



An evaluation of the hydrogen-chlorine flame as an excitation source for flame photometry
by William Kemp Johnston

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry

Montana State University

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Abstract:

Emission spectra were obtained in the ultraviolet and visible regions of the spectrum, 2500Å to 6500Å, for silver, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, sodium, nickel and strontium by aspirating ethanolic solutions of salts of these elements into a hydrogen-chlorine flame. The emission intensities were compared to those obtained in a hydrogen-air flame in order to evaluate the potential of a hydrogen-chlorine excitation source. Of these elements only silver, copper and magnesium gave emission intensities comparable to those obtained in the air supported source. Molecular chloride bands were observed in the case of calcium, copper and magnesium. The copper band was unusually strong compared to emission from this element in the air flame.

In addition to the elements already mentioned aluminum, gold, potassium, lithium and zinc were fed to this unusual flame to determine if they would emit in the halogen atmosphere. Emission was not detected in the 2500Å to 6500Å region.

In the hydrogen-air flame emission from copper, CuH, C₂, CH and OH was maximized by varying the total flow of gas to the burner, the ratio of oxidant flow to total gas flow and the aspiration rate. This was also done for copper, CuCl, C₂, CH and OH in the hydrogen-chlorine flame. Emission intensities from these species were also determined as a function of the height of observation above the tip of the burner.

Elements known for their formation of refractory oxides were fed to the hydrogen-chlorine source in an organic media. While band or line emission was not observed for vanadium, zirconium, niobium, tantalum, tungsten and the rare-earth elements, a weak band was observed for molybdenum when a sheathed hydrogen-chlorine flame was used.

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Chemistry

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Bozeman, Montana

March, 1969

ACKNOWLEDGEMENT

I would like to thank the Research Corporation, the National Science Foundation, and the Montana Agricultural Experiment Station for their support of this investigation.

I am grateful for the assistance and suggestions I received from Drs. G.L. Baker, E.E. Frahm and R.A. Woodriff. A thank you is also extended to Mr. H.D. Via and the Instrument Service for the fabrication of apparatus vital to my research.

The moral support I received from my wife Pat, and my children Anne Marie and Susan Lynn, is especially appreciated.

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ABSTRACT

Emission spectra were obtained in the ultraviolet and visible regions of the spectrum, 2500Å to 6500Å, for silver, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, sodium, nickel and strontium by aspirating ethanolic solutions of salts of these elements into a hydrogen-chlorine flame. The emission intensities were compared to those obtained in a hydrogen-air flame in order to evaluate the potential of a hydrogen-chlorine excitation source. Of these elements only silver, copper and magnesium gave emission intensities comparable to those obtained in the air supported source. Molecular chloride bands were observed in the case of calcium, copper and magnesium. The copper band was unusually strong compared to emission from this element in the air flame.

In addition to the elements already mentioned aluminum, gold, potassium, lithium and zinc were fed to this unusual flame to determine if they would emit in the halogen atmosphere. Emission was not detected in the 2500Å to 6500Å region.

In the hydrogen-air flame emission from copper, CuH, C₂, CH and OH was maximized by varying the total flow of gas to the burner, the ratio of oxidant flow to total gas flow and the aspiration rate. This was also done for copper, CuCl, C₂, CH and OH in the hydrogen-chlorine flame. Emission intensities from these species were also determined as a function of the height of observation above the tip of the burner.

Elements known for their formation of refractory oxides were fed to the hydrogen-chlorine source in an organic media. While band or line

emission was not observed for vanadium, zirconium, niobium, tantalum, tungsten and the rare-earth elements, a weak band was observed for molybdenum when a sheathed hydrogen-chlorine flame was used.

INTRODUCTION

The history of flame photometry dates back to the middle of the 18th century when chemists described the colors imparted to alcohol and candle flames by the introduction of metallic salts. However, chemists did not recognize the qualitative value of flame photometry until 1848. At that time Herschel in referring to metallic salts concluded that "the colors thus communicated by the different bases of flames, afford in many cases a ready and neat way of detecting extremely minute quantities of them". In 1870 Janssen first suggested the use of flame excitation sources for quantitative determinations. Three years later the first real instrument called a "spectronatromètre" was developed by Champion, Pellet, and Grenier. Capable of determining sodium with an accuracy of 2 to 5% this instrument was a significant advancement to the field of analytical chemistry (14, 19, 33, 39).

In this "spectronatrometre" sample was introduced into the flame by means of a platinum wire. The observed emission was compared to that obtained from excess sodium chloride placed in a platinum cone above a reference flame. Neutral wedges were used to reduce radiation from the reference flame and thus provide a reproducible means of matching intensities from the two sources (33, 39).

Modifications in the method of introducing sample into the flame by Gouy spectacularly improved the "spectronatrometre". Gouy aspirated solution into a city gas-air flame by means of a pneumatic atomizer. The advantage of this technique was that excitation conditions could be held constant thereby improving reproducibility (33,39).

Further improvements on the instrument designed by Champion, Pellet and Grenier were made by Lundegarh in 1928. In place of the insensitive method of matching intensities visually, emission from an acetylene-air flame was analyzed by a spectrograph and recorded on a photographic plate. The densities of the lines were then measured with a photoelectric densitometer (14,19,33,39).

Flame photometers as they are known today differ from Lundgarh's instrument in that they employ sophisticated photomultiplier-amplifier detector systems in conjunction with strip chart recorders for displaying the output. The burner systems used in current instruments have not changed a great deal from those used by Gouy in 1879. Pneumatic atomizers are relatively common although they are considerably more efficient than those employed by Gouy one hundred years ago.

Because of the advantages of flame photometric analyses (the amount of material required, the time per determination and the accuracy of the method) flame photometry is presently used in a variety of industrial applications ranging from the determination of lutetium formed by transmutation in irradiated hafnium to the determination of trace amounts of copper and iron in sugar syrup (17,33).

Because of its wide application in industry a great deal of effort has been put forth in attempts to improve the technique and make it even more useful. Research in flame photometry has quite naturally been concerned with increasing both the number of elements which may be determined and detection limits. The following dissertation is likewise directed toward these goals.

STATEMENT OF THE PROBLEM

The excitation source is obviously the heart of any determination by flame photometric techniques. In this respect a variety of flames, (hydrogen-air, hydrogen-oxygen, acetylene-air, acetylene-oxygen, natural gas-air, etc.) have been employed in an attempt to get elements to emit more intense and characteristic radiation. A brief consideration of the theoretical aspects involved in flame excitation explains why some unusual gas combinations have been investigated.

A flame is merely a means of providing energy to an atom so as to thermally excite it to emission. In the process of emitting a photon an atom moves from a high energy electronic state to a more stable lower energy state. The intensity of this emission is given by the following expression (33).

$$I = L S A N h \nu N (g_a/g_o) e^{-E_a/kT} \text{ erg/sec} \quad (1)$$

where L = flame thickness,

S = area of observation,

A = Einstein transition probability,¹

h = Plank's constant,

ν = the frequency of the spectral line emitted,

N = the number of atoms/cm³ in the flame,

g_a and g_o = statistical weights of the excited and ground states respectively,

E_a = excitation energy,

k = Boltzman's constant,

T = temperature in °K.

¹This is defined as the probability that the excited atom will make the transition in unit time with the emission of a photon.

Of these variables the number of atoms and the temperature are of immediate concern. The others remain constant for a given element with the exception of the flame thickness and the area of observation which are functions of the experimental arrangement. From the expression given above it is apparent that the intensity of emission for a given element can be increased by either increasing the temperature or the number of atoms or both. Thus any adjustment in the excitation source which affects either of these parameters will affect the intensity of emission.

With this theoretical basis investigators have looked for flame sources which would give higher temperatures. Hence, measurements of flame temperatures and calculations by thermodynamically minded chemists have led to the investigation of unusually high energy flames such as oxy-cyanogen (4,5,6), fluorine-hydrogen (17,21,37,50), ozone-cyanogen (54), ozone-hydrogen (53), perchlorylfluoride-hydrogen (45,46), and even atomic hydrogen (35,36). Although this approach has been moderately successful, it nevertheless has left something to be desired. In equation (1) relating emission intensity to temperature one cannot overlook the dependence on free atom concentration. As one increases the temperature of a source the degree of ionization likewise increases. In the case of alkali and alkaline-earth elements this effect is quite noticeable.

Chemical reactions involving free atoms and combustion products or reactants may decrease the free atom concentration and also adversely affect emission intensities. Since the analyte is generally introduced as an aqueous or organic solution, possible reactions involving the solvent must also be considered.

Because of these many complications a detailed explanation of flame processes has been difficult. Although somewhat simplified, the following describes in sequence what is known to take place when a solution of a metallic salt is aspirated into a flame.

As a sample droplet enters the reaction zone of a flame it acquires energy primarily through heat transfer so as to evaporate solvent associated with the sample. Depending on the energy available the resulting particle may then vaporize and dissociate to give free atoms, molecules or radicals. These in turn can react with combustion products, reactants or solvent to give additional species (1,2,14,19,31,33,39,42). The particular path which is followed quite naturally depends on the element involved and the characteristics of the excitation source. In the case of titanium, vanadium, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten and the rare-earths, in the usual oxygen supported flames, stable oxides are produced which do not emit useful radiation. Hence the determination of these elements by flame photometric techniques is troublesome.

Many of the high temperature flames mentioned earlier were used in an attempt to dissociate refractory compounds. However, Fassel and associates were more successful in approaching the problem with the intention of creating a reducing atmosphere to promote dissociation and thus obtain free atoms and atomic emission. To accomplish this they used fuel-rich oxy-acetylene flames along with organic solvents. Their success added support to the concept known as chemiluminescence² and provided the

²Chemical processes leading directly to the formation of an abnormally high population in the excited state (29).

analytical chemist with an improved method for determining rare earths, vanadium, niobium, rhenium, titanium, molybdenum and tungsten (18,23,24, 25,26,43).

As a substitute to the fuel rich oxy-acetylene flame the hydrogen-chlorine flame was suggested and is the subject of this dissertation. Use of chlorine in conjunction with organic solvents was expected to produce a reducing atmosphere (47) suitable for the determination of many refractory elements. By substituting chlorine for oxygen one would not expect formation of stable oxides. However, one might expect metal chlorides to form in place of oxides (13). A comparison of the limited data on free energies and enthalpies of formation for metal oxides and chlorides showed that in a number of cases the chlorides were less stable (10,11,27,32,34, 44,55,58). Hence, from a thermodynamic point of view use of a chlorine supported flame merited investigation.

In the event that the hydrogen-chlorine source lacked sufficient energy to dissociate even chlorides it was felt that molecular emission bands from these compounds might be of interest. Hydroxide and oxide bands for calcium and magnesium are intense enough and sufficiently narrow in band width so that they are commonly used in analytical determinations (14,33,39). If chloride bands shared these characteristics, they could also be useful analytically.

At this point in the discussion one may wonder why chlorine was chosen rather than one of the other halogens. Fluorine, bromine and iodine all had disadvantages which eliminated them from consideration. Bromine and iodine were known to produce low energy flames. Fluorine, on

the other hand, produces a very hot flame when combined with hydrogen (17,21,37,50). However, this particular halogen was not used because of problems involved in handling it safely.

Due to thermodynamic considerations hydrogen, acetylene and cyanogen were the only fuels which seemed worthwhile investigating. Acetylene, when combined with chlorine, produced an extremely bright flame due to incandescence from carbon particles. Although this type of atmosphere was desirable, the high background emission was a disadvantage. As an added complication chlorine and acetylene were known to ignite spontaneously at room temperature. References to a cyanogen-chlorine flame could not be found in the literature. Therefore, cyanogen was set aside for possible investigation at a later date.

As a result the hydrogen-chlorine flame was chosen for evaluation as an excitation source in flame photometry. The low temperature of this flame was recognized as a distinct disadvantage. Nevertheless it was anticipated that elements troubled by refractory compound formation in the conventional oxygen supported flames would emit useful radiation in this particular source.

EXPERIMENTAL

Emission Apparatus

The basic instrument used in this investigation was assembled from components from several manufacturers and as such was considered more versatile and far superior to any commercial instrument available. The heart of the instrument was a model 1700-111 3/4 meter Spex Industries Inc. monochrometer with a 1200 grooves/mm, 102x102 mm Bausch & Lomb grating blazed for 3000 Å, a continuously variable, servo-controlled, automatic scanning control and bilaterally opening to 3 mm wide by 50 mm high straightslits. The entrance slit also included a stepped fishtail and Hartman diaphragm shutter. The detector was a R106 photomultiplier tube having an S-19 spectral response from the Hamamatsu TV Company Ltd. The power supply for the photomultiplier was a model 412B from the John Fluke Manufacturing Company, Inc. The output from the photomultiplier was fed to a Princeton Applied Research Corporation type A preamplifier and from there to a model HR-8 lock-in amplifier from this same company. A model BZ-1 mechanical light chopper also from the Princeton Applied Research Corp. was used to modulate the light beam coming from the flame. The output from the amplifier was finally displayed on a Honeywell Lab 19 recorder operated on the 0-10 millivolt range. This experimental set up is illustrated schematically in Figure 1. as a matter of convenience.

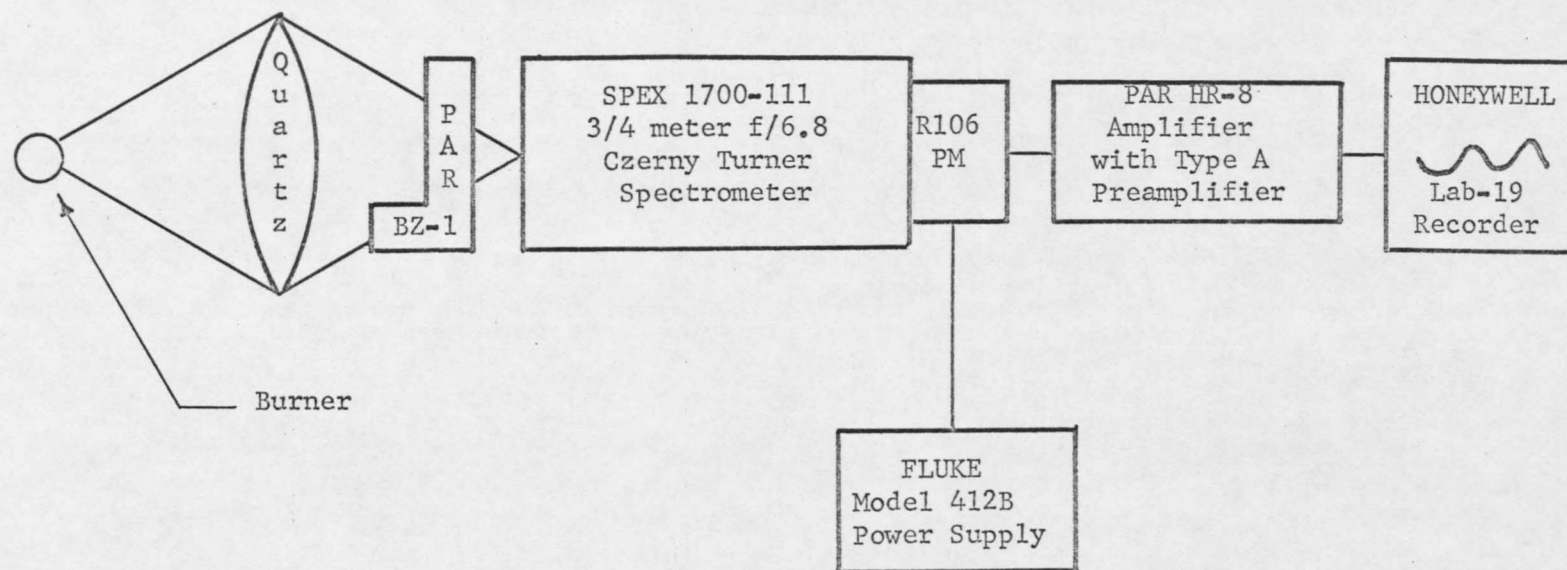


Figure 1. Flame Emission Apparatus.

Burner System

Finding a burner which would withstand the corrosive atmosphere created by the chlorine and yet maintain a stable flame was somewhat of a problem. The ordinary Beckman burners commonly used in flame photometry did not last long when hydrogen and chlorine gas mixtures were used in them. An all glass burner shown in Figure 2 was finally used to support the chlorine flame. An adjustable slide assembly with metric scale and vernier from Velmex, Inc. was adapted to the burner mount to permit adjustment of the horizontal and vertical position of the flame with respect to the optical axis of the instrument. A Sage model 249-2 constant speed syringe pump was used to feed solution to the flame while gas flow rates were monitored by Gilmont flow meters calibrated with a wet test flow meter. The automatic syringe pump was found to be very useful in that the rate at which sample was fed to the flame could be controlled without varying the flow of oxidant. With most commercial burners it is not possible to do this.

Choice of Solvent

Of all the factors influencing emission intensities the nature of the solvent has been investigated more intensively than any other (2,19, 23,31,48). Vaporization of an aerosol droplet is an important step in the sequence of processes leading to emission. Since vaporization depends on surface tension and temperature, emission intensities are affected by the choice of solvent. Although aqueous solvents are used a great deal, they are nevertheless undesirable since they cool the flame. Organic

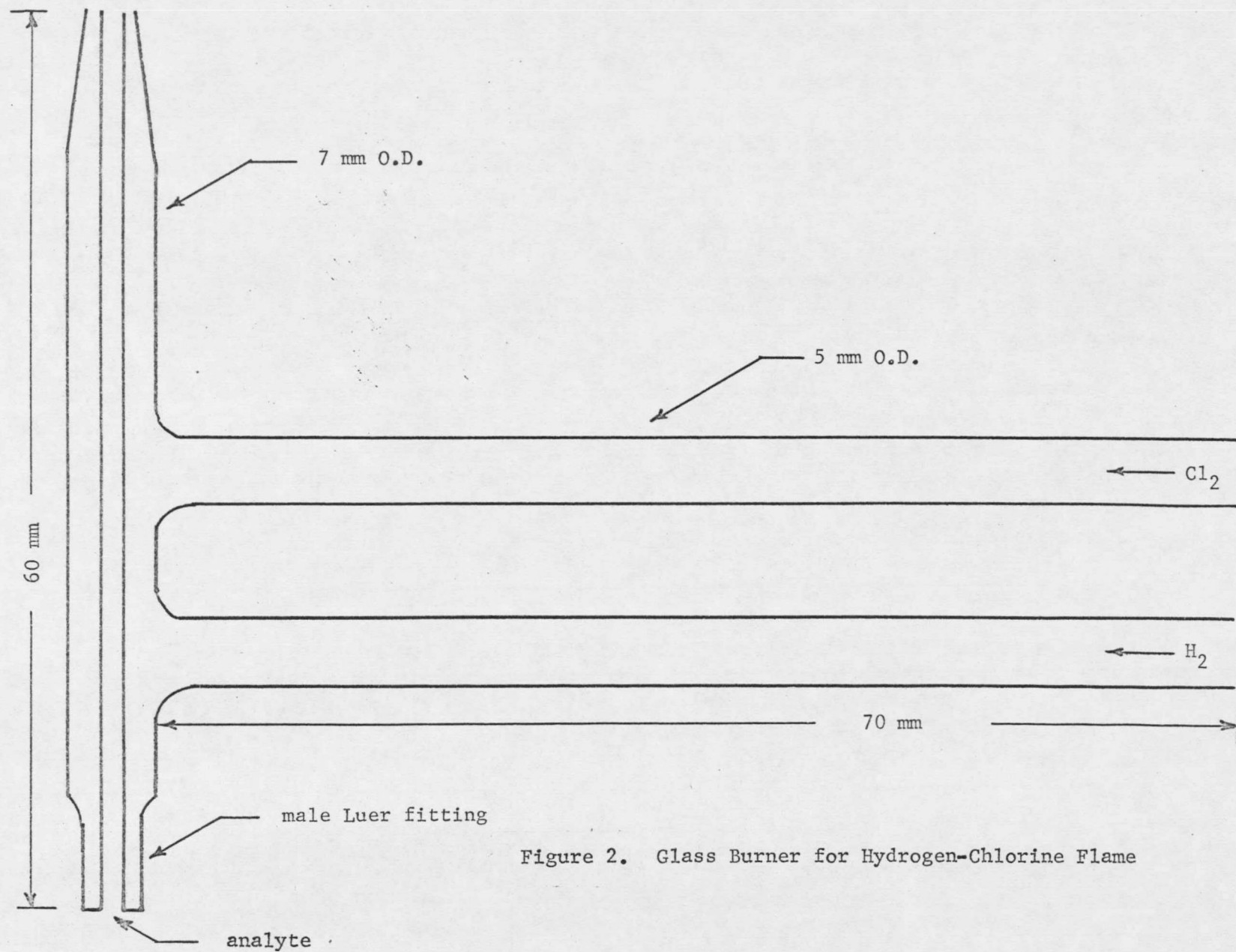


Figure 2. Glass Burner for Hydrogen-Chlorine Flame

solvents on the other hand do not have this effect (19,23,31,48). However, the limited solubility of metallic salts in organic solvents severely restricts their use. As far as organic solvents go, ethanol is generally considered the best all around choice. This particular solvent burns smoothly in the commonly used flames and yet many salts are moderately soluble in it. In this investigation ethanol was used whenever possible although acetonitrile, ethyl acetate and methyl isobutyl ketone were used in selected cases.

Cursory Investigation

At the beginning of this investigation it was felt that a study of the emission from a variety of elements would be worthwhile in view of the limited data reported on a hydrogen-chlorine excitation source. Hence, solutions of readily available compounds were prepared as indicated in Table I. Analysis of the emission spectra was achieved by aspirating these solutions into a hydrogen-chlorine flame and recording the amplifier output as one scanned the spectrum from 2500Å to 6500Å. A summary of these scans is presented in Table II, pages 14-17.

The intensities given represent the potential drop across a load resistor (470 K, 10%) connected between the anode of the photomultiplier tube and ground. Emission above background was measured as opposed to measuring over-all emission intensities.

Table I. Dissolution Procedures for Cursory Investigation.

Element	Dissolution Procedure
Aluminum	Anhydrous AlCl_3 (Baker & Adamson reagent) dissolved in absolute ethanol.
Calcium	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ("Baker Analyzed" reagent) dissolved in absolute ethanol.
Cadmium	$\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ("Baker Analyzed" reagent) dissolved in absolute ethanol.
Cobalt	Metal (Matheson, Coleman & Bell) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.
Copper	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker & Adamson reagent) dissolved in absolute ethanol.
Chromium	Metal (Fisher, 98%) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.
Iron	Metal ("Baker Analyzed" reagent) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.
Gold	$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ("Baker Analyzed" reagent) dissolved in absolute ethanol.
Lithium	LiCl ("Baker Analyzed" reagent) dissolved in absolute ethanol.
Magnesium	Metal (Baker & Adamson reagent) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.
Manganese	Metal (Baker & Adamson reagent) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.
Nickel	Metal (Baker & Adamson reagent) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.
Silver	AgNO_3 (Baker & Adamson reagent) dissolved in absolute ethanol.
Strontium	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ (Merck & Co. reagent) dissolved in absolute ethanol.
Zinc	Metal (Baker & Adamson reagent) dissolved in conc. HCl , evaporated to near dryness, followed by dissolution in absolute ethanol.

Table II. Emission Intensities in the Hydrogen-Chlorine and Hydrogen-Air Flames.

Element - Concentration Wavelength in Å	Emitting Species	Intensities Above Background in mv.	
		H ₂ -Cl ₂	H ₂ -Air
Ag 500 µg/ml			
3281	Ag	0.96	1.90
3383	Ag	1.10	2.30
Al 1000 µg/ml			
3944	Al	0.00	0.00
3962	Al	0.00	0.00
4842	AlO	0.00	0.00
4866	AlO	0.00	0.00
4888	AlO	0.00	0.00
5102	AlO	0.00	0.00
5123	AlO	0.00	0.00
Au 972 µg/ml			
2676	Au	0.00	0.00
Ca 250 µg/ml			
4227	Ca	0.06	9.40
5539	CaOH	0.00	9.95
5542			
5547			
5810	CaCl	0.03	0.00
5934	CaCl	0.31	0.20
6185	CaCl	0.11	0.60
6212	CaCl	0.08	0.80
Cd 1000 µg/ml			
3261	Cd	0.12	0.94
Co 1000 µg/ml			
3413	Co	0.48	1.12
3433	Co	0.20	0.42
3453	Co	0.50	1.40
3468	Co	0.30	0.86
3508	Co	0.41	1.04
3527	Co	0.50	1.54
3575	Co	0.28	0.52
3595	Co	0.24	0.20
3630	Co	0.19	0.06
3650	Co	0.25	0.04

Table II. (continued)

Element - Concentration Wavelength in Å	Emitting Species	Intensities Above Background in mv.	
		H ₂ -Cl ₂	H ₂ -Air
Co 1000 $\mu\text{g/ml}$			
3842	Co	0.15	0.26
3871	Co	0.30	0.70
3892	Co	0.23	0.26
3992	Co	0.11	0.20
4030	Co	0.00	0.04
4118	Co	0.09	0.20
Cr 1000 $\mu\text{g/ml}$			
3579	Cr	0.34	1.18
3594	Cr	0.24	1.10
3605	Cr	0.23	0.86
3891 (broad)		0.14	0.00
4254	Cr	0.57	5.00
4275	Cr	0.56	4.00
4290	Cr	0.54	3.50
Cu 500 $\mu\text{g/ml}$			
3248	Cu	0.72	1.52
3274	Cu	0.60	1.32
4265	CuCl	1.90	0.00
4280	CuH	0.00	0.54
4293	CuCl	4.00	0.00
4328	CuH	0.00	0.20
4334	CuCl	2.10	0.00
4359	CuCl	6.00	0.00
4416	CuCl	2.40	0.00
4446	CuCl	4.00	0.00
5240	CuOH	0.00	0.10
5300	CuOH	0.00	0.08
5370	CuOH	0.00	0.09
Fe 1000 $\mu\text{g/ml}$			
3441	Fe	0.07	0.65
3477	Fe	0.09	0.20
3491	Fe	0.15	0.15
3570	Fe	0.13	0.15
3581	Fe	0.05	0.30
3648	Fe	0.13	0.15
3706	Fe	0.07	0.15

Table II. (continued)

Element - Concentration Wavelength in Å	Emitting Species	Intensities Above Background in mv.	
		H ₂ -Cl ₂	H ₂ -Air
Fe 1000 $\mu\text{g/ml}$			
3720	Fe	0.22	2.20
3737	Fe	0.22	1.85
3746	Fe	0.23	1.65
3823	Fe	0.11	0.85
3860	Fe	0.26	2.25
3886	Fe	0.14	0.80
3900	Fe	0.16	0.45
3930	Fe	0.09	0.60
5647	FeO	0.00	0.18
5819	FeO	0.00	0.13
5868	FeO	0.00	0.21
5903	FeO	0.00	0.26
5975	FeO	0.00	0.00
6095	FeO	0.00	0.01
6109	FeO	0.02	0.03
6181	FeO	0.02	0.02
6219	FeO	0.00	0.00
K 1000 $\mu\text{g/ml}$			
4044	K	0.00	3.90
4047			
Li 1000 $\mu\text{g/ml}$			
6104	Li	0.00	0.10
Mg 200 $\mu\text{g/ml}$			
2852	Mg	0.12	0.36
3625	MgOH	0.16	0.45
3687	MgCl	1.20	1.10
3691	MgCl	1.10	1.60
3700	MgOH	0.56	1.85
3745	MgCl	1.38	0.90
3749	MgCl	1.42	0.90
3755	MgCl	1.32	0.80
3761	MgCl	1.28	0.80
3808	MgCl	0.98	1.40
3810	MgOH	0.76	1.50
3871	MgCl	0.40	0.70
3880	MgOH	0.22	1.40

Table II. (continued)

Element - Concentration Wavelength in Å	Emitting Species	Intensities Above Background in mv.	
		H ₂ -Cl ₂	H ₂ -Air
Mn 1000 $\mu\text{g/ml}$ 3500-4200 (board)	MnOH	1.20	1.60
4031	Mn	1.80	31.50
4033			
4035			
5159	MnO	0.00	0.45
5192	MnO	0.00	0.38
5360	MnO	0.00	0.55
5390	MnO	0.00	0.86
5632	MnO	0.00	0.46
5790	MnO	0.00	0.90
5810	MnO	0.00	0.62
Na 25 $\mu\text{g/ml}$ 5890	Na	2.00	71.00
5896			
Ni 1000 $\mu\text{g/ml}$ 3371	Ni	0.12	0.45
3394	Ni	0.18	0.60
3414	Ni	0.44	1.40
3438	Ni	0.22	0.45
3449	Ni	0.26	0.65
3460	Ni	0.46	1.40
3491	Ni	0.36	0.94
3514	Ni	0.40	1.25
3522	Ni	0.69	1.95
3569	Ni	0.27	0.40
3619	Ni	0.42	0.80
3854	Ni	0.44	0.20
Sr 250 $\mu\text{g/ml}$ 4078	Sr	0.00	0.07
4216	Sr	0.00	0.06
4607	Sr	0.05	20.00
6035	SrOH	0.00	1.00
6059	SrOH	0.00	1.50
6359	SrCl	0.01	0.00
Zn 1000 $\mu\text{g/ml}$ 2500-6500		0.00	0.00

Instrument Settings for Table II.

Flow Rates: Oxidant 1.8 l/min Fuel 7.2 l/min Aspiration Rate: 0.746ml/min
Entrance Slit: 750u Exit Slit: 750u Slit Height: 2mm
PM Voltage: 800V Time Constant: 1 sec.
Region Viewed: 2.5-7.5 cm above burner tip. Solvent: absolute ethanol.

The results of the cursory investigation summarized in table II seem to indicate that the hydrogen-chlorine flame could be used in the determination of silver, copper and magnesium. Emission intensities for these elements were comparable to intensities obtained in the hydrogen-air flame. In the case of copper the CuCl band at 4359Å was four times as intense as the strongest line or band obtained in the air supported flame.

On the other hand, although emission from calcium, cadmium, cobalt, chromium, iron, manganese, sodium and nickel was observed in the unusual source, it wasn't equivalent in strength to that observed in the air supported flame. In the case of lithium, potassium and strontium the hydrogen-air flame produced very intense line emission while in the chlorine flame emission was not observed.

The sodium doublet at 5890.0Å and 5895.9Å was observed in many samples as a result of contamination. Although the intensity of this emission was considerably less than that observed in the corresponding hydrogen-air flame, it is worth noting, as Sloodmaekers and Van Tiggelen did not observe emission from sodium in the hydrogen-chlorine flame (50).

Maximization of Copper Emission

The greater intensity of the copper chloride band in the chlorine flame compared to that of the atomic copper line in the air supported flame was impressive. However, at this point a great deal of significance

could not be placed on this comparison. For the given data the levels of the total flow rate of gas to the burner, the oxidant to-fuel ratio and the aspiration rate were chosen in order to give a stable flame. Since the particular choice of flame parameters could have led to false conclusions about the relative strength of emission for copper chloride and copper in the hydrogen-chlorine and hydrogen-air flames, an experiment was designed to maximize emission from CuCl and copper independently.

In this approach, the response surface design described by Box and Wilson (9) was adopted since it has been used successfully on many occasions in related problems of optimization in both flame emission and atomic absorption spectroscopy (15,41,48,49). In essence factorial experimentation is used to calculate linear equations relating a particular response to experimental variables. These equations indicate the direction one must move to approach a maximum. The levels of the variables are then shifted in the direction indicated by the sign of the coefficients of the linear equations and new equations are calculated from data taken at these levels. The process is repeated until the coefficients go to zero, indicating a maximum has been reached, or until the sign of the coefficients changes indicating one has passed the maximum. At this point central composite rotatable designs have been suggested for accurately specifying the maximum (16). However, in the experiment at hand this technique could not be used because the rate at which solution was fed to the flame could not be varied continuously, a necessary condition for a rotatable design. As a substitute a simple 3×3 factorial procedure was used to specify optimum excitation conditions.

Table III. Response Surface Methods Leading to Maximization of Emission for Copper, CuH and CuCl.

Experiment Number	X ₁ Total Gas Flow l/min	X ₂ Oxidant Flow Total Flow	X ₃ Aspiration Rate ml/min	Calculated Equations
Copper Emission in the Hydrogen-Chlorine Flame at 3247.5 Å				
1	9.0- 9.5	0.10-0.15	1.00 -3.00	I = 0.369 + 0.045X ₁ - 0.495X ₂ + 1.149X ₃
2	9.5-10.0	0.05-0.08	1.00 -3.00	I = 0.668 - 0.027X ₁ - 0.019X ₂ + 0.097X ₃
Copper Emission in the Hydrogen-Air Flame at 3247.5 Å				
1	8.8- 9.2	0.16-0.20	0.421-1.26	I = 0.505 + 0.085X ₁ - 0.080X ₂ + 0.240X ₃
2	9.4- 9.8	0.06-0.10	1.00 -3.00	I = 1.225 + 0.00X ₁ - 0.073X ₂ + 0.080X ₃
CuCl Emission in the Hydrogen-Chlorine Flame at 4359 Å				
1	9.0- 9.5	0.10-0.15	1.00 -3.00	I = 7.188 + 0.213X ₁ + 1.188X ₂ + 2.313X ₃
2	9.5-10.0	0.15-0.20	1.00 -3.00	I = 10.13 + 0.075X ₁ + 1.450X ₂ + 4.675X ₃
3	10.0-10.5	0.25-0.30	1.00 -3.00	I = 13.48 + 0.675X ₁ - 0.200X ₂ + 7.800X ₃
CuH Emission in the Hydrogen-Air Flame at 4280 Å				
1	8.8- 9.2	0.16-0.24	0.421-1.26	I = 0.022 + 0.002X ₁ - 0.002X ₂ + 0.012X ₃
2	9.4- 9.8	0.08-0.12	1.00 -3.00	I = 0.087 + 0.001X ₁ - 0.008X ₂ + 0.046X ₃
3	9.8-10.0	0.05-0.07	3.06 -4.59	I = 0.240 - 0.008X ₁ - 0.006X ₂ + 0.055X ₃

Table IV. Levels of Flame Parameters Giving Optimum Emission Intensities for Copper, CuCl, CuH, C₂, CH and OH.

Emitting Species	Wavelength in Å	Flame Employed	Total Gas Flow l/min	Oxidant Flow Total Flow	Aspiration Rate ml/min	Maximum Emission Intensity mv
Cu	3247.5	H ₂ -Cl ₂	9.50	0.05	4.59	1.02
Cu	3247.5	H ₂ -Air	9.00 8.80	0.10 0.06	4.59 3.06	1.46
CuCl	4359	H ₂ -Cl ₂	11.00	0.25	3.00	25.25
CuH	4280	H ₂ -Air	9.00	0.04	4.59	0.38
C ₂	5165	H ₂ -Cl ₂	11.00	0.30	3.00	19.60
C ₂	5165	H ₂ -Air	12.50	0.38	3.00	4.40
CH	4315	H ₂ -Cl ₂	10.00	0.30	3.00	9.70
CH	4315	H ₂ -Air	12.50	0.40	3.00	8.00
OH	3067.8	H ₂ -Cl ₂	11.00	0.15	3.00	14.20
OH	3067.8	H ₂ -Air	15.00 14.00	0.15	0.421	15.20

In table III the levels of the flame parameters and the linear equations leading to the determination of maxima are given for copper and CuH in the hydrogen-air flame and for copper and CuCl in the hydrogen-chlorine flame. Table IV, page 21, on the other hand, summarizes the results of the final factorial experiment to accurately determine optimum excitation conditions. In addition to giving the levels of the flame parameters (total flow of gas to the burner, ratio of oxidant flow to total gas flow and aspiration rate) table IV also gives the maximum emission intensities above background in millivolts for copper and CuH in the hydrogen-air flame and for copper and CuCl in the hydrogen-chlorine flame.

A study was also made of the variation in emission intensities for copper, CuCl and CuH as the flame region being observed was varied. To accomplish this the burner was lowered with respect to the optical axis of the instrument as copper solutions were fed to the chlorine and air supported flames while the emission intensities of the copper line and CuH and CuCl bands were monitored. The flame parameters were adjusted so as to give maximum emission as determined in the optimization procedures summarized in tables III and IV, pages 20 and 21 respectively.

Unlike the maximization data where a region above the burner tip from 2.5 cm to 7.5 cm was observed, this profile data was taken by locating the flame exactly at the focal point of the condensing lens. A light shield with a 4 mm diameter hole was used to restrict emission to the region of the flame desired. The results of this study are illustrated on figures 3 and 4 for copper and CuH, CuCl respectively. Data from the air and chlorine flames are shown on the same illustration to facilitate comparing the two flames.

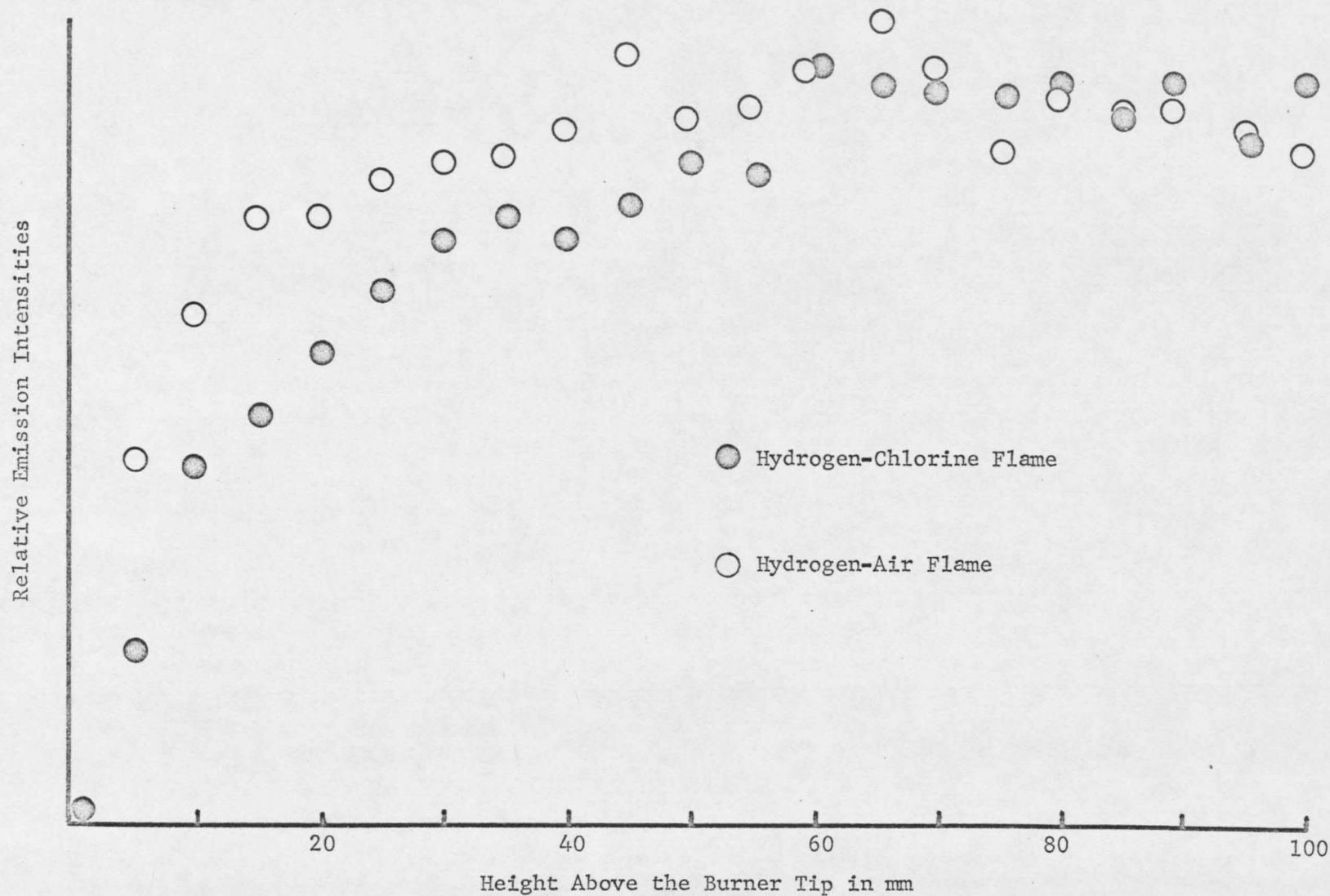


Figure 3. Emission Intensity for Copper at 3247.5 Å as a Function of the Height Above the Burner Tip in the Hydrogen-Chlorine and Hydrogen-Air Flames.

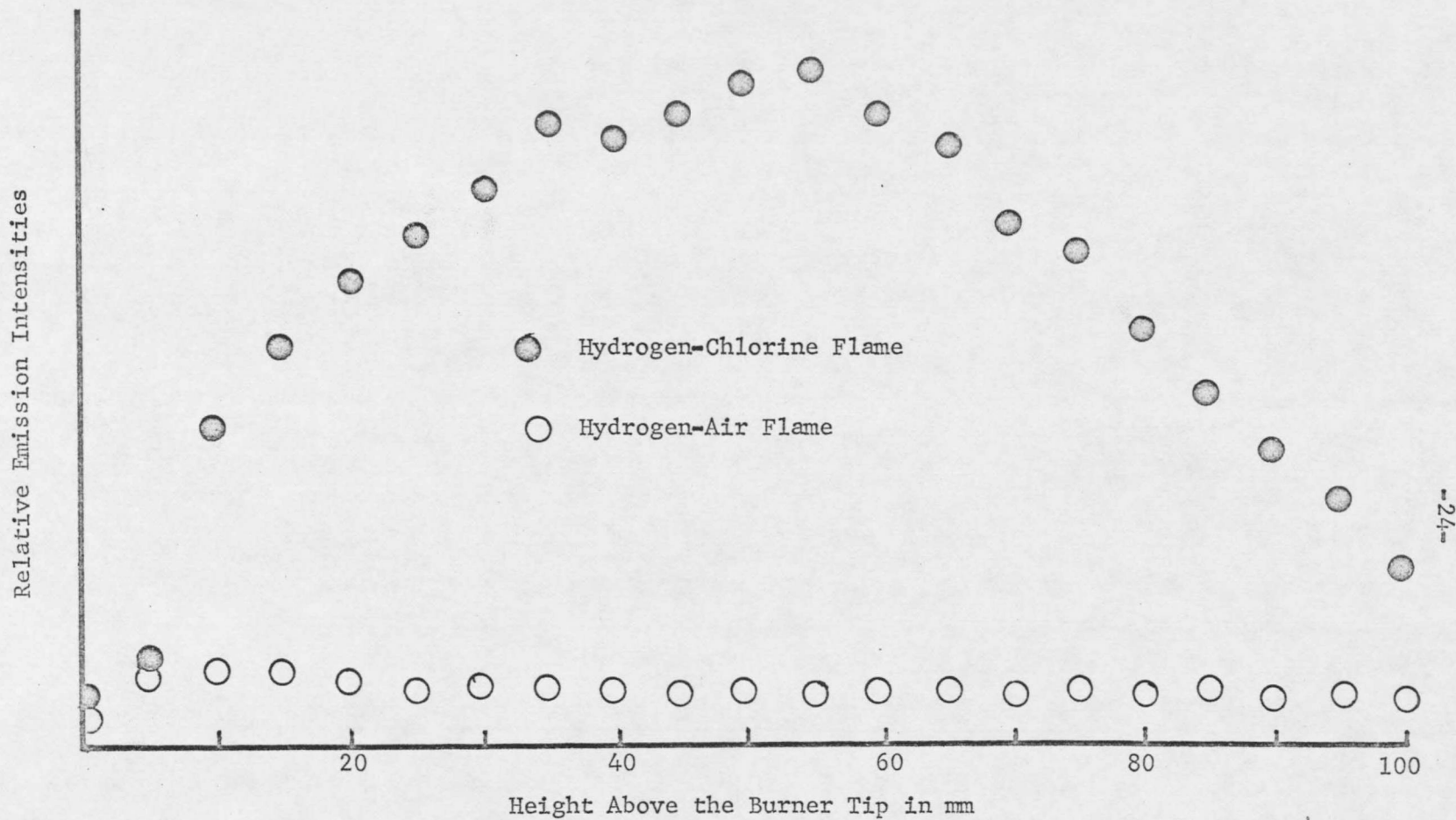


Figure 4. Emission Intensity for CuH at $4280\text{\AA}$ and CuCl at $4359\text{\AA}$ as a Function of the Height Above the Burner Tip in the Hydrogen-Chlorine and Hydrogen-Air Flames.

Atomic Absorption Measurements

Since atomic absorption measurements give information on ground state concentrations and are relatively independent of flame temperatures, it was felt that these measurements would be useful in the evaluation of the hydrogen-chlorine flame. If the difference between the atomic emission from copper in the air and chlorine flames resulted from differences in flame temperatures and not differences in copper concentration, atomic absorption would point this out.

Hence, modifications in the apparatus used for emission studies were made as illustrated in figure 5 and absorption data were taken at various positions in the flame for copper. Figure 6 illustrates these data for both the hydrogen-chlorine and hydrogen-air flames.

The hollow cathode tube employed was a Westinghouse type WL-22603* while the power supply was a Jarrel-Ash model 82-139. Although this particular power supply can be operated on both high intensity pulsed and straight D.C. modes, the D.C. mode was used exclusively. The Princeton Applied Research Corporation mechanical light chopper was placed between the flame and the light source to modulate the light so that it could be picked up by the A.C. amplifier which was used.

Emission from C_2 , CH and OH

Since the relative emission intensities of the C_2 molecule, the CH radical and the OH radical, commonly observed in flame excitation using organic solvents, reveal the chemical nature of the excitation source, maximization procedures identical to those used for copper emission were adopted to study the emission from these species in the chlorine supported

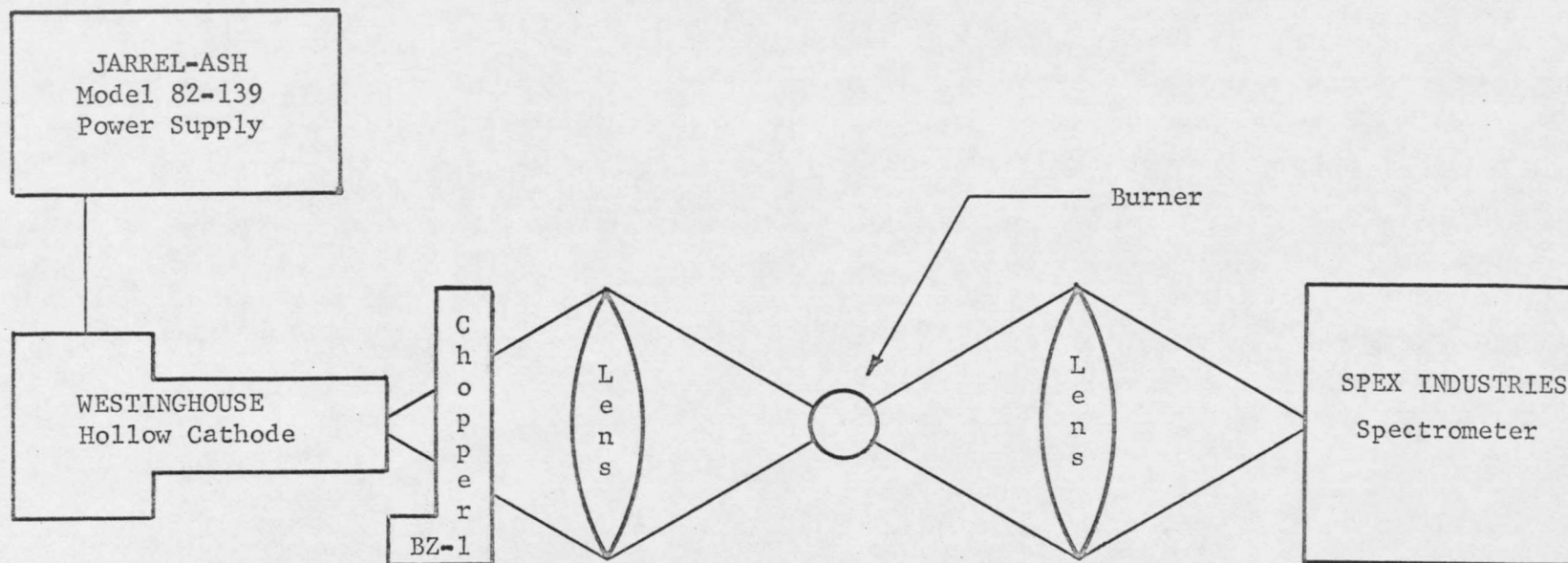


Figure 5. Modifications in the Optical Arrangement for Atomic Absorption.

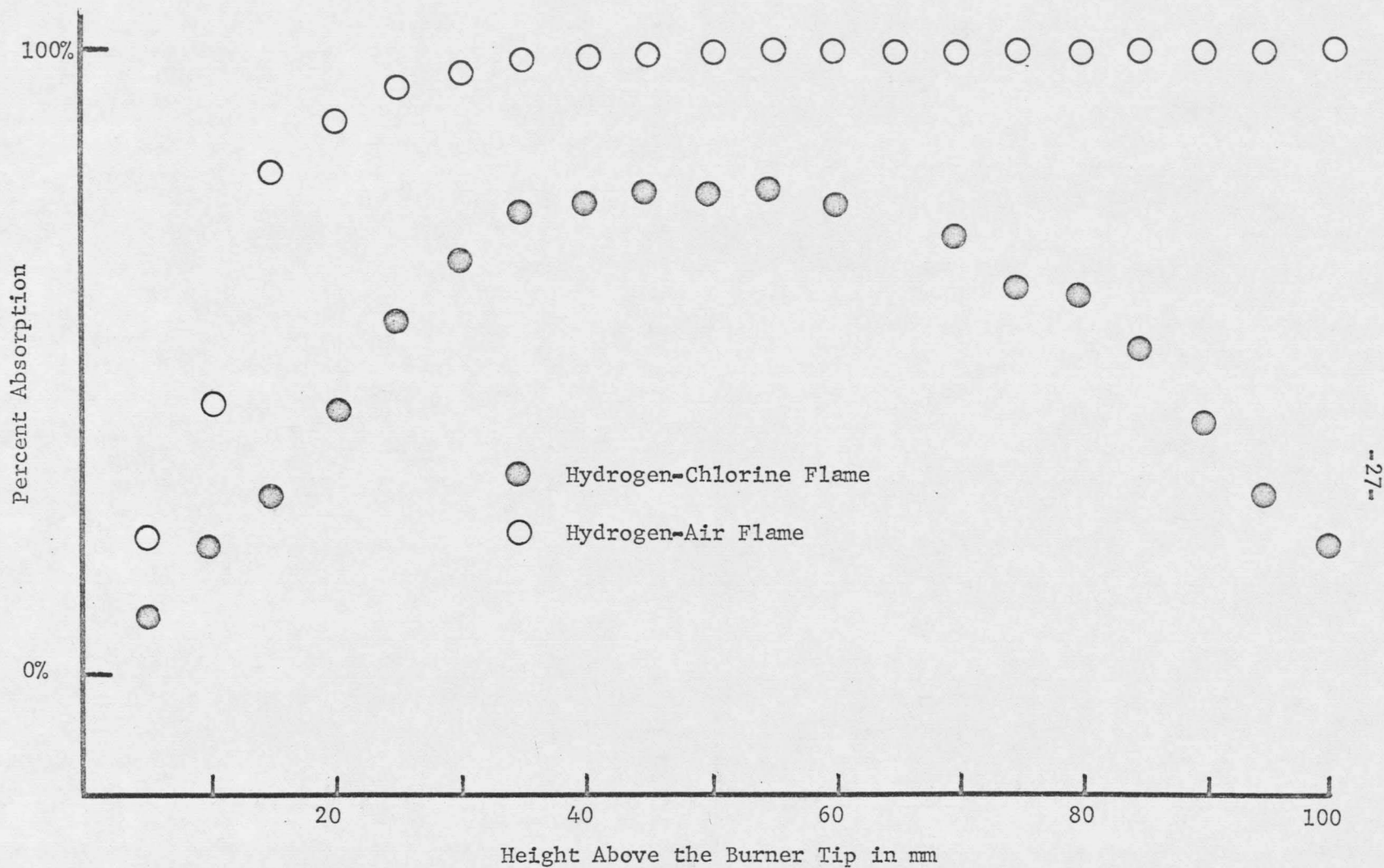


Figure 6. Percent Absorption for Copper at $3247.5\text{\AA}$ as a Function of the Height Above the Burner Tip in the Hydrogen-Chlorine and Hydrogen-Air Flames.

Table V. Response Surface Methods Leading to Maximization of Emission for C₂, CH and OH

Experiment Number	X ₁ Total Gas l/min	X ₂ Oxidant Flow <u>Flow</u> Total Flow	X ₃ Aspiration Rate ml/min	Calculated Equations
C ₂ Emission in the Hydrogen-Chlorine Flame at 5165 Å				
1	9.0- 9.5	0.10-0.15	1.00-3.00	I = 2.25 + 0.08X ₁ + 0.60X ₂ + 1.05X ₃
2	9.5-10.0	0.15-0.20	1.00-3.00	I = 4.97 + 0.47X ₁ + 1.36X ₂ + 2.13X ₃
3	10.0-10.5	0.25-0.30	1.00-3.00	I = 6.63 + 1.65X ₁ + 2.10X ₂ + 4.60X ₃
C ₂ Emission in the Hydrogen-Air Flame at 5165 Å				
1	10.0-10.5	0.20-0.25	1.00-3.00	I = 1.67 + 0.04X ₁ + 0.13X ₂ + 0.84X ₃
2	11.0-11.5	0.35-0.40	1.00-3.00	I = 2.58 + 0.05X ₁ + 0.00X ₂ + 1.34X ₃
CH Emission in the Hydrogen-Chlorine Flame at 4315 Å				
1	10.0-10.5	0.25-0.30	1.00-3.00	I = 4.66 + 0.02X ₁ + 0.09X ₂ + 2.72X ₃
CH Emission in the Hydrogen-Air Flame at 4315 Å				
1	11.5-12.5	0.35-0.40	1.00-3.00	I = 5.69 + 0.51X ₁ + 0.39X ₂ + 2.09X ₃

Table V. (continued)

Experiment Number	X ₁ Total Gas l/min	X ₂ Oxidant Flow <u>Flow</u> Total Flow	X ₃ Aspiration Rate ml/min	Calculated Equations
OH Emission in the Hydrogen-Chlorine Flame at 3067.8 Å				
1	10.0-10.5	0.25-0.30	1.00-3.00	$I = 6.88 + 0.28X_1 - 1.02X_2 + 2.75X_3$
2	10.0-10.5	0.10-0.20	1.00-3.00	$I = 10.5 + 0.20X_1 - 1.30X_2 + 1.20X_3$
OH Emission in the Hydrogen-Air Flame at 3067.8 Å				
1	11.0-12.0	0.30-0.40	1.00-3.00	$I = 9.88 + 0.42X_1 - 1.19X_2 + 1.04X_3$
2	12.0-12.5	0.20-0.30	1.00-3.00	$I = 12.8 + 0.35X_1 - 0.20X_2 - 0.03X_3$
3	13.0-14.0	0.10-0.15	1.00-2.00	$I = 12.9 + 0.29X_1 + 0.69X_2 - 0.44X_3$

flame. Absolute ethanol was used as the analyte in the investigation. It was anticipated that data on C_2 , CH and OH would show a relation to that obtained for copper and thus aid in the evaluation of the chlorine supported excitation source.

Table V gives the levels of the flame parameters chosen and the linear equations relating emission intensities to these parameters. The results of the final maximization by 3x3 factorial methods are presented in table IV, page 21, along with similar results for copper which were described earlier. The relations between emission intensities and flame positions are shown in figure 7, 8, and 9 for C_2 , CH and OH respectively. Once again data taken in the air and chlorine flames were placed in the same figure so that it would be easy to compare the chlorine flame to the more conventional hydrogen-air flame.

The Hydrogen-Chlorine Flame and Refractory Elements

At the beginning of this investigation little thought was given to the use of the hydrogen-chlorine flame in the determination of copper or any other element readily determined in more conventional flames. The primary concern was the determination of elements which form refractory oxides in conventional flames. In this respect an evaluation of the emission from titanium, vanadium, zirconium, niobium, molybdenum, lanthanum, tantalum, tungsten, and the rare earths was sought.

Because rare earths were used by Fassel in his illustrations of the value of fuel rich oxy-acetylene flames, they were an obvious beginning for the evaluation of the chlorine flame. Following the procedure outlined by Fassel (23) rare-earth oxides were converted to perchlorates and

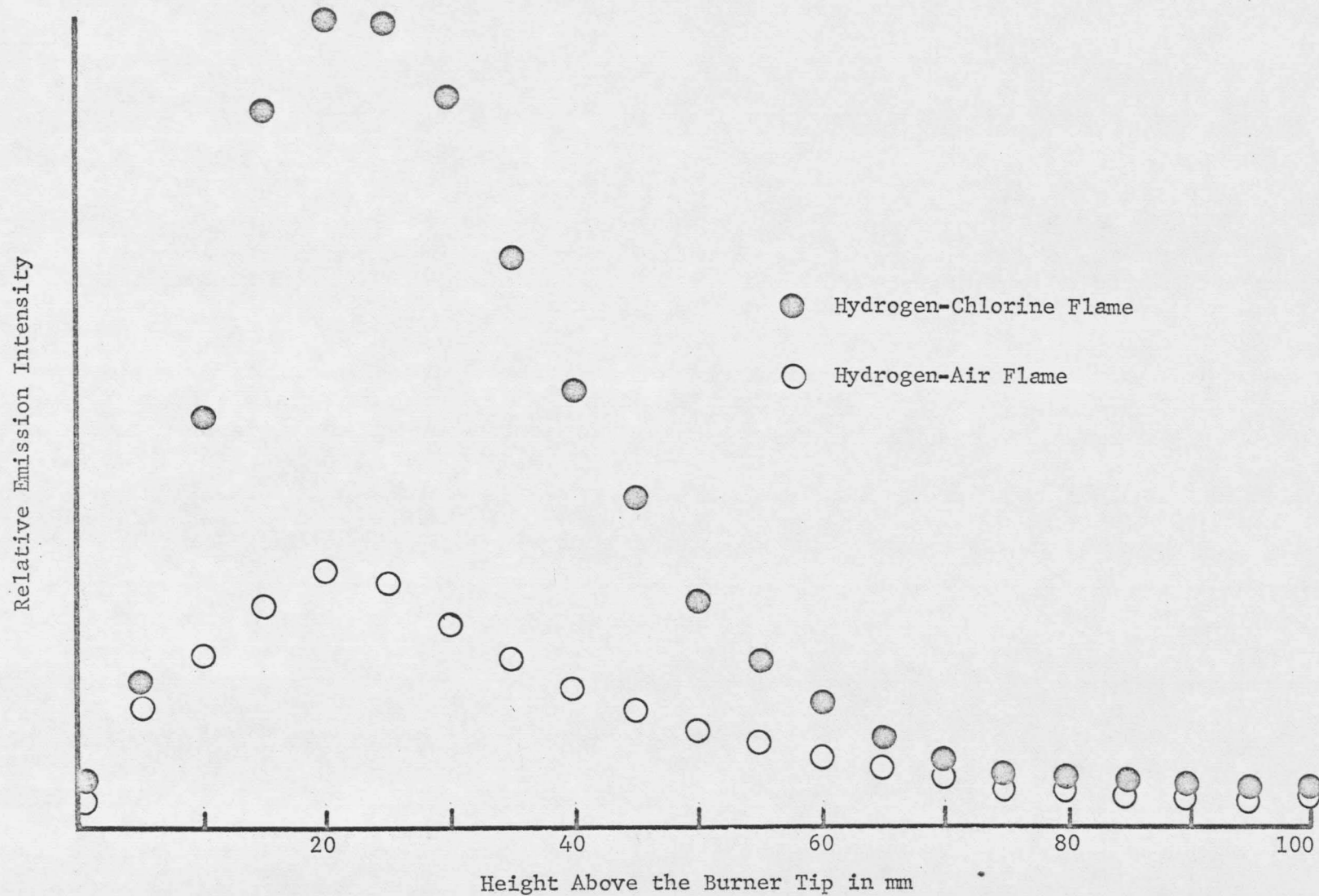


Figure 7. Relative Emission Intensity of the C₂ Molecule at 5165 Å as a Function of the Height Above the Burner Tip in the Hydrogen-Chlorine and Hydrogen-Air Flames.

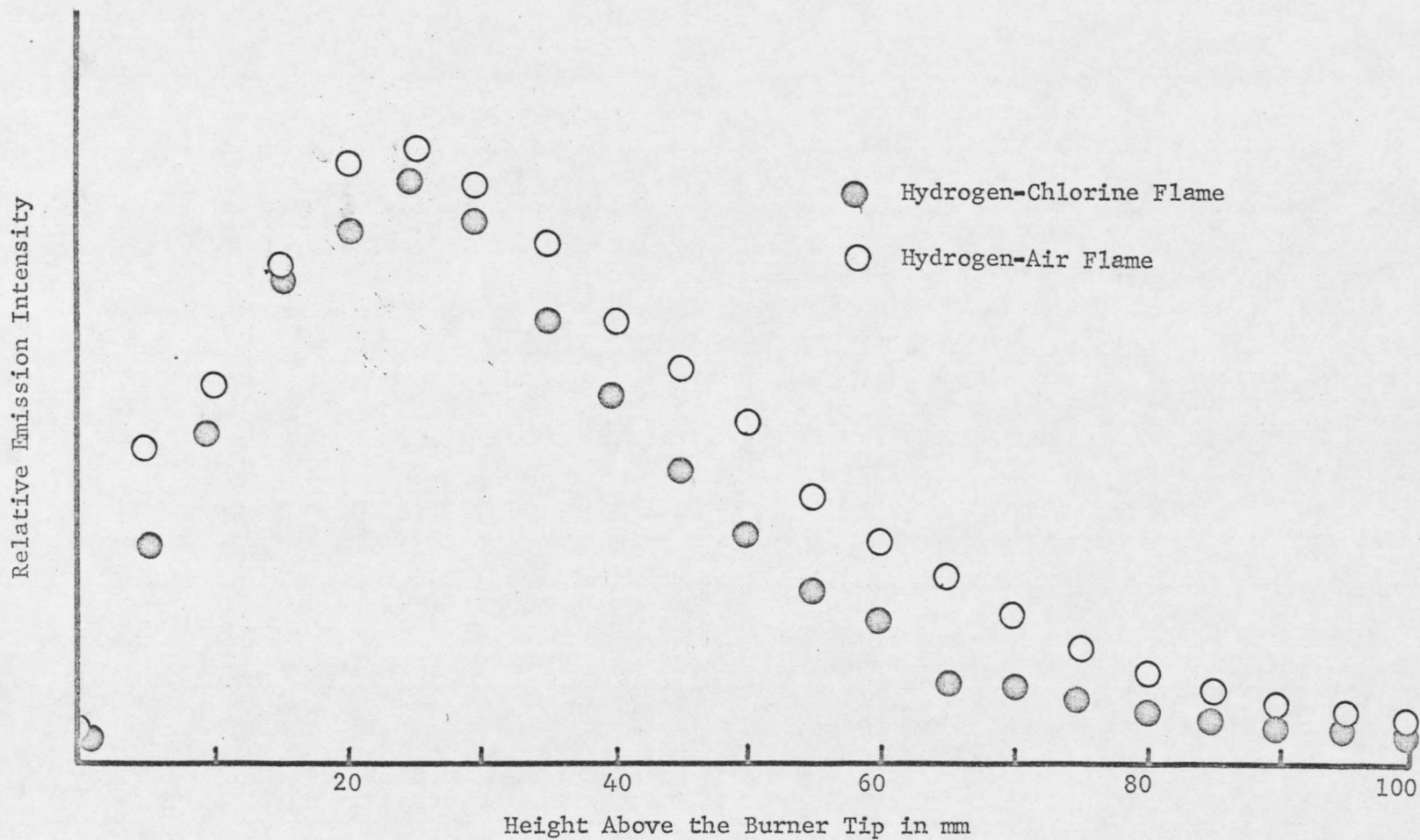


Figure 8. Relative Emission Intensity of the CH Radical at $4315\text{\AA}$ as a Function of the Height Above the Burner Tip in the Hydrogen-Chlorine and Hydrogen-Air Flames.

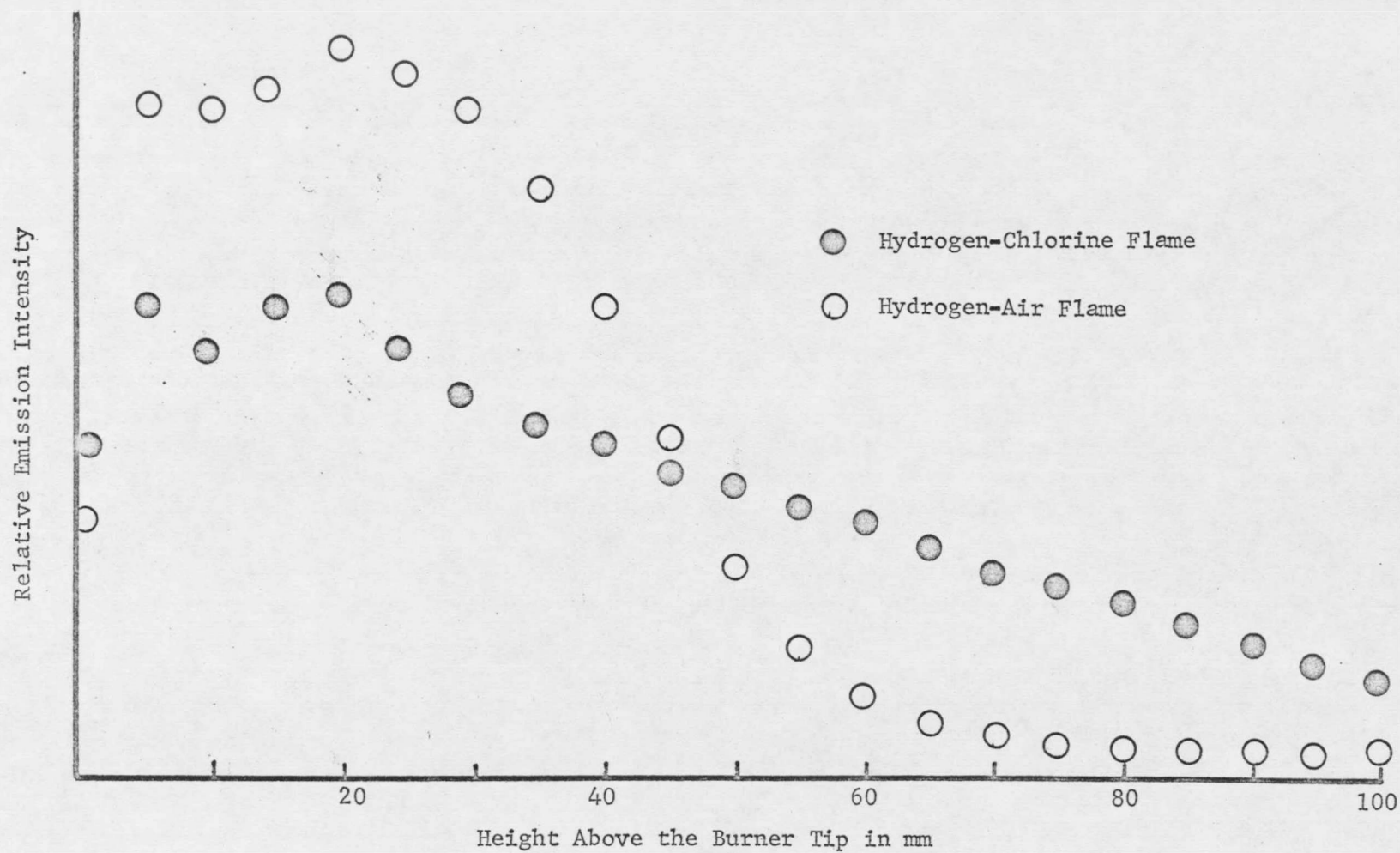


Figure 9. Relative Emission Intensity of the OH Radical at 3067.8 Å as a Function of the Height Above the Burner Tip in the Hydrogen-Chlorine and Hydrogen-Air Flames.

dissolved in absolute ethanol by the following procedure. Desired amounts of ignited oxides³ were dissolved in 50 ml of 1:1 perchloric acid (72%), and water. The resulting solutions were evaporated to near dryness and allowed to cool whereupon the liquid solidified. After further cooling to room temperature, the perchlorates were dissolved in absolute ethanol and diluted to volume to give the following weight percent solutions: yttrium, praseodymium, neodymium, holmium and lutetium - 0.1%; lanthanum - 1.0%; and gadolinium - 0.5%. These solutions were then aspirated into chlorine and air supported flames and the emission intensities recorded as the spectrum was scanned from 2500Å to 6500Å.

Peaks attributable to the rare earths were not observed for any of the compounds investigated nor were bands from chlorides or oxides seen. To further modify the atmosphere of the flame acetonitrile was used as the solvent in place of ethanol.

Rare-earth perchlorate solutions were prepared as were the ethanol solutions and aspirated into the hydrogen-chlorine flame. Once again when the spectrum was scanned from 2500Å to 6500Å, emission from the rare-earths was not detected. However, it may be interesting to note that very intense bands from the CN radical were observed arising from the solvent, acetonitrile. Bands from this species are illustrated in the appendix in recordings of the background emission obtained when acetonitrile was introduced into the chlorine flame.

³These compounds were purchased from Matheson, Coleman & Bell and were reported to be 99.9% pure.

Directing attention to molybdenum, tungsten and vanadium, 1000 $\mu\text{g/ml}$ aqueous solutions of these elements were prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{W}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ and NH_3VO_3 . The solutions were aspirated into the $\text{H}_2\text{-Cl}_2$ flame and the spectrum scanned. Emission from molybdenum, tungsten and vanadium was not detected. Since Fassel failed to get rare-earths to emit from aqueous solutions even in the fuel rich oxy-acetylene flame, this result was not entirely unexpected.

Molybdenum and vanadium were brought into organic solution by solvent extraction techniques described in the literature (38,40,51). Ammonium pyrrolidine dithiocarbamate, APDC, was used as the chelating agent and methyl isobutyl ketone (MIBK) as the solvent. Vanadium was also extracted with 8-hydroxyquinoline into methyl isobutyl ketone as was tungsten. A cupferron ethyl acetate extraction was also used in the case of vanadium. Neither of these elaborate procedures produced solutions whereby atomic or band emission could be detected in the hydrogen-chlorine flame. MIBK and ethyl acetate also did not burn satisfactorily in the chlorine flame. Excessive carbon formation at the tip of the burner was a constant problem in that this caused both the flame and aspiration rate to fluctuate.

Other elements which do not emit useful spectra in oxygen supported flames are niobium and zirconium. In an attempt to obtain spectra from these elements halides were dissolved in absolute ethanol which had had dry nitrogen bubbled through it. Tungsten was also treated in a similar manner. For this portion to the investigation samples of NbCl_5 from K & K Laboratories, Inc., ZrCl_4 from Pfaltz & Bauer, Inc. and WBr_5 from this same company were weighed out in a Dri Lab model HE-43-2 dry box from the

Vacuum/atmospheres Corporation. WBr_5 formed a precipitate when added to the ethanol necessitating the addition of 5 ml of 50% HF solution. The spectrum from $2500\text{\AA}$ to $6500\text{\AA}$ was then scanned as solutions of niobium, zirconium and tungsten were fed to the hydrogen-chlorine flame. In the recordings obtained no evidence for emission from these elements was detected.

Since emission from titanium hadn't been evaluated as yet, a 2000 $\mu\text{g/ml}$ solution of this element in 1:1 ethanol-water was fed to the chlorine flame. This solution was prepared by dissolving titanium in concentrated HCl, evaporating to near dryness and dissolving the remaining solution in absolute ethanol. As in the case of the other refractory elements, emission characteristic of titanium was not observed.

At this point it was apparent that elements known for forming refractory oxides would not emit radiation in the UV-visible region of the spectrum when aspirated into the hydrogen-chlorine flame. Although the atmosphere of this flame was more conducive to reduction, indicated by the increased C_2 and CH emission, (see appendix for recordings of background emission in the hydrogen-chlorine flame) refractory elements nevertheless did not emit the desired atomic line spectra. It was felt that turbulence in the hydrogen-chlorine flame may have brought oxygen in from the surroundings and defeated the whole purpose of using chlorine as the oxidant. For this reason the glass burner which had been employed throughout the investigation was modified by putting a glass sheath around the tip. Chlorine was passed through the sheath to shield the flame from the atmosphere.

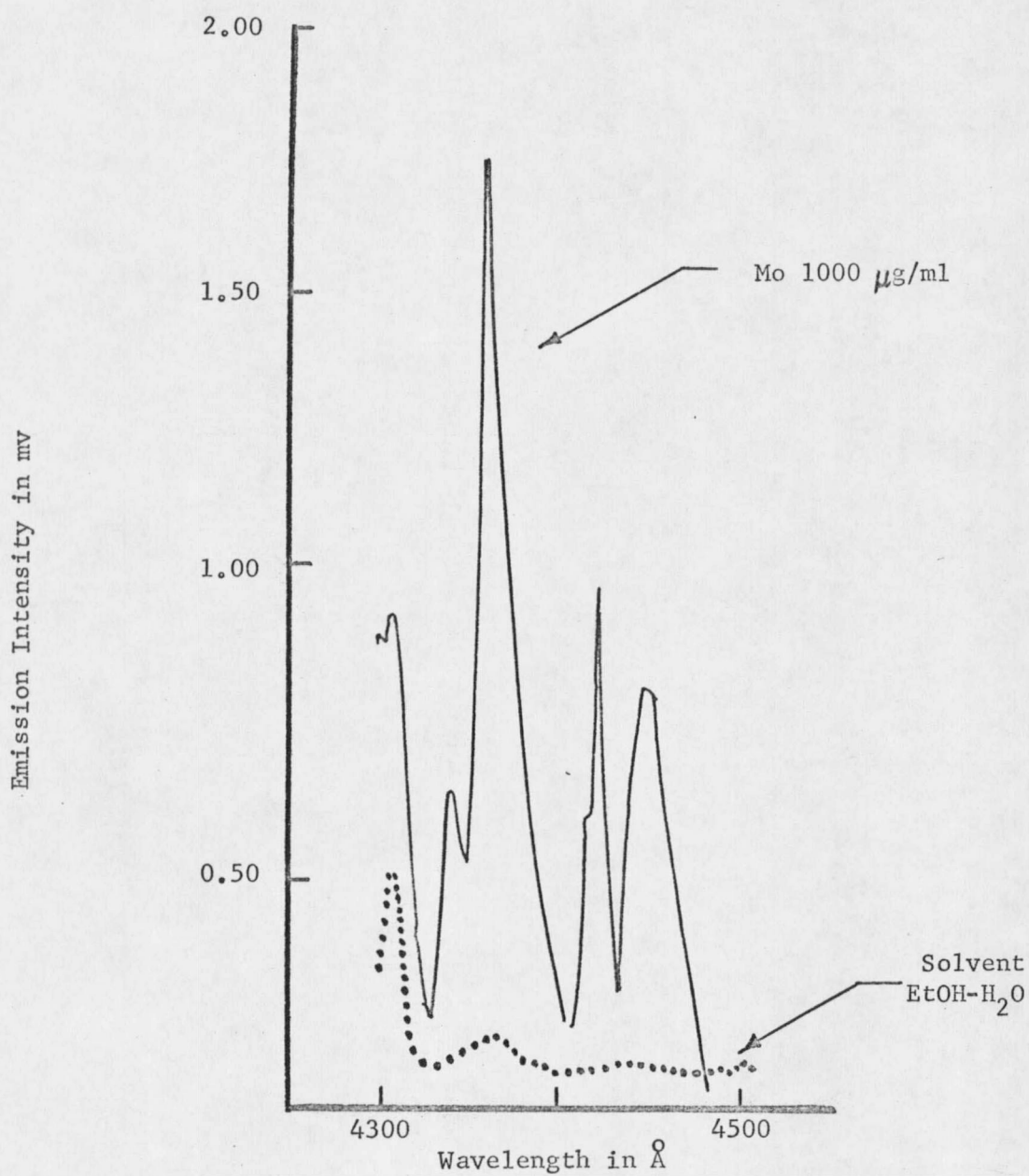


Figure 10. Recording of Emission Spectra for Molybdenum in the Sheathed Hydrogen-Chlorine Flame.

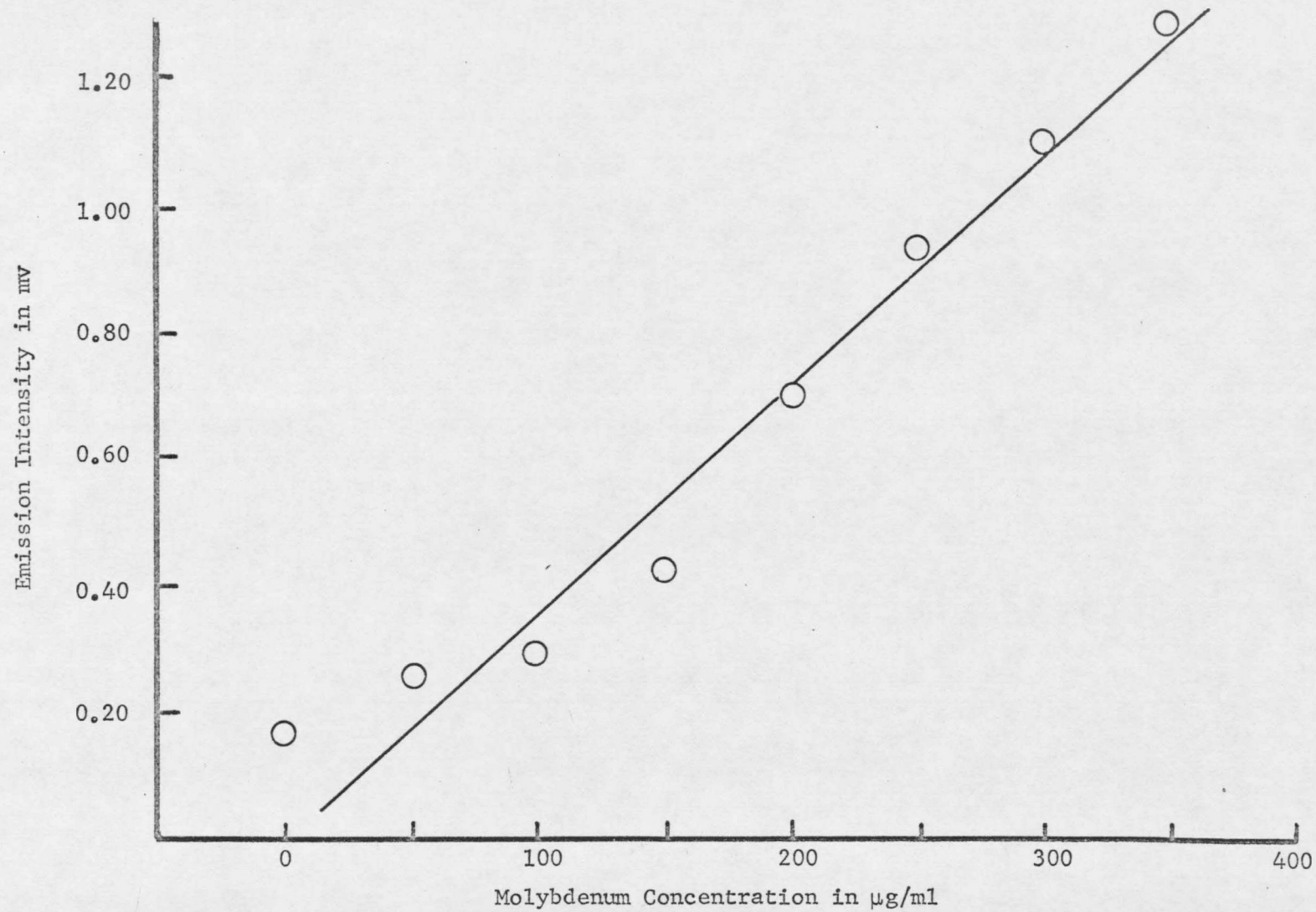


Figure 11. Emission Intensity of Molybdenum Band at $4366\text{\AA}$ as a Function of the Molybdenum Concentration

Solutions of molybdenum prepared by dissolving the metal in aqua regia, evaporating to near dryness and dissolving the resulting solution in a 3:1 mixture of absolute ethanol and water were now fed to the sheathed hydrogen-chlorine flame while the spectrum was scanned from 2500Å to 6500Å. A band between 4300Å and 4500Å was detected for 1000 µg/ml solutions of molybdenum. This region of the spectrum was also scanned when solvent without molybdenum was fed to the flame. Recordings of this data are illustrated in figure 10.

The width of the emission band observed indicated that the species responsible for the band was molecular rather than atomic in nature. To verify that the band was due to a molybdenum compound standard solutions ranging in concentration from 0 to 350 µg/ml were prepared from 99.8% molybdenum metal, Fisher Scientific Company, Baker & Adamson reagent grade acids and absolute ethanol from the U.S. Industrial Chemicals Company. Emission intensities for the observed band were plotted as a function of the concentration of the analyte. Figure 11, page 38, shows these data and verifies that the band is due to a molybdenum compound. To accurately identify the emitting species a high resolution instrument was required. The instrument used in this investigation would have been sufficient if the emission intensity of this particular band had been strong enough so that slit widths on the order of 8 microns could have been used. However, since this was not the case an accurate identification of the emitting species could not be made.

Emission intensities from the "MoCl" band appearing at 4366Å were determined for twenty-seven possible combinations of the total gas flow to

the burner, the chlorine flow to total gas flow ratio and the percentage of the total chlorine flow passing through the sheath rather than the burner. The aspiration rate was held constant because its affect on the emission was not that important. Furthermore, in the sheathed flame maintaining a stable flame front was difficult enough without complicating matters by varying the aspiration rate. Table VI gives the range of flame parameters studied along with the particular combination which produced the greatest emission intensity for molybdenum.

Table VI. Maximization of Emission from Molybdenum in the Sheathed Hydrogen-Chlorine Flame

	Total Gas Flow	Chlorine Flow	Chlorine Flow	Emission
	in l/min	Total Gas Flow	to Sheath Chlorine Flow to Burner	Intensity
Levels of Parameters Investigated	8.0-9.0-10.0	0.20-0.30-0.40	0.30-0.40-0.50	
Parameter Combination Yielding Optimum Emission	10.0	0.30	0.30	0.94 mv

Exactly why the unsheathed hydrogen-chlorine flame did not yield atomic emission from refractory elements was not entirely understood. It seemed as if chlorides were formed in place of oxides since oxide bands were not observed. To be certain that these elements did not exist in the

atomic state and did not emit because of the low temperature of the flame, atomic absorption measurements were made. Hollow cathode tubes were purchased from Westinghouse Electric for molybdenum and zirconium. If these elements were present in the atomic state, atomic absorption could be used to verify this.

Using the optical arrangement shown in figure 5, page 26, atomic absorption measurements were taken on solutions of both molybdenum and zirconium aspirated into the hydrogen-chlorine flame. For Mo a WL-22860* hollow cathode operated at 20 ma. was used while a WL-22937* tube operated at 25 ma. was used for zirconium.

Absorption was not detected in the unsheathed flame for either molybdenum or zirconium. Hence, this added support to our suspicions that these elements existed as chlorides in the reaction zone of the flame and that the desired atomic state did not exist.

Discussion

From the cursory investigation it was concluded that atomic emission from silver, copper and magnesium in the hydrogen-chlorine flame was somewhat less intense than similar emission in the hydrogen-air flame. Although intensities in the air flames are roughly twice those in the chlorine flame, this is not surprising since the hydrogen-air flame is approximately 200° to 300° hotter than the hydrogen-chlorine flame. In equation (1), page 3, it was shown that:

$$I \propto e^{-E_a/kT}$$

where I = Emission Intensity

E_a = Excitation Energy

k = Boltzmann's constant

T = Temperature

Substituting into this expression the flame temperatures of the excitation sources being compared⁴ one obtains the following range of values for the logarithm of the ratio of emission intensities:

$$\ln \frac{I_{H_2-Air}}{I_{H_2-Cl_2}} \approx 0.874 - 0.912$$

In table VII the values of this ratio are given for elements from the cursory investigation from which atomic spectra were obtained. As one can see logarithms of intensity ratios for silver, copper and magnesium agree rather well with the calculated ratio. This indicates that chlorine does not alter the concentration of atomic vapor in the flame.

⁴The temperature of the hydrogen-chlorine flame has been reported to be $2075^{\circ}K$ while that of hydrogen-air flame is reportably between $2275^{\circ}K$ and $2375^{\circ}K$ (17,14).

Table VII. Comparison of Atomic Emission Intensities.

Element Wavelength in Å	$\ln \frac{I_{H_2-Air}}{I_{H_2-Cl_2}}$	Element Wavelength in Å	$\ln \frac{I_{H_2-Air}}{I_{H_2-Cl_2}}$
Calcium			
4227	5.050	3720	2.303
		3737	2.129
Cadmium		3746	1.970
3261	2.058	3823	2.045
Chromium		3860	2.158
3579	1.244	3886	1.742
3594	1.522	3900	1.033
3605	1.319	3930	1.898
4254	2.171		
4275	1.966	Magnesium	
4290	1.869	2852	1.099
Cobalt		Manganese	
3413	0.846	4033	2.862
3433	0.742	Nickel	
3453	1.030	3371	1.322
3468	1.054	3394	1.203
3508	0.932	3414	1.157
3527	1.125	3438	0.715
3575	0.621	3449	0.916
3595	-0.183	3460	0.112
3630	-1.152	3491	0.956
3650	-1.833	3514	1.139
3842	0.548	3522	1.040
3871	0.846	3569	0.392
3892	0.122	3619	0.647
3992	0.599	3854	-0.787
4118	0.798	Silver	
Copper		3281	0.683
3248	0.747	3383	0.737
3274	0.788	Sodium	
Iron		5890	3.570
3441	2.228	Strontium	
3447	0.796	4607	5.991
3491	0.000		
3570	0.140		
3581	1.792		
3648	1.792		
3706	0.761		

In attempting to explain emission intensity ratios by temperature variations for calcium, cadmium, manganese, sodium and strontium one finds that the greater emission in the hydrogen-air flame cannot be explained. Values of $\ln I_{\text{H}_2\text{-Air}}/I_{\text{H}_2\text{-Cl}_2} \gg 0.874 - 0.912$ indicate that for these elements chlorine has an effect on emission intensities which cannot be accounted for by considering flame temperatures alone.

Since emission intensities are directly related to excited state concentrations, it is concluded that calcium, cadmium, manganese, sodium and strontium form chlorides in the hydrogen-chlorine flame decreasing the concentration of metallic vapor.

Chemiluminescence (footnote 2, page 5) has been shown to account for excitation in flames under a variety of conditions. If chemiluminescence is important in the hydrogen-chlorine flame, a second explanation for marked decreases in emission in the halogen flame is proposed. Halogens reportedly quench emission more than nitrogen and oxygen (50). Hence, large concentrations of chlorine could quench luminescence and thereby account for significant decreases in emission intensities in the hydrogen-chlorine flame.

For cobalt, chromium, iron and nickel a comparison of $\ln I_{\text{H}_2\text{-Air}}/I_{\text{H}_2\text{-Cl}_2}$ to the calculated temperature ratio yields inconsistent results. Depending on the emission line being observed for a particular element the logarithm of the $I_{\text{H}_2\text{-Air}}$ to $I_{\text{H}_2\text{-Cl}_2}$ ratio is less than, equal to, or greater than the $T_{\text{H}_2\text{-Cl}_2}$ to $T_{\text{H}_2\text{-Air}}$ ratio. This variation with the emitted radiation being considered is shown in table VII.

These apparent abnormalities were at first believed to be the result of poor data. Emission spectra for the transition elements are very complex and overlap background emission making the accurate determination of emission intensities difficult. Although this undoubtedly explains some of the variation, another explanation is suggested.

The reactivity of a particular atom is known to be a function of the electronic state of the atom. Hence, the formation of metal chlorides depopulates specific electronic states in varying degrees.

As explained in the introduction it was anticipated that refractory elements (titanium, vanadium, zirconium, niobium, molybdenum, tantalum, tungsten and rare earths) would emit line spectra in the hydrogen-chlorine flame. This was not observed experimentally even when special efforts were made to keep oxygen out of the system. Free energy of dissociation data for gaseous metal oxides and chlorides at high temperatures is not entirely reliable (11,58) and may explain these observations. Even though the chlorides of refractory metals are generally less stable than oxides the chlorides are relatively stable at the moderate temperature of the hydrogen-chlorine flame (50). Chloride band emission is seen for copper, calcium and magnesium. Hence, the lack of emission from chlorides of titanium, vanadium, zirconium, niobium, tantalum, tungsten, yttrium, lanthanum, praseodymium, neodymium and holmium was not expected. Molybdenum lived up to expectations in that a weak molecular molybdenum band was detected in a sheathed hydrogen-chlorine flame.

Chloride band emission from copper, calcium and magnesium has been

reported in the literature (17,45,46). Hence, these particular bands were expected although the strength of the copper chloride band was delightfully surprising. When emission intensities were maximized for CuCl emission in the hydrogen-chlorine flame and atomic copper emission in the hydrogen-air flame by varying flame conditions, the chloride band was found to be more than fifteen times as intense as the copper line emission obtained in a hydrogen-air flame. Atomic absorption measurements at numerous heights in the flame showed that for the hydrogen-air flame the atomic copper concentration rose sharply until it reached a maximum 35 mm above the burner tip. From 35 mm to 100 mm above the burner the concentration remained virtually constant. In the chlorine flame optimized for CuCl emission the concentration of atomic copper reached a maximum at a point 50 mm above the burner tip. Higher in the flame the copper concentration decreased steadily. This was expected since CuCl formation should be related to the time a copper atom spends in the chlorine atmosphere and the oxidative nature of the region being viewed. By integrating percent absorption over the entire flame, from the burner tip to a position 100 mm above the burner, for chlorine and air supported flames the concentration of copper in the hydrogen-chlorine flame can be calculated relative to the concentration in the hydrogen-air flame. In doing this it was found that the Cu concentration in the chlorine source was 83.9% of that in the air supported source. This value seems high in view of the intensity of the CuCl band. It is concluded that in the hydrogen-chlorine flame CuCl emits a very strong band suitable for the spectroscopic determination of copper.

Emission from C_2 , CH and OH observed when ethanol was used as the solvent was maximized by the procedure used in the optimization of copper emission. Comparing the optimum flame parameters for the emission from C_2 , CH and OH in the hydrogen-chlorine and hydrogen-air flames, one finds that excitation conditions for maximum emission are not significantly different. Total flow rates of gas to the burner were nearly the same in the chlorine and air flames for the emission from these species as were oxidant flow to total gas flow ratios. For C_2 and CH emission the maximum rate at which ethanol was aspirated into the flame produced the maximum emission in both flames. Emission from the OH radical did not follow this pattern. In the hydrogen-air flame emission intensities increased as the aspiration rate decreased while in the chlorine flame an opposite trend was observed. As the aspiration rate increased, increased intensities from the OH radical were observed. This behavior can be explained by considering the source of oxygen for the formation of the OH radical. If one neglects the possibility of drawing oxygen from the surroundings into the reaction zone of the hydrogen-chlorine flame, the only available oxygen is that contained in the absolute ethanol being fed to the flame by means of the capillary through the center of the burner (see figure 2, page 11). Hence, one would expect the emission intensity to be directly related to the rate at which ethanol was being fed to the flame.

In the hydrogen-air flame the situation is somewhat different. In addition to oxygen from the solvent the oxidant itself can provide for the formation of the OH radical. In fact in this particular flame the OH radical is necessary for the propagation of the reaction. This suggests

that the aspiration rate has a negligible affect on the OH emission provided the solvent being aspirated does not react with OH radicals and decrease their concentration. Experimentally it was observed that the intensity of the OH band was inversely proportional to the rate at which absolute ethanol was fed to the flame. Hence, in the hydrogen-chlorine flame it is concluded that ethanol decreases the concentration of this species.

A comparison of the emission intensities from C_2 and CH at various positions in the flame shows that the C_2 molecule and CH radical reach a maximum intensity 21 mm and 23 mm above the burner tip respectively in both flames. The OH radical reaches a maximum somewhat lower in the two flames at 19 mm.

From figure 8, page 32, it is apparent that CH emission in the air supported flame closely resembles that in the chlorine supported flame. This is not true of the C_2 molecule. As one can plainly see in figure 7, page 31, far greater emission from the C_2 molecule was obtained from the hydrogen-chlorine flame. Noting that emission in the air flame from the OH radical decreases as the aspiration rate of absolute ethanol increases and the C_2 emission is significantly less in the air flame, it may be concluded that the C_2 molecule, originating from the organic solvent, reacts with the OH radical and thereby decreases the observed intensities of bands from this species.

Finally it has been observed that emission from atomic copper occurs predominately when excess fuel is being furnished to the flames. In the H_2 -Air flame CuH emission is likewise increased when a fuel rich reducing

atmosphere is employed while the CuCl band is a maximum in a hydrogen-chlorine flame when less fuel and more chlorine is used. These results are what would be expected.

Conclusion

This investigation has attempted to determine the potential role of a hydrogen-chlorine flame excitation source in flame photometry. The results have led to the conclusion that silver, copper and magnesium emitted useful radiation although somewhat less intense than comparable emission in the hydrogen-air flame. Lower intensities were attributable to the lower temperature of the halogen flame. Chlorine decreased the concentrations of atomic calcium, cadmium, manganese, sodium and strontium in the hydrogen-chlorine flame. On the other hand, the affect of chlorine on individual atoms of cobalt, chromium, iron and nickel was found to depend on the particular electronic state of the atom involved.

Refractory metals (titanium, vanadium, zirconium, niobium, tantalum, tungsten, yttrium, lanthanum, praseodymium, neodymium and holmium) in general did not emit spectra when introduced into the hydrogen-chlorine flame. Molybdenum was an exception in that a weak molecular band was observed between $4300\text{\AA}$ and $4500\text{\AA}$ when a sheathed flame was employed. Copper on the other hand gave an intense CuCl band in the chlorine excitation source. The strength of this emission suggested that this flame may be useful analytically in the determination of copper.

Suggestions for Future Work

The results presented in the dissertation virtually rule out use of the hydrogen-chlorine flame in analytical determinations in the UV-visible region of the spectrum for elements other than copper. However, the apparent strength of the CuCl band and the conclusion that atomic line emission from refractory metals was not seen because of stable chloride formation suggests that molecular chloride bands may be worth further

consideration. The red end of the visible spectrum and the near infrared portion of the spectrum could not be observed with the equipment available. A study of the emission from refractory metals in a hydrogen-chlorine flame in this region may be worthwhile and is suggested for a future study.

The use of chlorine in conjunction with acetylene or possibly cyanogen may also be justified. The acetylene chlorine flame was considered briefly at the beginning of this investigation. The reducing atmosphere produced by this combination of gases appears promising. However, the nature of these gases and the high background emission are disadvantages which need to be carefully considered.

Use of cyanogen will require a more cautious approach than that of acetylene. Flames from chlorine and cyanogen have not been reported in the literature. Hence, it is pure speculation to suggest use of this combination for a flame photometric excitation source. One important advantage to using this combination of gases is that higher flame temperatures would be expected than those obtained from other chlorine supported flames.

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APPENDIX

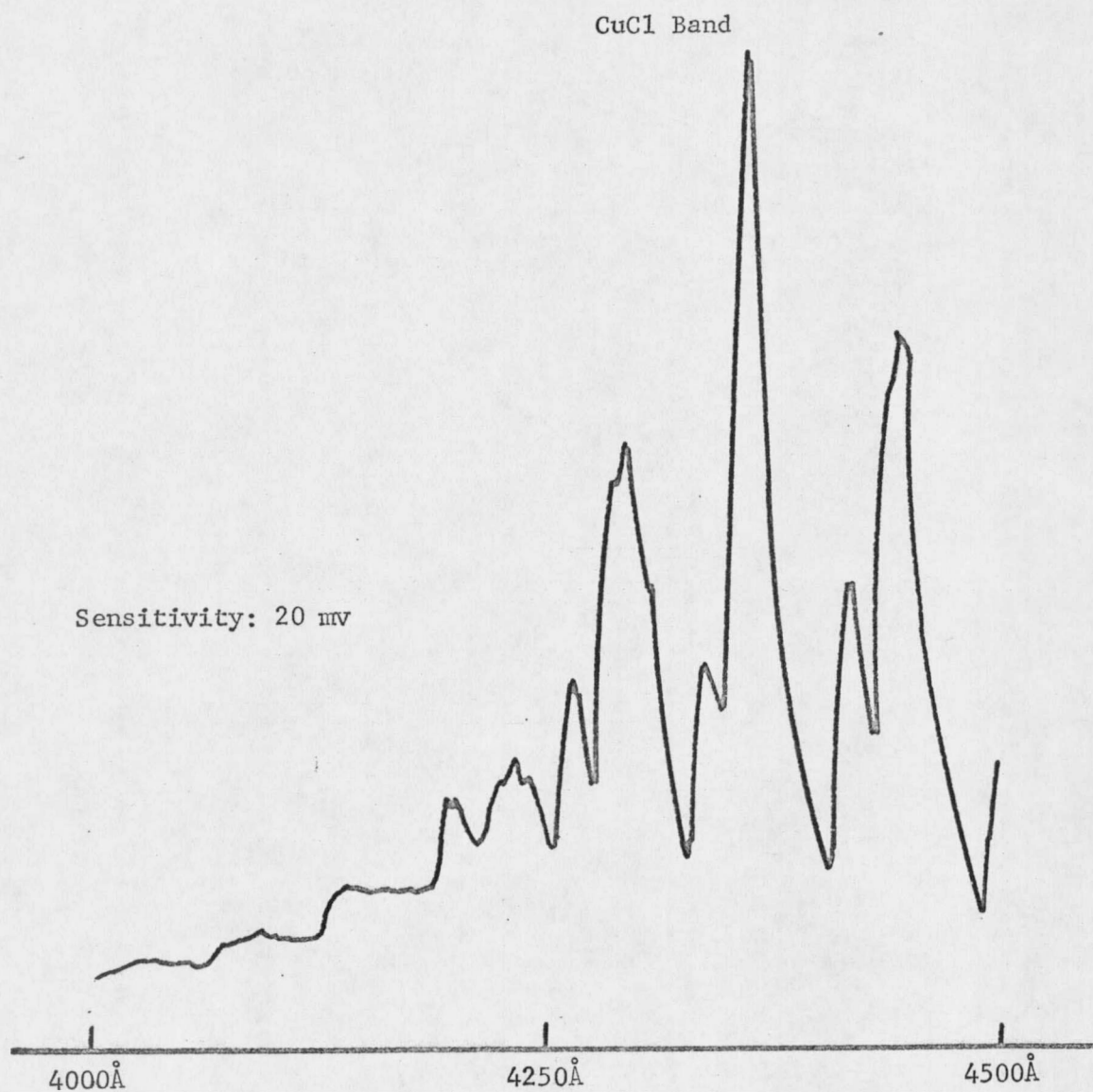


Figure 12. Copper Chloride Band Emission Obtained in the Hydrogen-Chlorine Flame.

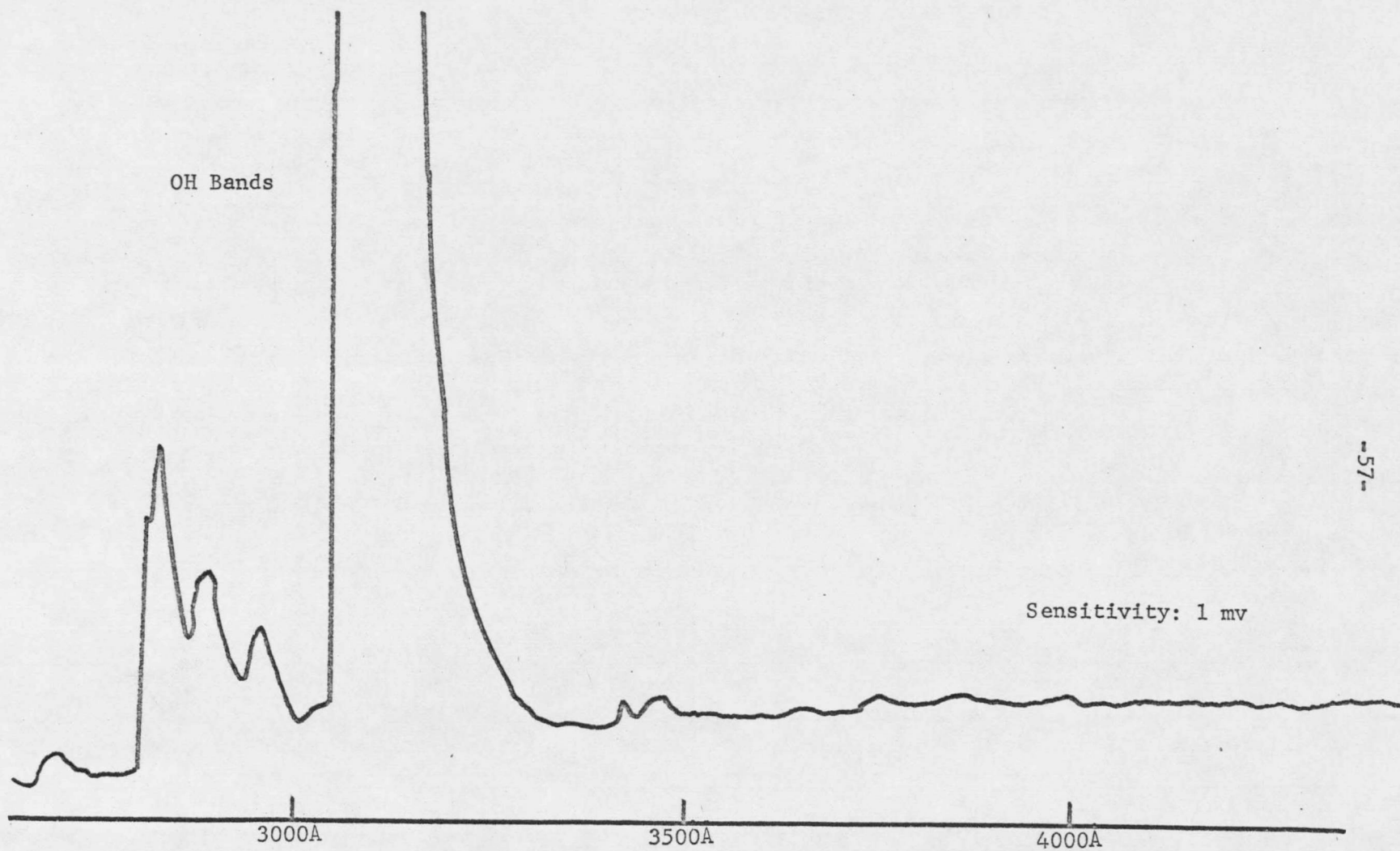


Figure 13. Background Emission from the Hydrogen-Chlorine Flame

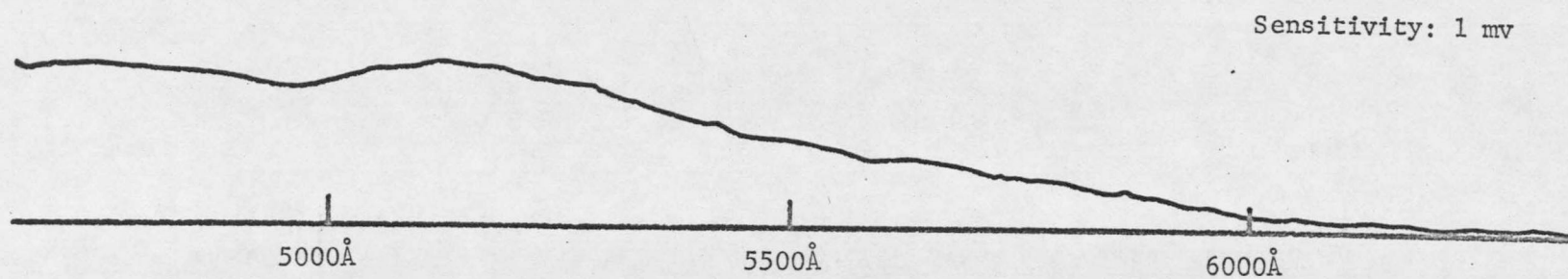


Figure 14. Background Emission from the Hydrogen-Chlorine Flame.

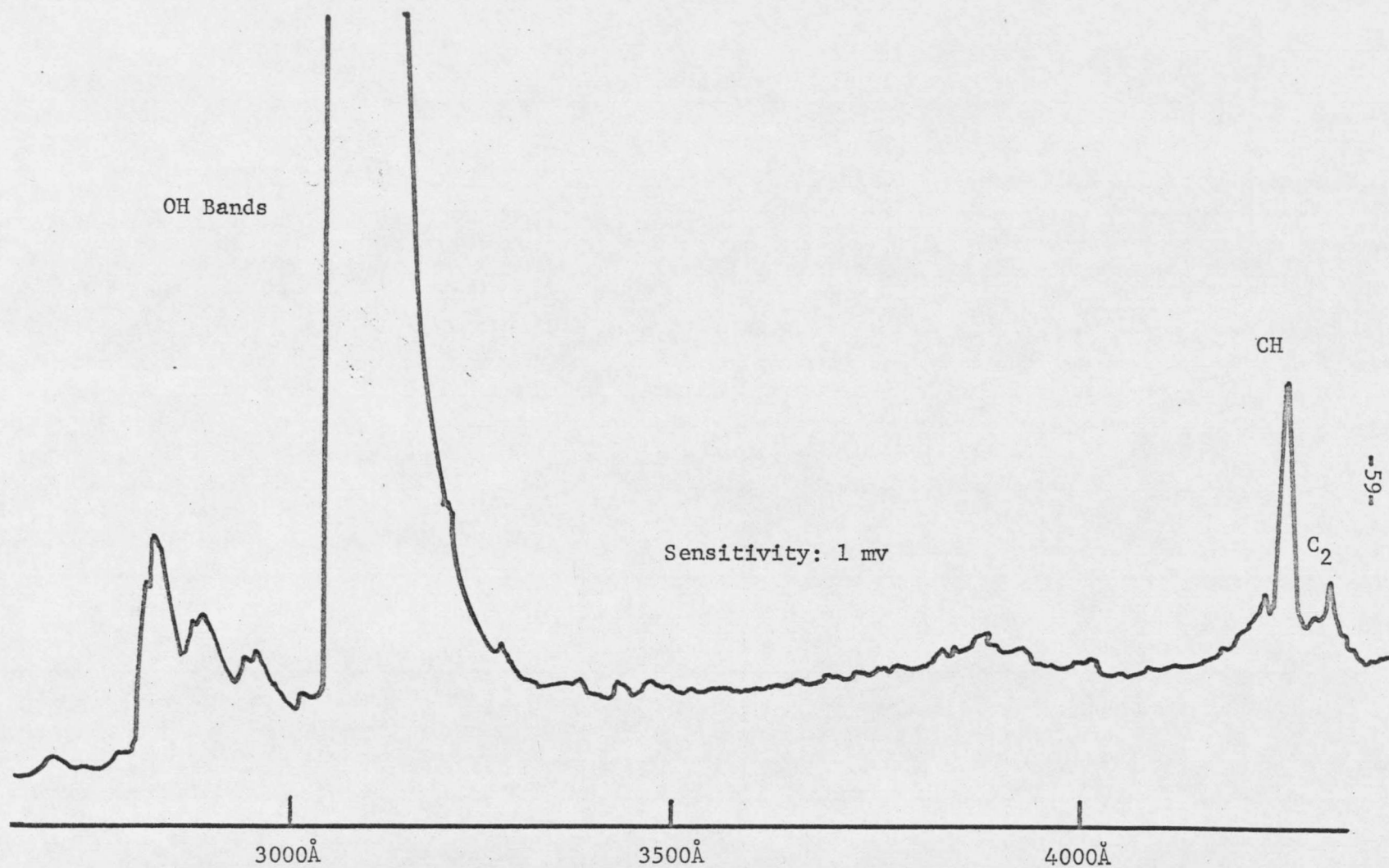


Figure 15. Background Emission from Absolute Ethanol in the Hydrogen-Chlorine Flame.

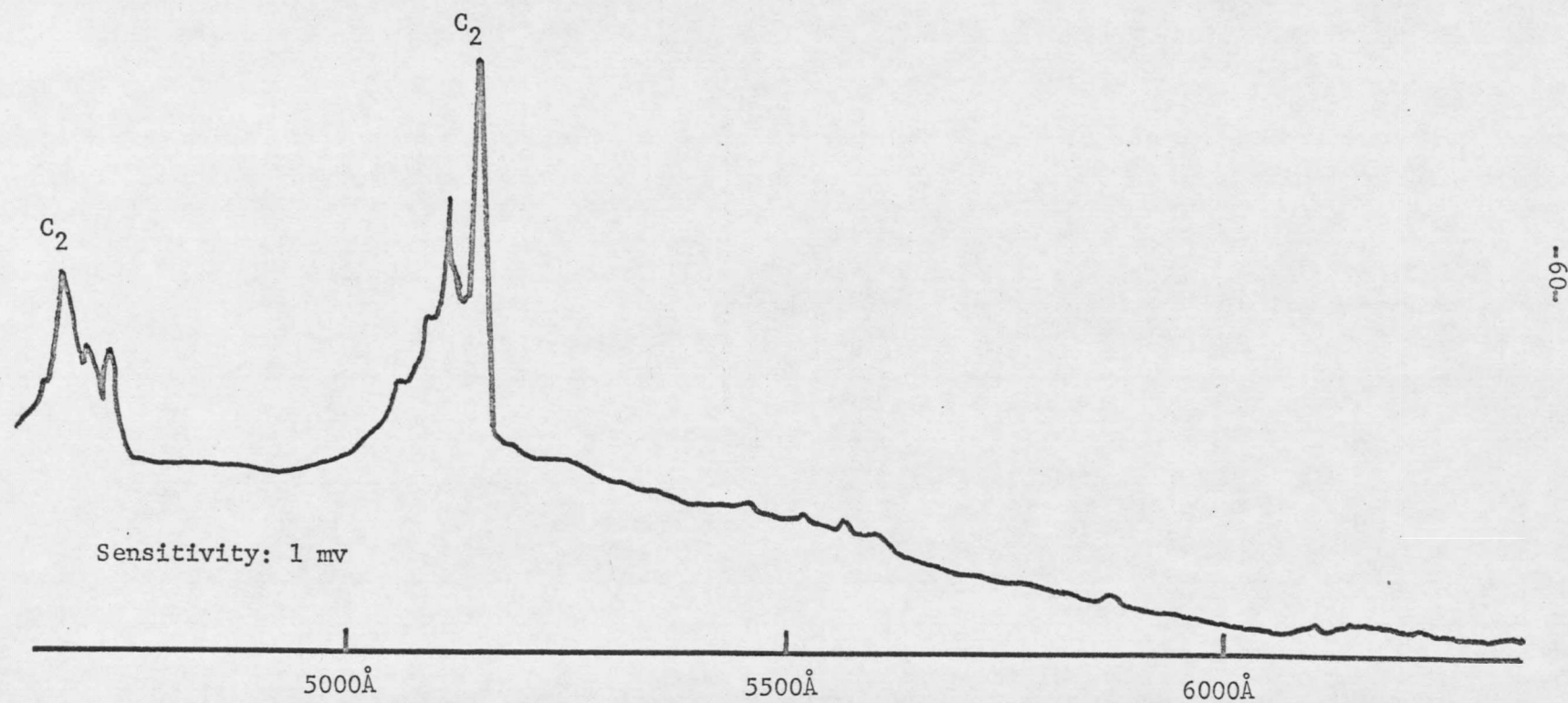


Figure 16. Background Emission from Absolute Ethanol in the Hydrogen-Chlorine Flame.

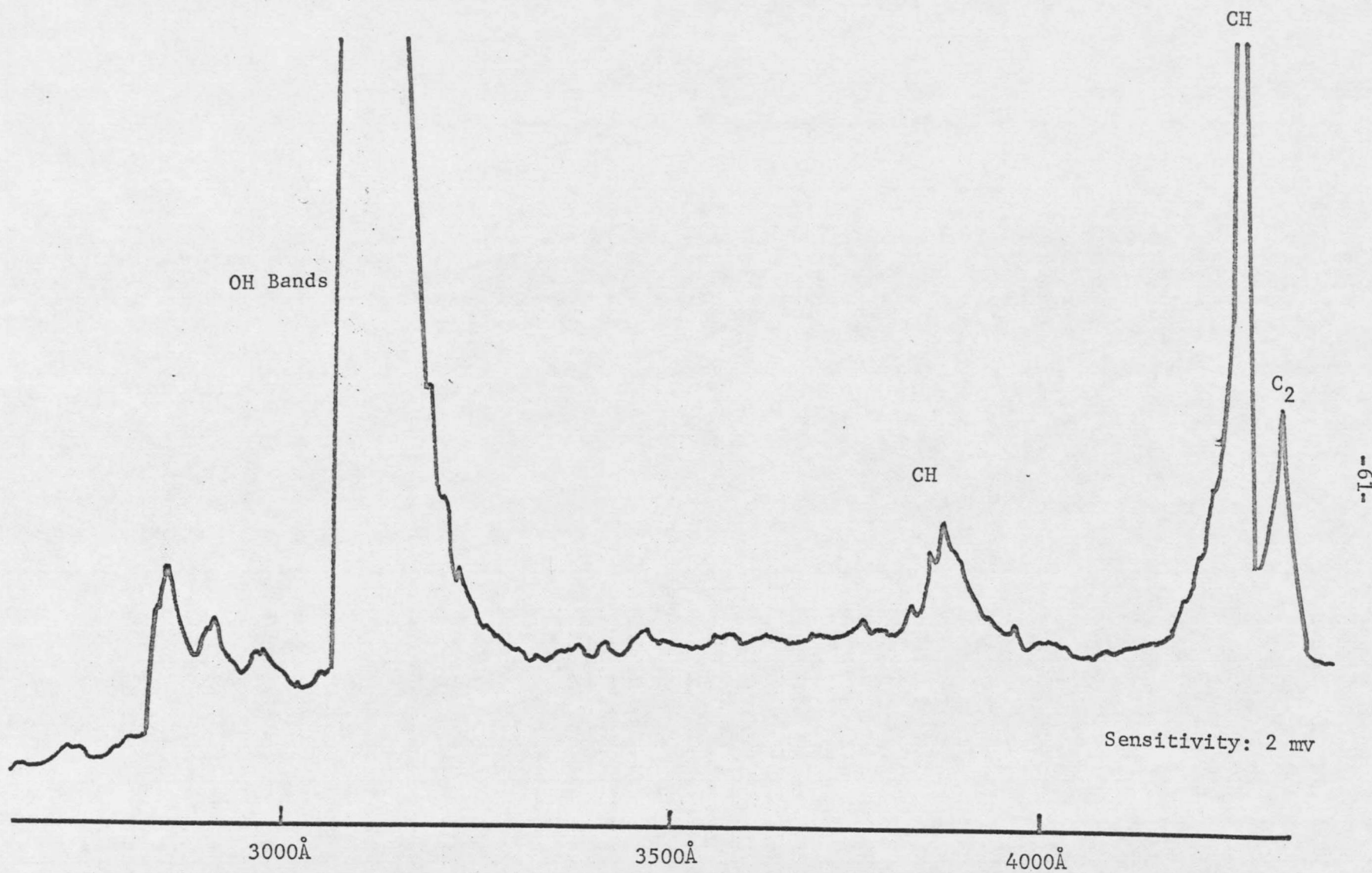


Figure 17. Background Emission from Ethyl Acetate in the Hydrogen-Chlorine Flame.

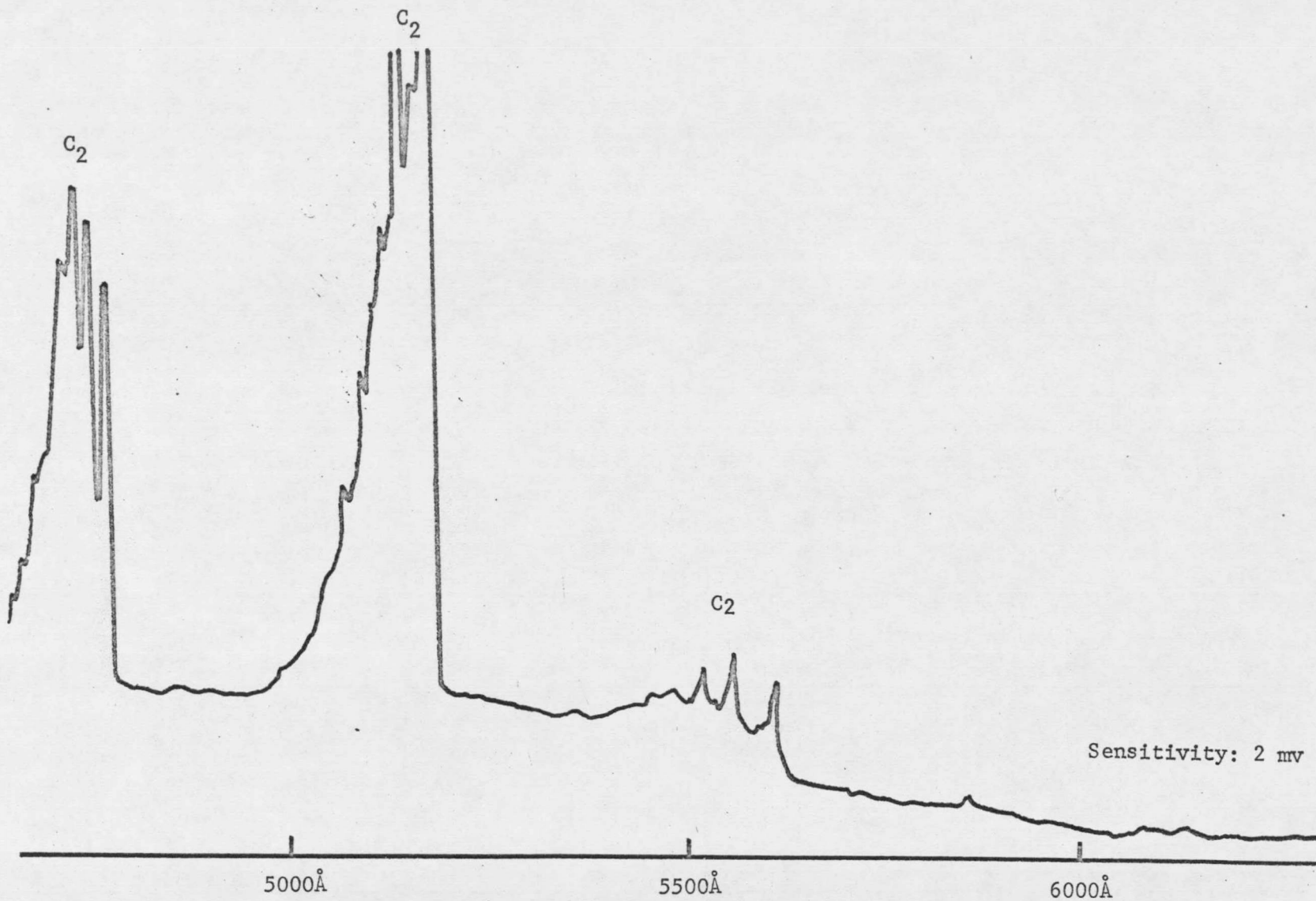


Figure 18. Background Emission from Ethyl Acetate in the Hydrogen-Chlorine Flame.

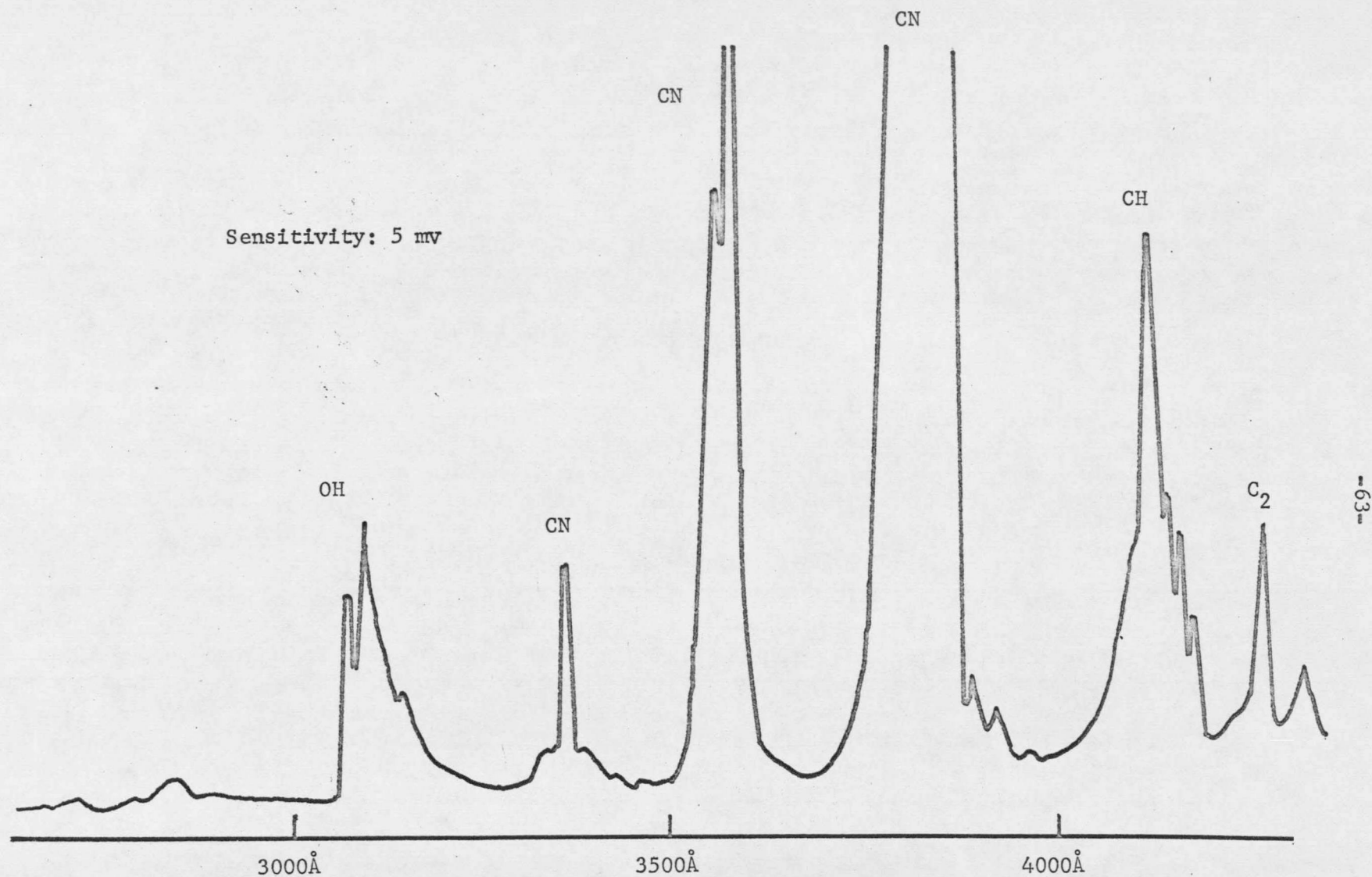


Figure 19. Background Emission from Acetonitrile in the Hydrogen-Chlorine Flame.

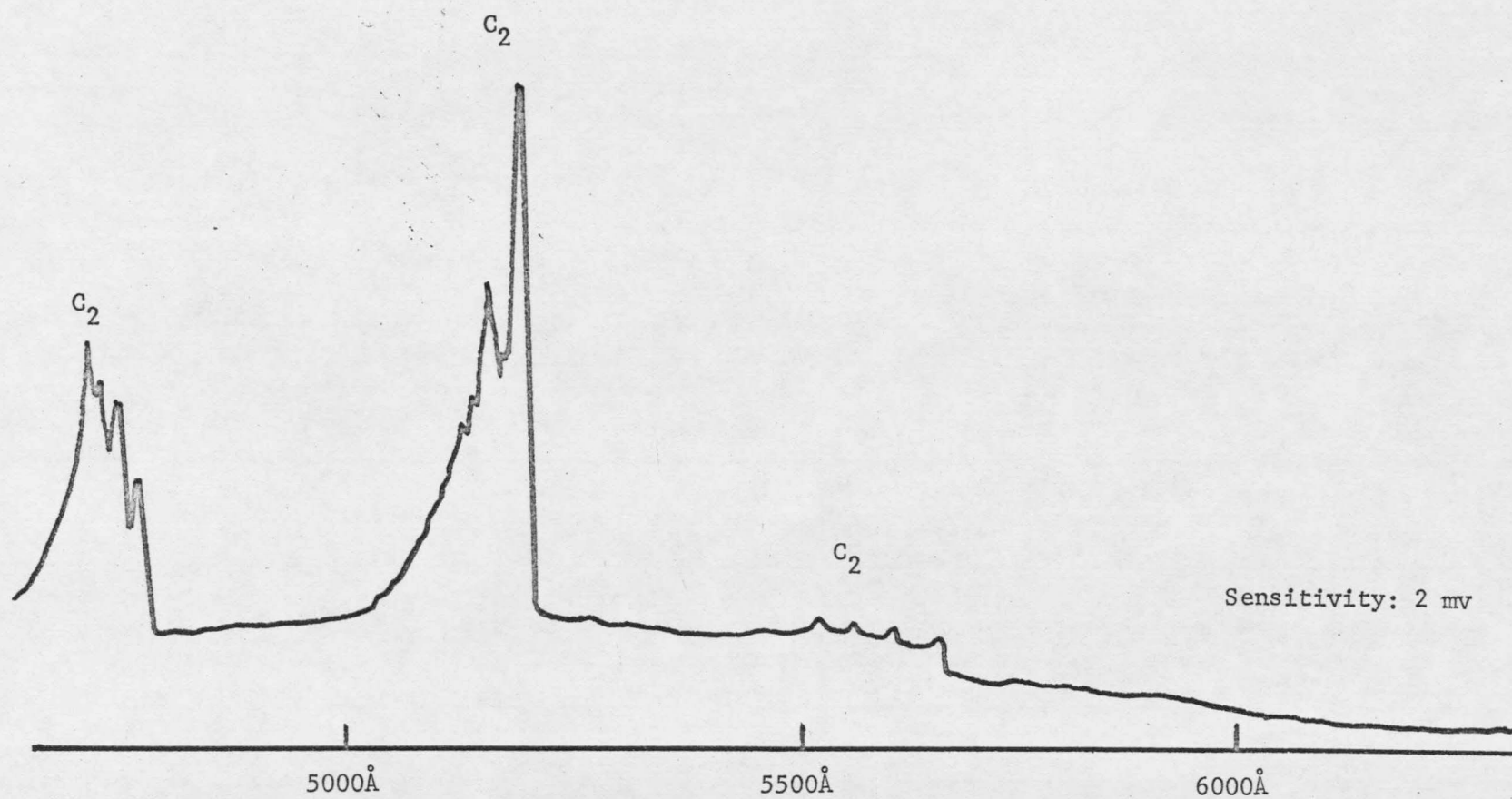


Figure 20. Background Emission from Acetonitrile in the Hydrogen-Chlorine Flame.

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