. In a methane-air flame, the sensitivity is poor whereas in the hotter acetylene-air flame the sensitivity is greatly increased. Table 1 contains the temperatures of some flames used in flame photometry.

TABLE 1

TEMPERATURES OF SOME FLAMES

Fuel	Oxidant	Temperature in °C	Ref.
Hydrogen	Air	2100	7
Hydrogen	Oxygen	2780	8
Hydrogen	Fluorine	4000	9
Acetylene	Air	2300	10
Acetylene	Oxygen	3080	10
Acetylene	Nitrous oxide	2955	10

Flame temperature not only effects excited state atom population, but also the amount of ionization, which in turn effects the amount of emission from a flame. Ionization of elements in a flame usually means that less emission is observed. Ions can emit radiation but it is less intense than the atomic line emission and is seldom observed in flames. The hotter the flame, the more easily ionized are the elements with low ionization potentials. Cesium, for example, emits strongly in an acetylene-air flame but only weakly in the hotter acetylene-oxygen flame. Table 2 contains the ionization potentials of some elements which are commonly determined by flame photometry.

TABLE 2

FIRST IONIZATION POTENTIAL

Element	Ionization Potential, Volts
Li	5.39
Na	5.14
K	4.34
Rb	4.18
Cs	3.89
Mg	7.65
Ca	6.11
Sr	5.69
Ba	5.21

A premixed laminar flame has several advantages over a turbulent flame(a flame from a conventional total consumption burner). These are:

1. A much lower flame background.[11]

2. A more stable and more reproducible flame.

3. A higher burning temperature because large water drops do not enter the flame.

One disadvantage is the threat of a flash back of the flame into the burner chamber. This flash back occurs when the burning velocity of the flame becomes greater than the velocity of the gasses leaving the burner. Table 3 shows the burning velocity of some of the common gasses used in flame photometry. Every attempt to use hydrogen-oxygen mixtures in a premixed burner has resulted in flash back problems. The inefficiency of premixed burners can be a problem if only small amounts of samples are available. Most of the solution in a premixed burner never reaches the flame and is drained away and discarded.

TABLE 3

MAXIMUM BURNING VELOCITY OF VARIOUS GASSES

Fuel	Oxidant	Diameter of Combustion Vessel in cm	Maximum Burning Velocity in cm/sec	Ref.
Hydrogen	Air	1.0	40	12
Hydrogen	Oxygen	2.5	3680	13
Hydrogen	Nitrous Oxide		11.5	14
Acetylene	Air	1.2	266	15
Acetylene	Oxygen	2.5	2480	13
Acetylene	Nitrous Oxide		180	16

Compound formation is another factor to be considered in flame emission. For some elements oxide formation severely hinders the atomic emission observed in flames. Compound emission can replace atomic emission; nevertheless, compound emission usually is not as sensitive or as selective, because the energy emitted is spread over a wide range of wavelengths. The refractory metals, e.g., aluminum, magnesium, molybdenum, titanium, tungsten, etc. show severe oxide formation. Knutson[17] has shown that magnesium has enhanced atomic emission by making the flame fuel rich. A fuel rich flame is a reducing flame, and therefore inhibts oxide formation. Fassel and associates also have shown that this effect is observed for many of the other elements which form stable oxides.

Flame background is another factor which effects the sensitivity observed for some elements. Magnesium, for example, has an atomic line at 285.2 mu and its sensitivity is severely effected by the OH band emission from the flame. In flames containing hydrocarbon fuels, the emission from some elements may be masked by carbon radical emission or cyanogen band emission. Fuel rich acetylene flames are particularly bad in this respect. The fuel rich hydrogen-nitrous oxide flame has a low background in comparison to the fuel rich acetylene-oxygen flame.

The hydrogen-nitrous oxide flame has several advantages in flame photometry. The flame has a fairly high temperature and should therefore be able to excite many elements. The burning velocity is low enough to be used safely in a premixed burner; this burner will allow a much lower flame background and a more stable and reproducible flame than the turbulent total consumption burners. The hydrogen-nitrous oxide flame can be used in the fuel rich state with a fairly low background emission as compared to the other flames available, and therefore should inhibit "oxide" formation.

The purpose of this research was to test these advantages with two end results in view. It was desired to learn something about the basic characteristics of the flame, such as flame background, emission intensity as a function of height in the flame, effect of the flow rate ratio of hydrogen to nitrous oxide, etc. It was also desired to determine the detection limits of certain elements in this flame for the purpose of analysis.

The alkaline earth elements were chosen for this study for the following reasons:

1. They can be usefully determined by atomic emission.

2. They are in the same group in the periodic table and show similar emission characteristics.

3. They form compounds in the flame which emit band radiation.

4. Some of the alkaline earth elements readily undergo ionization.

All of these factors can be studied as a function of the fuel to oxidant flow rate ratio in order to study flame parameters and determine optimum analysis conditions.

EXPERIMENTAL

A. Materials

The hydrogen, oxygen, and acetylene used in this study were obtained from Air Reduction Co. The nitrous oxide was obtained from the Matheson Co.

All solutions were prepared from distilled water which was subsequently passed through a mixed resin bed ion exchanger(Crystal Lab. Deeminizer). All chemicals were Mallinckrodt Chemical Works "Analytical Reagent" grade. These chemicals were used without further purification. Concentrated stock solutions were prepared for each element tested and dilutions of these stock solutions were used for all other solutions. The salts used and the concentration of each stock solution can be found in Table 4.

B. Equipment

A simplified block diagram of the apparatus used can be found in Figure 1.

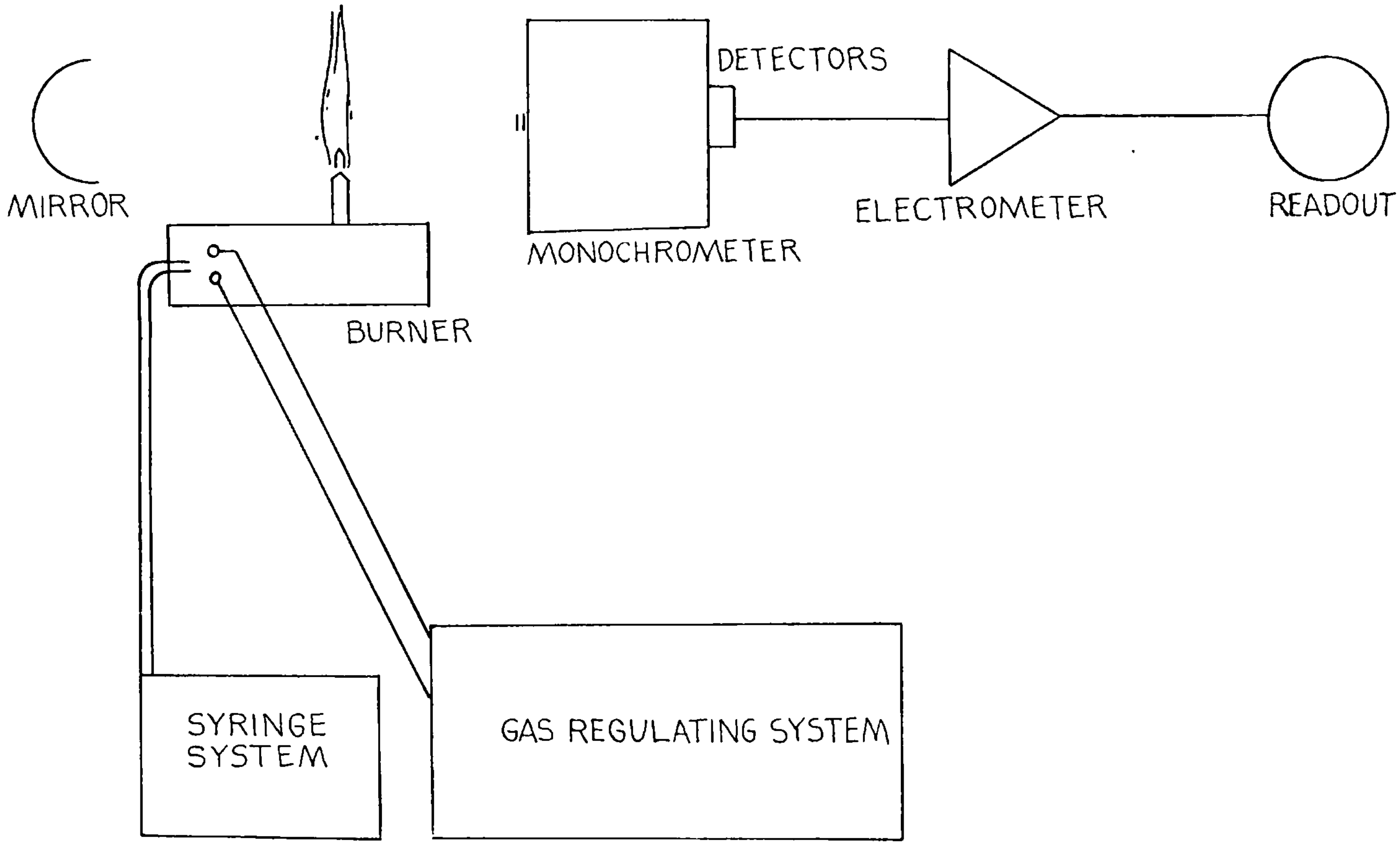
Light from the flame was focused unmagnified on the monochromator slits by an A. Jaegers Co. No. 5C2571 mirror of 150 mm focal length and 82 mm diameter. A Jarrel Ash Co. Model 82-410 0.25 meter Ebert monochromator was used to disperse the radiation from the flame. This monochromator

TABLE 4

SALTS USED TO PREPARE STOCK SOLUTIONS OF THE ELEMENTS TESTED

Salt	Element	Concentration in ppm
$AlK(SO_4)_2 \cdot 12H_2O$	Aluminum	500
$BaCl_2 \cdot 2H_2O$	Barium	100
$CaCO_3$ + HCl	Calcium	100
$Cr(NO_3)_3 \cdot 9H_2O$	Chromium	100
$CoCl_2 \cdot 6H_2O$	Cobalt	100
$Fe(SO_4)(NH_4)_2 \cdot 6H_2O$	Iron	100
$MgCl_2 \cdot 6H_2O$	Magnesium	5000
$MnSO_4 \cdot H_2O$	Manganese	100
$NiCl_2 \cdot 6H_2O$	Nickel	100
KCl	Potassium	100
NaCl	Sodium	100
$SrCl_2 \cdot 6H_2O$	Strontium	100

Figure 1.--Diagram of apparatus.


MIRROR
BURNER
MONOCHROMETER
DETECTORS
ELECTROMETER
READOUT
SYRINGE SYSTEM
GAS REGULATING SYSTEM

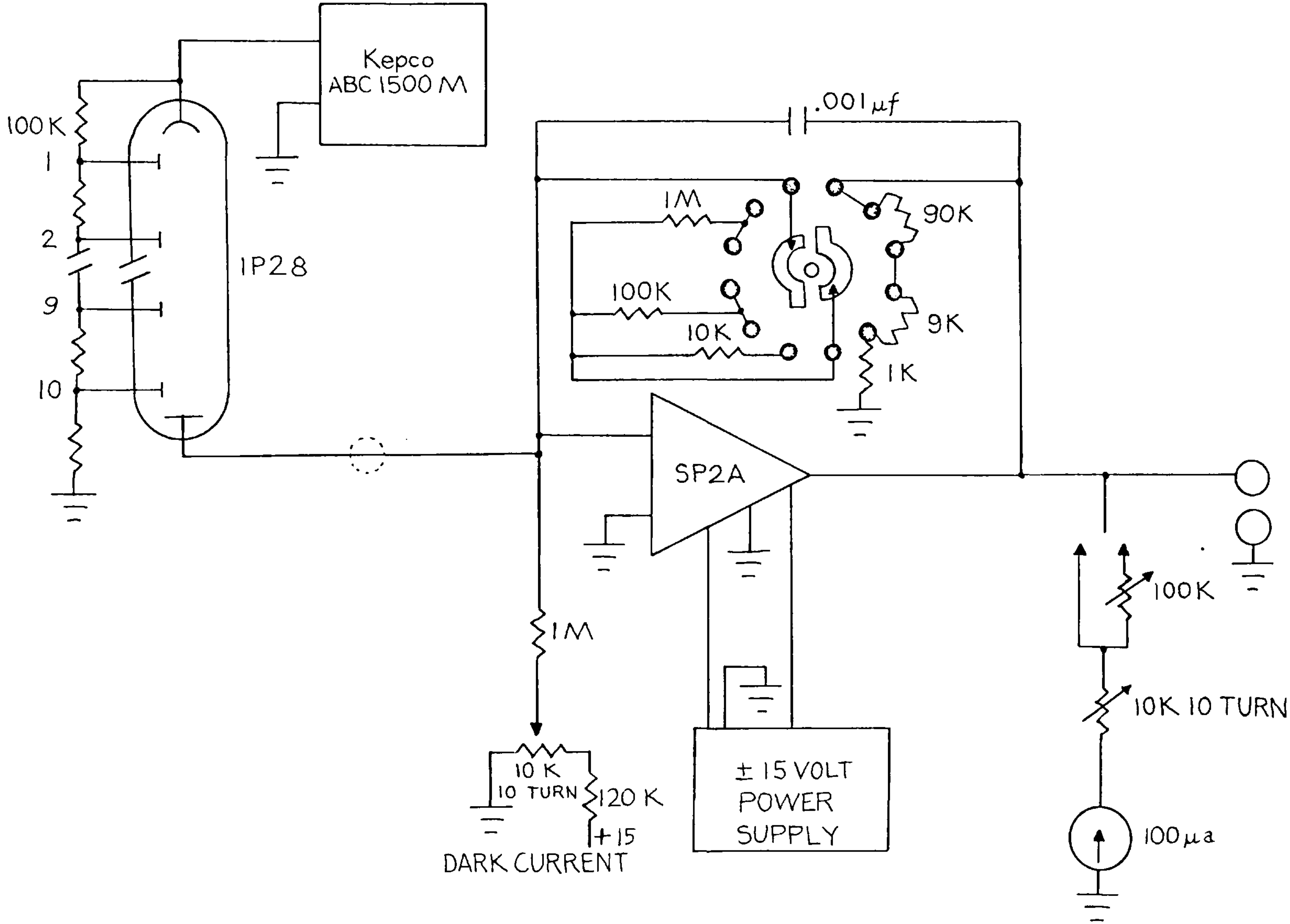
was equipped with two gratings of 1180 groves/mm, one blazed for 300 mµ the other for 600 mµ. The efficiency of each grating was checked and showed that the best results could be obtained by using the 300 mµ blaze for wavelengths below 450 mµ and the other grating for wavelengths above 450 mµ. Two sets of fixed slits were used with the monochromator, one of 25 µ and the other of 100 µ. The 25 µ slits produced a half band width of 0.2 mµ; the 100 µ slits produced a half band width of 0.5 mµ.

An adaptor was made for the input slit to the monochromator so that a Corning Glass No. 0-52 filter with a cut off of 340 mµ could be placed in front of the slit to eliminate second order interferences. Two scan motors allowed the wavelength passed by the monochromator to be changed by 10 mµ/minute and 25 mµ/minute.

Radiation at the exit slit of the monochromator was detected with an RCA 1P28 photomultiplier tube contained in a Jarrel-Ash Model 83-021 housing. Power to the detector was supplied by a Kepco Model ABC 1500M power supply. The supply voltage to the photomultiplier was kept constant at 1000 volts for most of the work but was varied to give the best signal to noise ratio when detection limits were determined.

The electrometer for the detector system consisted of a G. A. Philbrick Researches SP2A operational amplifier. The circuit diagram is shown in Figure 2. The operational

Figure 2.--Diagram of electrometer circuit.


Kepco
ABC 1500 M
100 K
1
2
9
10
1P28
.001 μf
1M
90K
100K
10K
9K
1K
SP2A
1M
10 K
10 TURN
120 K
+15
DARK CURRENT
± 15 VOLT
POWER
SUPPLY
100K
10K 10 TURN
100 μa

amplifier was powered by a $\pm$ 15 volt power supply, regulated with a Burr Brown Research Corp. Model 1515 dual regulator. The electrometer had a current range of 10^{-10} to 10^{-3} amps for a full scale reading on a 100 μa meter. This meter had an internal resistance of 1050 Ω and an accuracy of 0.5 percent. The electrometer circuit had a time constant of one second on the most sensitive range. Either a Leeds and Northrup Model "H" AZAR or a Heath Model EUW-20M recorder was used as a readout device in addition to the meter. Under these conditions the electrometer had a full scale range of 10^{-11} to 10^{-5} amps. Because of the wide range of chart speeds available, the Heath recorder was used to record the spectra of the flames.

A diagram of the gas regulating system is presented in Figure 3. Matheson two stage regulators were used on the gas cylinders with the second stages having ranges from 0-100 psi. Beckman type 9220 regulators were used for fine control of the pressure to the rest of the regulating system. The Beckman regulators were used without the rest of the regulator system when Beckman atomizer burners were used for comparison purposes. The needle valves were Nupro type 2MA. The flow meters were purchased from the Matheson Co.(Cat. No. 622PB). The nitrous oxide flow meter was equipped with Tube No. 603 and the hydrogen flow meter with Tube No. 602. The flow meters were calibrated by measuring the time that it took the gas to replace the

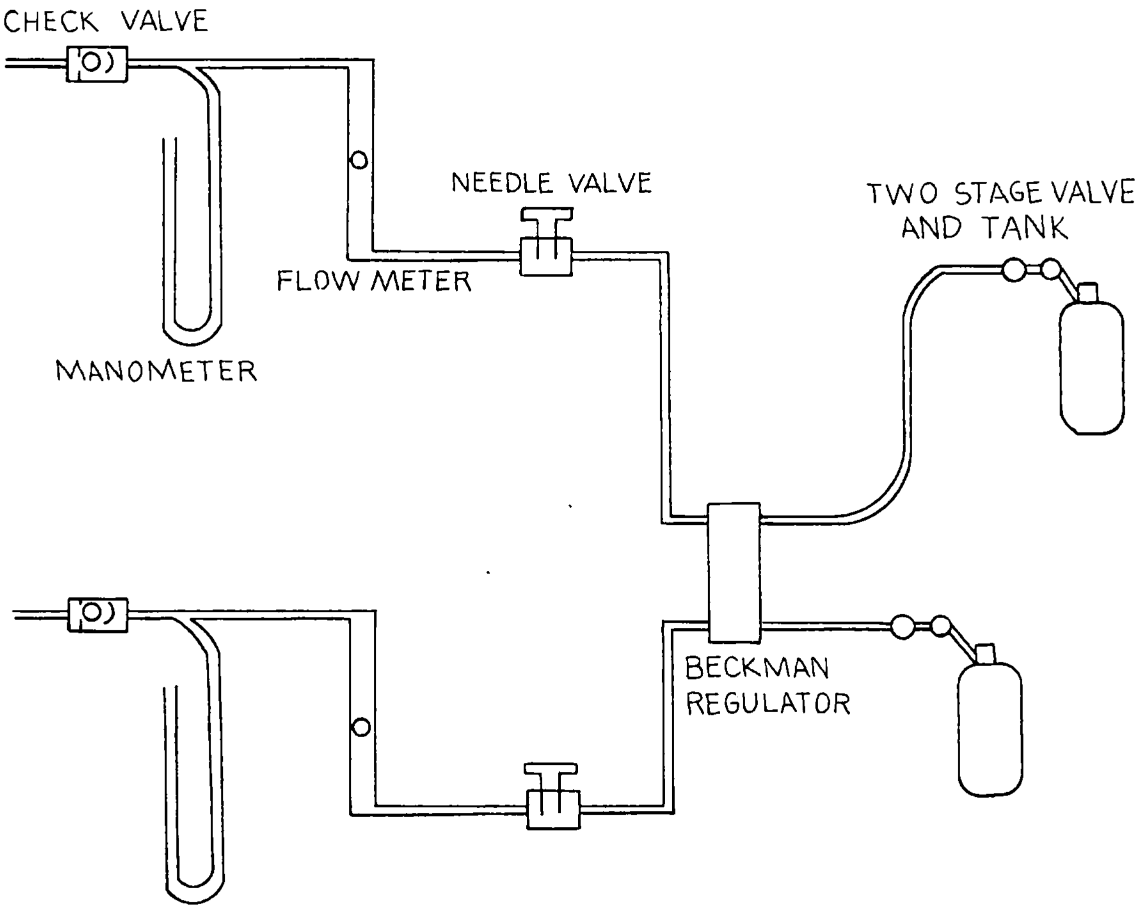


Figure 3.--Diagram of gas regulating system.

mercury in a 250 ml volumetric flask which was inverted in mercury. The calibration curves are shown in Figure 4 with flows corrected to one atmosphere pressure and 25^{o} centigrade. Manometers made from pyrex glass and filled with mercury were used to measure the pressures of the gasses coming from the flow meters. Check valves from the Matheson Co.(type 401) were used to protect the system in case of flash back and explosion.

The burner was constructed from type 303 stainless steel. The parts, shown in Figure 5, are as follows:

1. A plastic safety window which would rupture in case of a flash back.

2. A drain to remove excess sample from the aspiration system.

3. An inlet for hydrogen with a large diameter orifice.

4. An inlet for nitrous oxide with an orifice of 0.016 inches.

5. A syringe needle for sample injection with the tip at a right angle and close to the tip of the inlet jet for nitrous oxide.

6. Two burner heads were used, one with an orifice diameter of 0.040 inches, the other with orifice diameter of 0.052 inches.

Aspiration was accomplished by passing the solution through a Hamlton Co. 2", 90^{o} syringe needle type N726 at a

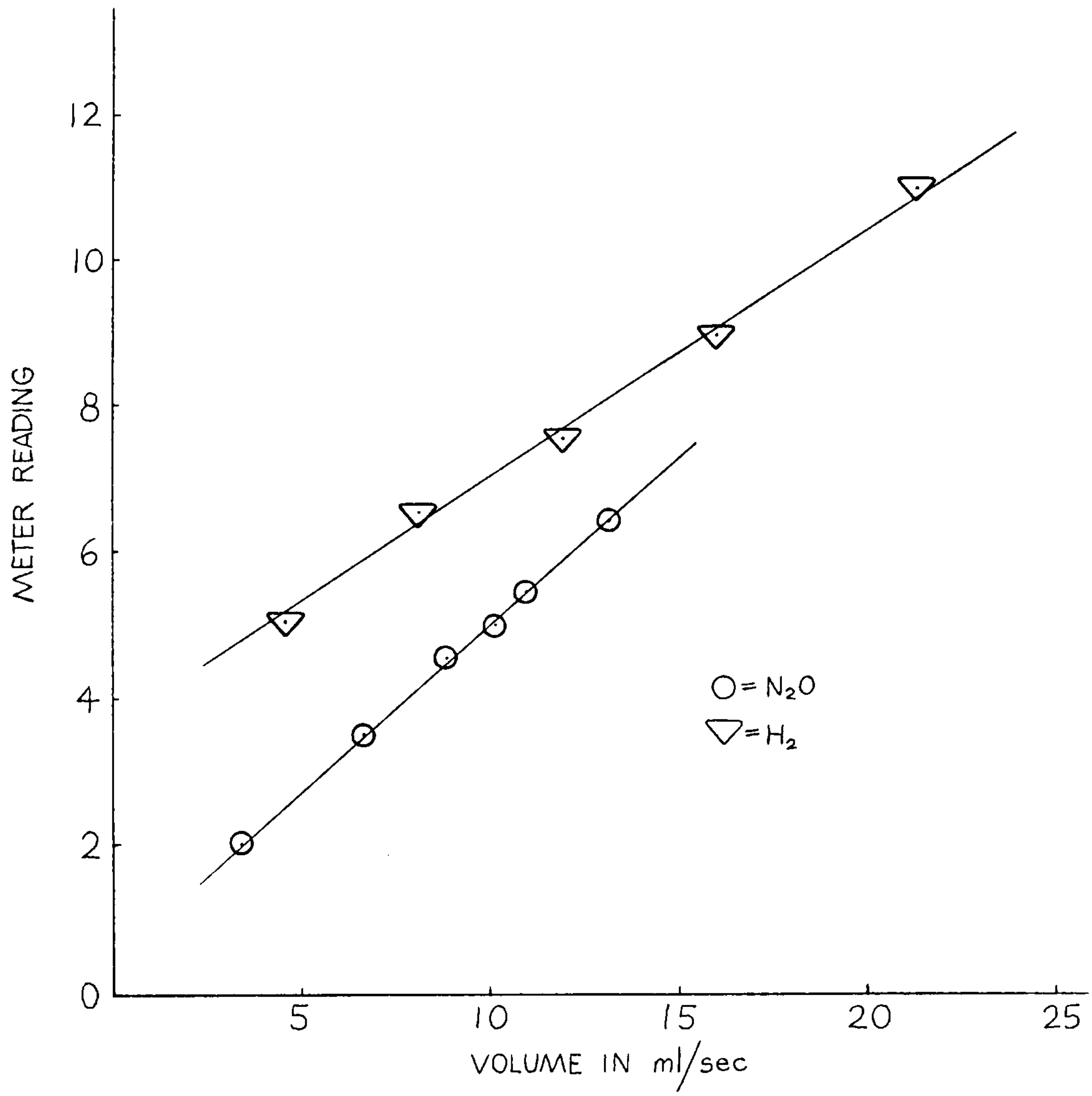


Figure 4.--Flow meter calibration curves.

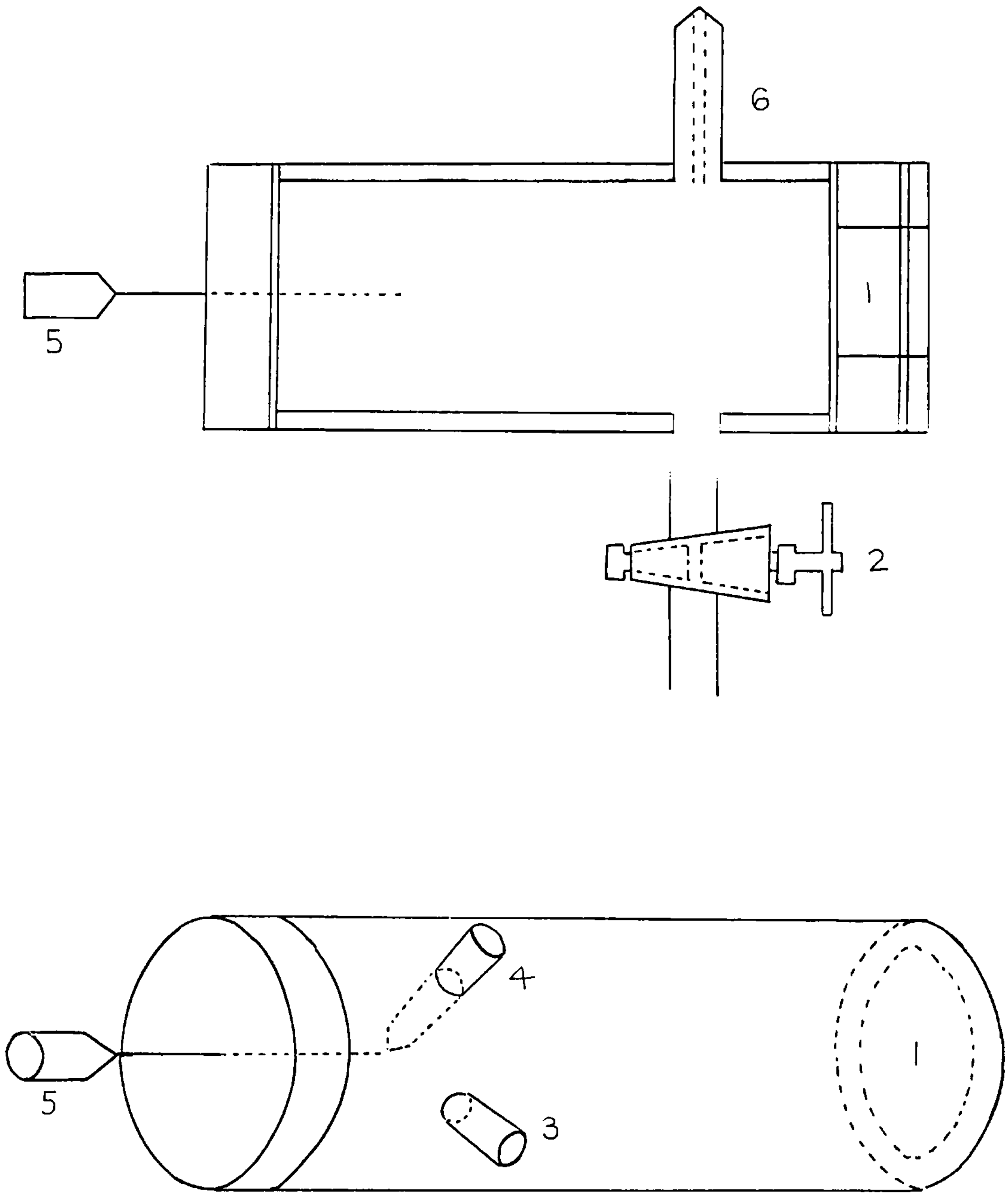


Figure 5.--Burner diagram for premix flame.

right angle to the tip of the nitrous oxide jet. The needle was positioned so that maximum aspiration was obtained. An attempt was made to aspirate with two gas jets, one using nitrous oxide and one hydrogen, to determine if this would improve the efficiency of aspiration. This proved to be unsatisfactory because it was impossible to maintain the aspiration efficiency constant while the flow rate of one of the gasses varied. When using two jets if either flow rate was changed the aspiration rate changed. By using only one jet for aspiration, the aspiration rate was independent of the flow of gas coming from the non-aspirating jet.

For comparison purposes Beckman burners were used for hydrogen-oxygen flames(Model No. 4020) and for oxygen-acetylene flames(Model No. 4030).

The height of the burners in relation to the slits could be varied through a worm gear drive system to allow the study of different parts of the flame.

The apparatus for feeding the solutions to the burner consisted of a Syringe Microburet Model No. SB2 manufactured by Micro-Metric Instruments Co. The microburet was powered by an electric motor whose speed could be adjusted by changing the gears in the drive system. The syringe used in the microburet was a 10 ml glass type with a Lur Lock fitting. The syringe was connected to the syringe needle in the burner through a piece of small diameter Teflon spaghetti. To complete the connection several small fittings were made from brass.

RESULTS

A. Characteristics of the Premix Burner

A graph showing the relationship between the flow rate of nitrous oxide and intensity of sodium emission is presented in Figure 6. The graph indicates that a flow of at least 6.0 ml/second must be used to cause any aspiration of a sample into the flame. With the flow rate of nitrous oxide at about 10 ml/second, it was found that the burner had an aspiration efficiency of about 4 percent. The efficiency was determined by weighing the sample put into the burner and the amount drained away. This is only an approximate number due to the large errors involved in its determination. The burner had a large hold up volume of solution and did not drain evenly every time.

The aspiration efficiency of the burner was also dependent on the concentration of other elements in solution. Figure 7 shows the relationship between the intensity of sodium emission and molarity of KCl in the solution. The observed intensity was corrected for the amount of sodium in the KCl as an impurity. The effect of adding a large amount of potassium to the solution should be to increase the sodium emission observed. Potassium was easily ionized in the flame and the electrons from this ionization should depress the ionization of sodium atoms resulting in an

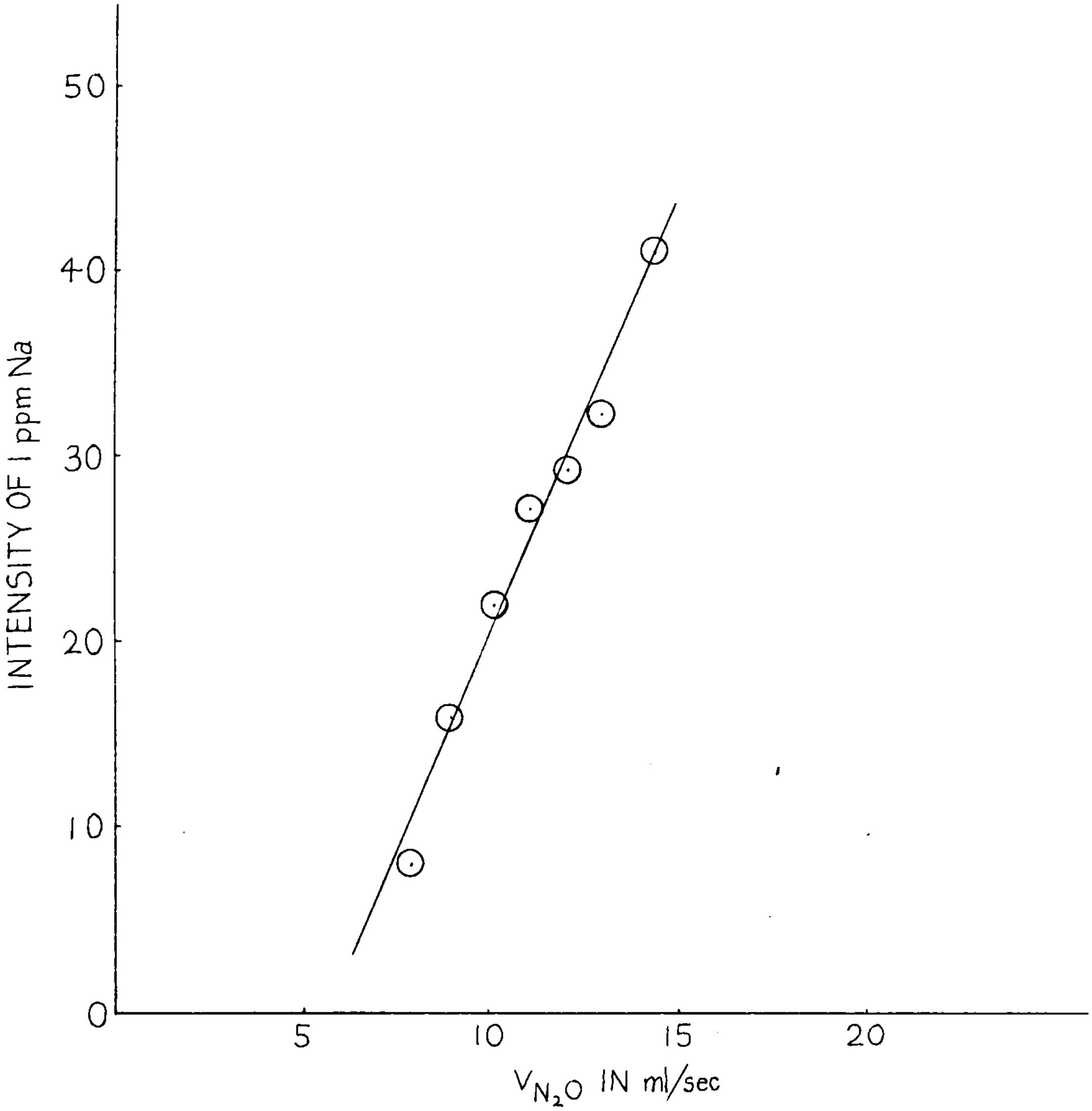


Figure 6.--Flow rate of nitrous oxide versus aspiration efficiency.

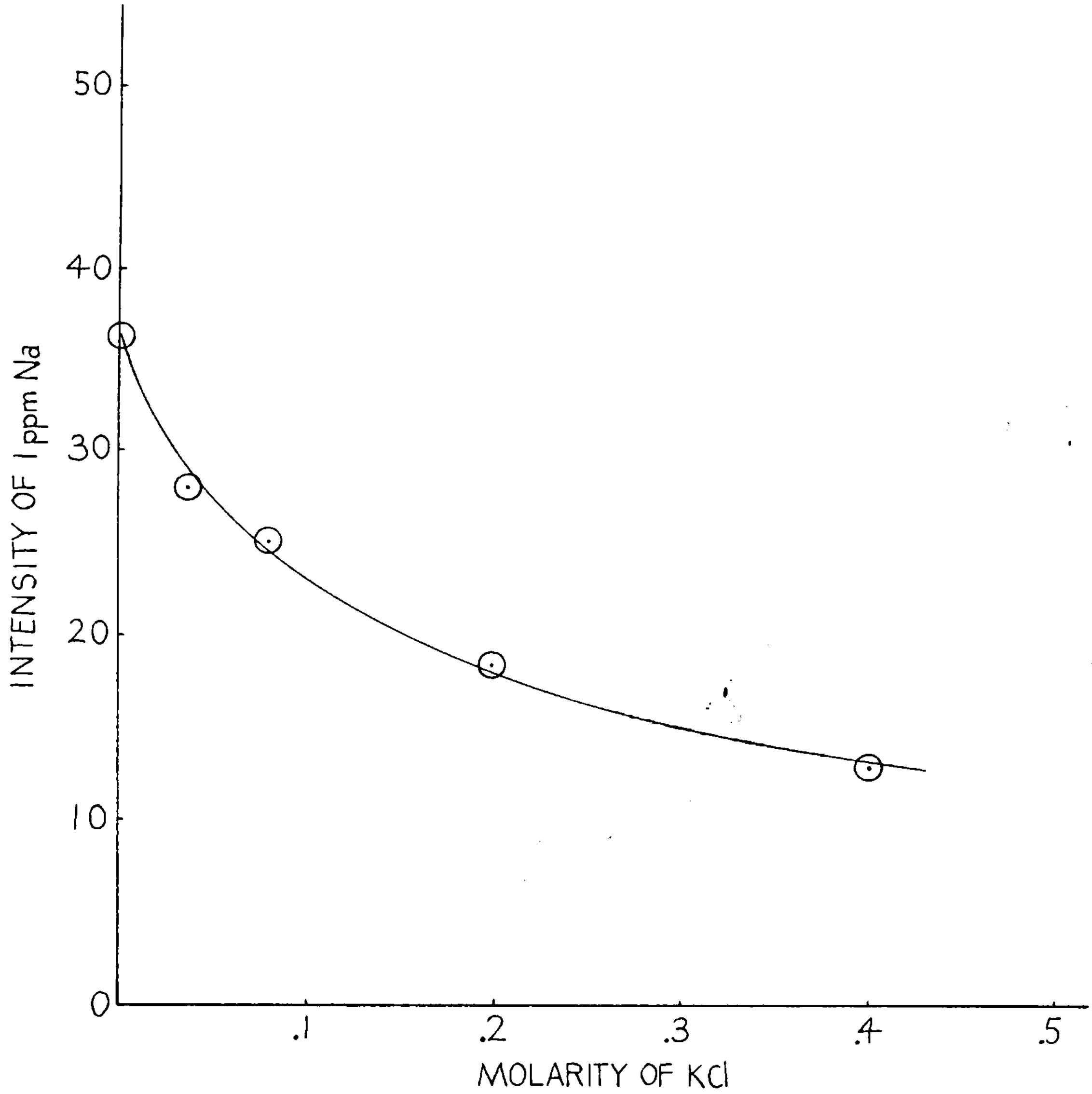


Figure 7.--Concentration effect on aspiration.

increase in atomic emission. The opposite was observed. This decrease in sodium emission when an inert salt was added was therefore probably caused by changes in density, viscosity, and surface tension of the solution.

B. Flame Characteristics

The hydrogen-nitrous oxide flame is a slightly white, almost colorless flame. The inner cone appears at the bottom of the flame as an area that has a higher luminosity than the rest of the flame. The inner cone has the same color as the outer cone.

Figure 8 shows the variation of the heights of the inner and outer cones of the flame with the ratio of the flow rates of hydrogen to nitrous oxide. During a given experiment the nitrous oxide flow rate was held constant. While the height of the inner cone of the flame stayed fairly constant, the total height of the flame continued to rise fairly rapidily as the flow rate of the hydrogen increased. The total height of the flame depended on the rate of air diffusion into the flame to burn any excess hydrogen and also the time for the gasses to completely react in the flame. The inner cone height of the flame varied with the volume of gasses coming out of the burner head and with the burning velocity of the hydrogen-nitrous oxide mixture. Thus the inner cone height changed less rapidly with flow rate than the outer cone height.

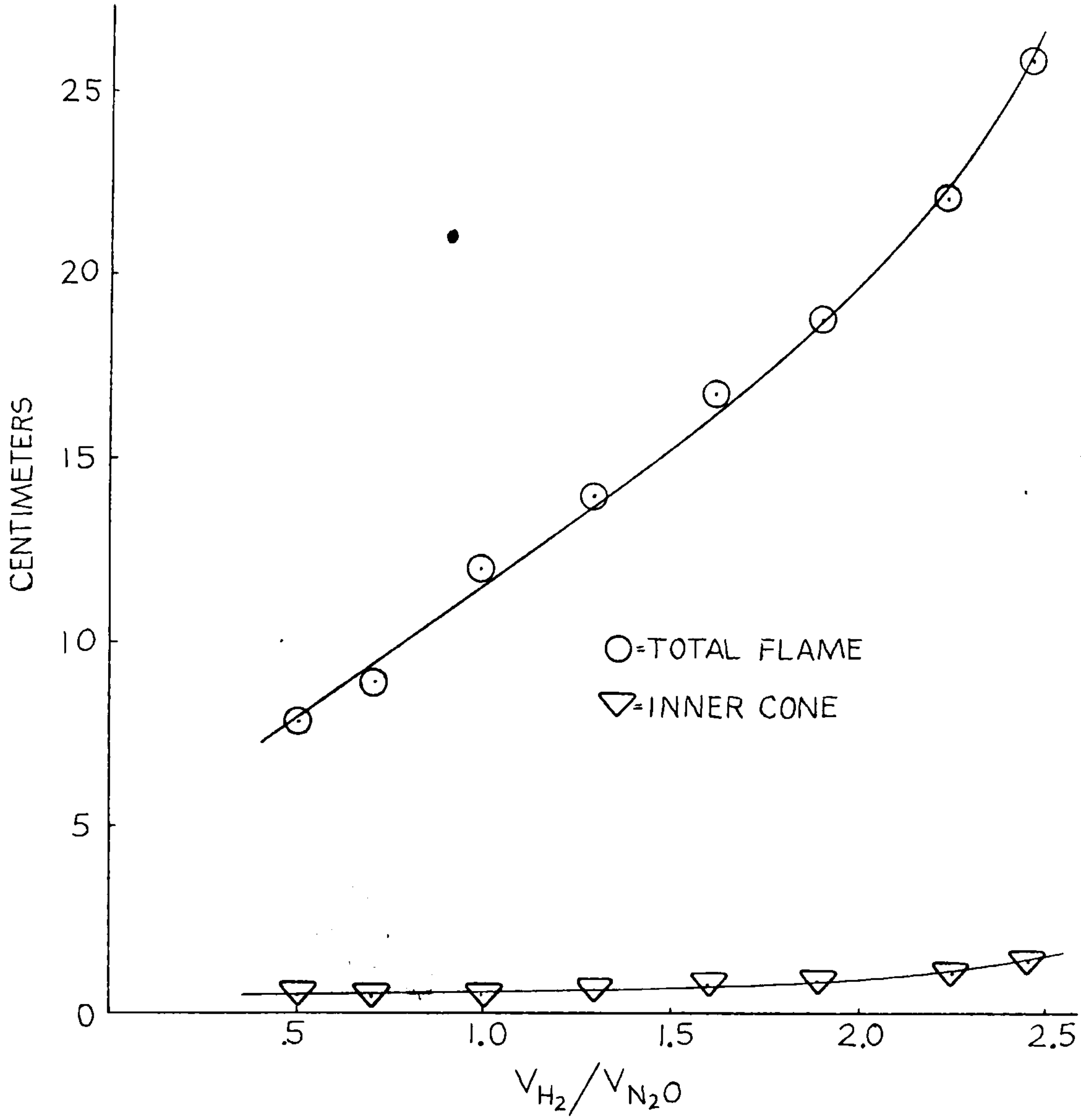


Figure 8.--Height of inner and outer cone of hydrogen-nitrous oxide flame.

The spectra of several different flames can be seen in Figures 9, 10, 11, and 12. These spectra were taken using 25 μ slits with a 4 mm vertical window at a scan rate of 25 mμ/minute. At 450 mμ the gratings were switched from the 300 mμ blaze to the 600 mμ blaze. The Corning filter to eliminate second order distortions was also placed in front of the entrance slit at 450 mμ. No solvent or solutions were aspirated into the flames in these runs.

In the analysis of the spectra one must consider that the photomultiplier response starts to fall off above 650 mμ and is very poor above 700 mμ. Air(oxygen) begins to absorb the radiation emitted below 200 mμ and almost all of the radiation emitted by the flame is absorbed at 175 mμ.

Figure 9 shows the flame background from a turbulent flow hydrogen-oxygen flame. Figure 10 shows the spectrum of the inner cone of a fuel rich hydrogen-nitrous oxide flame, and Figure 11 shows the outer cone of the same flame. Many similarities are noted between the hydrogen-oxygen and hydrogen-nitrous oxide flames. Most of the features in both the hydrogen-oxygen flame and in the hydrogen-nitrous oxide flames are due to OH band emission in the flame. The one extra peak at 336 mμ in Figure 10 is due to NH emission. The OH band emission is greater in the inner cone of the hydrogen-nitrous oxide flame; the band between 285 mμ and 295 mμ is particularly intense.

Figure 9.--Flame background for fuel rich hydrogen-oxygen flame.

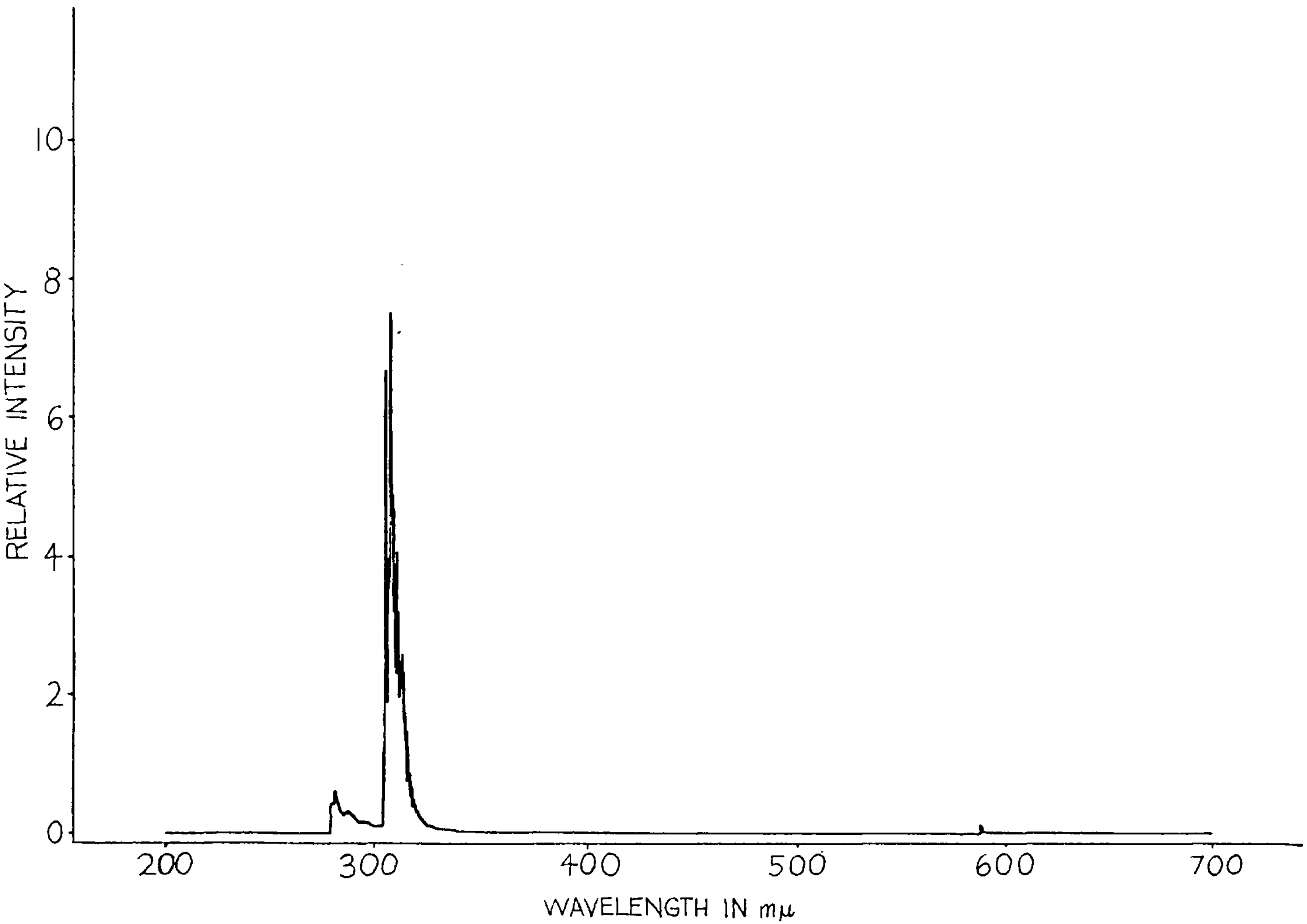

RELATIVE INTENSITY
0
2
4
6
8
10
200
300
400
500
600
700
WAVELENGTH IN mμ

Figure 10.--Flame background for inner cone of fuel rich hydrogen-nitrous oxide flame.

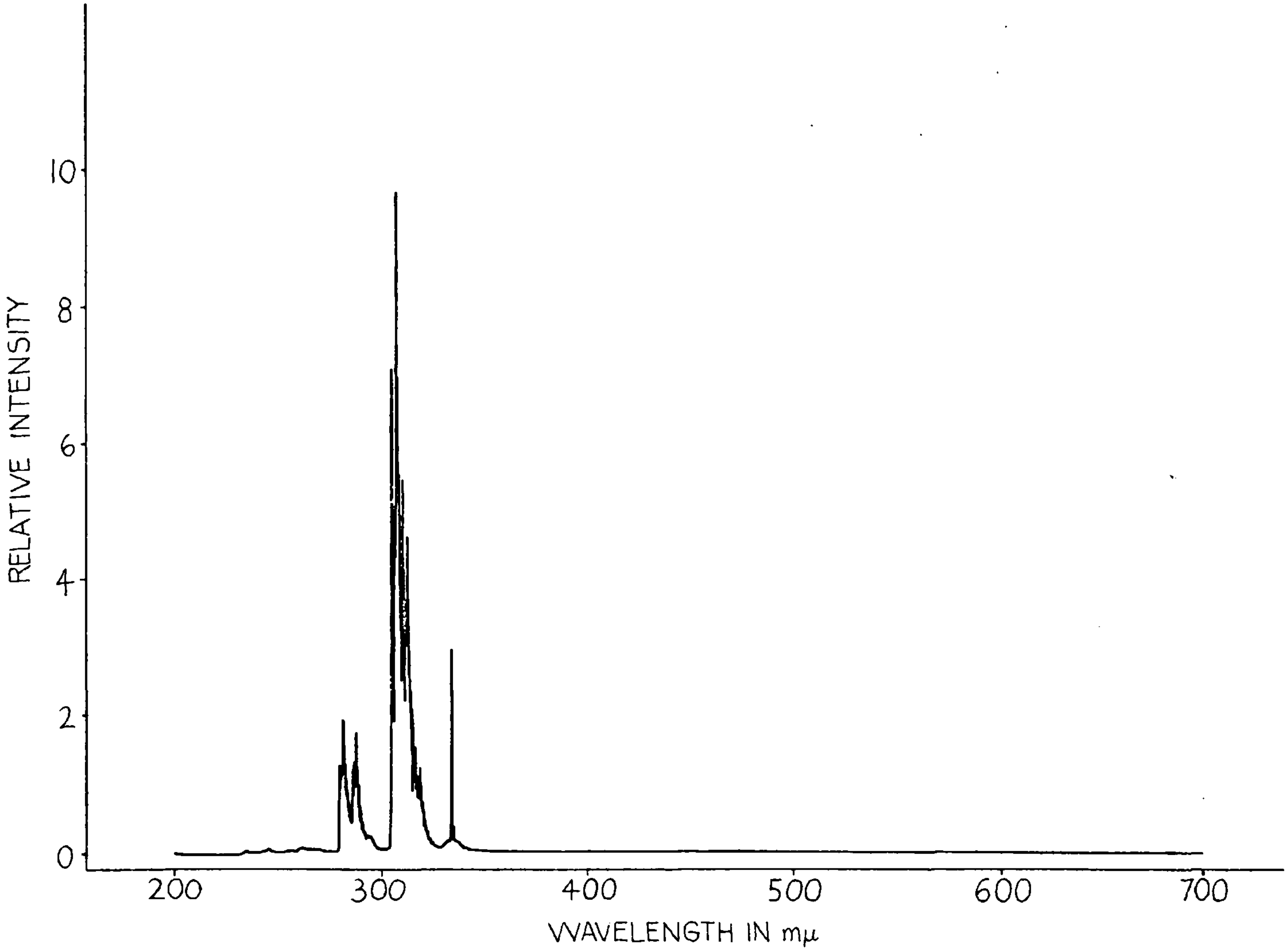

RELATIVE INTENSITY
0
2
4
6
8
10
200
300
400
500
600
700
WAVELENGTH IN mμ

Figure 11.--Flame background for outer cone of fuel rich hydrogen-nitrous oxide flame.

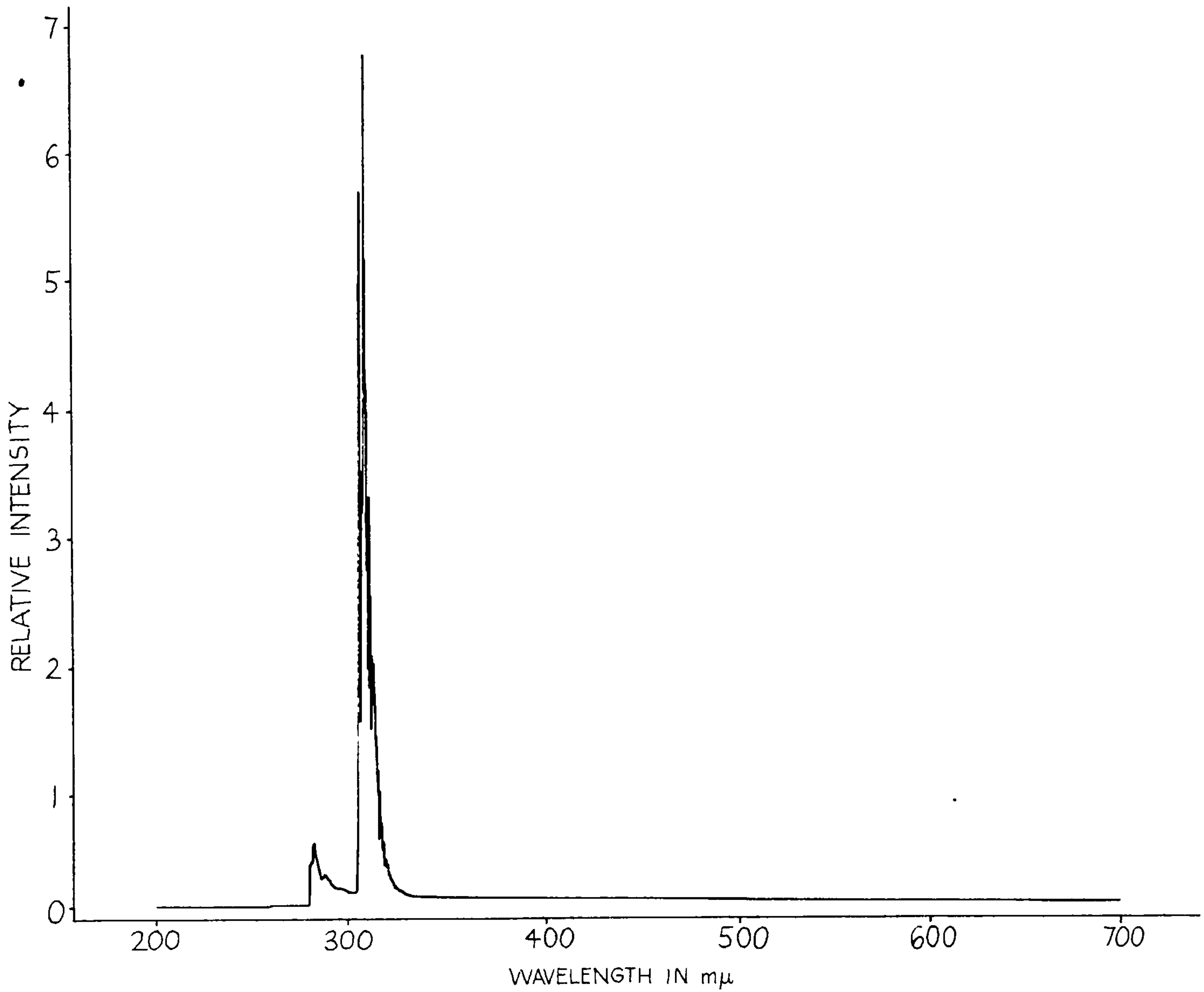
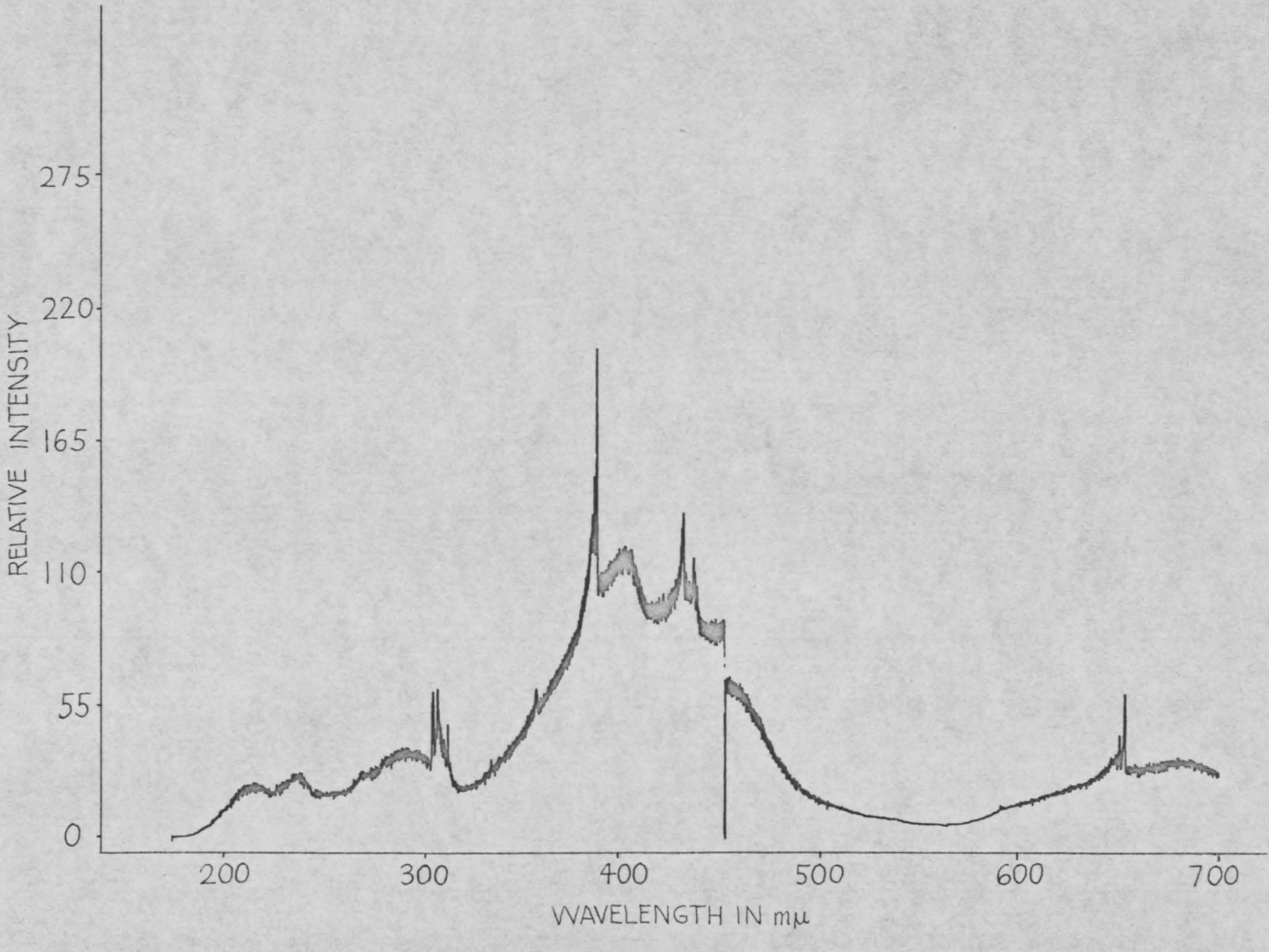

RELATIVE INTENSITY
0
1
2
3
4
5
6
7
200
300
400
500
600
700
WAVELENGTH IN mμ

Figure 12.--Flame background for fuel rich acetylene-oxygen flame.


RELATIVE INTENSITY
275
220
165
110
55
0
200
300
400
500
600
700
WAVELENGTH IN mμ

From the comparison of the relative intensities of the different spectra, it can be seen that a premixed hydrogen-nitrous oxide flame has a very low background in comparison to that of the fuel rich turbulent acetylene-oxygen flame shown in Figure 12. The C_2 and CN band emission are more intense than the OH emission in the latter flame. The discontinuity in the acetylene-oxygen spectrum at 450 mμ is due to the switching of grating and inseration of the filter.

C. Emission Characteristics

The main factors that effect flame emission are compound formation, ease of excitation, ease of ionization, and the rate of sample introduction. The first three of these effects are strongly influenced by flame temperature. The temperature of the hydrogen-nitrous oxide flame is a maximum when the ratio of the flow rates of hydrogen to nitrous oxide is between about 1.0(stoichiometric flame) and 1.1. The temperature of the flame decreases to either side of this range.

Compound formation in a flame can lower the atomic emission observed. For stable compounds such as oxides, fluorides, hydroxides, etc., the energy necessary to dissociate the compounds may be large so that little atomic emission will be observed. Compounds can emit radiation but it is in the form of band emission and usually not as intense as atomic emission.

The temperature or energy necessary to excite atoms or compounds which emit light at a short wavelength will be greater than the energy necessary to excite atoms that emit light at a long wavelength. A high temperature may not be an advantage for some elements, because ionization may become a predominate factor in a hot flame.

Sample introduction into a flame is mostly a mechanical problem. Sample introduction will have the following effects on the flame:

1. The more sample that can be placed in the flame per unit time, the greater the emission.

2. The more water, if water is used as solvent, placed in the flame the greater the cooling of the flame and the less emission.

3. A lower flame background is observed when water is used as solvent because of the cooling of the flame.

4. A higher flame background is observed when organic solvents are used because of carbon radical and cyanogen emission.

No attempt was made to adjust sample introduction into the flame to give maximum emission.

Figures 13, 14, 15, and 16, show the relationship between the emission observed from the alkaline earth elements and the ratio of fuel to oxidant flow rates.

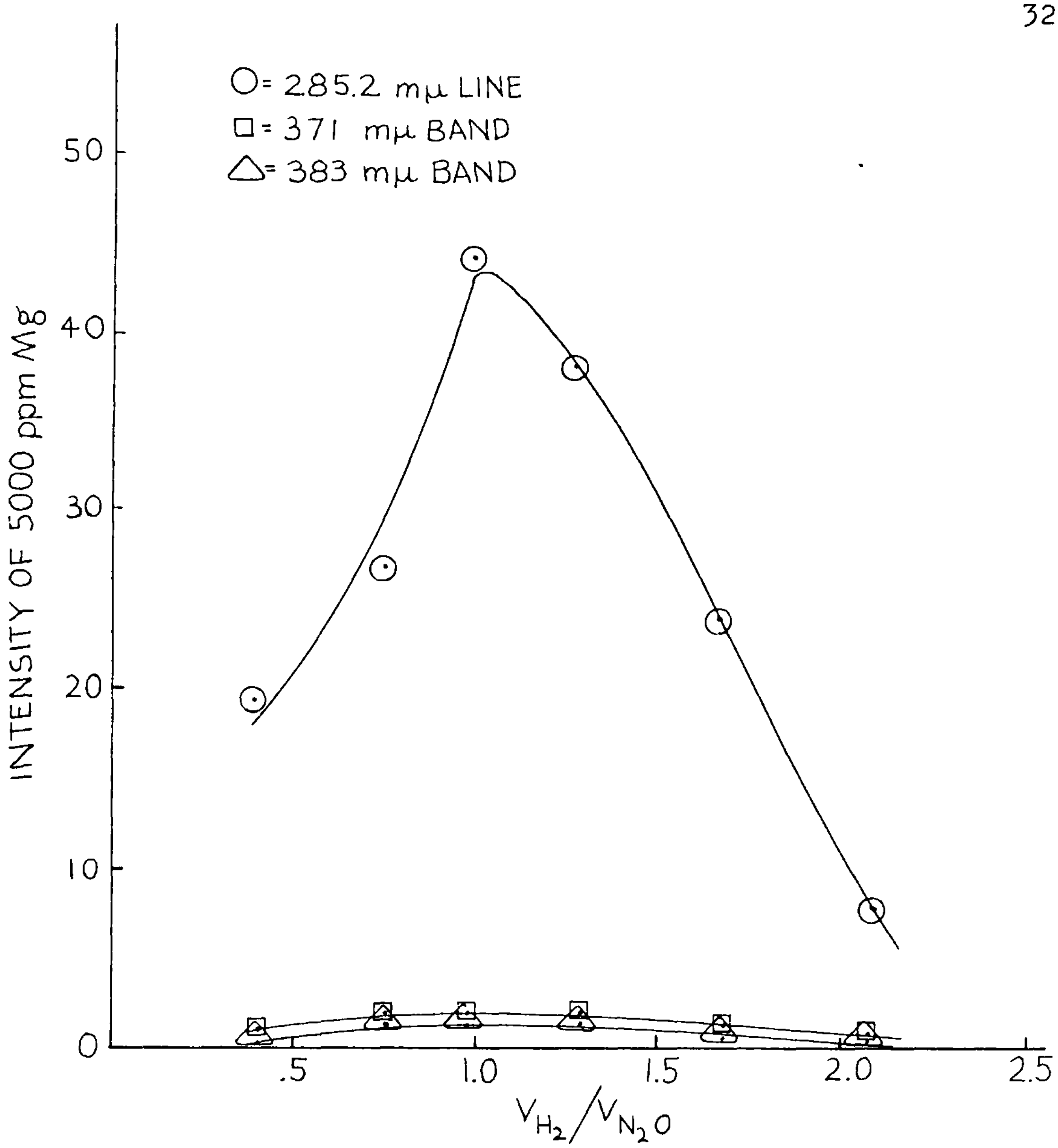


Figure 13.--Magnesium emission versus hydrogen to nitrous oxide flow rate ratio.

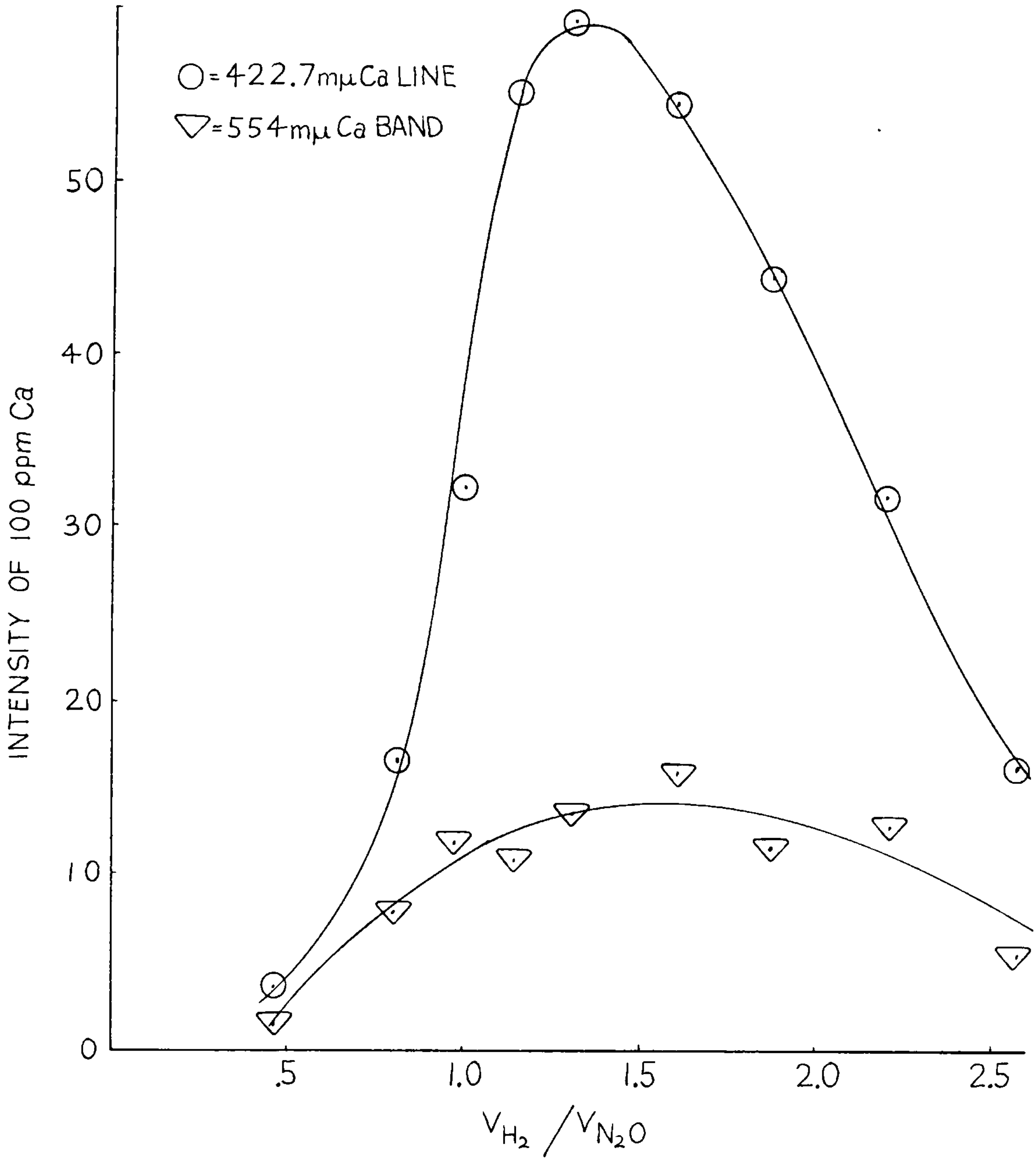


Figure 14.--Calcium emission versus hydrogen to nitrous oxide flow rate ratio.

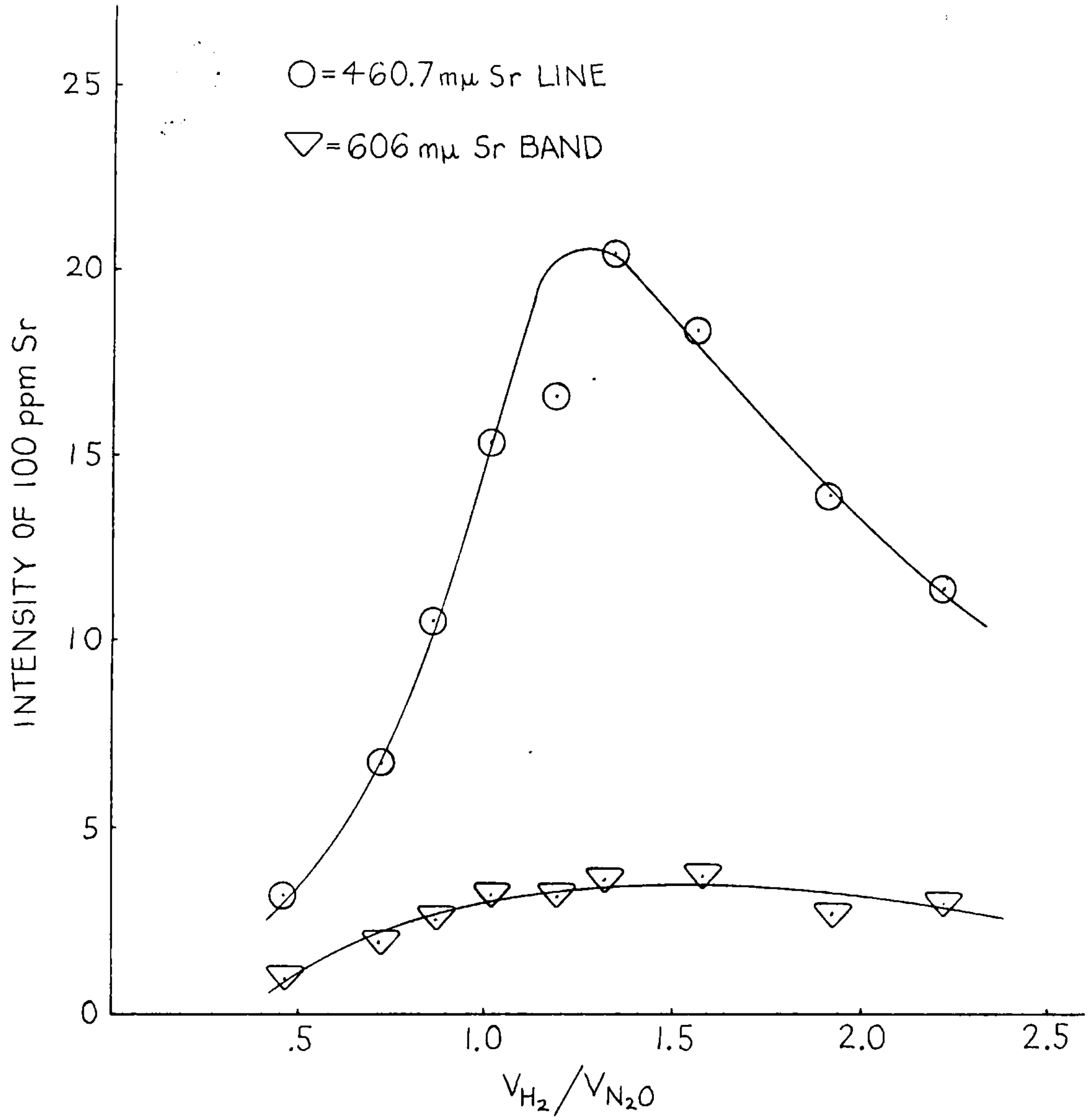


Figure 15.--Strontium emission versus hydrogen to nitrous oxide flow rate ratio.

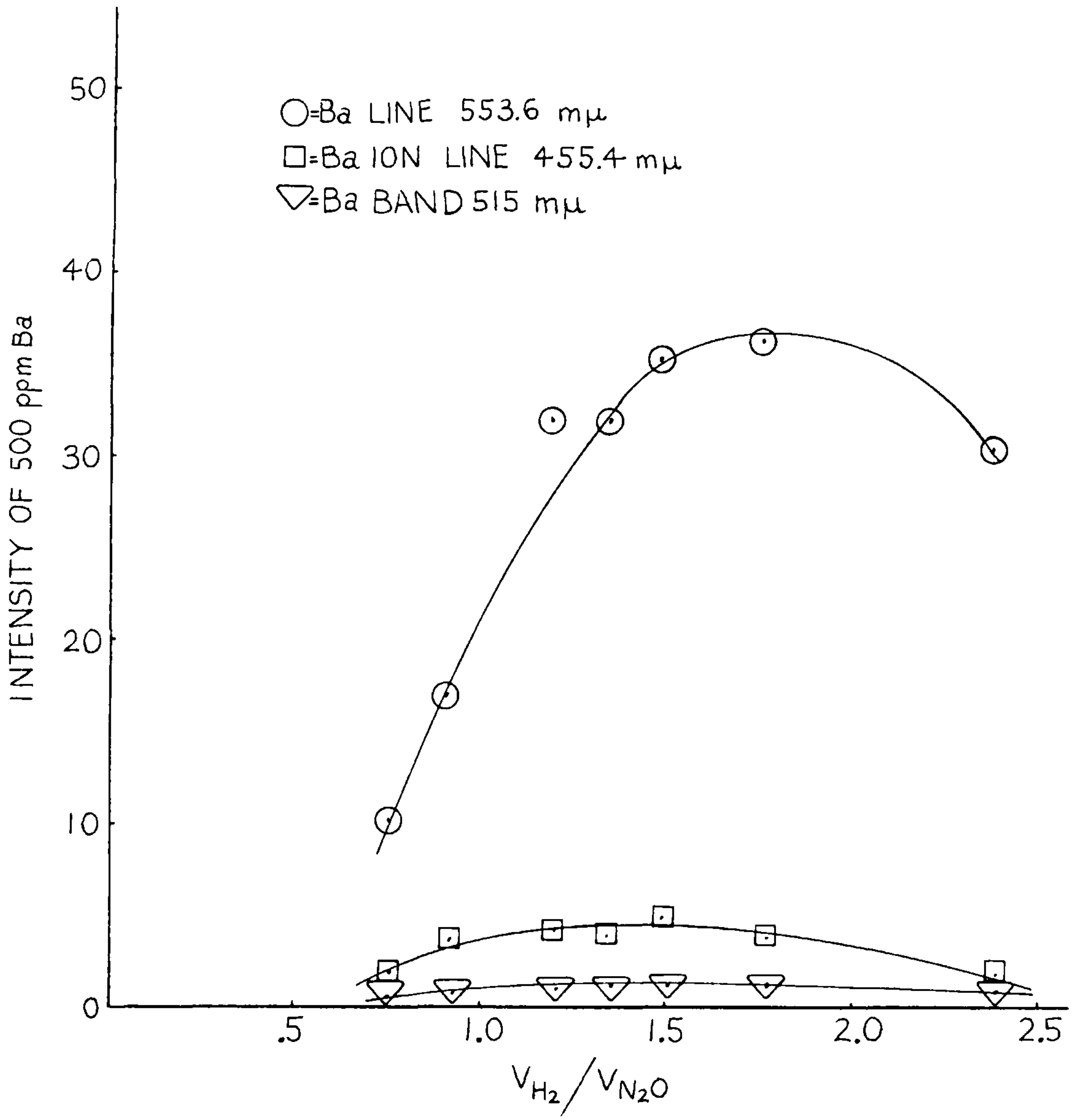


Figure 16.--Barium emission versus hydrogen to nitrous oxide flow rate ratio.

Analogous data for sodium are presented in Figure 17. Each set of points was measured using a constant nitrous oxide flow rate(10 ml/second) and varying the hydrogen flow rate. The intensities were measured at the height above the burner that gave maximum emission.

TABLE 5

FLOW RATE RATIO OF FUEL TO OXIDANT FOR MAXIMUM ATOMIC EMISSION

Element	Wavelength in mμ	Ratio V_{H_2}/V_{N_2O}
Magnesium	285.2	1.1
Calcium	422.7	1.3
Strontium	460.7	1.3
Barium	553.6	1.7

For the elements in Table 5, there is a correlation between excitation energy(atomic emission wavelength) and the flow rate ratio of hydrogen to nitrous oxide for maximum sensitivity. A similar correlation holds for ionization potentials as noted in Table 2. This table indicates that the emission of elements that are easily ionized and emit radiation at a long wavelength is favored in a cool fuel rich flame. The lower flame temperature decreases the extent of ionization and thereby increases the number of atoms available for atomic emission. For

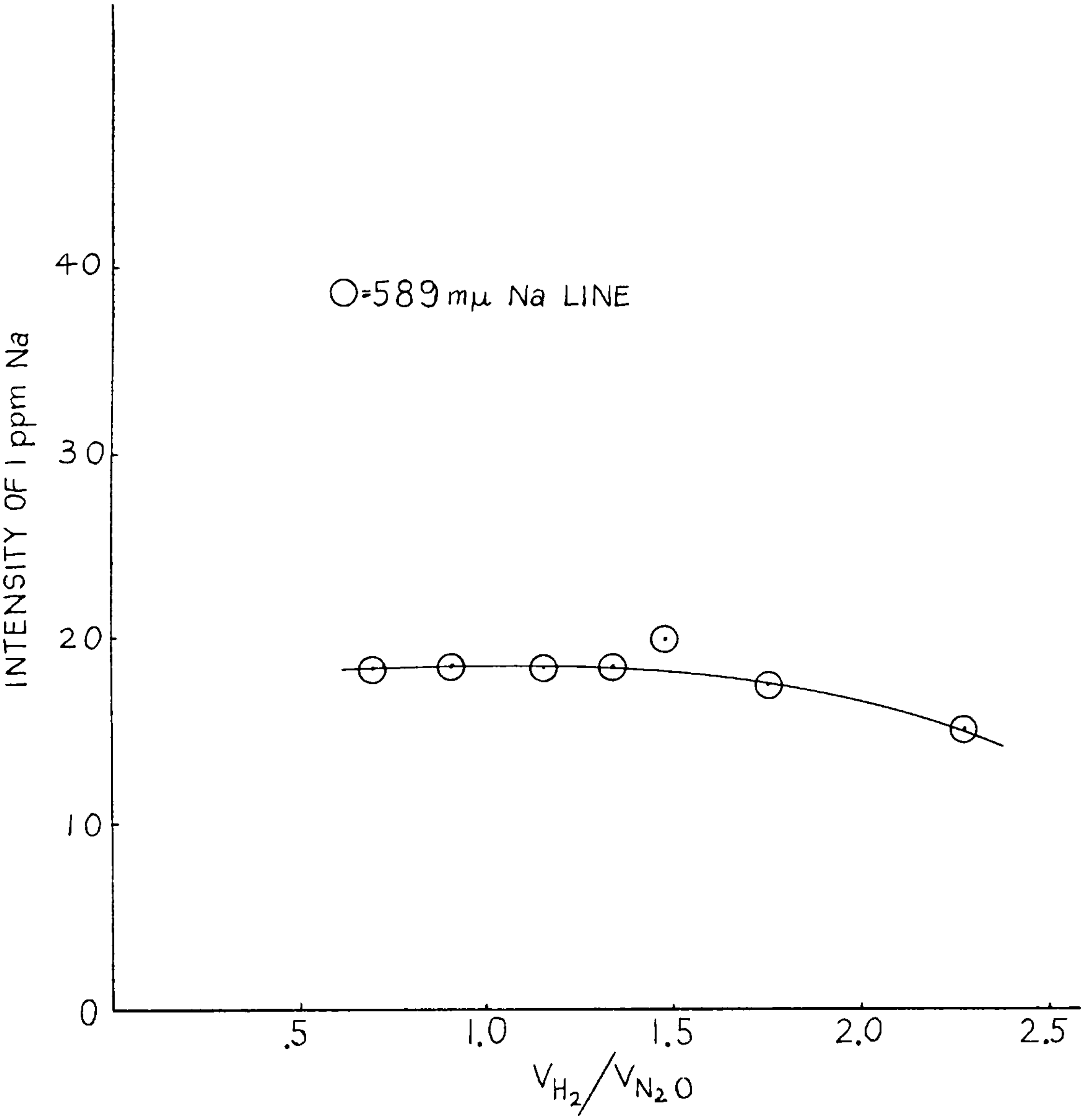


Figure 17.--Sodium emission versus hydrogen to nitrous oxide flow rate ratio.

elements that are not easily ionized and emit at a short wavelength, emission is favored in a hotter flame. The hotter flame is needed to excite these elements.

Figure 18 represents the effect of adding an easily ionized element(potassium) to a solution of barium. The electrons released by the ionization of potassium atoms will depress the ionization of the barium atoms. The effect of the addition was to decrease the intensity of the ion line of barium until it was no longer observed, and to slightly increase the barium band and atom line emission. This is as expected. By decreasing the number of barium ions, the number of atoms and molecules capable of excitation and emission is increased. Comparing Figure 16 and Figure 18, the curves are almost identical except for the slight increase in emission due to depression of the ionization of barium by potassium.

If one examines the vertical dimension of a flame, the flame temperature would probably increase from the burner to a maximum near the tip of the inner cone and then would slowly decrease. If the oxidant flow rate were held constant and the flame made more fuel rich, the height of the inner cone would increase slowly. The region of maximum temperature would also move farther above the burner.

The portion of the flame sampled was varied by adjusting the burner height relative to the monochromator system. Figure 19 shows a graph of the ratio of hydrogen

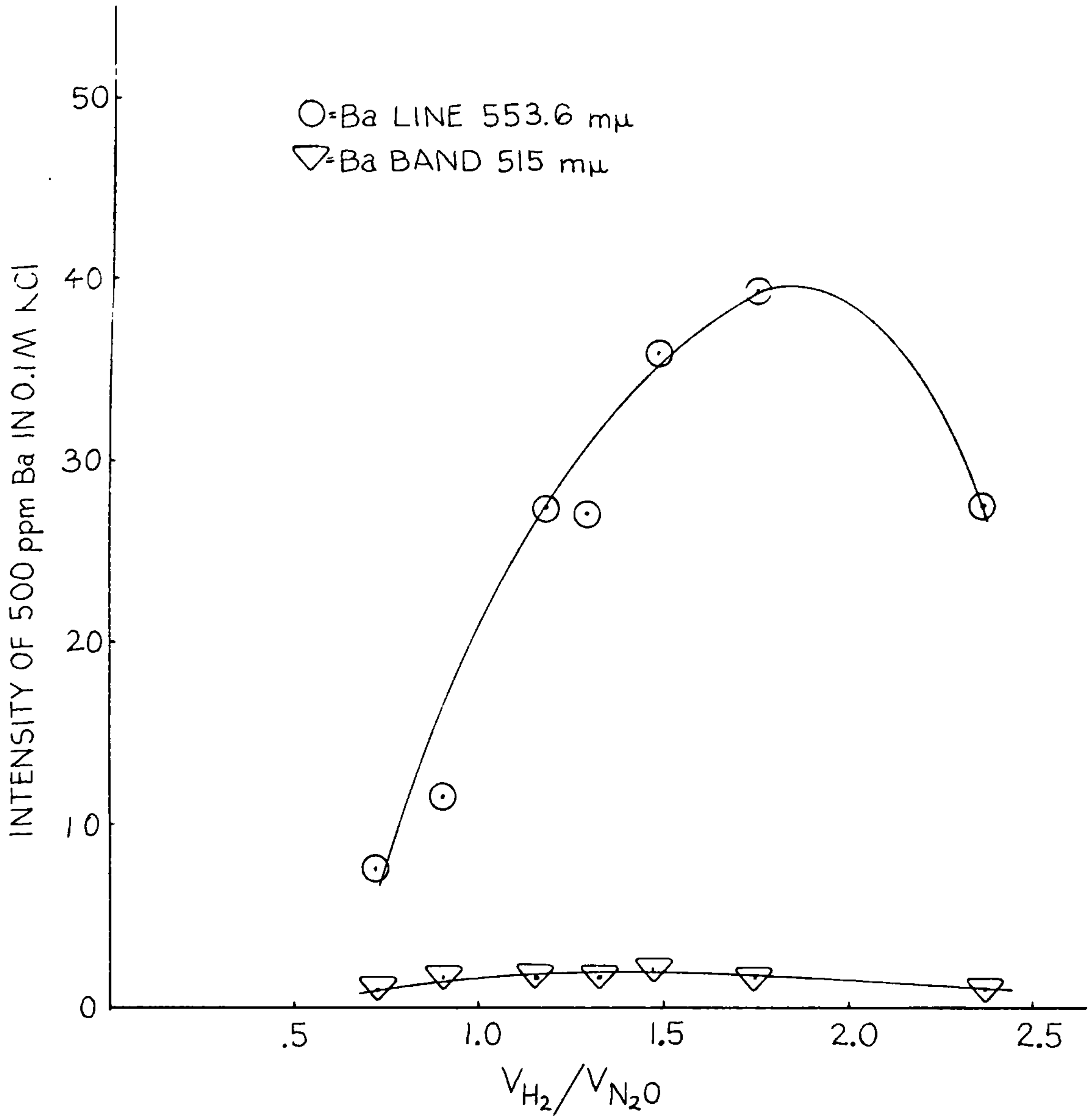


Figure 18.--Barium emission in KCl versus hydrogen to nitrous oxide flow rate ratio.

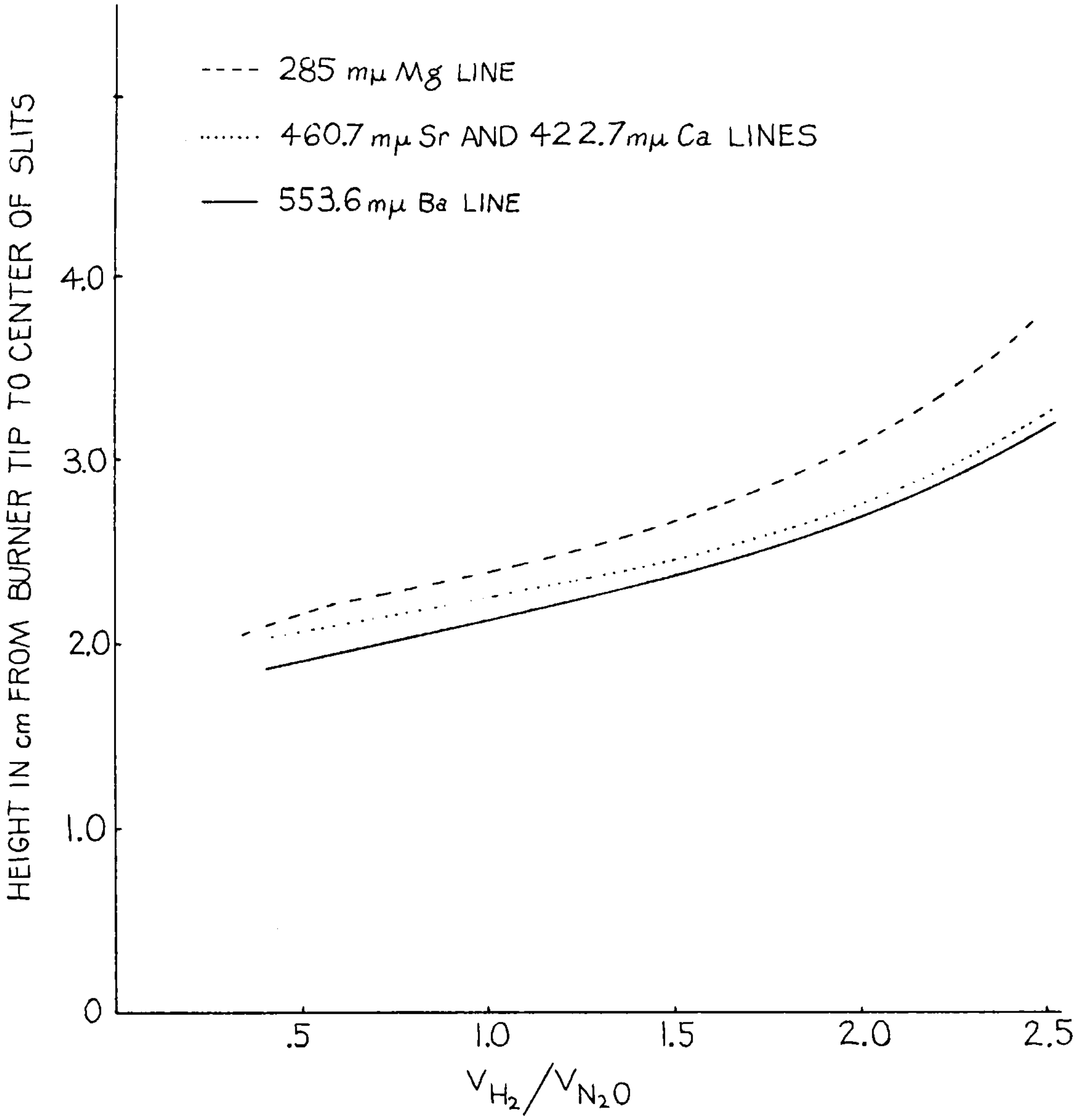


Figure 19.--Height of emission in flame versus hydrogen to nitrous oxide flow rate ratio.

to nitrous oxide flow rates versus height for maximum emission for the alkaline earth elements. The deviations from the lines were about $\pm$ 1 mm, probably due mostly to inaccuracies in height measurement. As seen in Figure 19, magnesium is excited higher in the flame and therefore in a hotter portion of the flame than the other elements studied. Barium is excited in a cooler flame, calcium and strontium are intermediate. The reason for this was given previously. The rise in the maximum emission height as the flame becomes fuel rich, is caused by the rise in the height of the maximum temperature region of the flame above the burner.

A comparison of Figures 8 and 19 shows that the region of maximum sensitivity is considerably above the tip of the inner cone. Two possible explanations are as follows: The slits were about 1.5 cm in height and the distance above the burner for maximum sensitivity was measured to the center of the slits. The slits in effect averaged the emission over a fairly wide region of the flame. The position of maximum emission and the actual position of peak emission need not be the same. Also the samples introduced into the flame may not have been completely vaporized and excited by the time that they reached the maximum temperature region of the flame.

For the elements in Table 6, a correlation exists between excitation energy and the flow rate ratio of fuel to oxidant for maximum band emission. The change in emission with flow rate was not as great as that of the atomic line emission and was fairly flat for most of the elements. The order followed that of increasing wavelength and ease of excitation as in atomic line emission. This was as expected. Surprisingly the emission was a maximum in a fuel rich flame. The hydroxide or hydroxyl radical was thought to be the favored species to be excited.[1] This would indicate that the hydroxide formation was favored in a fuel rich flame. This does not eliminate the possibility of oxide formation in a more oxidizing flame.

TABLE 6

FLOW RATE RATIO OF FUEL TO OXIDANT
FOR MAXIMUM BAND EMISSION

Element	Emitter[1]	Wavelength in mµ	Ratio V_{H_2}/V_{N_2O}
Magnesium	MgO or MgOH	383 & 371	1.3
Barium	BaOH	515	1.5
Calcium	CaOH	554	1.6
Strontium	SrOH	606	1.6

D. Detection Limits

From Table 7 the detection limits in the hydrogen-nitrous oxide flame can be compared to the detection limits reported for turbulent flames. The detection limits observed are close to those reported by others. The detection limits reported for the hydrogen-nitrous oxide flame could be lowered if the aspiration efficiency of the burner could be improved. The making of an effective aspiration system is an art, and extreme care and a great deal of experimentation must be used in its construction. The poor detection limit for magnesium was caused in part by the monochromator which was unable to resolve the magnesium line and one of the strong OH lines. A better monochromator would improve all the detection limits reported.

Optimum excitation conditions were not determined for elements other than the alkaline earths. Thus the detection limits listed in Table 7 do not necessarily represent the lowest obtainable for non-alkaline earth elements.

TABLE 7

DETECTION LIMITS OBSERVED FOR SOME ELEMENTS

Element	λ mµ	$H_2 - N_2O$ Flame Detection Limit in ppm	Others	Ref.
Iron	372.0	5.0	1.0	21
Manganese	493.1	0.2	0.1	19
Cobalt	353.0	9.0	4.2	19
Nickel	352.5	4.0	1.6	19
Magnesium	285.2	10	0.6	20
Calcium	422.7	0.07	0.08	19
Strontium	460.7	0.06	0.07	19
Barium	553.6	2.5	1.0	19
Aluminum	392.6	500		
Sodium	589	0.004	0.001	19

SUMMARY

In general the hydrogen-nitrous oxide flame has a lower flame background than hydrocarbon flames used in flame photometry. A fuel rich hydrogen-nitrous oxide flame has a much lower flame background than a turbulent fuel rich acetylene-oxygen flame. Since many elements are most sensitive in a fuel rich enviroment, the hydrogen-nitrous oxide flame has a considerable advantage.

The hydrogen-nitrous oxide flame has the advantage that it can be used premixed. The burning velocity of hydrogen-nitrous oxide is low enough to be used safely in a premix burner. Flash back is the largest disadvantage to premixed flames and the hydrogen-nitrous oxide flame overcomes most of this hazard.

The premixed hydrogen-nitrous oxide flame has the advantage that the flame is very reproducible and stable. Besides being reproducible and stable, the flame has a very low noise level and a low flow rate of gasses. These advantages make the flame very desirable to work with and more economical than turbulent flames.

For the elements studied, the maximum emission was observed in a fuel rich flame. All the elements studied gave maximum emission above the inner cone of the flame.

The ratio of atomic line to band emission was greatest in a fuel rich portion of the flame with the detection limits being about equal to those observed for turbulent flames.

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