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Atomic spectroscopic techniques for the measurement of elemental concentrations in oil shales

ATOMIC SPECTROSCOPIC TECHNIQUES FOR THE  
MEASUREMENT OF ELEMENTAL CONCENTRATIONS  
IN OIL SHALES

M. K. AMINI

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ATOMIC SPECTROSCOPIC TECHNIQUES  
FOR THE MEASUREMENT OF ELEMENTAL CONCENTRATIONS  
IN OIL SHALES

by

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## Abstract

Three atomic spectroscopic techniques including Atomic Emission, Atomic Absorption, and Inductively Coupled Plasma Emission were used in the determination of elemental concentrations of Kansas shales. The effects of different parameters such as atom reservoir; fuel and oxidant flow rates; extent of different types of interferences and methods for their elimination; detection limits; precision; and sample preparation, pretreatment, extraction and measurement techniques are presented. Some major, minor and trace elements were determined in five different types of shales varying from a black (reduced) to a red (oxidized) coloration.

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## Chapter I

### Introduction

The importance of atomic spectroscopic techniques, including atomic emission (AE), atomic absorption (AA), atomic fluorescence (AF) and inductively coupled plasma atomic emission (ICP), for elemental analysis, especially of trace elements, is well known. The wide popularity of these techniques can be related to high precision and accuracy, procedural simplicity, high selectivity, low detection limits and relative freedom from interferences. These techniques are used for the measurement of elemental concentrations at major, minor and trace levels. Different types of samples such as air, water, biological tissues and fluids, and geological, petrochemical, metallurgical and industrial products have been analyzed very successfully.

The objective of this work is the analysis of some Kansas shales varying from a black (reduced) to a red (oxidized) coloration, for determination of some elemental concentrations. Oil shales are important from the viewpoint of their high concentration of organic matter, which is considered a potential source of synthetic oil. These materials are also important because of their relatively high content of some metals with potential economic value. Extraction of oil from shale on a commercial scale requires a very large amount of this material to be processed daily, which will create some

environmental problems, partially due to the trace element content of the shales.

Owing to the relatively high concentration of some major constituents of the shales such as Fe, Al, Ca, Mg, Si and P, and various trace element species in the shales, there is a complex matrix and many analytical problems will arise. Metal concentrations cannot be compared with matrix-free standards in many cases. Thus some pretreatment techniques should be considered.

In the first part of this work the principles of flame atomic spectroscopic methods and ICP are reviewed. This is followed in Chapter III by a discussion of atom reservoirs, which are considered to be the most important part in atomic spectroscopic systems. Different types of interferences and ways of minimizing their effects are discussed in Chapter IV.

After a thorough discussion of atom reservoirs and interferences, there is a chapter on optimization which deals with some of the important parameters already discussed in the previous chapters. Solvent extraction methods in trace element analysis are discussed in Chapter VI.

In Chapter VII the importance of oil shales, dissolution procedures, sample pretreatments and methods of analysis are presented. This is followed by the results of analysis of the shales with AE, AA and ICP.

## Chapter II

### Basic Concepts of Flame Atomic Spectroscopy

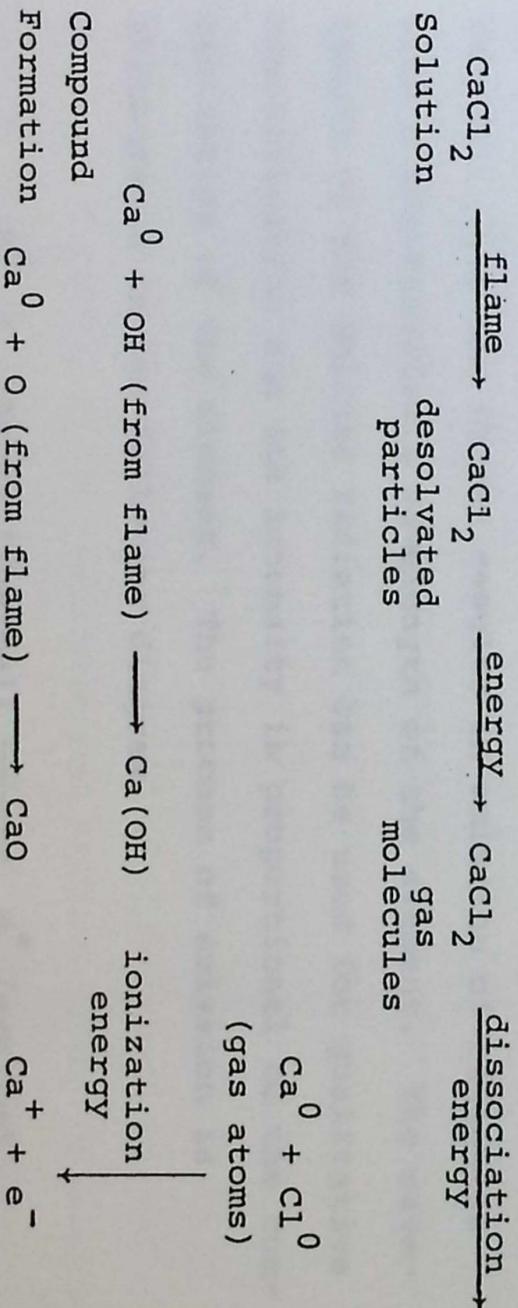
#### A. Introduction

Flame atomic spectroscopic techniques including atomic emission (AE), atomic absorption (AA), atomic fluorescence (AF) and, more recently, inductively coupled plasma emission spectroscopy (ICP), have developed as sensitive, precise, reliable and widely used means to meet the requirements for elemental analysis of many different types of samples. The rapid emergence and wide popularity of these techniques lie in several of their advantages such as procedural simplicity, little influence of coexisting elements due to high selectivity, and ability to carry out successive or simultaneous measurements for many elements. With these techniques, concentrations of major, minor and trace elements can be measured. Concentrations may be as low as parts per billion (ppb or  $\text{pp}10^9$ ) or as high as a hundred or more parts per million (ppm or  $\text{pp}10^6$ ).

There has been a great interest in the development of multi-element systems. ICP is usually considered as a multi-element system. Other techniques, *i.e.*, AE, AA and AF, usually have been used as single element methods. However, with the progressive advancement that has been made in the

Last few years in instrument design and use of electronic systems, particularly microprocessor control, automatic sampling, automatic background correction and automatic readout systems, multielement capability of these three techniques has increased. These advancements have also increased the speed of analysis and improved the accuracy and reproducibility of the measurement.

The basics of the atomic spectroscopic techniques are the same. The sample, usually in the form of a solution, is aspirated through a nebulizer into the flame or plasma, and then several physical and chemical processes occur as follows: desolvation, vaporization, atomization, ionization, compound formation, excitation, and emission. These processes can be shown with the following example, where a solution of calcium chloride is aspirated into the flame (1):

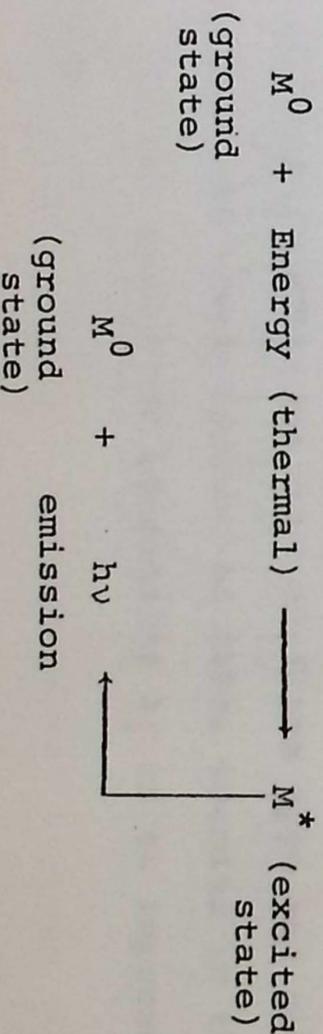


The purpose of these processes is to produce neutral atoms (or, in some cases, ions when an ionic line is used in AE or

ICP) with the highest possible population in the atom cell. Thus any process that decreases the number of atoms of analyte is undesirable and is considered an interference. These undesirable processes are discussed in Chapter IV. All of these techniques utilize free atoms except some cases in ICP or AE. However, the method of excitation and/or deexcitation may be different. For a detailed discussion of theory and instrumentation, the following references may be consulted (2-8).

#### 1. Flame Atomic Emission Spectroscopy

Flame atomic emission spectroscopy is based on the excitation of free atoms by thermal energy through collision with high temperature atoms and molecules of the flame. Excited species are not stable and relax to the ground state either by radiational deactivation or radiationless deactivation. Only the former results in emission of radiation with a characteristic wavelength of the element. The wavelength of the emitted radiation can be used for qualitative identification and its intensity is proportional to the concentration of the element. The process of emission is illustrated in the following diagram.



Emission intensity depends on the number of atoms in the excited state that return to the ground state by emitting radiation, and the number of atoms in the excited state depends on the fraction of analyte present as neutral atoms in the ground state. The fraction of neutral atoms either in the ground or excited state depends on several factors, the most important of which are analyte concentration in the sample and flame energy. When the flame is at thermal equilibrium, the distribution of the analyte atoms in different energy levels is determined by the Boltzmann distribution

Law (4):

$$n_j = n_0 \frac{g_j}{g_0} \exp\left(-\frac{E_j}{kT}\right)$$

In this equation  $n_j$  and  $n_0$  are the number of atoms in the excited state and ground state, respectively;  $g_0$  and  $g_j$  are the statistical weights of the ground state and excited state atoms, respectively;  $E_j$  is the energy of excitation;  $T$  is absolute temperature; and  $k$  is Boltzmann's constant.

The number of atoms in the excited state ( $n_j$ ) is a fraction of the ground state atoms ( $n_0$ ) and this is very small relative to the total number of analyte atoms in the sample. However,  $n_j$  can be increased significantly by selection of suitable conditions such as flame type and composition, solvent and concentration of other species in the sample. The net result of increasing  $n_j$  is to improve the sensitivity.

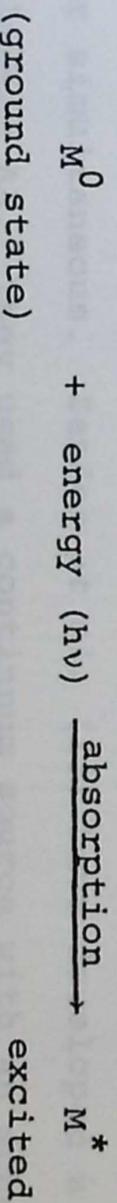
There is a great interest in the application and use of flame AE (FAE) for routine analysis, especially for determination of alkali metals in biological samples, because the technique is very simple, has multielement analysis capability, requires no external light source and exhibits higher sensitivity for some elements. Unfortunately, FAE does not have good sensitivity for many elements with resonance emission line below 350 nm and suffers from interferences more than do AA and AF. However, the use of hot flames such as  $N_2O$ -acetylene in AE has improved the sensitivity and decreased some of the interferences. In comparing AE and AA, Christian and Feldman found that 15 elements have lower detection limits with FAE (9). Spillman and Malmstadt (10) have described a computer-controlled AF/AE spectrometer for sequential multielement determination of up to 25 elements in atomic emission mode. Busch and coworkers (11) have developed a simultaneous multielement AE spectrometer by using a silicon diode vidicon detector and have measured 8 elements (Mo, Fe, Da, Al, Ti, W, Mn, and K) simultaneously. However, the reported detection limits are higher than single element AE values, as is generally true for all multielement systems.

## 2. Flame Atomic Absorption

Atomic absorption is based on the absorption of a characteristic wavelength by the neutral atoms of the analyte present in the flame cell. Radiation of proper wavelength emitted by an external light source passes through the

atomization cell containing neutral atoms of analyte; those atoms that are in the ground state can absorb the radiation and result in a subsequent decrease in the intensity of the light source. The decrease in intensity can be calculated by measuring the source intensity before and after absorption. This is done electronically and the actual signal is  $\log(I_0/I_t)$ , which is called absorbance. This value is proportional to the number of free atoms in the flame and thus to the concentration of analyte. In this equation  $I_0$  and  $I_t$  are the source intensity and transmitted light intensity, respectively.

The most important factor in AA is the population of neutral atoms in the ground state, and thus, unlike AE, the atomization devices are used only for the production of ground state atoms. The process of AA is illustrated in the following diagram.



As mentioned earlier and will be discussed in later chapters, this is not the only process in an atomic absorption measurement; other processes such as thermal excitation, ionization and molecular formation will occur, which may interfere and change the absorbance.

Requirements for AA measurement, besides a light source and atomization cell, are a monochromator, a photomultiplier

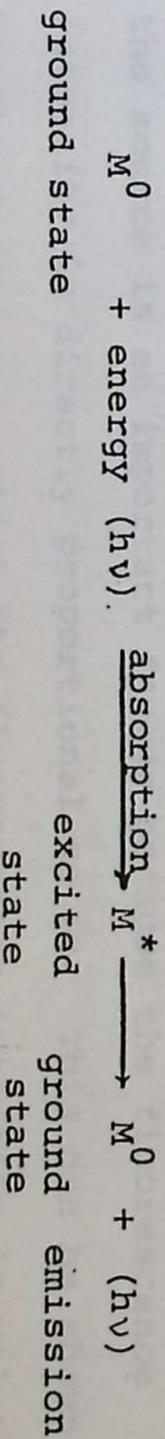
tube and a readout system. Radiation sources used in AA are usually conventional hollow cathode lamps (H.C.L.). Other radiation sources such as electrodeless discharge tubes and continuum sources have been used by some workers (2). Keller and Wohlers (12) have used a 200-W Hg-Xe lamp with a high resolution echelle grating monochromator and compared it with H.C.L.'s for elements with the resonance line below 320 nm. They have reported that almost all of the elements normally determined with H.C.L.'s can be measured using the continuum source.

AA has been accepted as a routine method of analysis in almost all laboratories. More than 60 elements can be determined with high precision, very low detection limits, good accuracy for many elements in different samples, and fewer interferences compared to atomic emission and atomic fluorescence. These advantages of AA have created a great interest in the development of multielement AA, either sequential or simultaneous. Zander *et al.* (13) have developed a multielement AA. They used a continuum source with an echelle monochromator, wavelength modulated via a quartz plate for correction of background absorption and elimination of spectral interferences. Multielement AA systems have been developed by many other workers (14-16). Recently, Harnly *et al.* (17) have developed a simultaneous multielement AA by using a 300-W Xenon-arc continuum source and a wavelength-modulated direct reading echelle polychromator. They have measured up to 16 elements with either flame or furnace

atomization system, double beam background corrected with detection limits comparable to those of single element AA and comparable to or an order of magnitude better than ICP.

### 3. Atomic Fluorescence Spectroscopy

Atomic fluorescence spectroscopy is an absorption-emission technique based upon the absorption of radiation of a characteristic wavelength by the analyte atoms and subsequent radiational deactivation of the excited atoms. The flame in AF as in FAA is used only for the production of ground state free atoms and an external light source is used for excitation. The radiation emitted by the analyte atoms is called fluorescence and, since the method is emission, the signal is fluorescence intensity. Fluorescence intensity is proportional to the concentration of analyte in the sample. The process of AF is illustrated in the following diagram.



In AF both the absorption and emission wavelengths are characteristics of the element, but they may be different as shown in the previous diagram. There are actually four types of fluorescence (2,3): (a) resonance fluorescence, with the emission and absorption wavelengths being the same; (b) direct line fluorescence, with the emission wavelength longer than the absorption wavelength; (c) thermally assisted fluorescence, with longer absorption wavelength; and (d) sensitized fluorescence in which the atoms emit radiation after collisional activation by other excited states.

The excitation source in AF can be either a spectral line source such as H.C.L.'s or a continuum source such as tunable dye lasers and Xe-arc lamps. A continuum source has the advantage that it can be used for many elements and offers the possibility of multi-element analysis, while H.C.L.'s are specific to the elements. Tunable dye lasers with the possibility of tuning at any discrete wavelength, the small area into which the light beam may be concentrated, and their high intensity, are very good sources for AF. Intensity of the source is an important factor because the fluorescence intensity is directly proportional to it. This can be shown by the equation in which the fluorescence intensity is related to the concentration.

$$F = \phi I_0 K_Y N_0$$

$N_0$  = number of free atoms in the ground state which is proportional to the concentration of analyte in the sample

$K_Y$  = probability factor for transition

$I_0$  = source intensity

$\phi$  = quantum efficiency

F = fluorescence intensity

The signal can be increased by increasing the intensity of the source. Attempts have been made by many workers to use intense sources or to improve the present sources such as H.C.L.'s. Pulsed H.C.L.'s have been used successfully in AF (18-21). Continuum sources, as mentioned earlier, offer the advantages of using only one source for several elements and the possibility of multi-element analysis (22,23). A detailed discussion on the use of these and other sources, such as electrodeless discharge lamps and lasers can be found in the literature (2,24-26).

Other requirements of AF are the same as for AA, i.e., monochromator, detector and readout system. However, in AF the source is not placed in view of the monochromator entrance slit (usually at right angles).

#### 4. Inductively Coupled Plasma Emission Spectroscopy (ICP)

The basis of this technique is actually the same as FAF; the only difference is in the excitation source, which is

briefly described here. For more discussion the reader is referred to the following references (27-34). The excitation source, which is similar to flames, is called the inductively coupled argon plasma discharge (ICP). This type of plasma is a partially ionized argon gas. It is formed electromagnetically by the coupling of high frequency energy with ionized argon gas. The plasma consists of a torch (three concentric quartz tubes) through which the argon gas flows, surrounded by a water-cooled induction coil. A radio frequency generator supplies power to the coil. An intense magnetic field develops at the torch area inside the coil. The argon gas is then exposed to a Tesla coil discharge to produce "seed" electrons. The argon gas is ionized by these electrons and becomes conductive. The interaction of the ionized argon gas with the intense electromagnetic field produces a stable flame-shaped plasma near the top of the torch. The temperature of the plasma is about  $10,000^{\circ}\text{K}$ , which is much higher than flames (see Table 1). Thus it is necessary to isolate the plasma from the torch by flowing argon gas through the outer tube to prevent overheating. This also serves to center and stabilize the plasma and to create a low pressure zone in the axial channel of the tube (27).

The sample is aspirated through the nebulizer, which may be either pneumatic or ultrasonic, to produce an aerosol of very fine particles in the expansion chamber. A few percent of the sample are transported to the plasma through the

inner quartz tube. The sample is introduced in the low pressure zone of the plasma, where there is a high and uniform temperature. This zone ensures long residence time for complete vaporization, and almost complete atomization, excitation and/or ionization of the analyte atoms. Deexcitation of the excited atoms produces intense emission lines characteristic of the elements, with the intensity being dependent on concentration.

ICP usually has been used as a simultaneous multi-element technique with the capability of measuring up to 70 elements. The requirements for measuring the intensity of several elements simultaneously include a high dispersion grating spectrometer equipped with separate detectors for each element and a computer for data handling and processing. ICP also has been used for sequential multi-element analysis where a scanning monochromator is used.

Multi-element analysis capability of the ICP is the most important advantage of this technique over flame methods. This is due to the characteristics of the plasma, with its high temperature and stability, so that when a sample of a complex matrix is introduced into the plasma most of the elements will emit one or more intense lines even at concentrations in the ppb range. Another important advantage of the plasma over flames is its relatively greater freedom from chemical interferences such as vaporization, compound formation and ionization interference. Ionization interference is not as important in ICP as it is in flames because of the

very high population of neutral atoms present in the plasma, and the conditions can be adjusted to minimize the ionization. For some elements ionic lines are used because of higher intensity and lower interferences.

Interferences in ICP are mainly due to sample transport, scattered light and spectral interferences. These interferences are discussed in Chapter IV. Spectral interferences can be minimized by applying correction techniques. Spectral interference due to background variation or molecular emission bands can be minimized by using wavelength modulation techniques. The basis of this technique is measurement of signals at two different wavelengths, one at the emission wavelength of the element of interest and the other just off the peak. The effect of background is then compensated for by using either the response difference or taking the ratio of the signals at these two wavelengths.

## Chapter III

### Atom Reservoir

#### A. Introduction

The atom cell is probably the most important component of the atomic spectrometer system because the precision, accuracy, sensitivity and detection limits are highly dependent on this part. Different types of atom reservoirs have been used in atomic spectrometers and, in general, they are classified as flame and non-flame types. Chemical flames are the most widely used in AA, AF and AE. Some advantages of flames are good stability (for high accuracy and precision), simplicity, ease of operation and low cost. However, there are some disadvantages to the use of flames. The main ones are the problem of high background emission, difficulty of close control over the flame environment and problems in the analysis of small samples.

Non-flame methods have been used in recent years mainly for AA. The most successful non-flame atomization system is the high temperature graphite furnace, which was probably the first non-flame cell. Analytical methods based on the use of these devices were pioneered by L'vov (35). A small and fixed sample volume is introduced into the furnace, usually a graphite tube. After pretreatment for drying and ashing, it is thermally atomized by resistive heating in an inert or reactive atmosphere and a transient signal is

obtained. Other similar devices consisting of thermally heated graphite cups, graphite rods, metal furnaces, wire loops and some other types have been used in the last few years. Advantages of thermal atomization systems include: much higher conversion efficiency, which results in higher sensitivity and low detection limits; capability of having the desired atmosphere such as Ar to eliminate the interference effect of  $O_2$  or other species from the atomization cell; close control over temperature; and the possibility of using very small sample volumes, as low as a few microliters. In spite of these advantages over flames, there are some interferences which sometimes result in poorer accuracy and precision as compared to flames. Some disadvantages of thermal atomization systems are: memory effect; problem of reproducible sample deposition; need for a large power supply; and cost of operation. Reviews and articles on non-flame techniques can be found elsewhere (35-39).

#### B. General Flame Characteristics for Atomic Spectroscopy

The main requirements of a flame cell for AA, AE and

AF are:

- 1) high vaporization efficiency to give sufficient breakdown of the sample and prevent interferences from sample matrix.
- 2) high atomization efficiency to produce high populations of the analyte atoms for good sensitivity and low detection limits.

- 3) Low ionization to prevent decrease in the atom population or high ionization when an ionic line is used.
- 4) high stability and reproducibility of the flame and nebulizer for high precision and accuracy of the measurements.
- 5) Long residence time of the analyte atoms in the optical path.
- 6) Low flame background emission.
- 7) safety.

There are some special requirements for each technique. For example, high excitation efficiency for AF, low concentration of quenching species for AF, and low scattering of excitation beam for AA and AF.

The first three conditions are highly temperature-dependent. Condition 4 depends on several factors such as fuel and oxidant, burner design, and nebulizer efficiency. Condition 5 is also an important factor; the longer the free atoms remain in the flame in view of the entrance slit, the greater the probability of excitation, deexcitation or absorption. To have a long residence time, burning velocity of the flame gases must not be large. Condition 6 depends on fuel and oxidant gases and also on solvent. Hydrocarbon flames give a higher background level than hydrogen flames. The use of an inert gas for sheathing decreases the background to very low levels. For a better understanding of these conditions

it is necessary to deal with different parameters in the following sections.

### 1. Flame Temperature

Temperature of the flame is an important factor governing different processes in the flame, including desolvation, vaporization, atomization, excitation (in AE) and ionization. Therefore, one of the major parameters for selection of a fuel-oxidant mixture is the flame temperature. The temperatures of typical flames are shown in Table 1.

Table 1

Fuel	Oxidant	Support gas	Temperature	Ref.
H <sub>2</sub>	O <sub>2</sub>	---	2800 °C	8
H <sub>2</sub>	Air	---	1950	40
H <sub>2</sub>	entrained air	Ar	1600	8
C <sub>2</sub> H <sub>2</sub>	O <sub>2</sub>	---	3000	8
C <sub>2</sub> H <sub>2</sub>	Air	---	2150	41
C <sub>2</sub> H <sub>2</sub>	N <sub>2</sub> O	---	2795	41
Propane	O <sub>2</sub>	---	2800	8
Propane	Air	---	1900	8

Maximum temperature is obtained when the fuel/oxidant ratio is stoichiometric. The temperature of the flames depends on various factors such as fuel/oxidant ratio, type of oxidant and fuel, flow rate of the gases, aspiration rate

of the solution, and solvent.  $O_2$ -fuel flames have higher temperatures than air-fuel flames. This is due to more rapid consumption of  $O_2$  flames. When air is used some of the energy is lost to heat up nitrogen. For most flame analysis, hot flames are advantageous, due to reduction in chemical interferences. High temperature causes increases in vaporization efficiency, and decreases in compound formation with species present in the flame. Hot flames are particularly important in AE, where the energy of the flame is used for excitation of the atomized species.

Hot flames are not advantageous for all elements, as they contain enough energy to ionize an appreciable fraction of the neutral atoms. The result is a decrease in population of free atoms. The approximate degree of ionization for alkali and alkaline earth metals at different temperatures are shown in Table 2. Other elements have low ionization at these temperatures and in many cases it can be ignored.

Table 2

Ionization of Metal Atoms at Different Temperatures  
(approximate values) (1)

Metal	Ionization Potential	Percent Ionized		
		2000 K	2500 K	2800 K
Na	5.21	0.3	5.0	26
K	4.32	2.0	32	82
Rb	4.16	14	44	90
Cs	3.87	28	70	96
Ca	6.11	<0.11	1.0	7.3
Ba	5.21	1.0	9	43

The extent of ionization of these metals indicates the need for use of low temperature flames and a way to eliminate or decrease ionization. The use of  $H_2$ -air is a good choice for alkali metals to reduce ionization. There is an effective way of suppressing ionization in very hot flames, by adding an excess of an easily ionized element which is called an ionization buffer. The effect of the buffer is to create a large density of electrons and thus decrease the ionization of the element sought.

## 2. Burner System

In general, two types of burners have been used in flame atomic spectroscopy: total consumption and premixed. With the total consumption burner, which is sometimes called direct injection burner, the oxidant gas enters the burner at high pressure and surrounds a capillary tube connected to the sample reservoir; the high pressure of the gas produces a "venturi" effect and draws the solution up into the gas stream where the solution is broken into an aerosol of small particles. Advantages of total consumption burners are:

- (1) all of the sample is aspirated into the flame with the following advantages:
  - a. high analyte concentration in the flame
  - b. no error due to loss of some volatile components if they are present
- (2) no memory effect
- (3) easy to clean

- (4) capability of using a wide variety of flame mixtures
- (5) no danger of flashback

Disadvantages of total consumption burners are:

- (1) variation in droplet size and possibility of passing large droplets into the flame
- (2) incomplete evaporation
- (3) high acoustic noise
- (4) relatively low temperature due to a large volume of sample aspirated into the flames
- (5) clogging the burner, which will cause a change in aspiration rate
- (6) light scattering due to large particles
- (7) poor flame geometry
- (8) high background emission which is due to extended reaction zone and entrainment of oxygen from atmosphere.

Large droplets, which pass through the flame do not have the opportunity to be completely atomized and even droplets could pass without complete vaporization. This results in vaporization interference in all three flame methods and a large scatter of the incident beam in AA and AF (42, 43).

In a premixed burner, the solution is aspirated into a premixing chamber by means of the support gas. It is then mixed with the fuel and sometimes an auxiliary oxidizing agent or supporting gas. The mixture passes through the

burner head and produces a laminar flow. Premixed designs have the following advantages over the total consumption burner:

- (1) the flame is more steady
- (2) only small droplets will pass through the flame, large droplets are condensed in spray chambers, which in turn have the following advantages:
  - a. reduced vaporization interferences
  - b. reduced scattering of the incident light source in AA and AF
  - c. the analytical signal is less noisy
  - d. optical transparency of the flame cell
- (3) possibility of having different geometries
- (4) no acoustic noise
- (5) lower background levels

In spite of these advantages, there are some disadvantages relative to premixed burners, including:

- (1) memory effect
- (2) hard to clean
- (3) less choice for fuel and oxidant due to danger of flashback
- (4) when the solutions contain more than one solvent the more volatile components are drawn to the flame and less volatile components are drained off
- (5) low efficiency of sample introduction to flame

Disadvantages mentioned above are not severe in many measurements and do not limit the use of premixed systems.

### 3. Types of Flames

There is an enormous amount of literature about the flames, dealing with types of flames, their composition, and characteristics for different atomic spectroscopic methods. The purpose of the following discussion is to compare the analytical utility of the most popular flames from the literature. The fuels and oxidants usually used with AA, AF and AF are air,  $O_2$ ,  $N_2O$ ,  $C_2H_2$  and  $H_2$ . Sometimes an inert gas such as Ar or  $N_2$  is used as a support or sheath.

#### a. Hydrogen-fueled flames

$H_2$  flames have the lowest flame emission background. For many flame studies  $H_2$ -air or  $H_2-O_2$  are good choices and result in a considerably large signal/noise ratio and low detection limits.  $H_2$ -fueled flames have lower temperatures as compared to  $C_2H_2$  or hydrocarbon flames in general.  $H_2$ -air or  $H_2-O_2$  flames are especially good in AE analysis of alkali metals and metals which are easily atomized. For some of the less readily atomized elements, fuel-rich  $H_2-O_2$  flame can improve the atomization efficiency significantly (44). For AF,  $H_2$  flames seem to be the best for many elements and many workers have preferred  $H_2$  flames. For some elements which exhibit little tendency to form refractory oxides,  $H_2$ -entrained air has been shown to be a good flame and limits of detection obtained are less than that of  $H_2-O_2$  (45-48).  $H_2$ -air flames give a smaller flame background than  $H_2-O_2$  (49).  $H_2$  flames have limited reducing properties

and refractory elements are not adequately atomized (50). Gutzler and Denton (51) used a premixed  $H_2O_2$  flame combined with an ultrasonic nebulizer for AE. They have indicated a substantial improvement in detection limits for a number of elements in comparison to those obtained using  $N_2O-C_2H_2$ ,  $O_2-C_2H_2$  or total consumption  $H_2-O_2$  flames. Zacha and Winefordner (52) used Ar- $H_2$  entrained air with a total consumption burner for determination of Ba, Ca, Co, Ni, Cu, Ga, Th, Ag, In, Cd, Mg, Sr, Mn and Cr by AE. They have reported very low detection limits, near the ppb range, for these elements. However, most of this work has been done on matrix-free standards and when a complex matrix is used for the analysis, it will certainly affect the detection limits to a high extent. Ar- $H_2$  entrained air is much more transparent at wavelengths below 200 nm than hydrocarbon flames and has found particular application for the determination of As and Se (53,54). The major disadvantage of  $H_2$  flames is the danger of explosion, especially when used with  $O_2$  in a premixed burner.

b. Acetylene-fueled flames

Acetylene-fueled flames, including air- $C_2H_2$ ,  $N_2O-C_2H_2$ ,  $O_2-C_2H_2$ , and some other combinations, have been used in all three methods (AA, AE, and AF) more than any other fuel. Air- $C_2H_2$  flame provides sufficient atomization for many elements with a temperature of about 2300° C. This temperature is not sufficient for efficient atomization of a

large number of elements. Elements that form stable oxides in the flames (refractory elements) such as Al, Ti, Zr, Si, V and B are not efficiently atomized and there are a lot of interferences. For these elements, a higher temperature flame such as  $O_2-C_2H_2$  or  $N_2O-C_2H_2$  is required.  $O_2-C_2H_2$  flame has a temperature around  $3000^\circ C$ , thus it is very efficient in atomization of refractory elements. This flame has been used by many workers for determination of refractory elements (55-57). The formation of refractory oxides is much faster in fuel-lean than in fuel-rich flames, because fuel-rich flames, especially  $O_2-C_2H_2$ , result in a reducing atmosphere which is a necessary condition for the production of a large population of free atoms of refractories (55). In spite of the high temperature advantage of  $O_2-C_2H_2$  flame, it is very difficult to handle it with a premixed burner system because of the danger of explosion. It is possible to use  $O_2-C_2H_2$  with air,  $N_2$ , Ar or use  $N_2O-C_2H_2$  to decrease the burning velocity and reduce the danger of flashback.  $N_2O-C_2H_2$  offers a favorable chemical environment, especially for refractory elements, and it is largely free of interferences (58-61). Air- $C_2H_2$  provides a stable, reproducible and safe flame. This flame has been used in all three techniques. It is suitable for AE of alkali metals and a few other elements. For determination of many other elements by the AE technique, a hotter flame such as  $O_2-C_2H_2$  or  $N_2O-C_2H_2$  is required. Some of these elements are Ca, Ba, Sr, Al and La. In AA air- $C_2H_2$  can be used for determination of more elements

because the flame is not used for excitation. Elements such as Ca, Co, Ba, Sr, Mg, Mn, Zn, Fe, Ni, Cr, Mo, Pb, Cd, Cu and Ag can be analyzed using air-C<sub>2</sub>H<sub>2</sub> flame. However, alkali earth elements may suffer from chemical interferences in air-C<sub>2</sub>H<sub>2</sub> and it is advantageous to use N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> to minimize this problem. There are two other groups of elements that are difficult to measure with air-C<sub>2</sub>H<sub>2</sub> flame. One group is the refractory oxide-forming elements such as those elements previously mentioned. The second group includes elements such as As, Se, Sn or hydrides of As, Sb, Se, Te, Ge and Bi. For these elements, which are volatilized at the high temperature of N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> and even the moderate temperature of air-C<sub>2</sub>H<sub>2</sub>, air-H<sub>2</sub> or Ar-H<sub>2</sub> entrained air flames are useful.

#### c. Separated flames

To discuss the effect of separation or shielding on flames it is necessary to understand the flame structure. The structure of a typical flame is shown in Figure 1. It consists of different parts. The preheating zone is where the main combustion reactions take place and there is not a complete thermal and chemical equilibrium. Strong molecular spectra such as CN, CH, C<sub>2</sub>, OH and NH come from this region. Adjacent to the primary reaction zone is the interconal zone, which is sometimes called the reaction-free zone. In this zone there is complete thermal and chemical equilibrium. The advantages of this region of the flame are that it has a higher temperature relative to other zones, it is almost non-

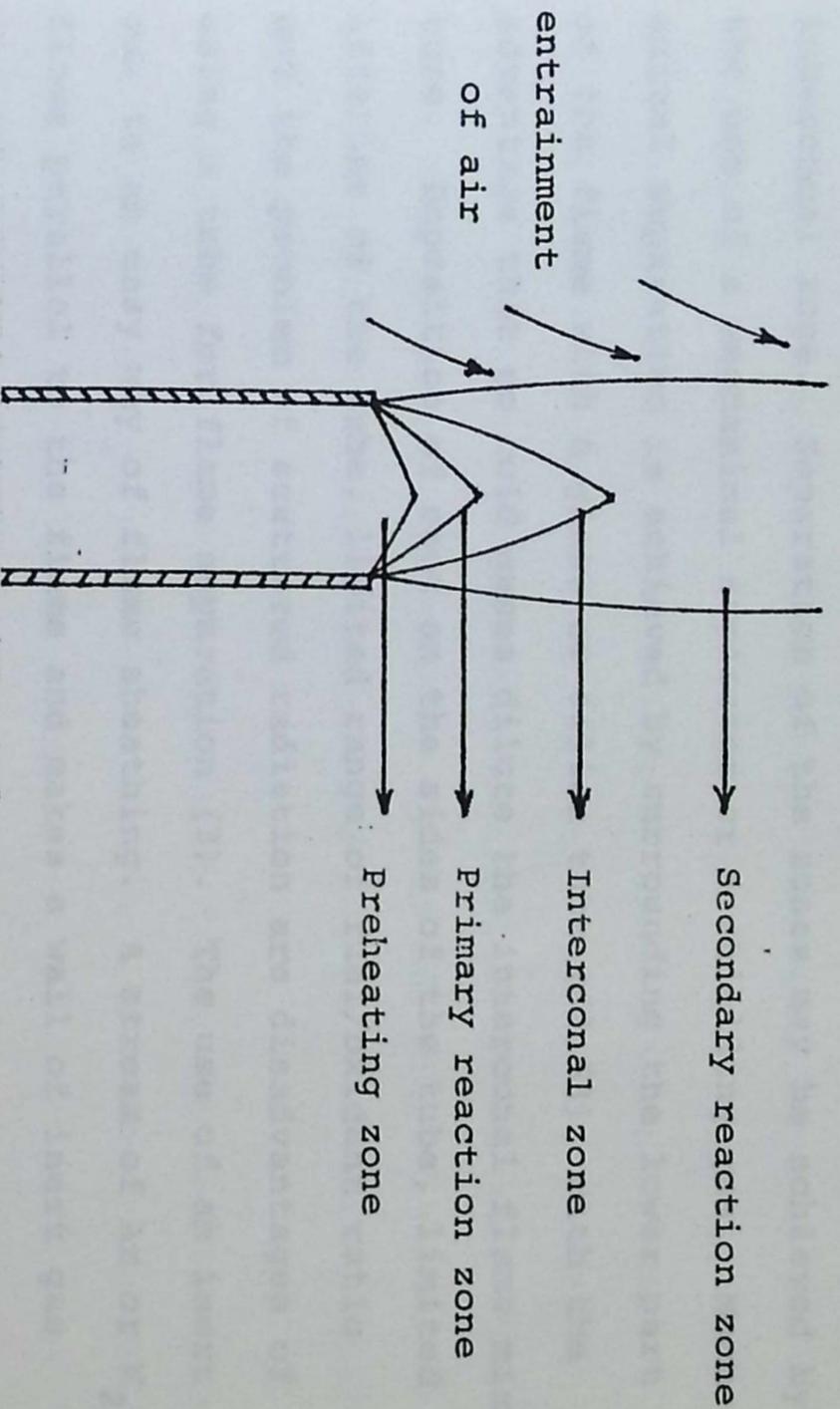


Figure 1. Structure of a typical flame

Luminous, and it is transparent. Thus, it has the optimum characteristics for use in atomic spectroscopy. The thickness of the interconal zone depends on various factors such as the gas mixtures, the ratio of the fuel/oxidant, the burner system and many other factors. By increasing the fuel/oxidant ratio (fuel-rich), this region can be extended. Above this region is the secondary reaction zone, which is the major part of the flame. In this region the composition of the flame is affected by diffusion of the surrounding atmosphere. The major background of the flames comes from the secondary reaction zone.

The purpose of separation or shielding is to eliminate or shift away the secondary reaction zone and extend the

interconal zone. Separation of the zones may be achieved by the use of a mechanical separator or a shielding gas. Mechanical separation is achieved by surrounding the lower part of the flame with a glass or silica tube (62,63), with the advantage that no cold gases dilute the interconal flame mixture. Deposition of soot on the sides of the tube, limited lifetime of the tube, limited range of fuel/oxidant ratio and the problem of scattered radiation are disadvantages of using a tube for flame separation (3). The use of an inert gas is an easy way of flame sheathing. A stream of Ar or  $N_2$  flows parallel to the flame and makes a wall of inert gas around the flame to prevent entrainment of atmospheric gases into the flame. Thus, the secondary reaction zone is shifted away and the region of the flame between the two zones (interconal zone) is extended. A separated flame has many advantages, including: (a) decrease in the background emission up to several orders of magnitude, because the flame is sealed off from the surrounding atmosphere (63); (b) suppression of the molecular OH band emission (64,65); (c) extension of the interconal zone and prevention of the entrainment of atmospheric oxygen, which results in higher sensitivity for determination of elements which form refractory oxides. Table 3 shows relative emission and detection limits of several elements with  $N_2O-C_2H_2$ ,  $N_2$ -sheathed  $N_2O-C_2H_2$  and Ar-sheathed  $N_2O-C_2H_2$  flames (61); (d) decrease in scattering, especially in AF (66); (e) decrease in the concentration of quenchers, thus improving the fluorescence intensity in AF,

since quenchers such as atmospheric nitrogen decrease the fluorescence intensity; (f) absorption by the flame at wavelengths below 200 nm is much less in the separated flame. This is due to removal of the oxidizing secondary reaction zone and lack of oxygen species in the interconal zone (67, 68). The resultant transparency has an advantage in the determination of elements such as Se and As with much higher sensitivity.

Many workers have used separated flames for measurement of elements. Kirkbright *et al.* (63) have described the use of  $N_2$ -sheathed  $H_2$ -air flame. Martin *et al.* (66) have compared three different burner systems, a turbulent (total consumption) burner, a premixed and a premixed separated burner. They have reported that for all wavelengths, the flame backgrounds of the premixed, turbulent and separated flames are in the approximate ratio of 100:10:1 for equal fluorescence signals derived from a 1 ppm Zn solution. These workers obtained detection limits five times lower for the separated compared to two other flames. Johnson and Winefordner (69) used an Ar-sheathed Ar- $O_2$ - $C_2H_2$  flame and compared it with an Ar-sheathed air- $C_2H_2$  for use in AF. They have reported about 5-fold improvement in the detection limits for a wide variety of elements when Ar- $O_2$ - $C_2H_2$  is used instead of air- $C_2H_2$ .

Table 3.

Element	Wavelength (nm)	Relative Emission			Detection Limits (ppm)		
		1	2	3	1	2	3
Al	395.15	100	87	197	0.4	0.04	0.02
Be	234.86	100	41	62.5	1.5	0.3	0.15
Mo	319.40	100	61	103	20	0.5	0.3
Nb	405.89	100	127	334	0.5	0.09	0.06
Si	251.61	100	43	96.5	60	10	6
Ti	365.35	100	128	206	7	1	0.5
	399.86	100	132.5	208	5	0.4	0.2
V	437.92	100	124	254	2	0.08	0.05
W	400.88	100	117.5	235	10	0.8	0.4
Zr	351.96	100	72	167	9	2	1.2

1. Ordinary  $N_2O-C_2H_2$  flame
  2. Nitrogen-sheathed  $N_2O-C_2H_2$  flame
  3. Argon-sheathed  $N_2O-C_2H_2$  flame
- Reference (61).

### C. Burner Design

Requirements for a burner for the different atomic spectroscopic techniques are different. Premixed burners of different design have been used for commercial AA spectrometers. The burner body, including nebulizer and spray chamber, is basically the same, but different burner head designs can be found in the literature, including single circular, long path, and circular capillary burner ports. The circular, single port burner head is not suitable for mixtures of high burning velocity because of the danger of explosion (40). Long path burner heads of different designs usually have been used in AA. An interesting burner head design is the capillary burner head, which is a versatile design for AE, AF and, in some cases, for AA. Different burner head designs are found in the literature (70-73). Usually, capillary tubes are bonded together with a high temperature-resistant epoxy resin (70). A very even gas flow is established because of the large number of capillary tubes. Flow is very stable and flames are extremely laminar and by suitable choice of capillary diameter, all gas mixtures can be used without any danger of explosion.

The burner system used in FAE and FAA studies and measurements is based on the design of Martin (74), which has the following components:

Spray Chamber:    Varian burner bowl (08-10047-00)

                  Varian burner bowl sleeve (01-10008-00)

                  Varian spray chamber (01-100254-00)

Burner Head: Capillary burner head with sheath  
capillaries for AE measurements  
Varian long path burner for AA  
measurements

Nebulizer: Perkin-Elmer adjustable nebulizer  
(303-0352)

The constructed capillary burner head is shown in Figure 2. Modification of this burner from the design suggested by Martin is that it has removable sheath capillaries which can be adjusted to the desired position. The burner assembly with the capillary burner head is shown in Figure 3. For a detailed discussion of the design and construction of the burner system, the reader is referred to reference (74).

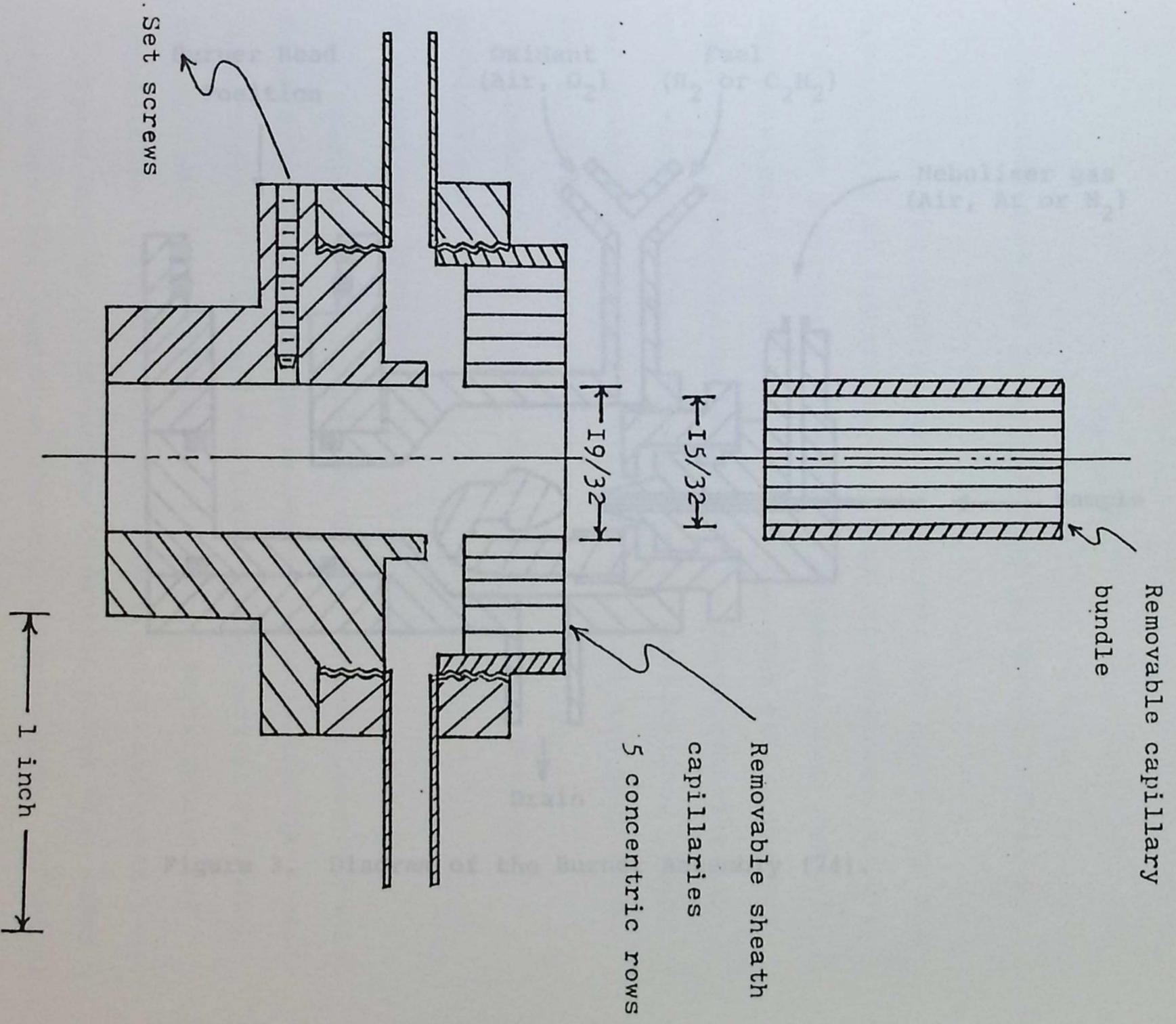


Figure 2. Schematic diagram of the capillary burner head

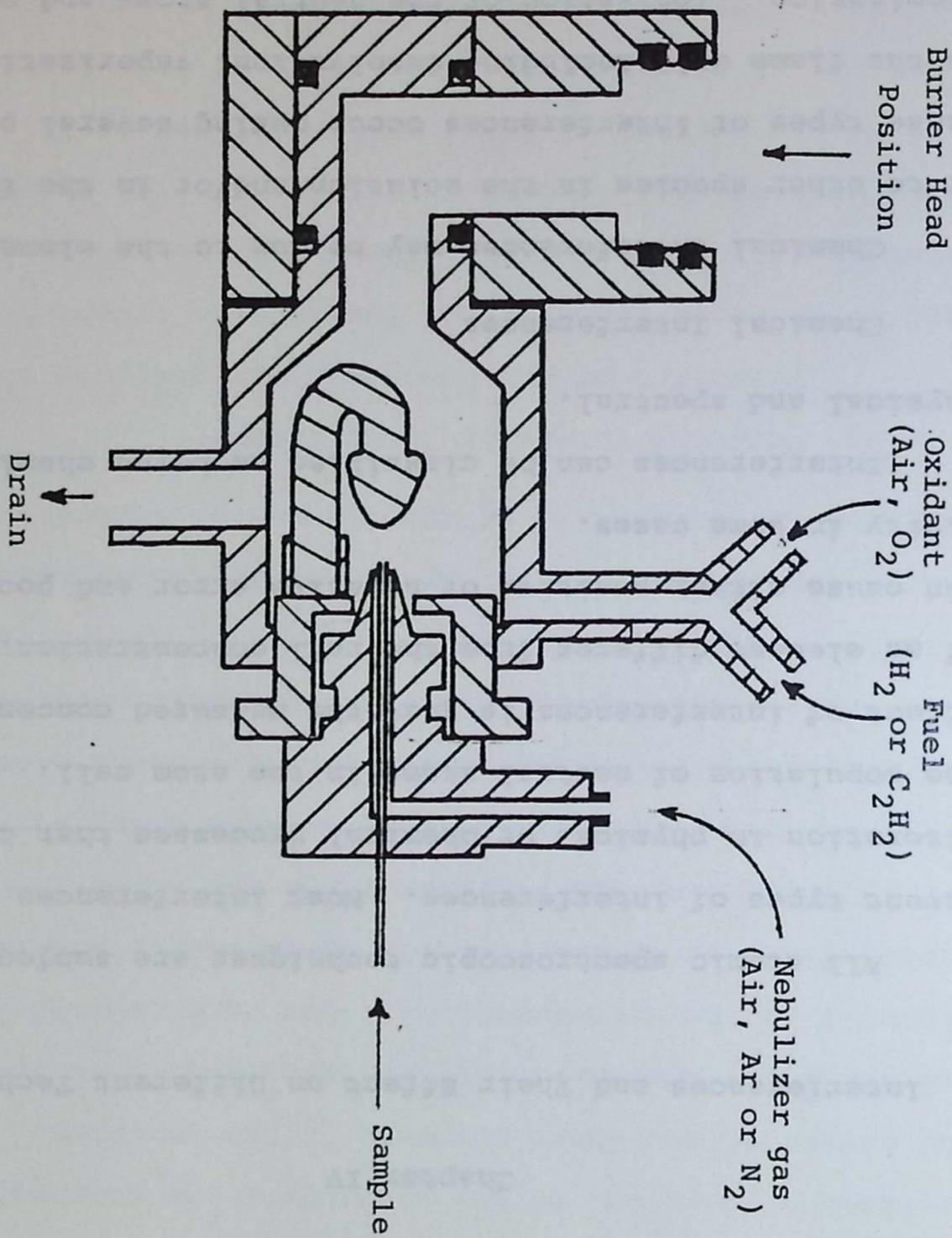


Figure 3. Diagram of the Burner Assembly (74).

## Chapter IV

### Interferences and Their Effect on Different Techniques

All atomic spectroscopic techniques are subject to different types of interferences. Most interferences cause an alteration in physical or chemical processes that control the population of neutral atoms in the atom cell. The net effect of interferences is that the measured concentration of an element differs from the real concentration. This can cause either positive or negative error and poor sensitivity in some cases.

Interferences can be classified as being chemical, physical and spectral.

#### A. Chemical Interferences

Chemical interferences may be due to the element itself, or to other species in the solution and/or in the flame cell. These types of interferences occur during several processes in the flame cell including desolvation, vaporization and atomization. Ionization of the neutral atoms and other processes such as recombination of neutral atoms with other species also are considered chemical interferences. Chemical interferences are subdivided into different classes as follows:

##### 1. Ionization Interferences

Ionization interference, as discussed in Section (III-B1)

is due to the element itself and depends on factors such as ionization potential of the element, flame temperature, and the nature of the other elements in the solution. Ionization decreases the population of neutral atoms, lowering the sensitivity of the measurement. It can be minimized by using a cooler flame or by the addition of an easily ionizable element. Decreasing the temperature of the flame is not an effective way of minimizing this interference, because vaporization, desolvation and atomization processes also may decrease and cause a reduction in the total number of neutral atoms. Usually elements such as K, Li or Cs, which are called ionization buffers, are added to the solution to suppress the ionization of the element of interest.

## 2. Compound Formation Interference

Formation of any compound that prevents the atomization of an element can be considered as a compound formation interference. In principle, there are two reasons for the occurrence of this type of interference: (a) compound formation of the element of interest with cations or anions in the solution. These compounds are stable or slow to vaporize, therefore they reduce the population of neutral atoms in the flame. It is also called vaporization interference. (b) compound formation of atoms of interest with atoms and radicals in the flame. This contributes to vapor phase interferences; formations of oxides, hydroxides and hydrides are considered as vapor phase interferences. The effect of both interferences on the measurement depends on many factors including

Flame type and temperature, nebulization efficiency, burner system (total consumption or premixed), sample composition, and observation height.

There is an enormous amount of literature concerning these types of interferences and their elimination. A well-known example of anion interferences is the depressing effect of phosphate, sulphate and silicate on determination of Ca, Mg and Sr (75-78). These interferences are due to the presence of strong metal-anion bonds, therefore high energy is required for dissociation. Al interference on Ca and Mg is an example of cation interference. The interference is probably due to the formation of compounds such as  $MgAl_2O_4$  (79), which are difficult to dissociate.

Eliminating or decreasing these types of interferences can be carried out by different methods including selection of a suitable flame and optimized fuel/oxidant ratio, the addition of releasing and complexing agents, and matrix matching methods in order to have the same concentration of interfering species in samples and standards. Phosphate interference on Ca and Mg can be eliminated by the addition of other elements such as Sr, Ba and La (80-82). La eliminates the effect of phosphate, sulphate and silicate on alkaline earth elements (80). EDTA is sometimes used as a complexing agent in the measurement of Ca and Mg. Sr also has been used as a releasing agent to remove the interferences in determination of Ca, Cu, Mg, Mn and Zn in soil and Mg in aluminum alloys by AF (83,84). The standard addition

method is a useful technique in dealing with chemical interferences. The main advantage of this method is that exact matching of the sample and "standard" solutions is achieved automatically (2). Some workers, however, have reported that the standard addition method is not a reliable solution in some cases (123). Matrix matching is rather inconvenient because the concentrations of interfering species are not known in many samples. Selection of a suitable flame and optimizing the fuel/oxidant ratio is very helpful in minimizing the compound formation interferences. For example, use of  $N_2O-C_2H_2$  flame with its high temperature, significantly decreases the phosphate, sulphate and silicate interference on alkaline earth elements. To decrease the formation of oxides and hydroxides, high temperature flames with reducing atmospheres are very useful.

#### B. Spectral Interferences

All three methods of atomic spectroscopy are subjected to this type of interference. The interference is due to the radiation being emitted or absorbed by species other than the analyte. It can be classified as: (a) emission and absorption by non-analyte atoms; (b) emission of the analyte (in AA and AF); (c) emission and absorption by molecules; (d) light scattering; and (e) self-absorption.

##### 1. Emission by Analyte and Non-analyte Atoms

Emission by non-analyte atoms is particularly important in AF when the lines of two different elements overlap.

This interference is due to inability of the monochromator to resolve these lines. It is only possible to eliminate this interference by doing the measurement at a different line, separating the species from each other before measurement or minimizing the interference by using a high dispersion monochromator and/or a smaller spectral slit width. A lot of observed and predicted direct spectral overlaps are listed in "Handbook of Flame Spectroscopy" (85). Some examples are: Cd, 228.802 nm and As, 228.812 nm; Hg, 253.652 nm and Co, 253.649 nm; and Fe, 271.903 nm and Pt, 271.904 nm. Ar lines emitted from the plasma may cause spectral interference in some cases. This is especially severe at wavelengths above 475 nm, which Ar exhibits considerable line broadening (88). Some examples of Ar interference are La, 294.910 nm and Ar, 394.898 nm; Sc, 346.770 nm and Ar, 256.766 nm; and Na, 588.995 nm and Ar, 588.859 nm.

Emission of the analyte and non-analyte atoms are both considered as spectral interferences in AA and AF. Complete correction for these interferences may be made through modulation of the incident light (86,87). Using a smaller spectral bandpass causes a significant improvement in this case.

## 2. Absorption by Non-analyte Atoms

Absorption by the non-analyte atoms or absorption line interference is small in AA because of the narrow width of the light source. Therefore, if there is another element with an absorption line within the bandpass of the monochromator, it still cannot absorb. However, if the lines

are too close, the interfering element can absorb the radiation meant for the analyte and result in serious errors. The possibility of the interference increases when multielement H.C.L.'s or demountable H.C.L.'s are used. Some examples of these types of interferences are: Fe, 271.902 nm and Pt, 271.904 nm; Al, 308.215 nm and V, 308.211 nm; and Cu, 324.745 nm and Eu, 324.753 nm (89). A number of workers have studied this type of interference (89-93). Elimination of this type of interference depends on wavelength separation of the two adjacent lines. Using narrow bandpass may decrease the interference, but it is not effective in most cases because it should be comparable to the separation between two lines. Several workers have used wavelength modulation techniques (13,91,92). Recently Koizumi (94) has reported correction of this type of interference by Zeeman Atomic Absorption Spectroscopy. In this method a strong magnetic field is applied to the sample vapor in the graphite furnace, which causes splitting of the absorption spectrum. By passing a polarized light source radiation through the sample, a double beam system is produced. The difference in absorption at the perpendicular and parallel components of the light source is proportional to the analyte concentration without the effect of molecular absorption or light scattering. The advantages of this technique over other methods of background correction are precise correction at exactly the same wavelength and the possibility of correction for direct spectral overlap interferences.

The presence of a non-absorbing line close to the analyte line which is not absorbed by the analyte atoms can be used for background correction, providing the background is the same in both lines (95). This technique requires a double beam spectrometer. One channel is set to the analyte line and the other to the non-absorbed line. By taking the ratio or the difference response of the two channels, a background corrected signal results. Dual beam spectrometers can also be used for measurement of two elements simultaneously, for internal standardization methods in which the non-analyte channel is set to the internal standard wavelength, or for continuum source background correction technique, in which the non-analyte channel is used for the continuum source.

### 3. Molecular Emission or Background Emission Interference

This type of interference results from various molecular species produced by the flame gases, such as OH, CH, NH and CN, or molecular species formed from the components of the solution in the flame, such as oxides and hydroxides of some elements. The molecular spectrum is a broad band and interference occurs when it overlaps the analyte line. The interference depends on many factors such as type of flame gases, oxidant/fuel ratio, observation height, and sample matrix. This type of interference is particularly important in AE and, if it is not corrected, serious errors may result. If the flame background is stable in AE, it can be simply compensated for by the blank solution. If the back-

ground is not stable or is due to sample matrix, possible methods include using a smaller spectral bandpass or applying a wavelength modulation technique (96). Background emission in AF has the same effect as in AE. Complete elimination of the background can be accomplished in AA and AF using light source modulation (86,87). Using a smaller spectral bandpass also decreases the interference significantly.

#### 4. Molecular Absorption Interference

Molecular absorption interference, which is sometimes called background absorption, results from the formation of spectrally active molecular species in the flame which absorb incident light. This interference will arise especially when solutions of high salt content are aspirated into the flame. The interference in this case depends on many factors such as flame temperature, which is discussed in Chapter III, B.1, matrix components, observation height and intensity of the light source. This is one of the most severe and troublesome interferences in AA, especially for the measurement of trace elements in a complex matrix (97). A typical example is the interference of CaOH band in the measurement of Ba with AA in air-C<sub>2</sub>H<sub>2</sub> at 553.6 nm (2). This interference effect is eliminated by using a hot flame such as N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>. Different schemes have been designed for correction of molecular absorption interferences. Continuum source background corrections in which the absorbance from the continuum radiation is subtracted from the absorbance of H.C.L. can be made. Hydrogen

or deuterium lamps are usually used. However, the radiation intensity of the continuum source is higher in the UV region and lower in the visible region compared to the H.C.L. Thus there is the problem of balancing energy between the two light sources, which makes the determination of elements in the visible region difficult (101). Most commercial equipment is equipped with this type of background corrector. Zeeman effect for background correction is one of the most useful methods which has been applied for this type of interference (98,99). Wavelength modulation (13,91,92) and non-absorbing line methods are other approaches for correction of molecular absorption interference. Several other methods, including temperature control by changing the fuel/oxidant ratio, use of a flame with less background absorption, use of a separated flame, matrix modification (*i.e.*, addition of some compounds to the solution in order to decrease molecular species), and matrix matching (*i.e.*, make the standards have the same matrix as the samples, excluding the element of interest), have all been used for correction of this type of interference. Fry *et al.* have reported that the molecular band spectra due to undissociated inorganic polyatomic species with a premixed burner is approximately 150 times less than long path total consumption burner (97,100). Background absorption in AF is not as significant as it is in AA, the effect of which is attenuation of the source intensity(2).

## 5. Light scattering

This spectral interference is due to scatter of incident radiation by solvent droplets and solute particles. It depends on many factors such as the sample nature, wavelength, flame and nebulizer. Solutions of high salt content produce a high concentration of molecular species in the flame which cause an increase in scatter. Any factor that reduces the particle size and increases the vaporization efficiency can be applied to minimize scatter. In AA, scattering results in a positive effect on the analytical signal. Correction for light scatter in AA may be made by the use of a continuum source (102). The effect of scattered light is particularly important in AF, especially when a continuum source is used as the excitation source. The interference is eliminated in AF when non-resonance fluorescence wavelengths are used for measurement. Correction for scattered radiation in AF may be made by wavelength modulation (103).

## 6. Self Absorption and Quenching

These types of interferences arise from reabsorption of radiation emitted from the element by other unexcited atoms or molecules present in the cooler part of the flame. The effect of the interference is a decrease in emission intensity. The extent of radiation loss by self absorption is highly concentration-dependent. Self absorption is important in AE and AF and causes curvature of calibration curves at high concentrations. The effect is much less

important in AA because it is not an emission technique.

Quenching is the result of collisional deactivation of the excited atomic species with other species present in the flame, the effect of which is important in AF. Quenching does not affect significantly AF and AA methods.

These interferences can be minimized by dilution of the samples and elimination of molecular species such as  $O_2$  from the flame surroundings, by shielding the flame with an inert gas.

### C. Physical Interferences

Physical interferences depend on physical properties of the sample (such as viscosity, surface tension, vapor pressure and density) and characteristics of the nebulizer. These factors affect the aspiration rate, nebulization and vaporization efficiency. The interference will occur when these factors vary between samples and standards, and results in variation of the fraction of the sample present in the flame as neutral atoms per unit time. Nebulizer characteristics, as long as they act the same on samples and standards, do not contribute to physical interferences. Efficient nebulizers which produce a fine aerosol of very small and uniform droplet size improve the whole process of atomization and decrease some of the interferences. The flow rate of the solution into the nebulizer depends upon the solution viscosity, and particle size depends on the surface tension. So the viscosity and surface tension of the samples and standards must

be the same.

There are different ways to eliminate physical interferences. If samples with high salt content have to be measured, ultrasonic nebulizers are very helpful in preventing burner clogging and memory effect (104). Use of organic solvent with samples and standards improves the aspiration rate, decreases the droplet size and improves the vaporization process. Other methods of minimizing physical interferences are: standard addition, internal standardization, and dilution techniques.

## Chapter V.

### Optimization of Parameters in Flame Atomic Spectroscopic Techniques

#### A. Introduction

There are many factors in atomic spectroscopic methods which require optimization. Optimization consists of the selection of values of parameters in order to obtain the best signal-to-noise ratio (S/N). Maximum S/N ratio results in high precision and low detection limits.

Factors influencing the signal and noise can be divided into instrumental parameters and interferences. Different types of interferences have been discussed already and only the instrumental parameters will be considered here. Before discussing the important parameters in optimization, it is necessary to define different sources of instrumental noise.

1. White noise: has the same power density at all frequencies. Examples are the PMT shot noise which results from the random arrival of photons at the photocathode, and Johnson noise or thermal noise, which is related to the electronics.

2. Flicker noise: sometimes called drift noise or  $1/f$  noise. It has a high power density at low frequencies. This type of noise is common in amplifiers and radiation sources.

3. Interference noise: this type of noise is due to pickup of signals from the environment and occurs at discrete frequencies.

These types of noises can be discriminated against by performing the measurements at frequencies where there is little interfering noise.

#### B. Experimental Parameters

The most important experimental parameters influencing the S/N ratio in a given flame atomic spectroscopic method can be summarized as follows (105).

1. Nebulizer
  - a. aspirating gas flow rate
  - b. particle size
  - c. solution flow rate
2. Atomizer
  - a. fuel flow rate
  - b. oxidant flow rate
  - c. sheathing gas flow rate
  - d. height of flame (burner position)
  - e. type of fuel and oxidant
  - f. flame geometry
3. Radiation source
  - a. source intensity
  - b. source position
  - c. modulation frequency (in source modulated techniques)

4. Optical factors
  - a. slit width
  - b. wavelength setting
  - c. modulation frequency (in wavelength modulated techniques)
5. Detector and readout system
  - a. PMT voltage
  - b. readout gain

Optimization can be carried out by increasing the signal, decreasing the noise, or accomplishing both. In each case, an attempt should be made to increase the S/N ratio. Some of these factors are independent and can be adjusted separately for maximum S/N ratio. Among the above parameters, excitation source, PMT voltage and readout gain are independent variables. The PMT voltage and readout gains do not greatly affect the S/N ratio, unless a very large voltage is applied to the PMT; or very large gains are used to the amplifiers, which increase the noise and result in reduced S/N ratio (85). Type of flame gases and flame geometry are usually predetermined before a measurement and are not considered in the optimization process. For example, in AE and AF, burners of circular cross-section and in AA long path burner heads are commonly used. Type of flame gases were discussed in Chapter III, selection of the gases depends on the mode of measurement (whether AE, AA or AF), element to be measured, and matrix constituents.

Modulation frequency in wavelength-modulated techniques and wavelength setting are independent variables and should be adjusted separately. However, frequency of modulation in source-modulated systems is a dependent factor, determined by other variables of the source such as pulse width, pulse height, duty cycle and dc level.

#### C. Noise Reduction

Modulation techniques are very efficient in reducing the effect of noise and, thus, increasing S/N ratio. Modulation is transformation of the dc into an ac signal and shifting the measurement frequency to a region of low noise density. Wavelength modulation methods have been widely used in atomic spectroscopy not only to reduce some interferences (see Chapter IV,B), but also for reduction of some types of instrumental noise. Source modulation techniques are employed in AA and AF to increase S/N ratio. This method has the capability of not only reducing interferences and instrumental noise, but also of increasing the signal. This is achieved by applying a large current to the light source for a short period of time, which increases the radiation intensity of the source and leads to an increased signal in AF.

#### D. Optimization, Results and Discussion

Optimization can be carried out in different ways. The single factor method keeps all the variables but one constant,

and determines the optimal S/N ratio for that variable (106). Optimization in this way has the following disadvantages. First, other factors may influence the result, so the optimal value is not real, and, secondly, for a large number of variables, it takes a long time (107). Because of the large number of interdependent variables in atomic spectroscopy, this method of optimization is not very efficient and multi-factor optimization methods should be employed. Simultaneous optimization techniques such as factorial design require carrying out a large number of experiments according to a pre-arranged plan (105). This method also is inadequate where complete knowledge of the response is not initially available (108). The sequential optimization method consists in carrying out only a few (often one) measurements at a time. By using the S/N ratio from the previous measurements, new values of the variables are determined before the next measurement. The simplex method is an example of sequential optimization.

The simplex optimization method has been used by some workers in studying the optimum S/N ratio for several elements. Parker *et al.* (109) employed this technique in FAA for investigation of absorbance response as a function of five variables: acetylene flow rate, air flow rate, lamp current, burner height, and an insignificant factor which was the volume of water in a 100 ml graduated cylinder some distance from the instrument. They found optimal values of the significant variables for Ca in an air-C<sub>2</sub>H<sub>2</sub> flame. The insignificant

nificant factor was found to be "significant" in some cases. Johnson *et al.* (110) used simplex optimization for pulsed H.C.L.'s. Factors varied included pulse height, dc level, pulse width, average current, and duty factor. They have reported optimum values for several H.C.L.'s.

In this study some of the parameters were roughly optimized. The most important variables, *i.e.*, flame height, oxidant flow rate and fuel flow rate, were adjusted to obtain a reasonable S/N ratio. Optimization was carried out by choice of a flame weight and an oxidant flow rate, then fuel flow rate was adjusted for maximum S/N ratio. Then flame height and fuel flow rate were kept constant and oxidant flow rate was adjusted. The procedure was then repeated for other variables.

Signal, background and S/B characteristics of several elements vs. fuel flow rate are illustrated in Figures 4 to 20. With H<sub>2</sub>-fueled flames, the background intensity does not vary as signal does, thus a very large S/N ratio can be obtained by varying the H<sub>2</sub> flow rate. Unfortunately, H<sub>2</sub>-fueled flames are not efficient in many cases, because of relatively low temperature. C<sub>2</sub>H<sub>2</sub>-fueled flames show much higher background variation upon changing the fuel flow rate. It should be emphasized that these figures do not show the real optimum fuel or oxidant flow rate; rather, they are optimum for the conditions indicated on each separate graph. In order to obtain a rough optimum value of variables, S/N

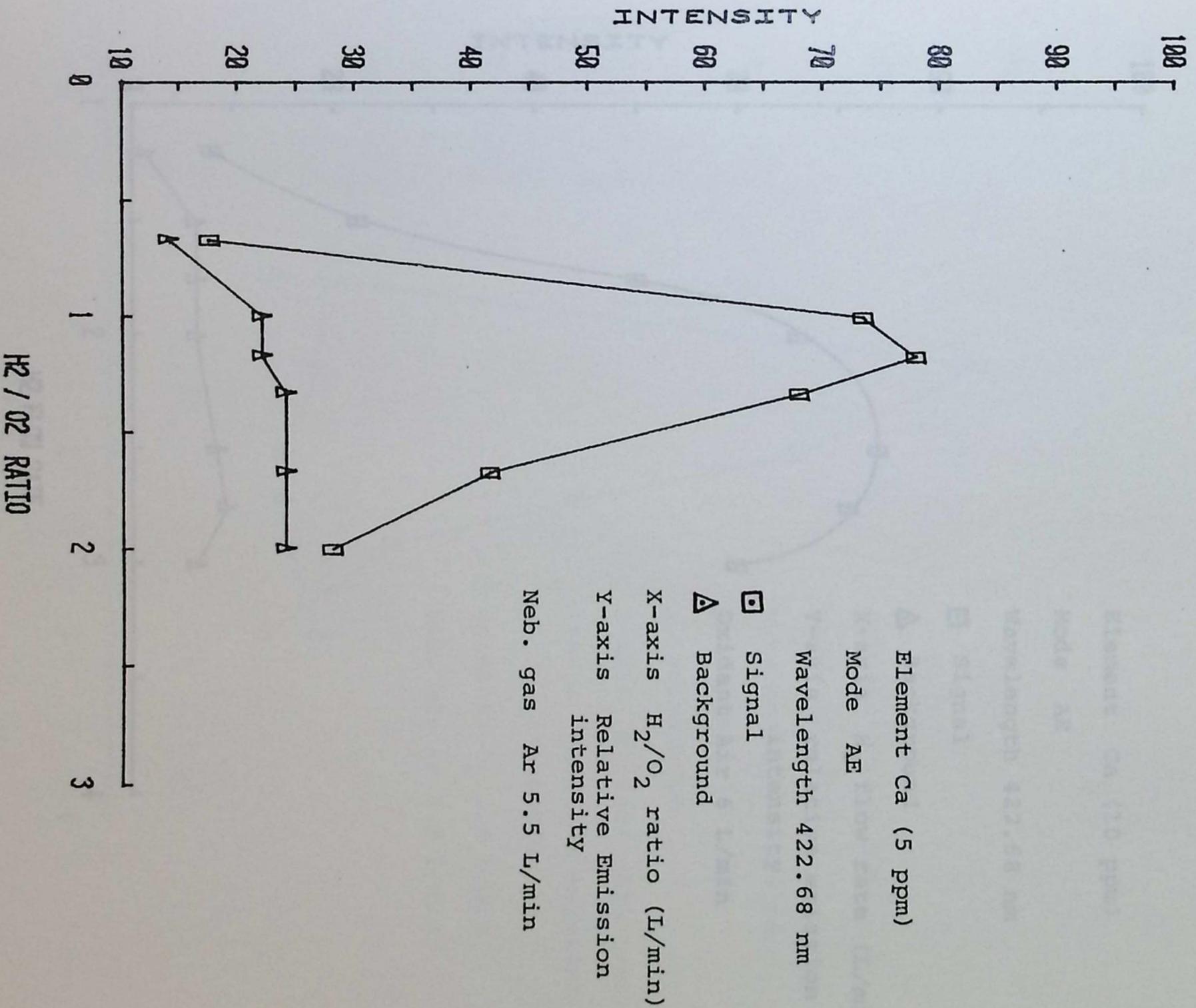


Figure 4

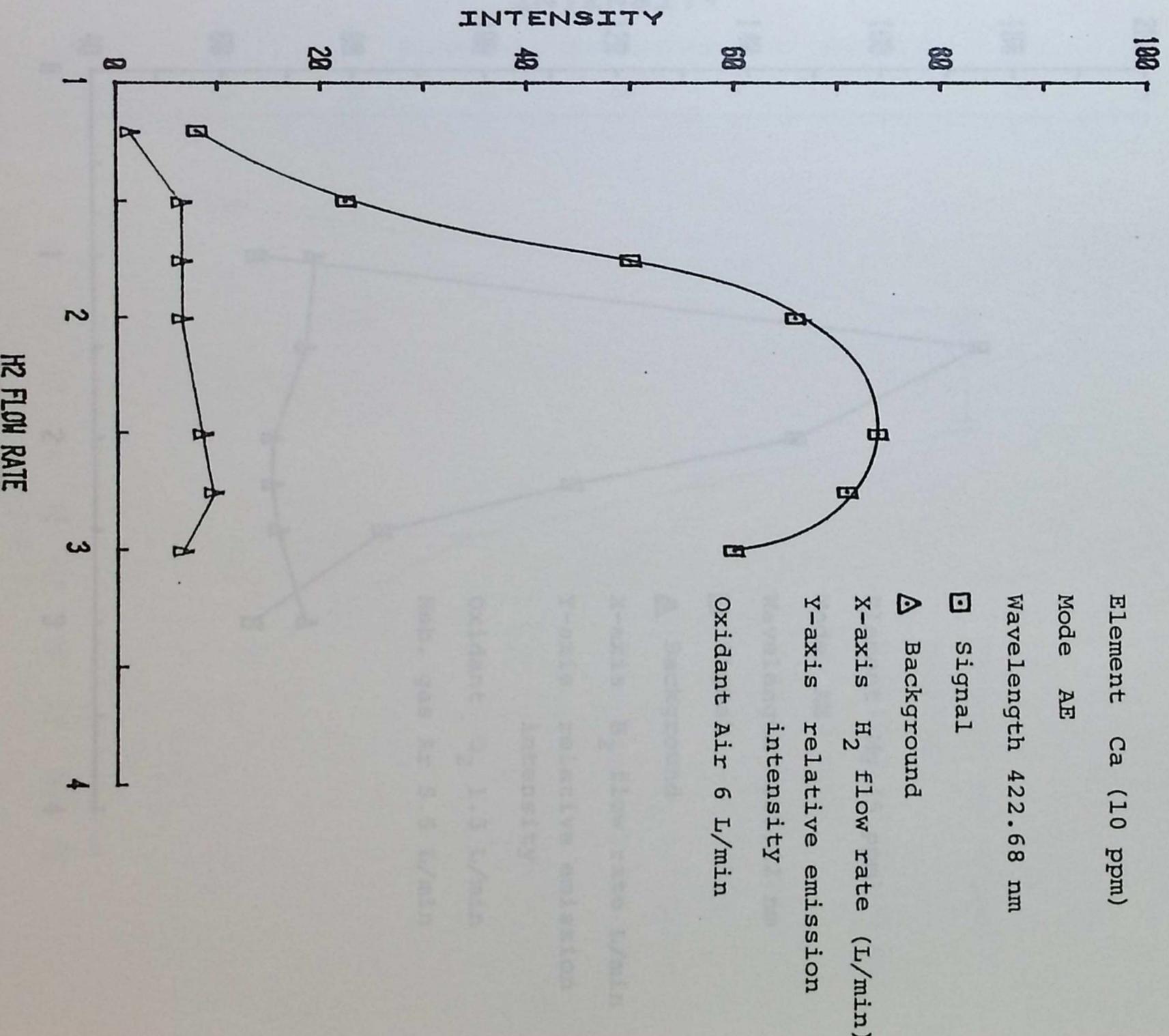


Figure 5

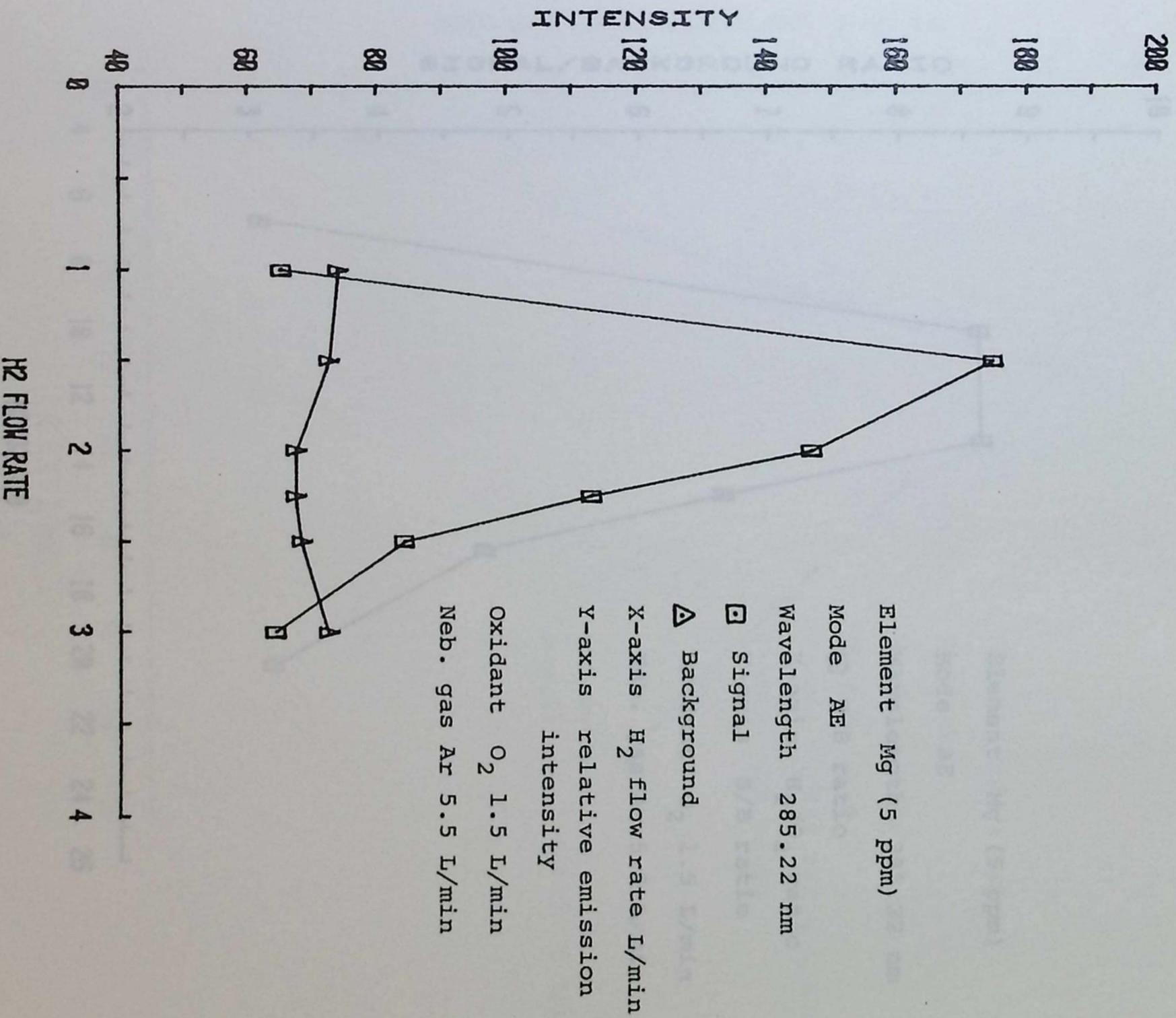


Figure 6

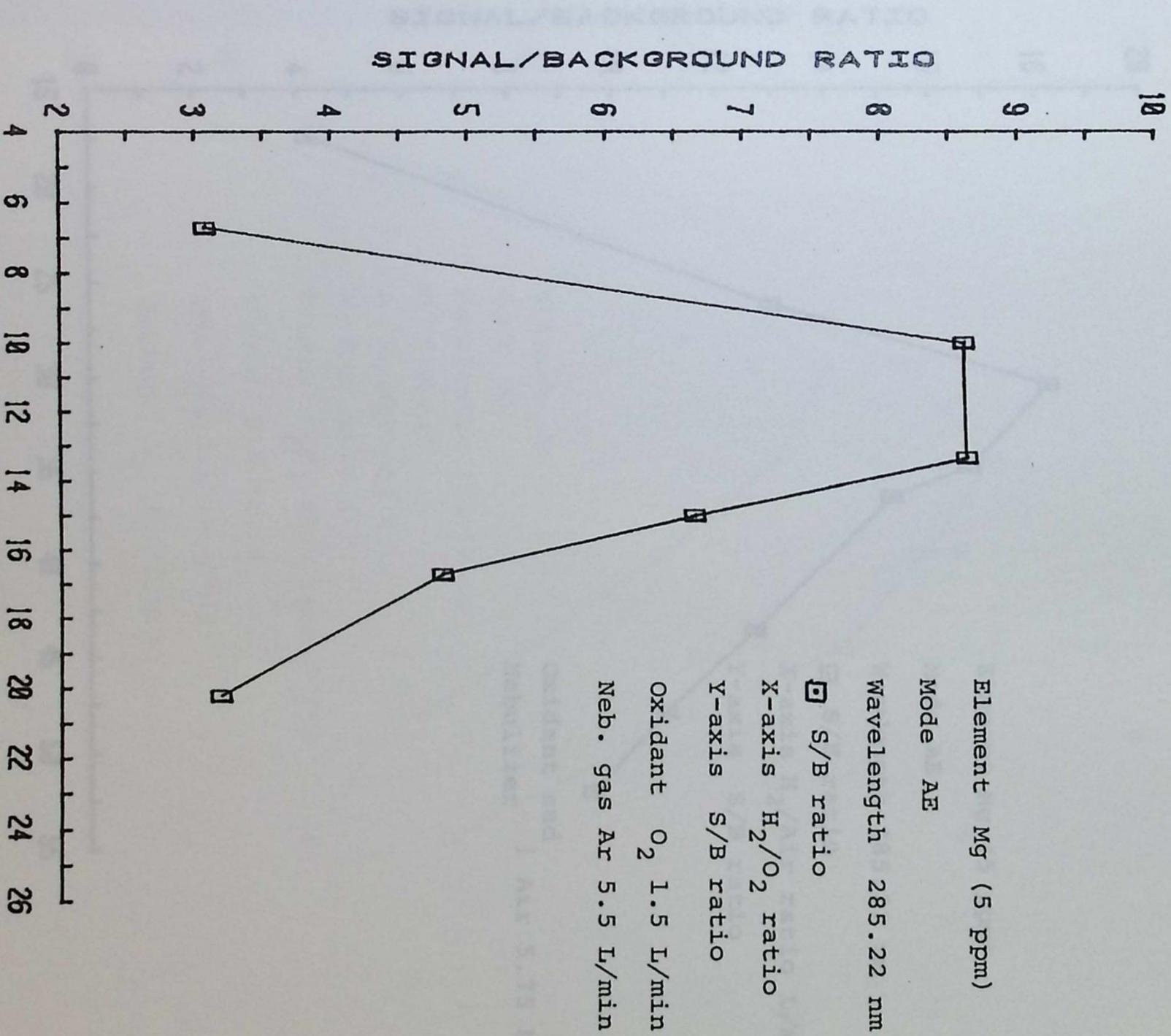


Figure 7

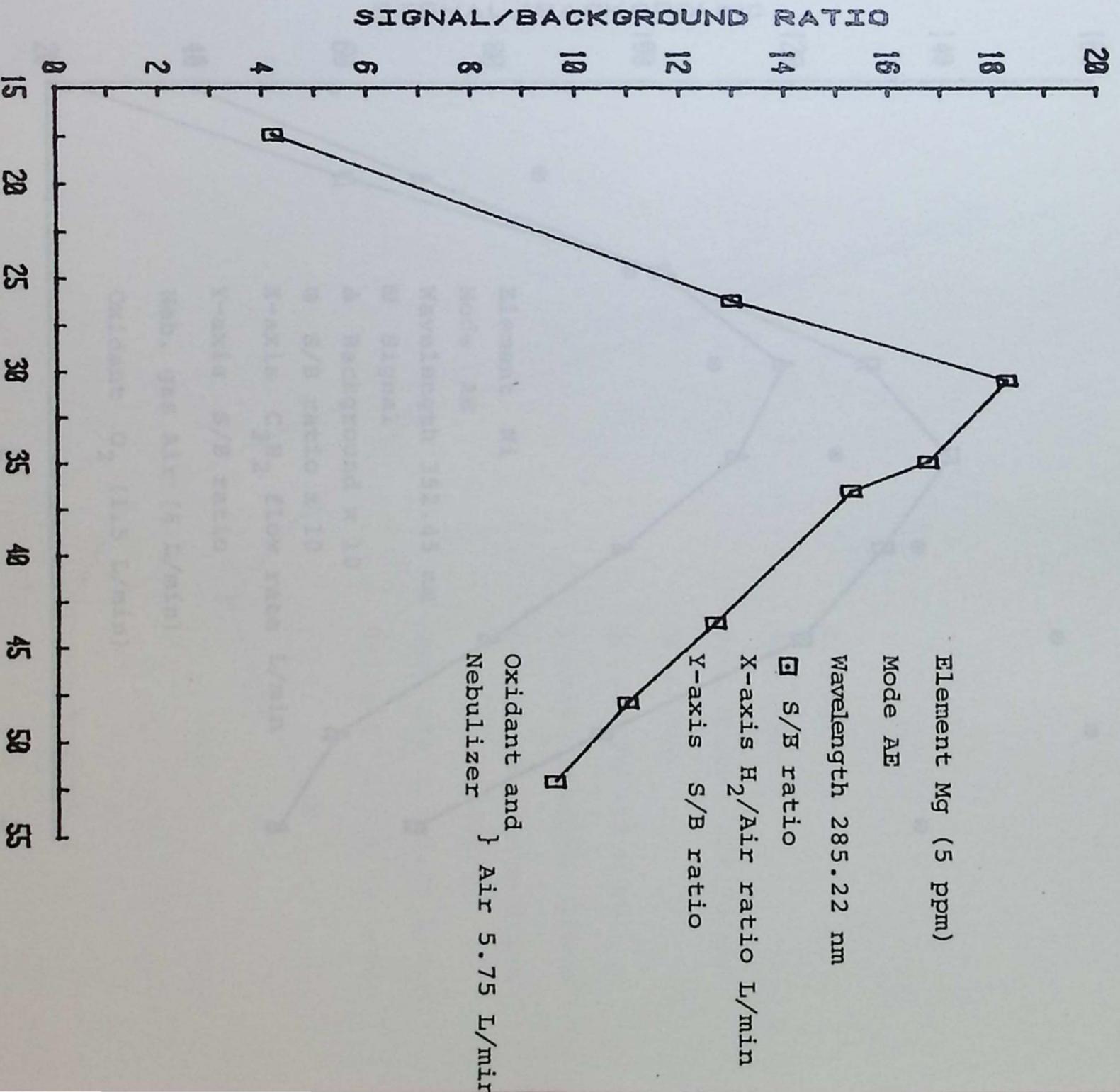


Figure 8

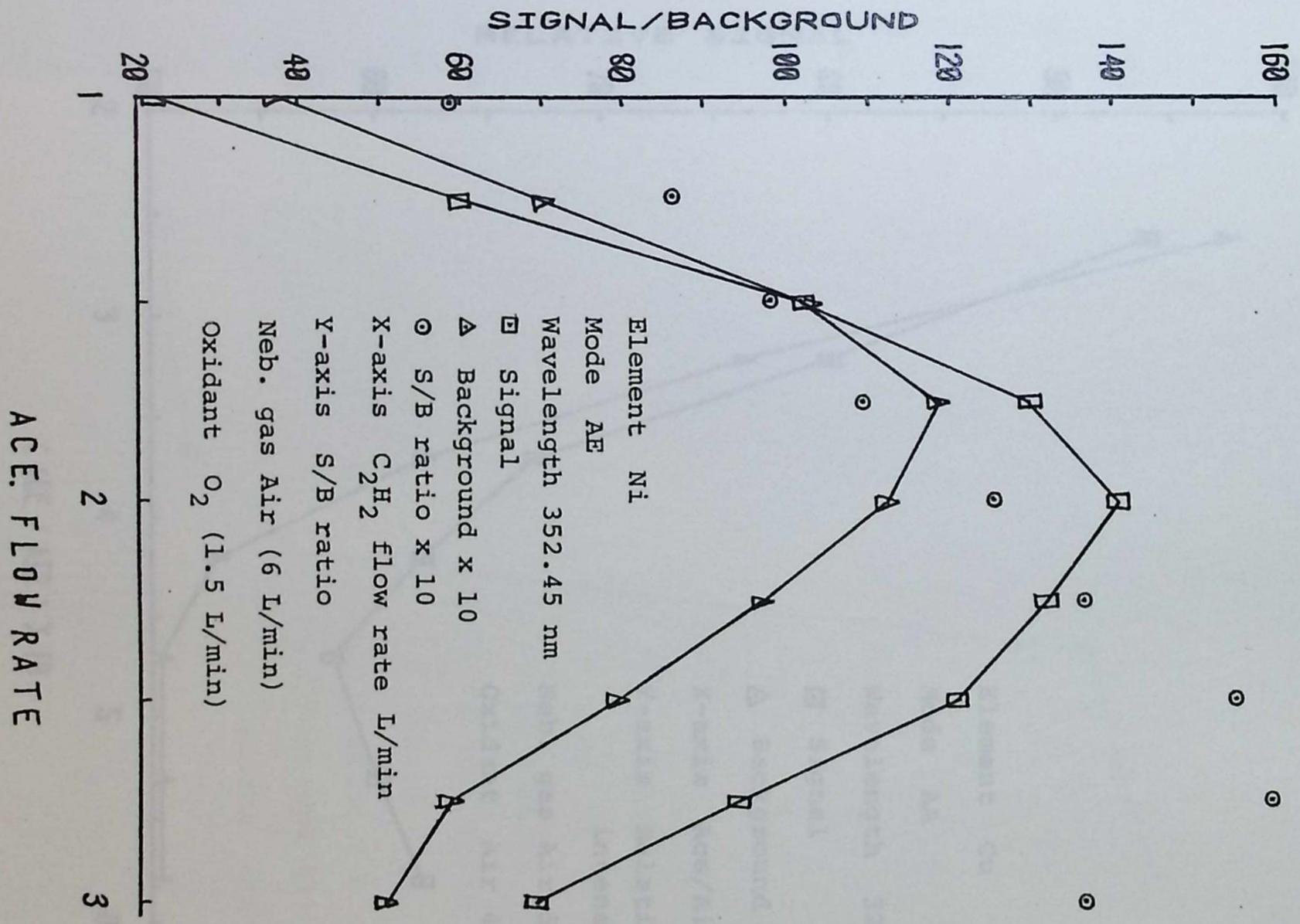


Figure 9

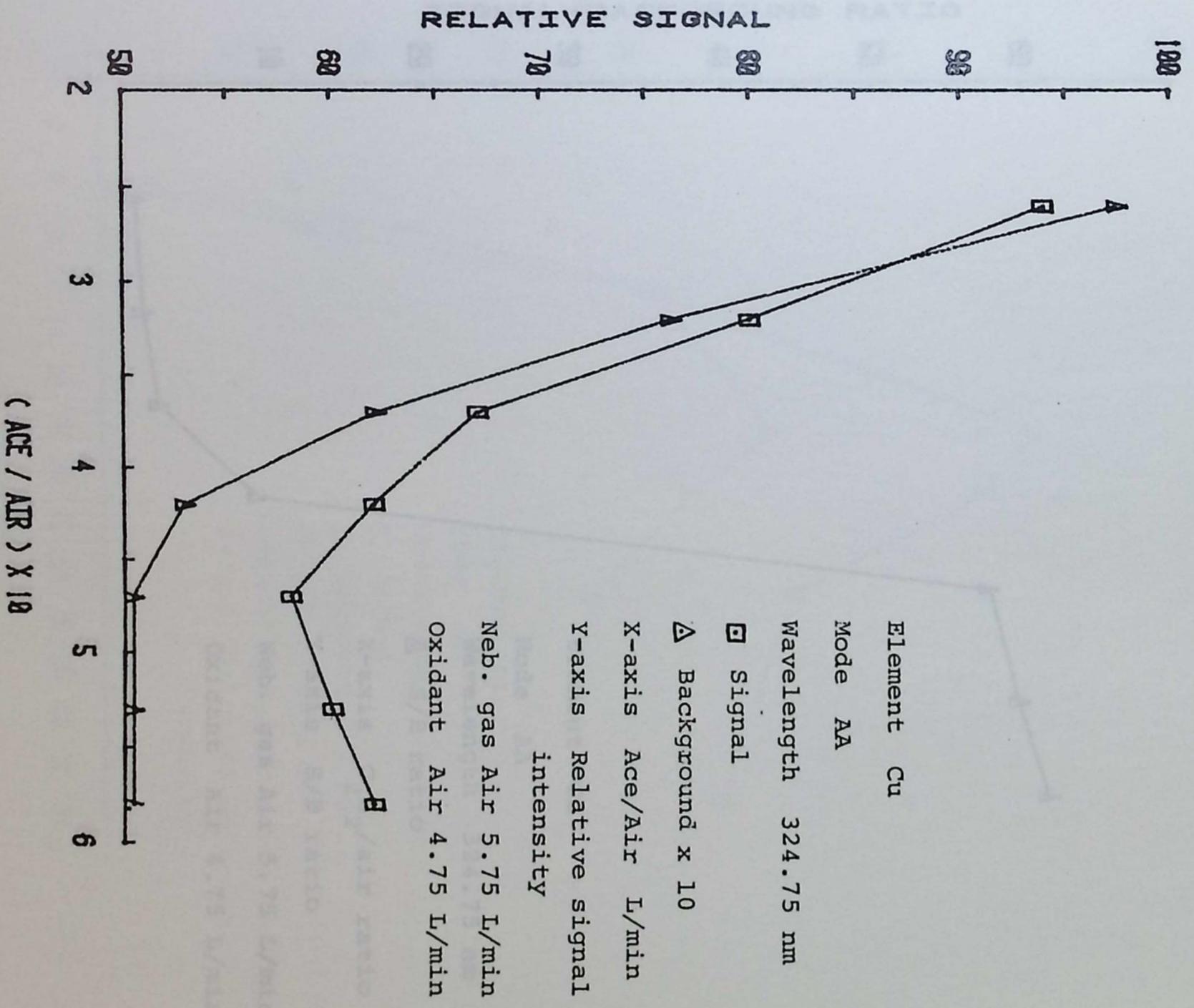


Figure 10

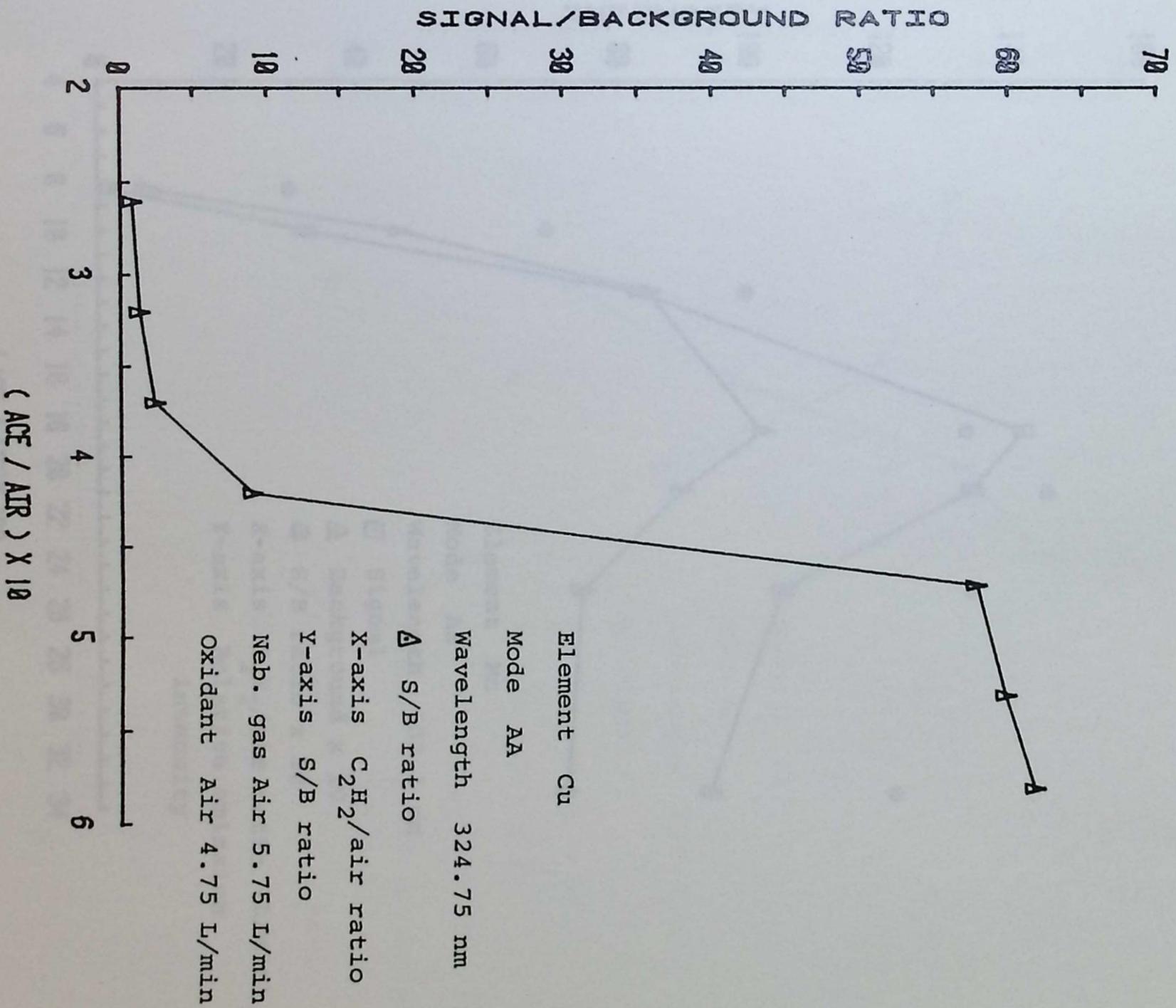
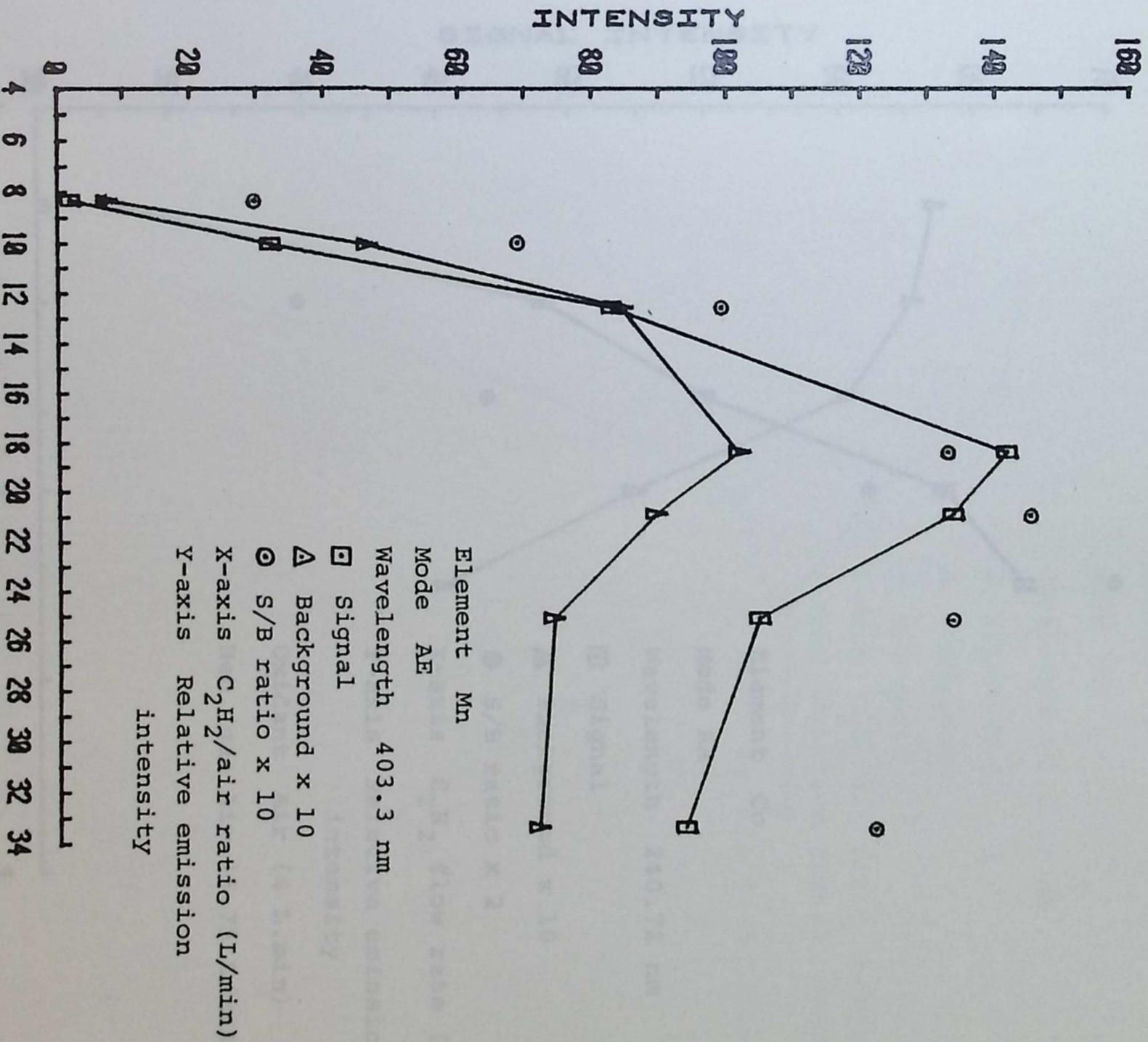


Figure 11



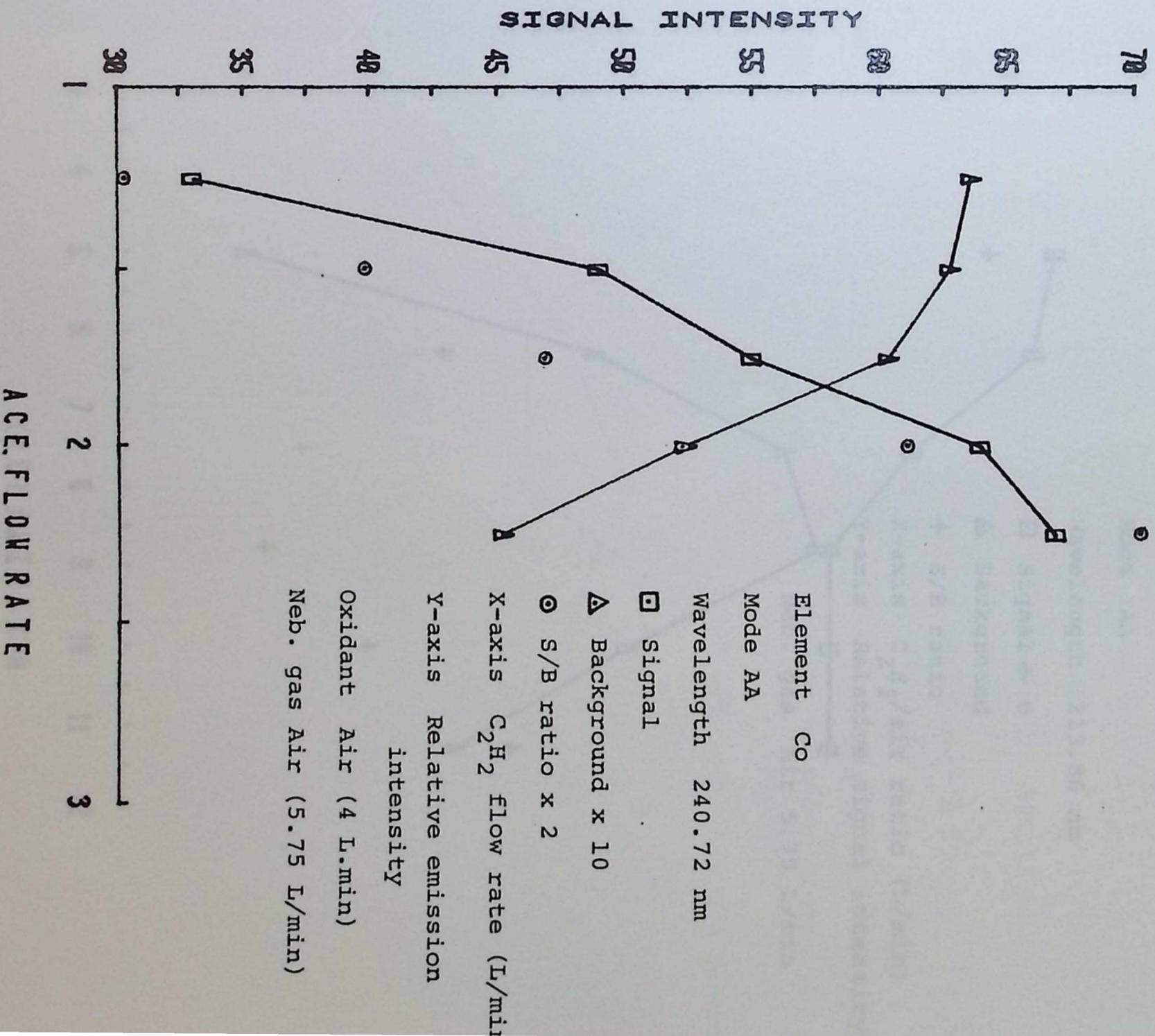


Figure 13

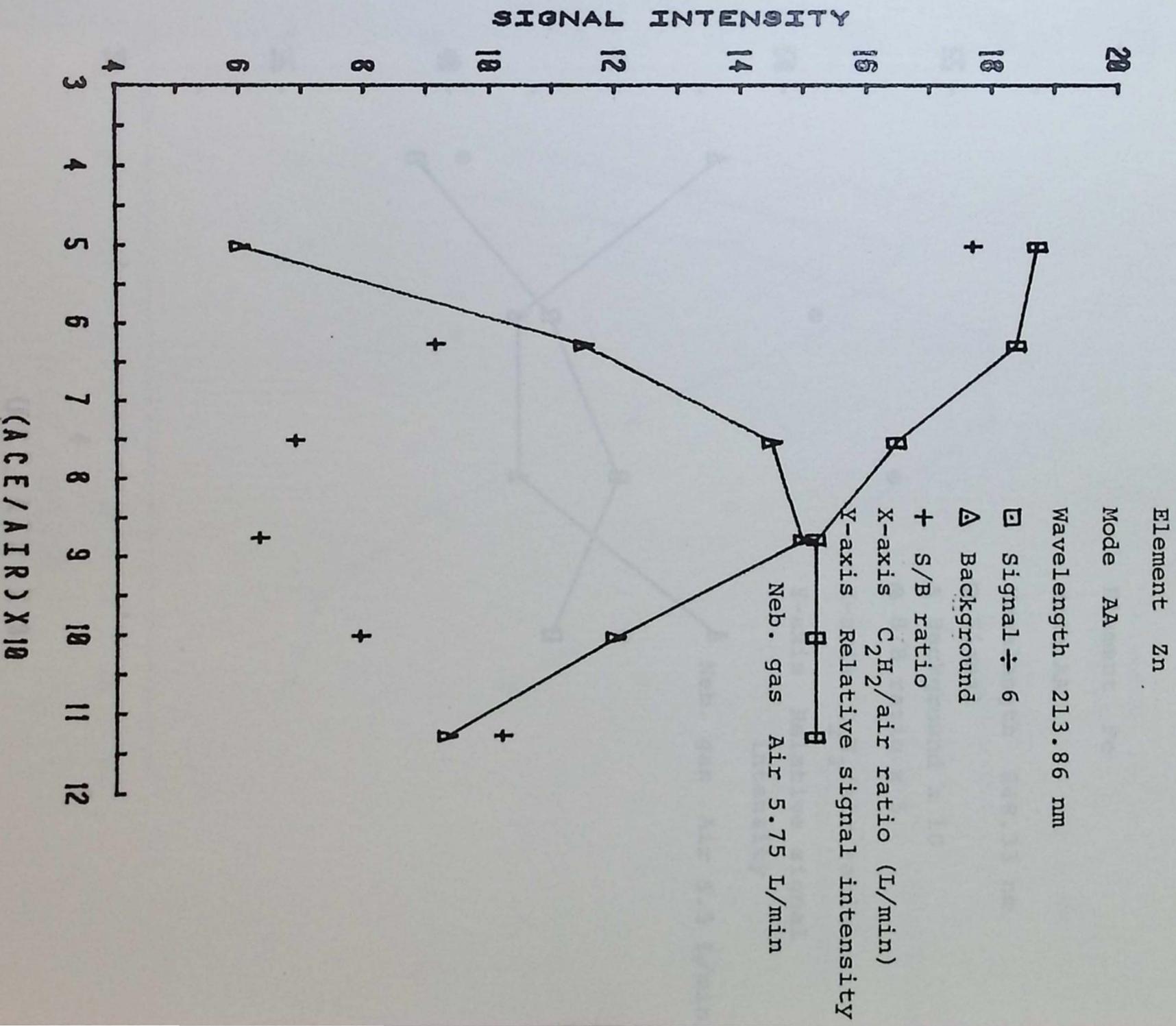


Figure 14

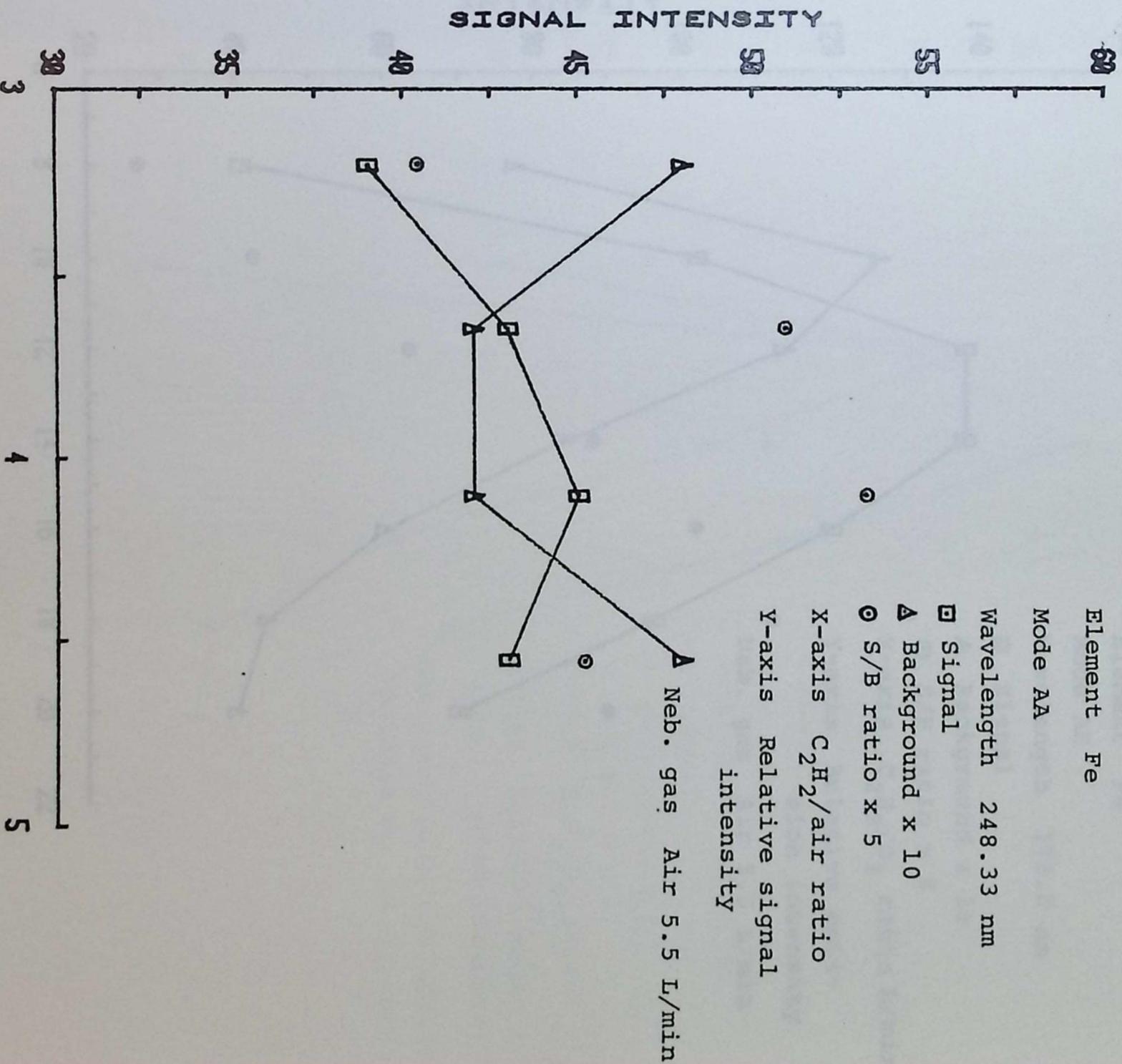
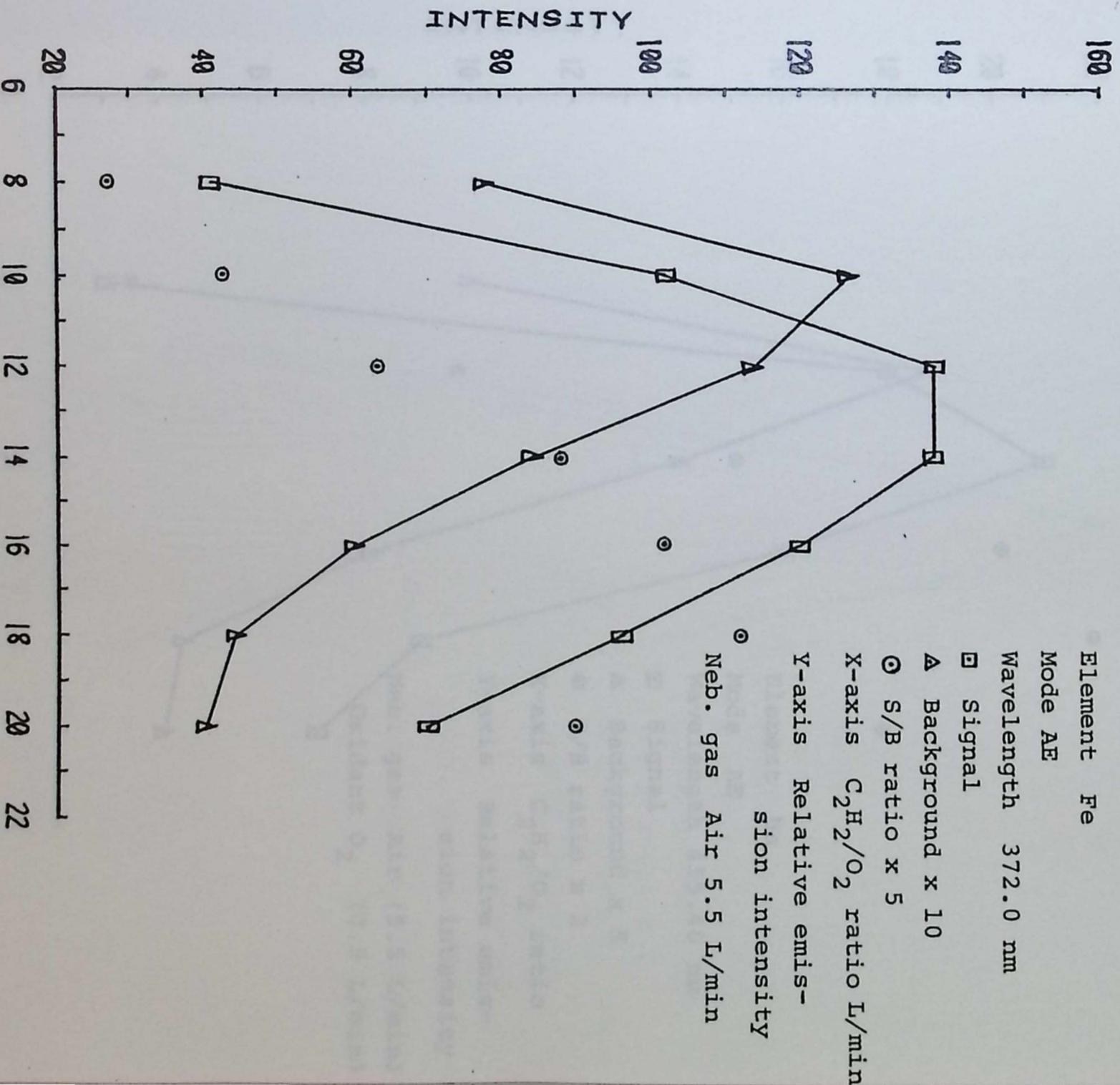
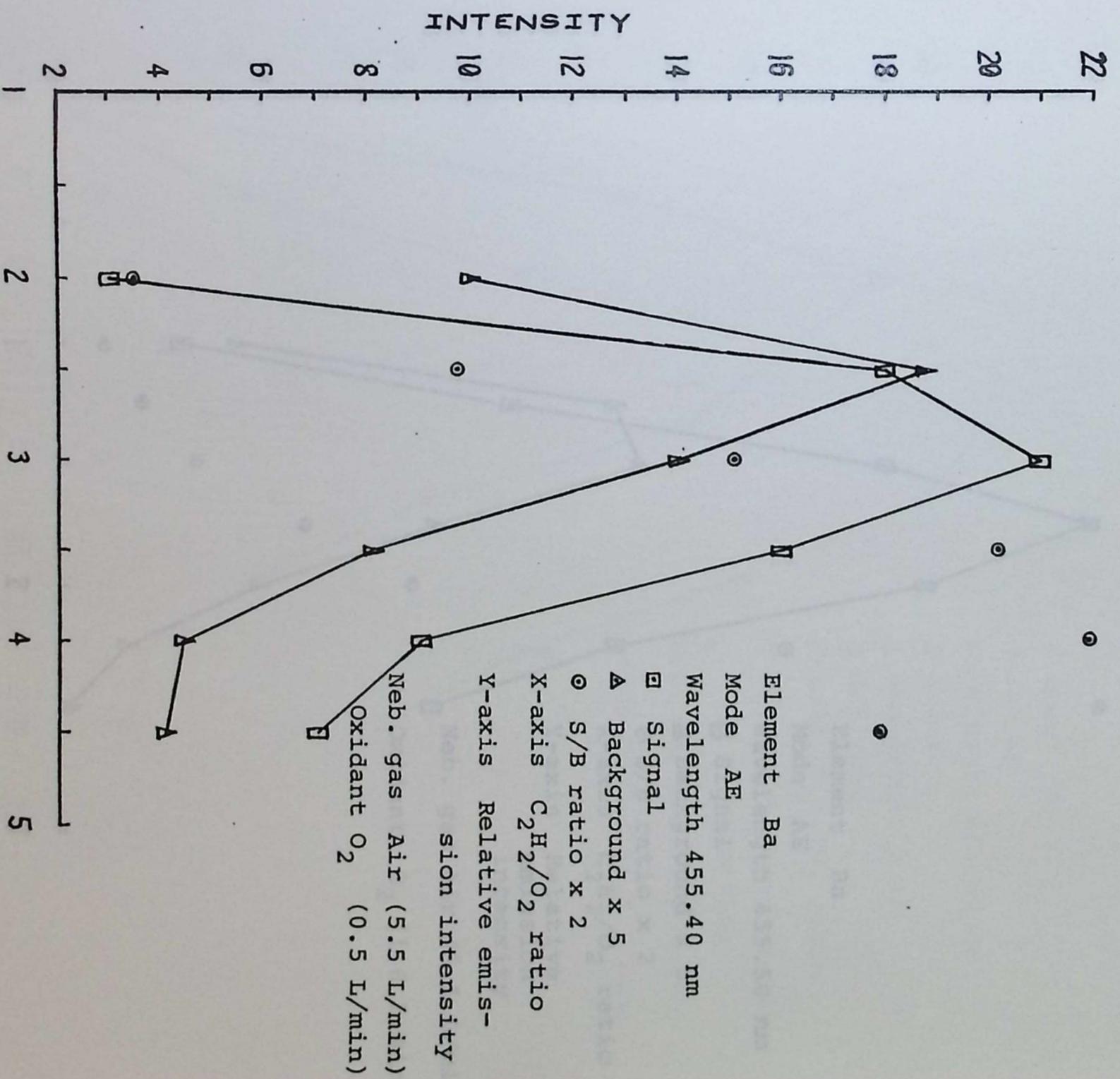


Figure 15



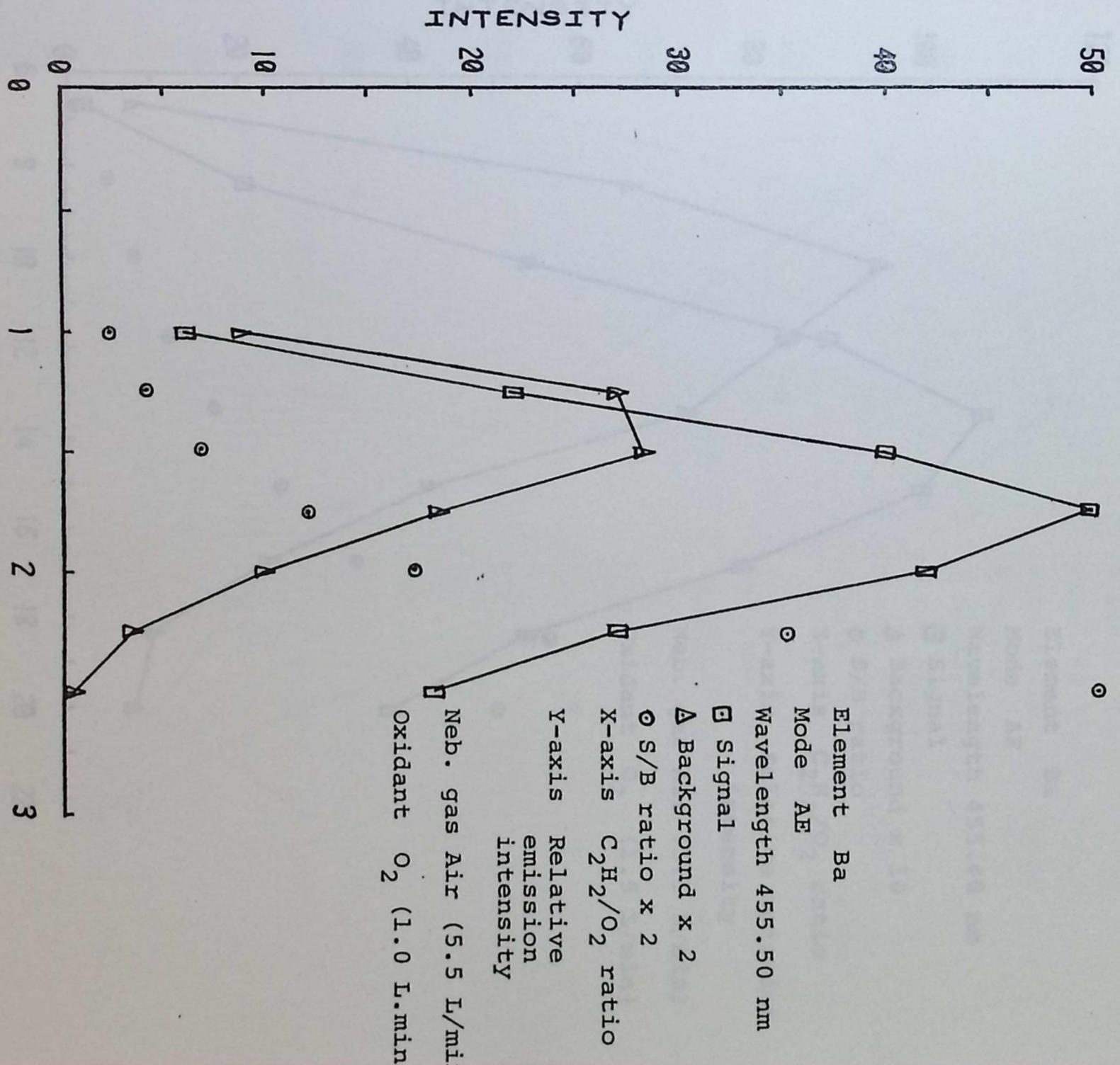
(A C E. / 02 ) X 10

Figure 16



(ACE./O2) X 10

Figure 17



( A C E . / O 2 ) X 1 0

Figure 18

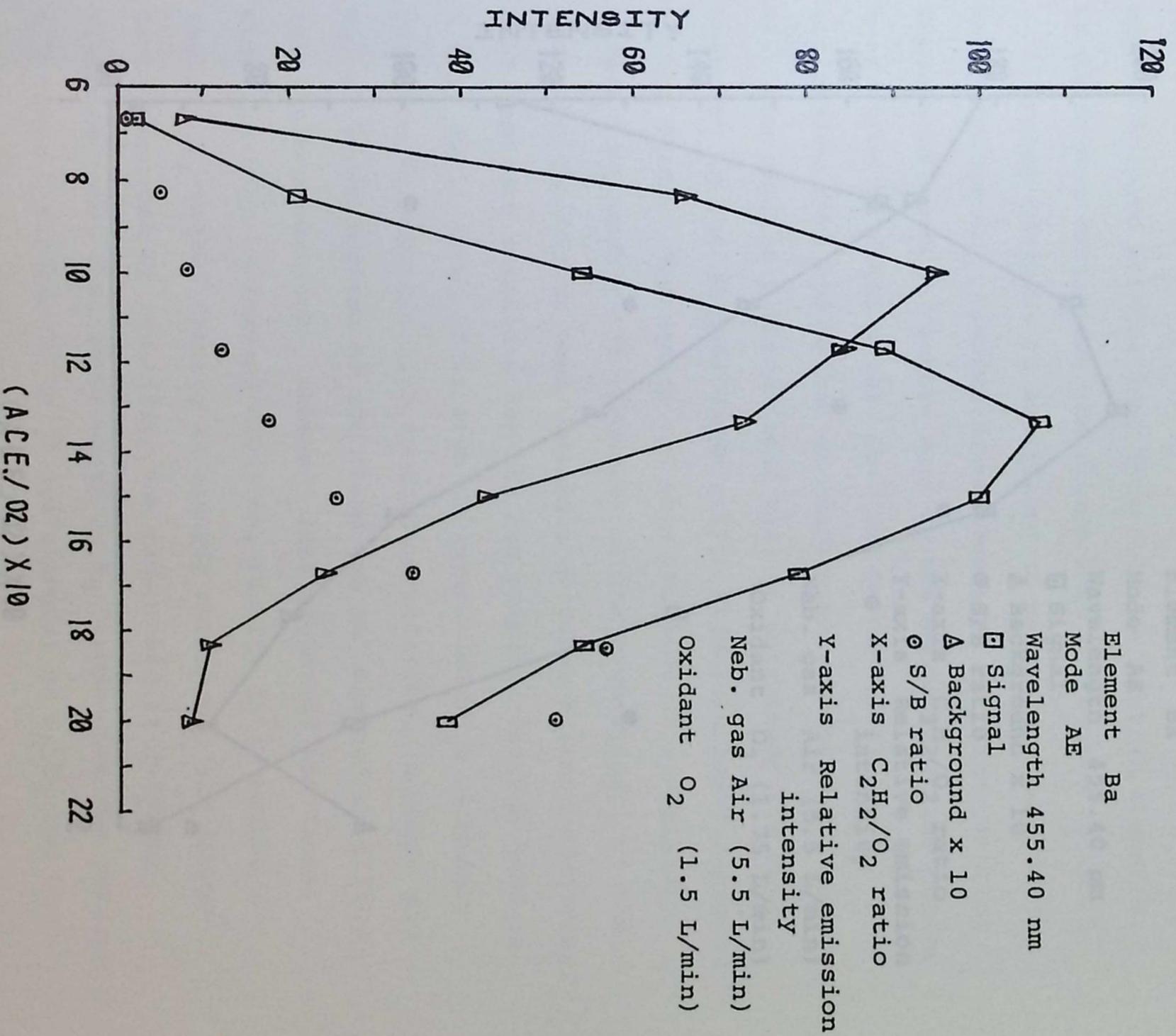
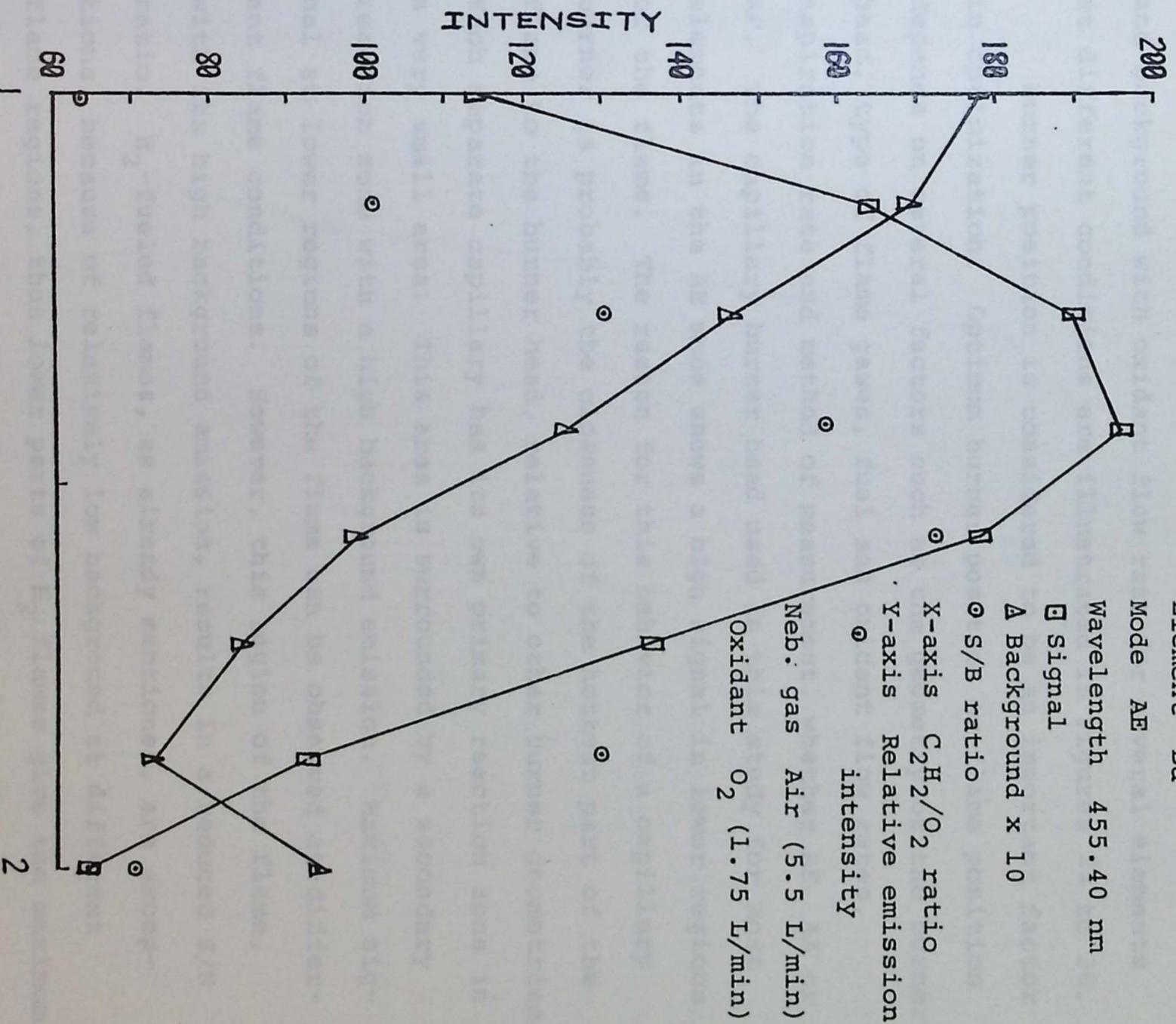


Figure 19



(ACE./02) X 10

Figure 20

ratio was examined at other conditions, i.e., different oxidant flow rates and burner positions. Variations of signal and background with oxidant flow rate for several elements at different conditions are illustrated in Figures 21 to 30.

Burner position is considered to be an important factor in optimization. Optimum burner position or flame position depends on several factors such as the geometry of the burner head, type of flame gases, fuel and oxidant flow rates, aspiration rate and method of measurement, whether AE, AA or AF. The capillary burner head used in this study for most elements in the AE mode shows a high signal in lower regions of the flame. The reason for this behavior of a capillary burner is probably the closeness of the hottest part of the flame to the burner head, relative to other burner geometries. Each separate capillary has its own primary reaction zone in a very small area. This area is surrounded by a secondary reaction zone with a high background emission. Maximum signal at lower regions of the flame can be observed at different flame conditions. However, this region of the flame, with its high background emission, results in a reduced S/N ratio.  $H_2$ -fueled flames, as already mentioned, are exceptions, because of relatively low background at different flame regions, thus lower parts of  $H_2$  flames give the maximum S/N ratio. Figures 31 to 34 are examples of  $H_2-O_2$  and  $H_2$ -air flame characteristics.

Acetylene flames, either air- $C_2H_2$  or air- $O_2-C_2H_2$ , unlike

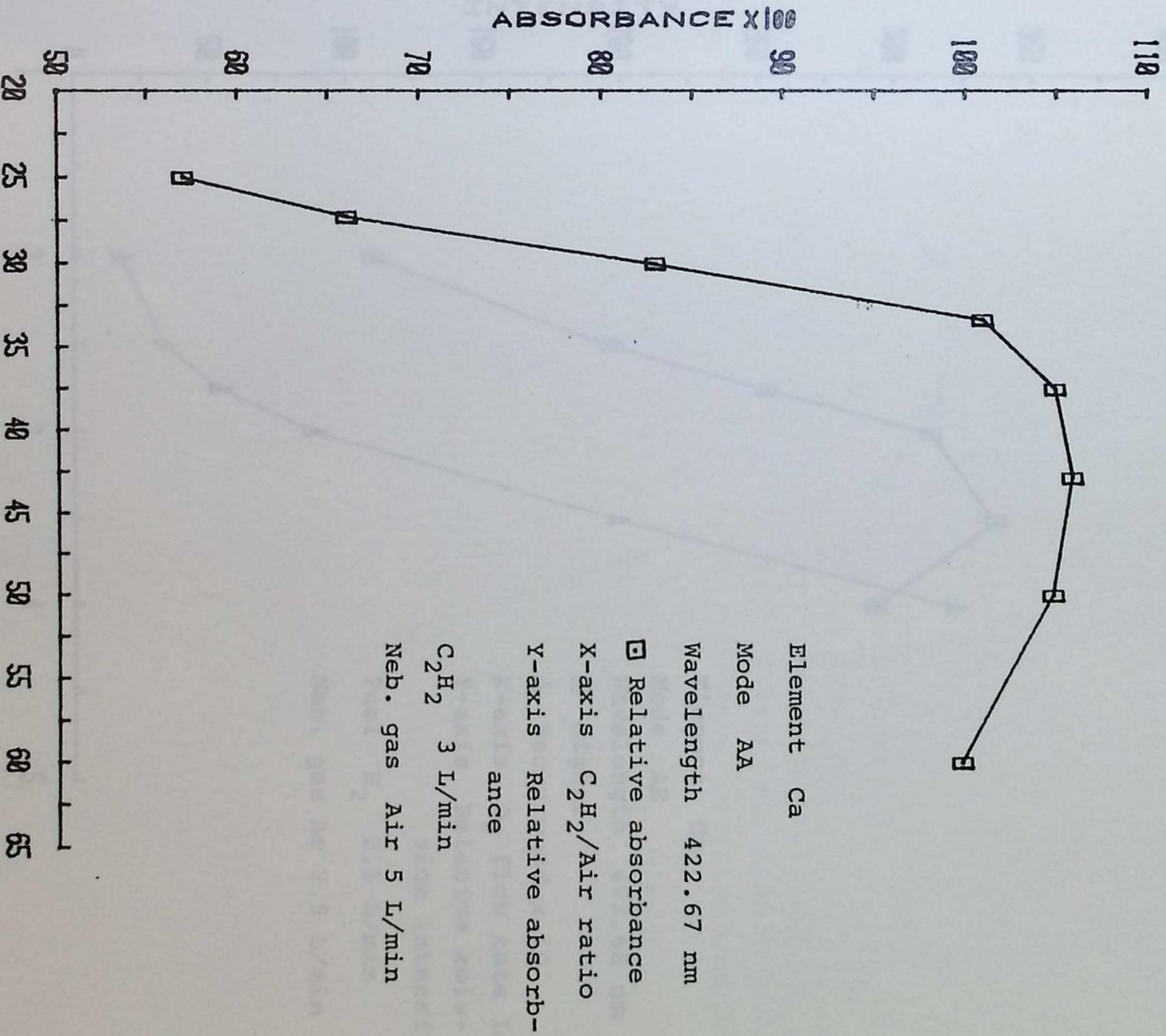


Figure 21

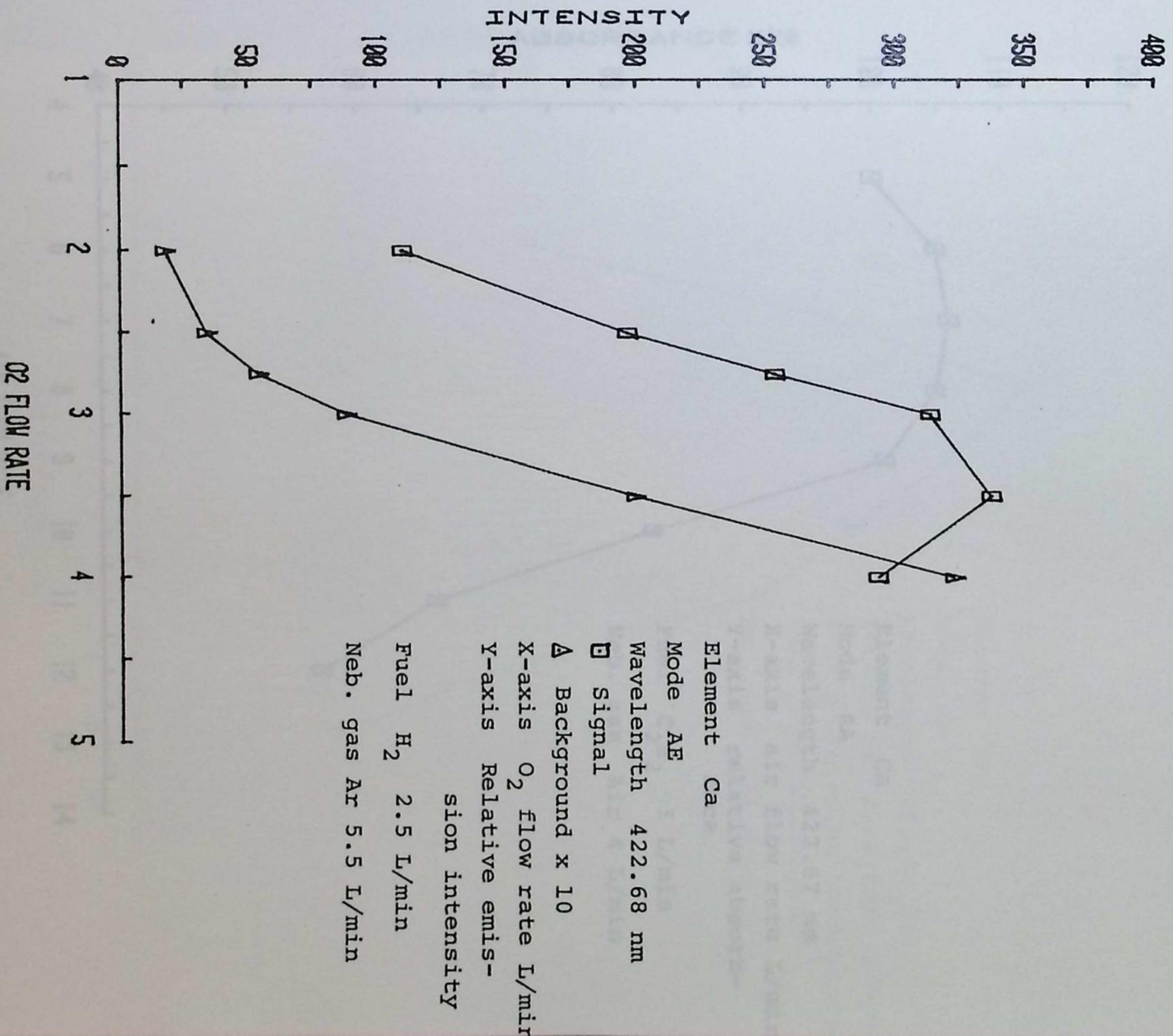


Figure 22

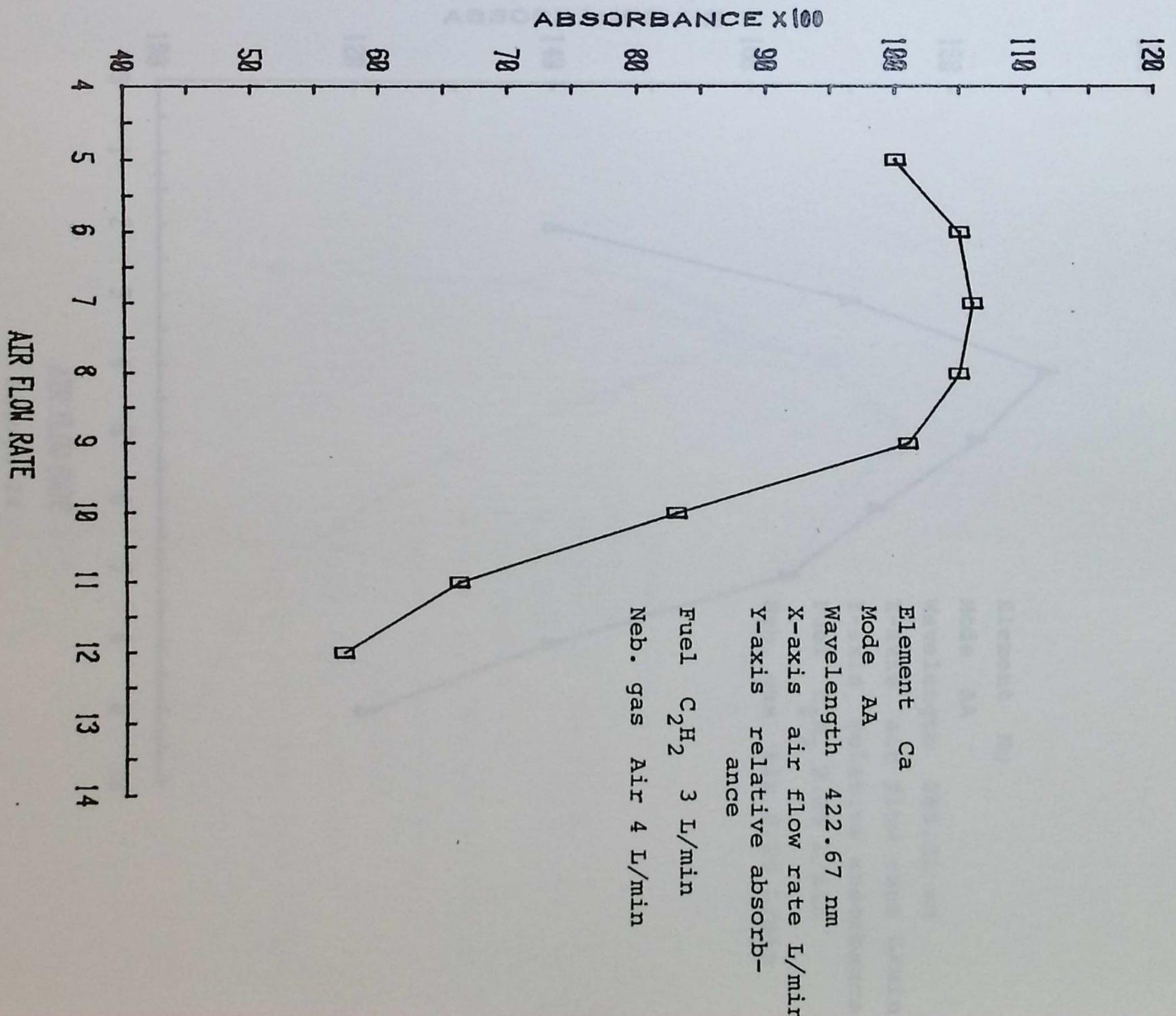


Figure 23

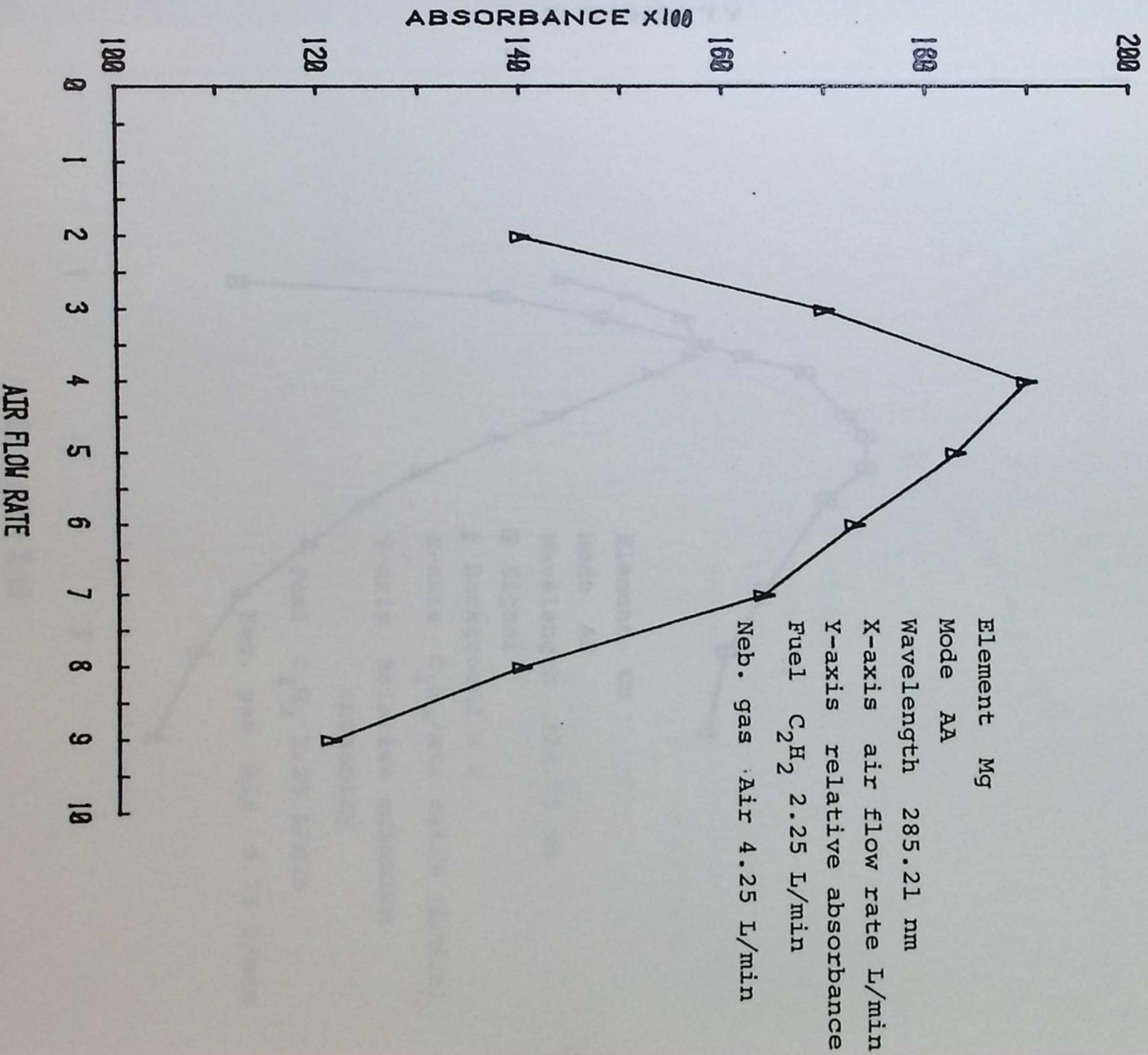
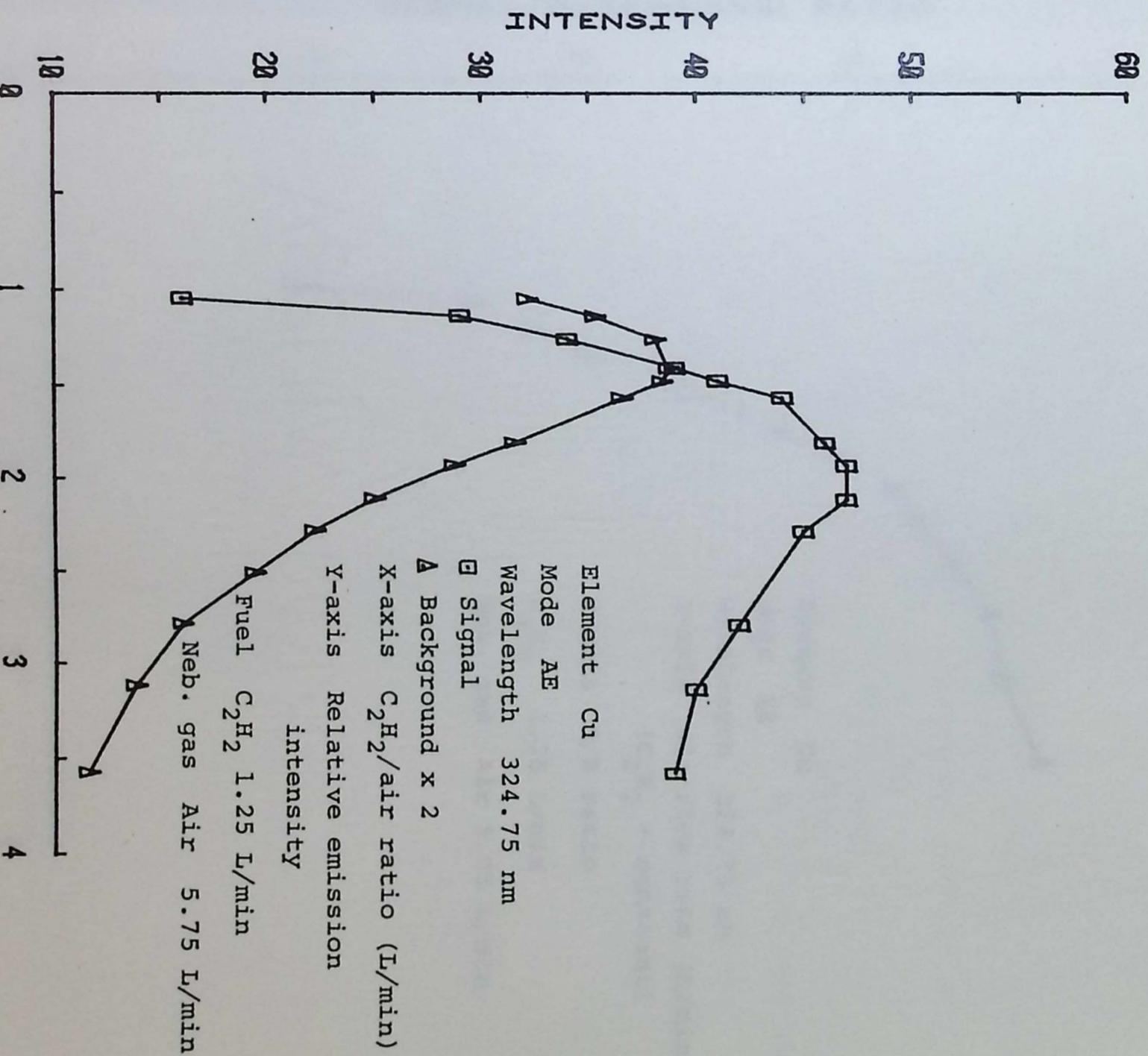


Figure 24



(ACE / ATR ) X 10

Figure 25

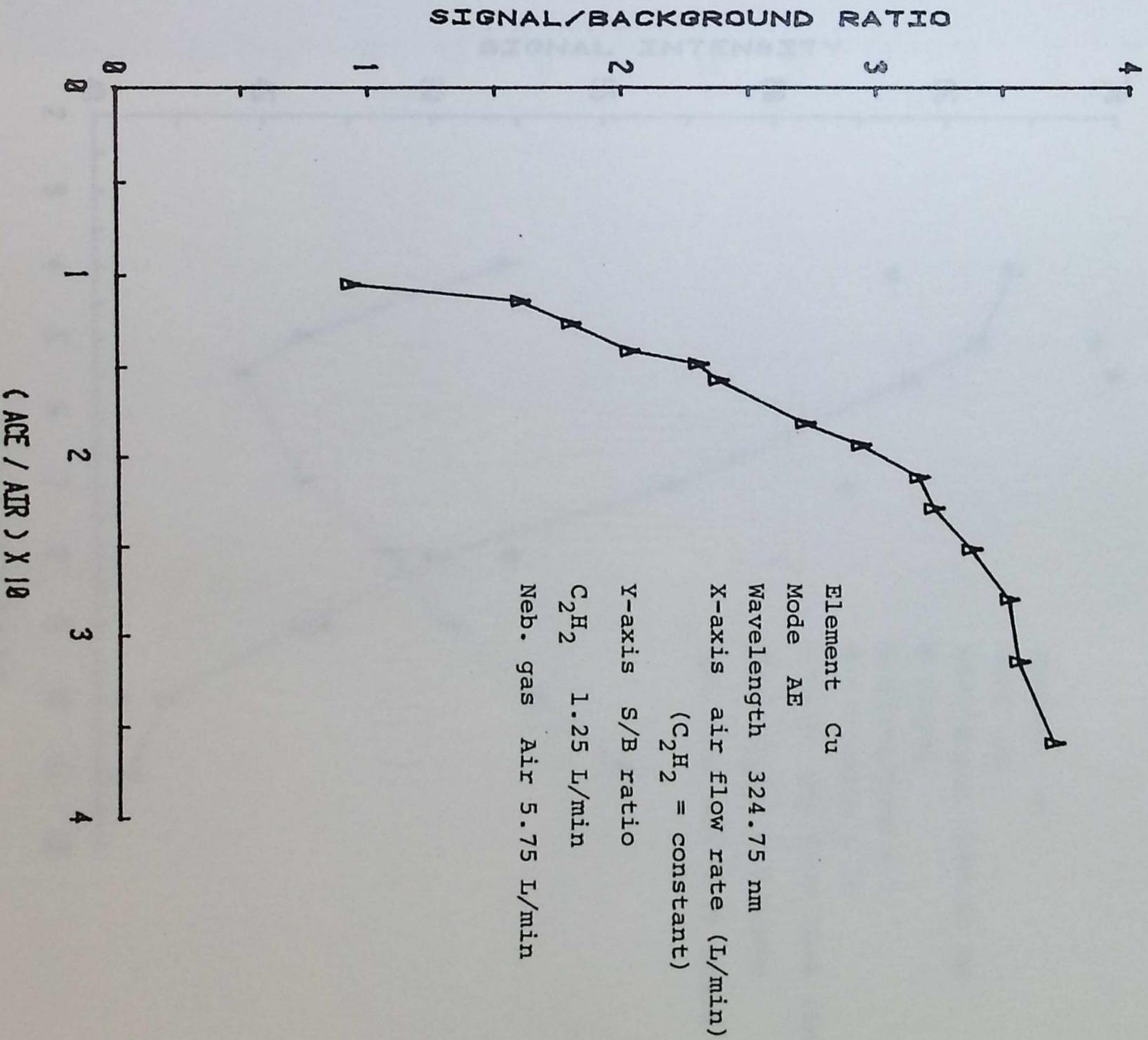


Figure 26

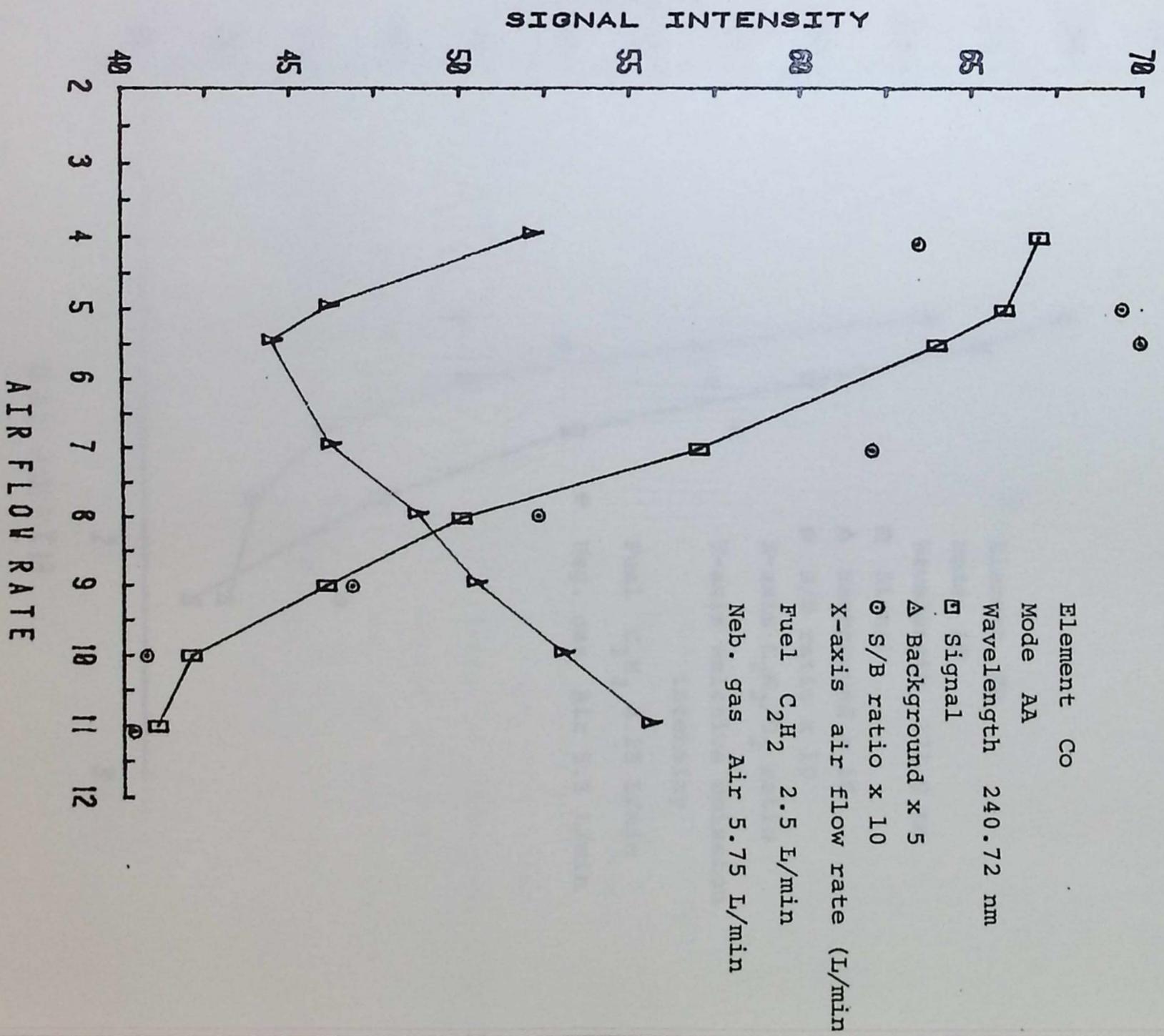
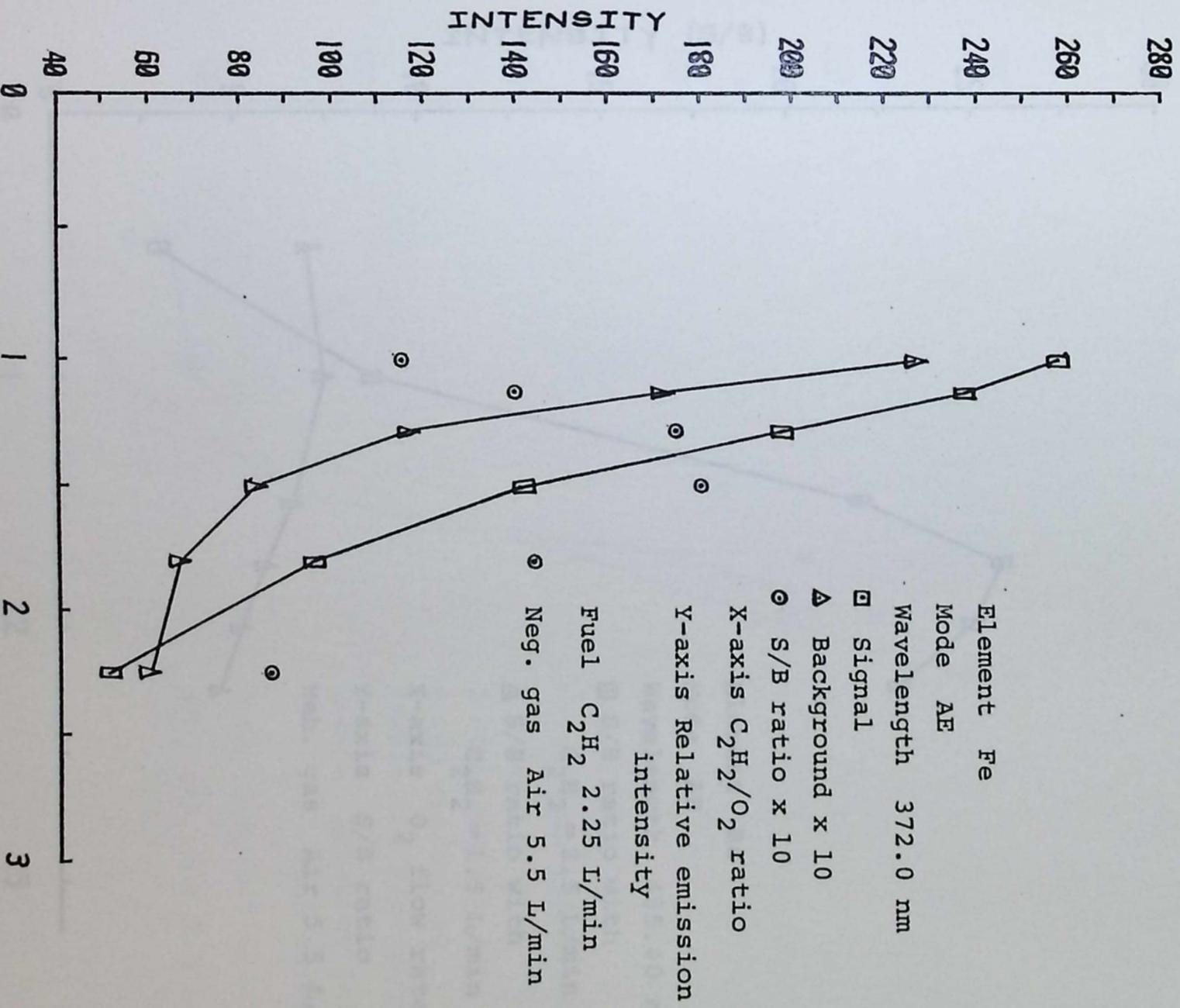


Figure 27



(A C E. / 02 ) X 10

Figure 28

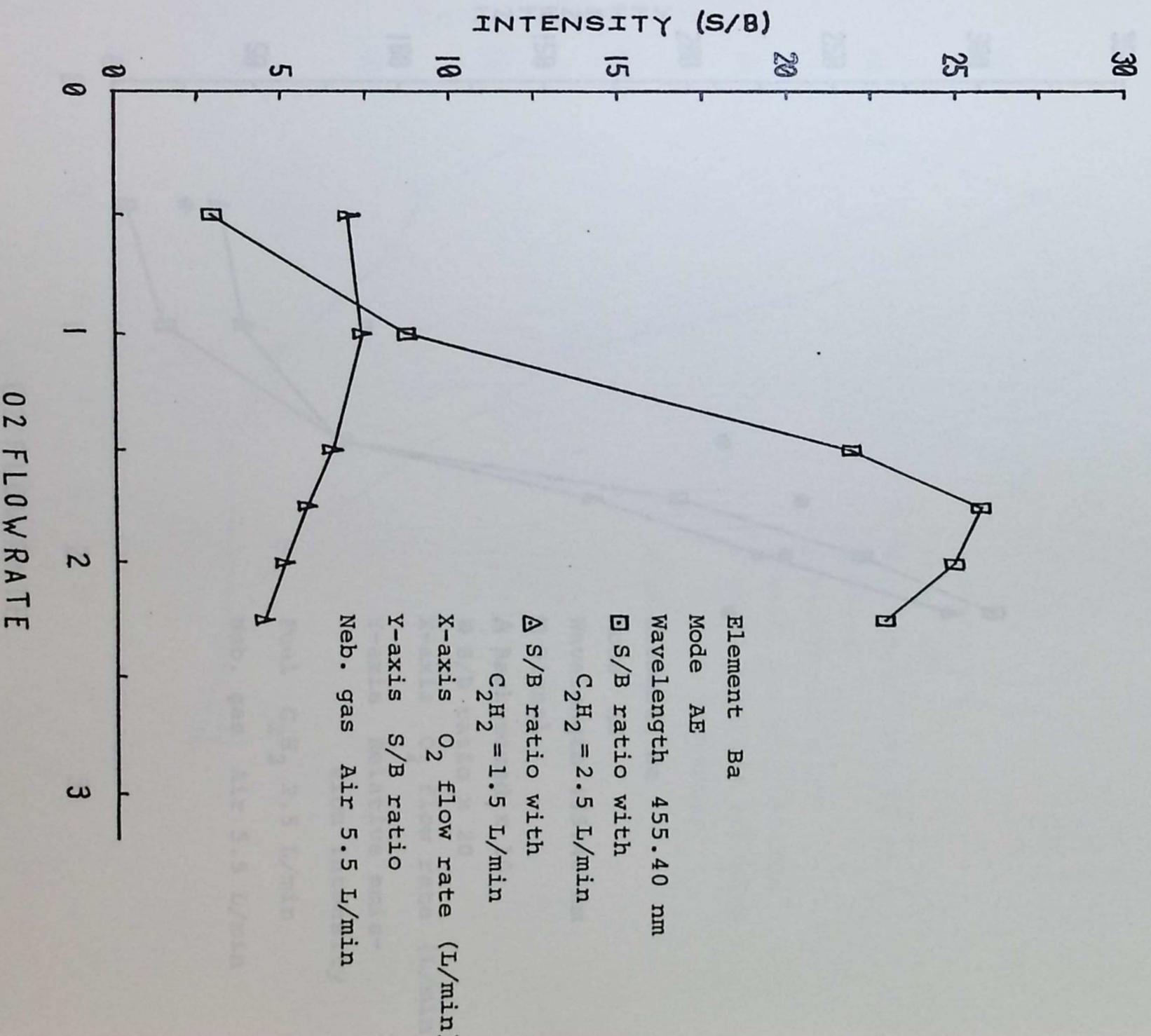
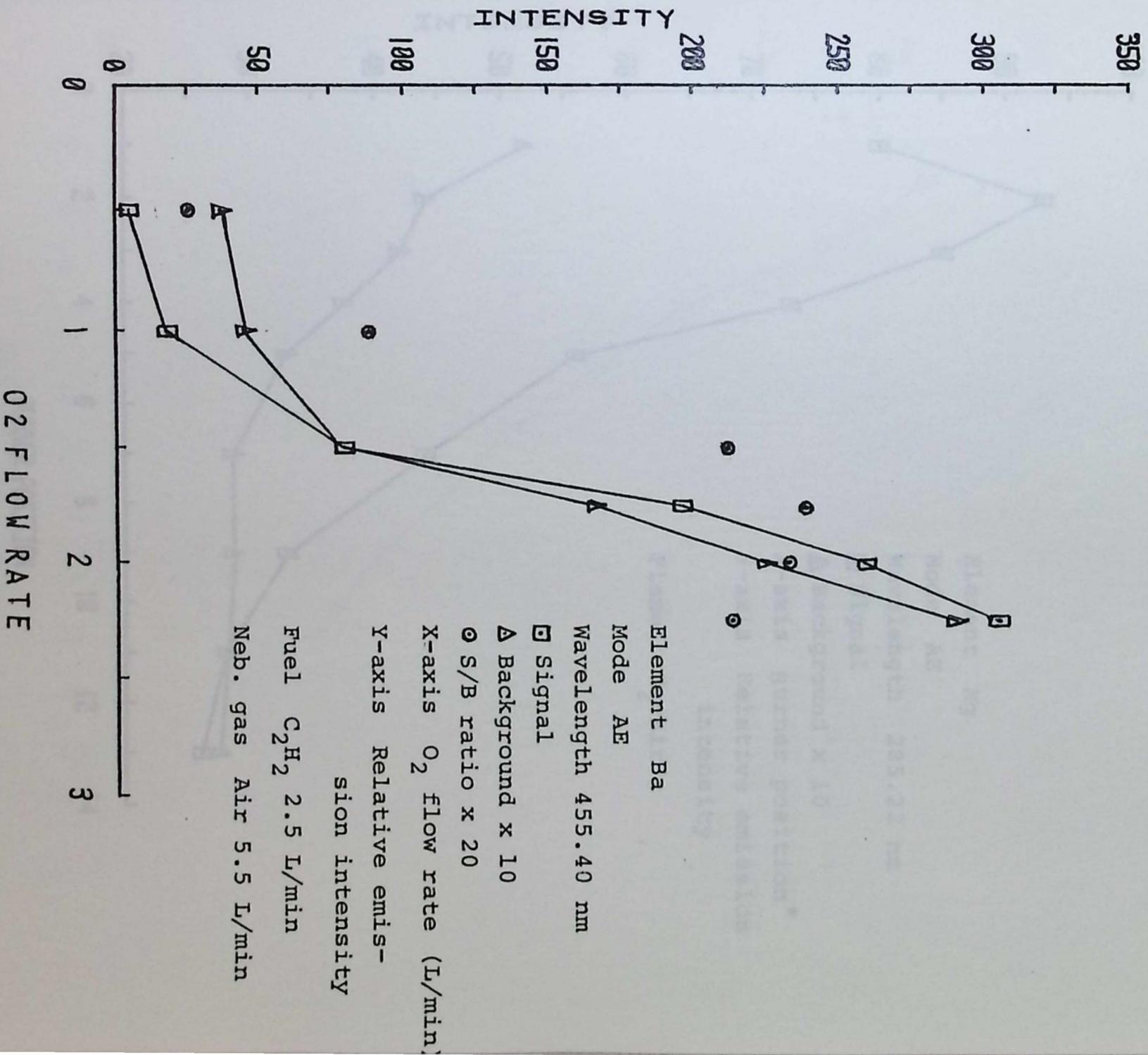


Figure 29



O<sub>2</sub> FLOW RATE  
Figure 30

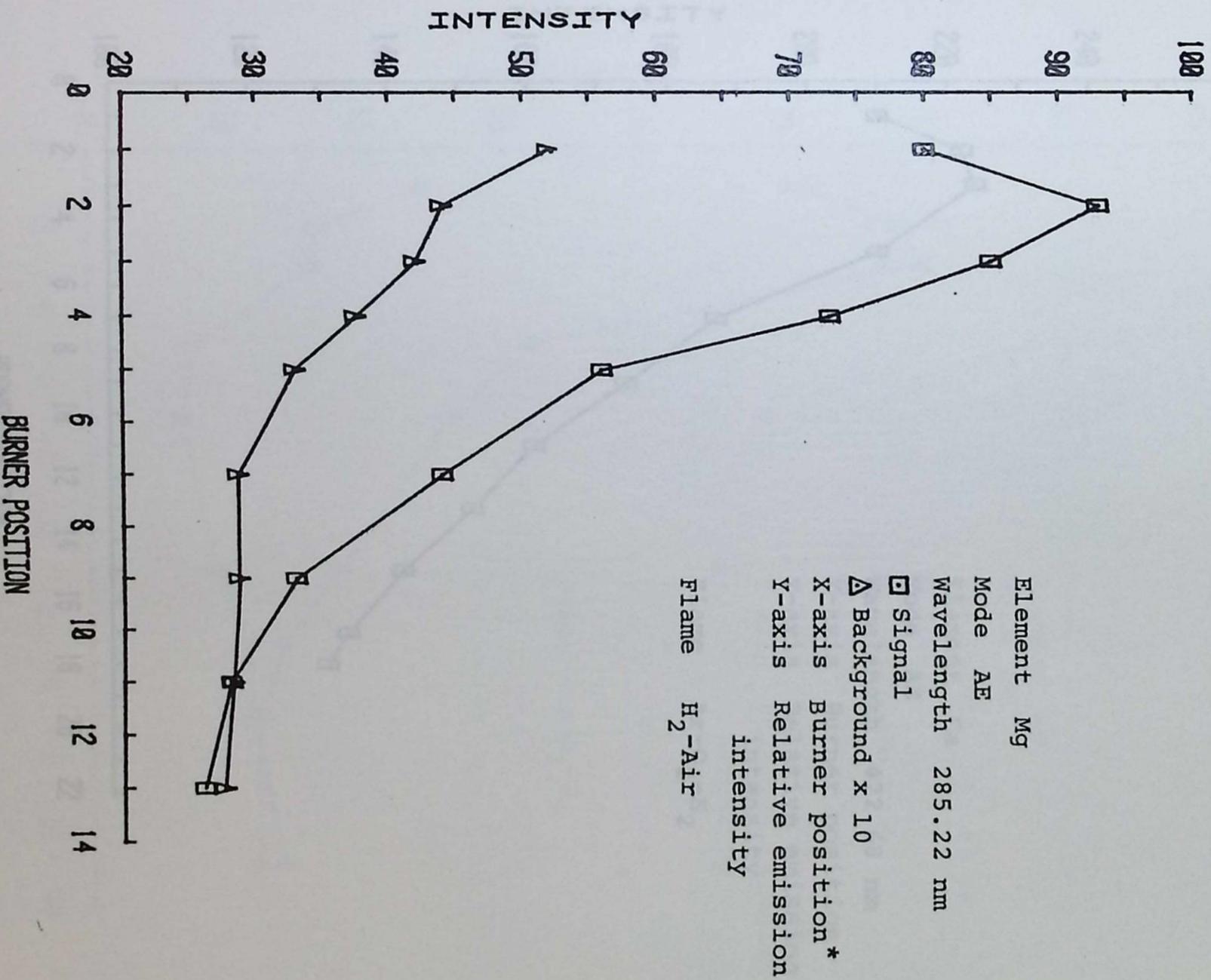
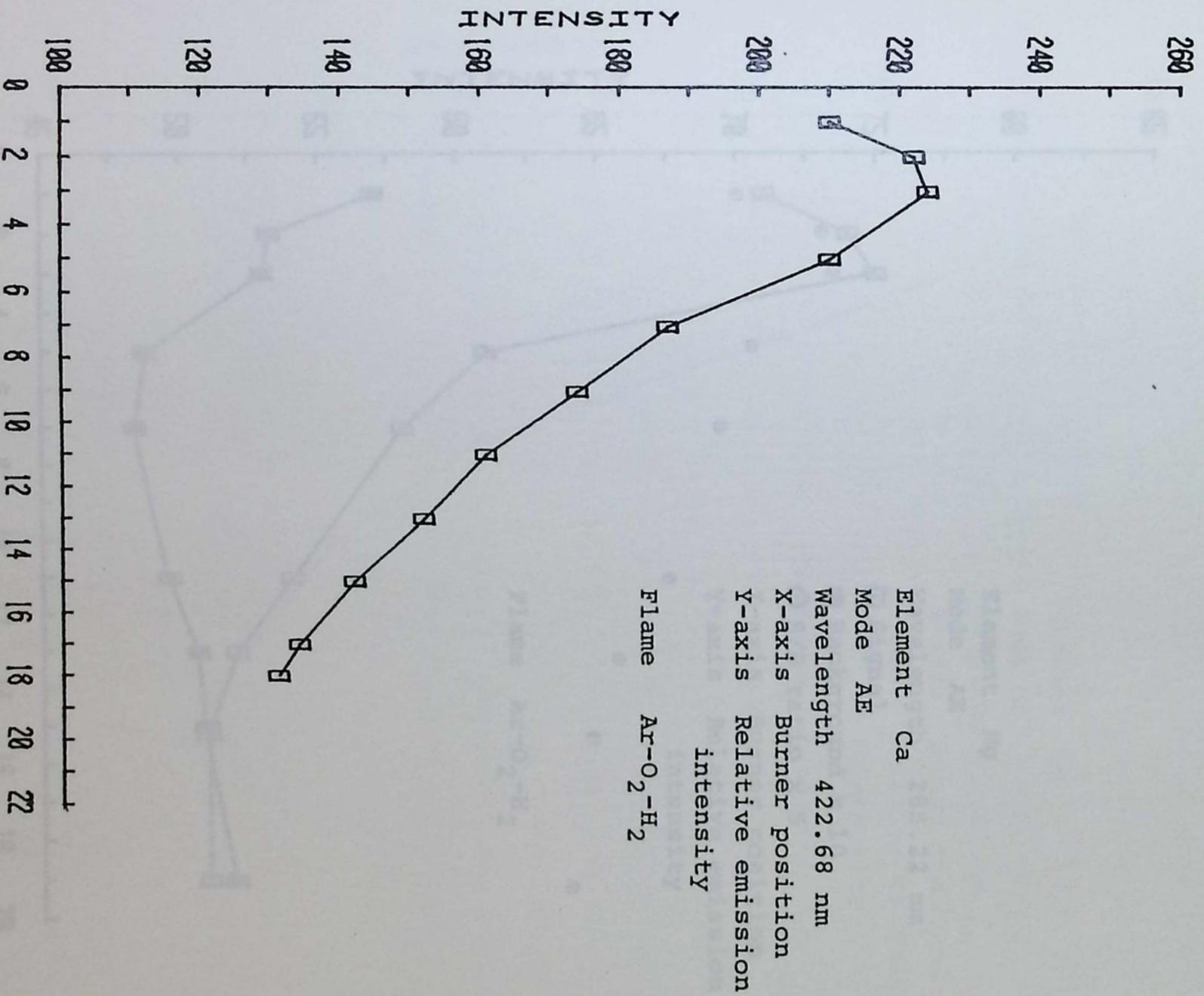


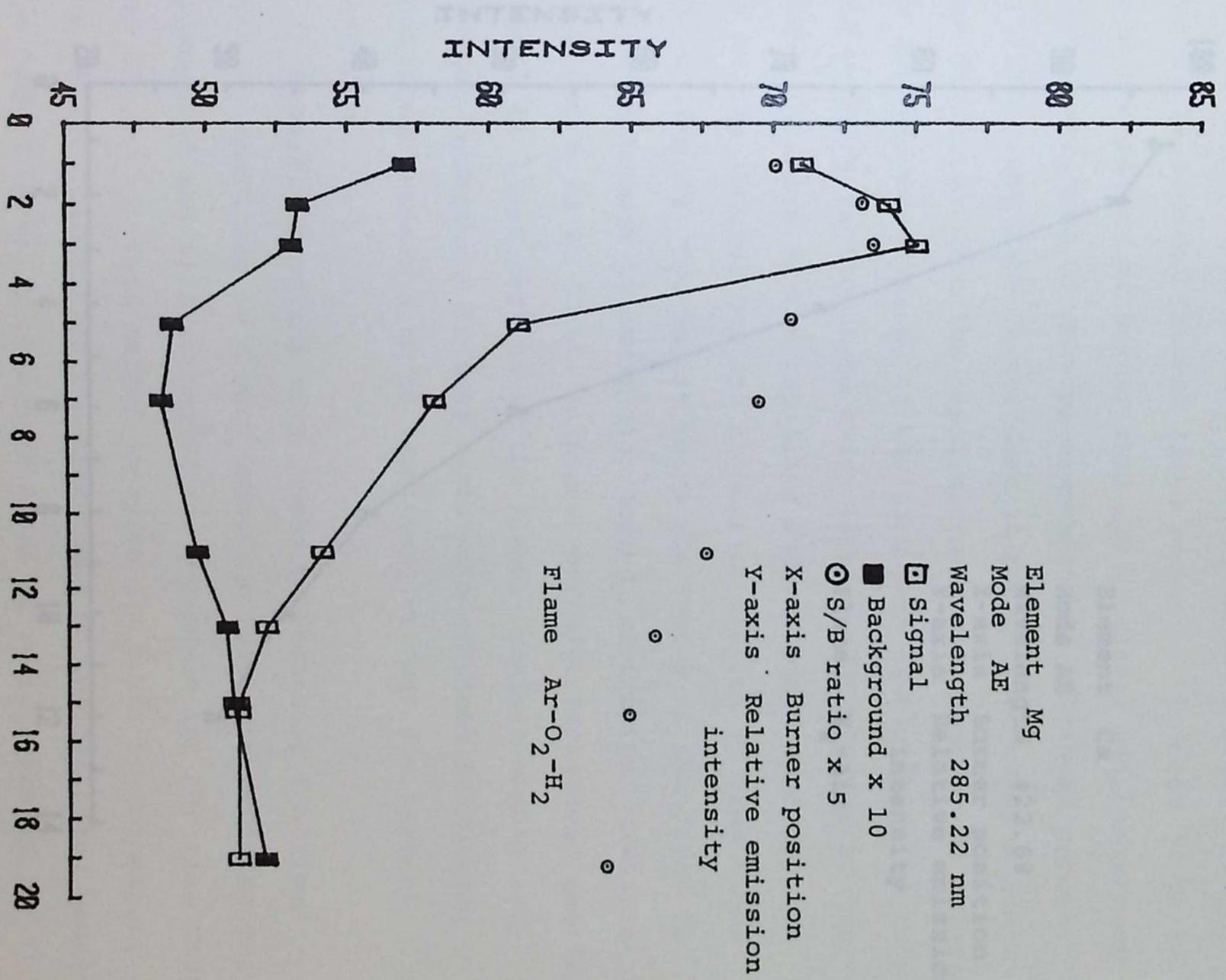
Figure 31

\* Burner positions are taken as the observation height in mm above the burner head.



BURNER POSITION

Figure 32



BURNER POSITION

Figure 33

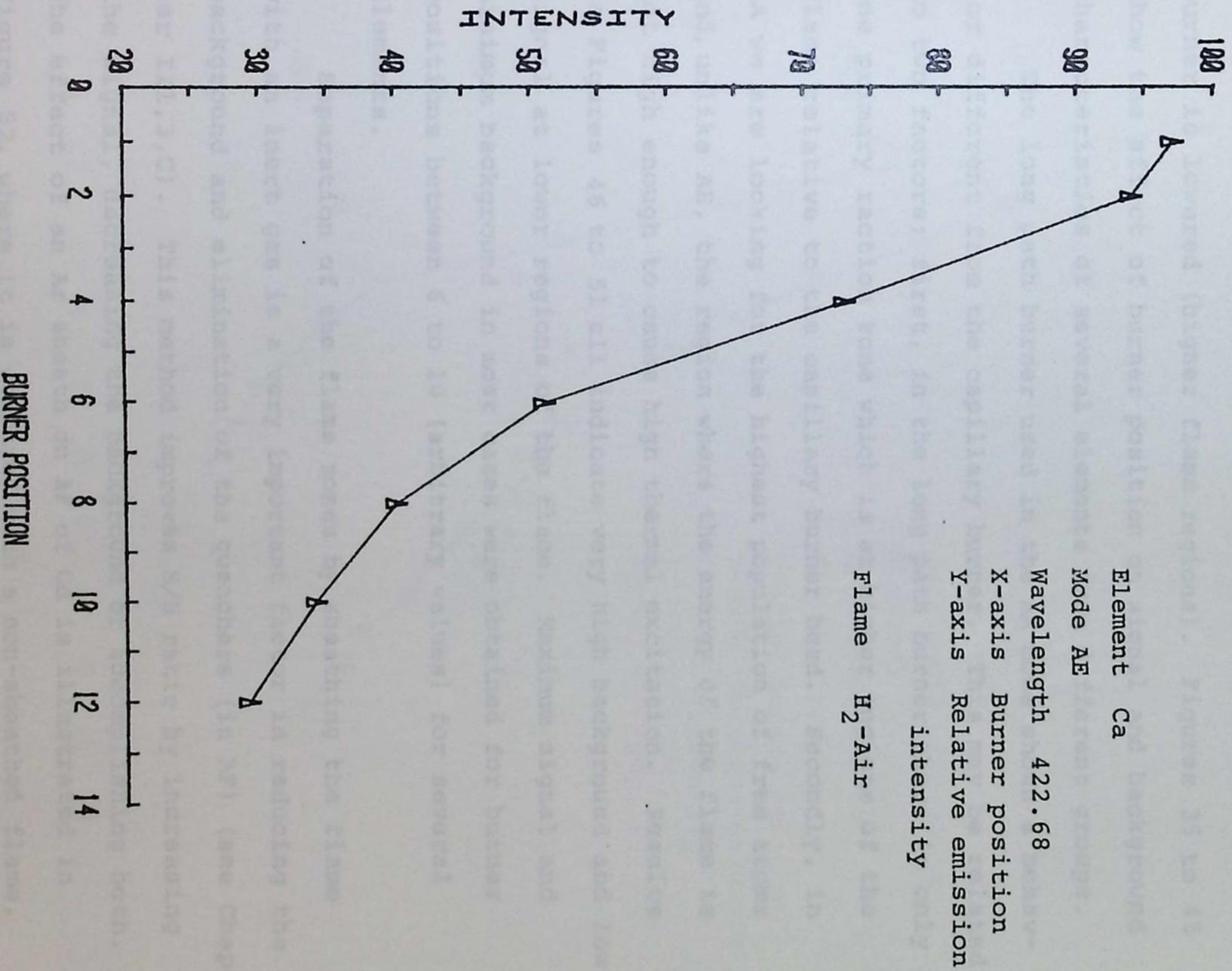


Figure 34  
BURNER POSITION

H<sub>2</sub> flames, show a large background at lower flame regions along with a large signal. S/N ratio will increase as the burner is lowered (higher flame regions). Figures 35 to 45 show the effect of burner position on signal and background characteristics of several elements from different groups.

The long path burner used in the AA mode shows a behavior different from the capillary burner. This may be related to two factors; first, in the long path burner there is only one primary reaction zone which is at higher regions of the flame relative to the capillary burner head. Secondly, in AA we are looking for the highest population of free atoms and, unlike AF, the region where the energy of the flame is not high enough to cause high thermal excitation. Results in Figures 46 to 51 all indicate very high background and low signal at lower regions of the flame. Maximum signal and minimum background in most cases were obtained for burner positions between 6 to 10 (arbitrary values) for several elements.

Separation of the flame zones by sheathing the flame with an inert gas is a very important factor in reducing the background and elimination of the quenchers (in AF) (see Chapter III,3,C). This method improves S/N ratio by increasing the signal, decreasing the background or accomplishing both. The effect of an Ar sheath on AF of Cd is illustrated in Figure 52, where it is compared with a non-sheathed flame, other conditions being the same. The results show an improvement in S/N ratio which may be discussed in terms of an

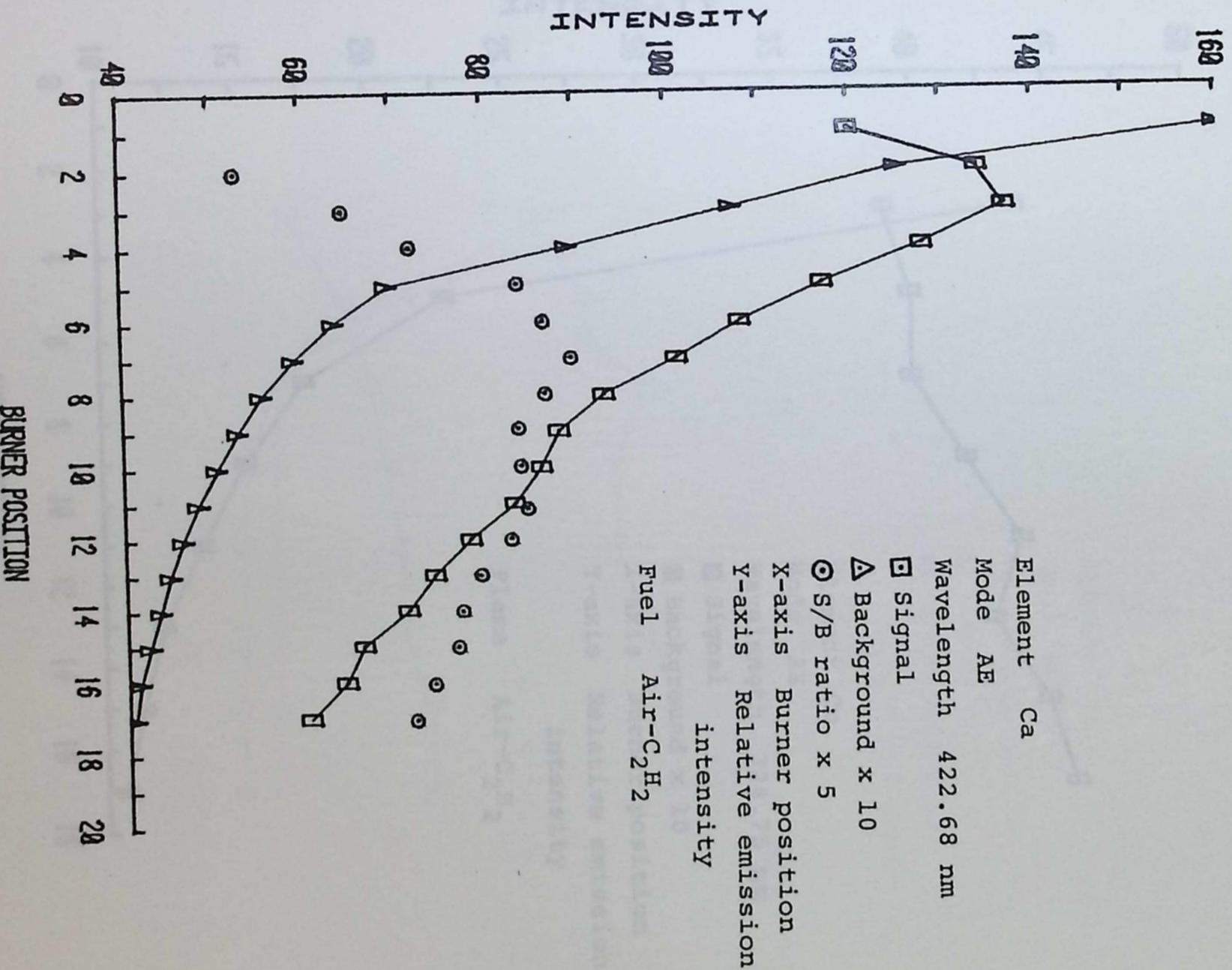


Figure 35

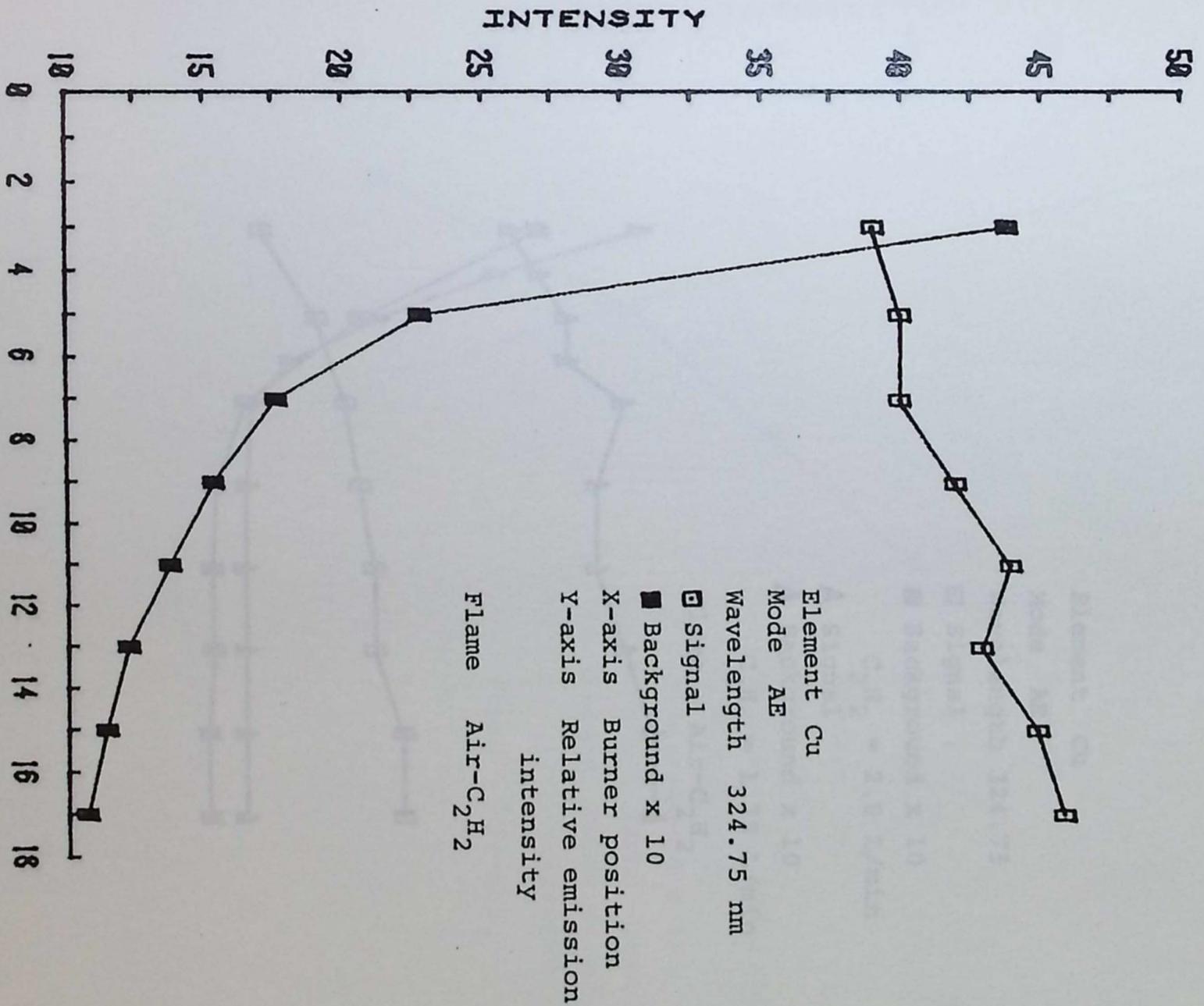
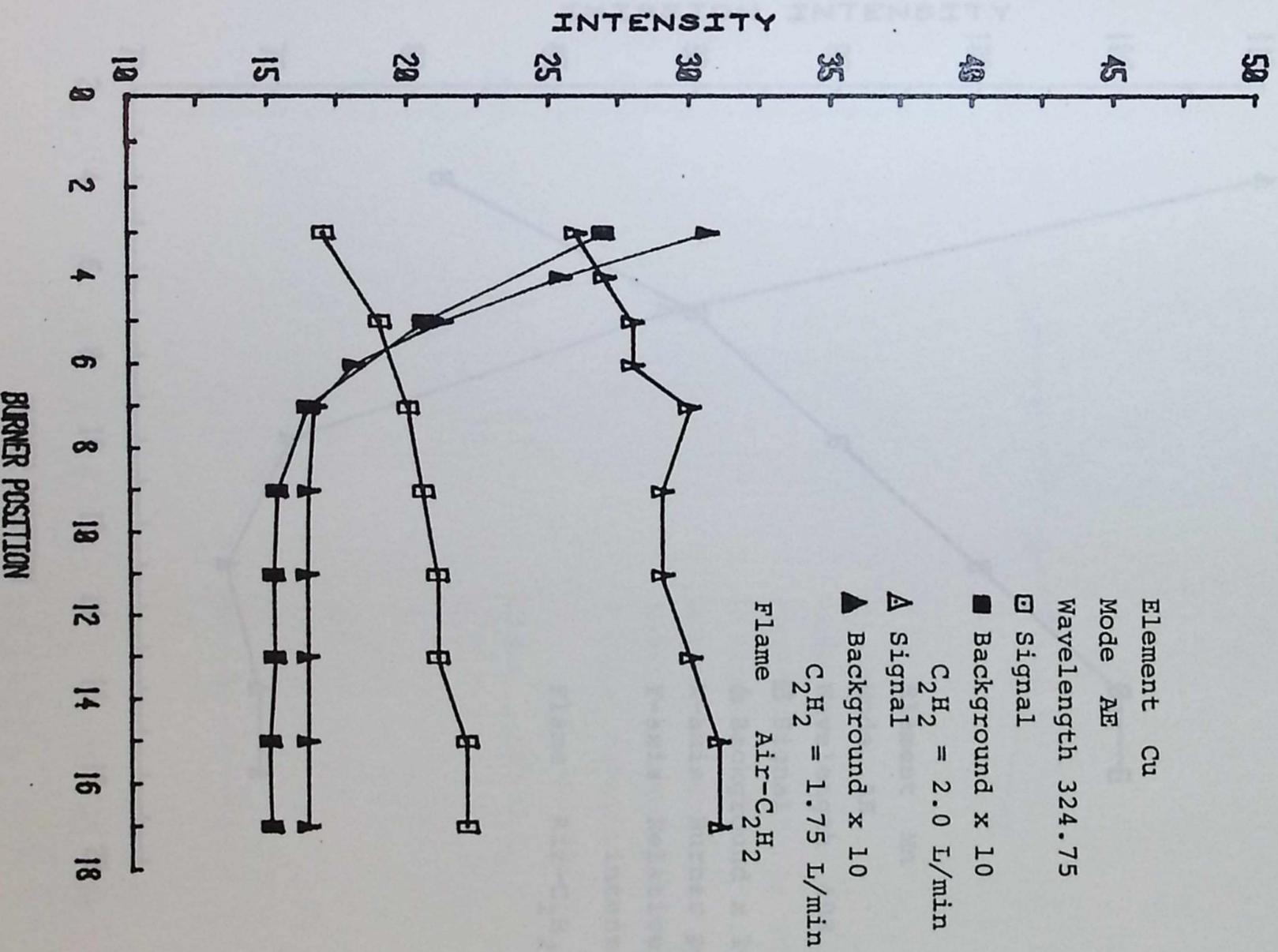


Figure 36



BURNER POSITION  
 Figure 37

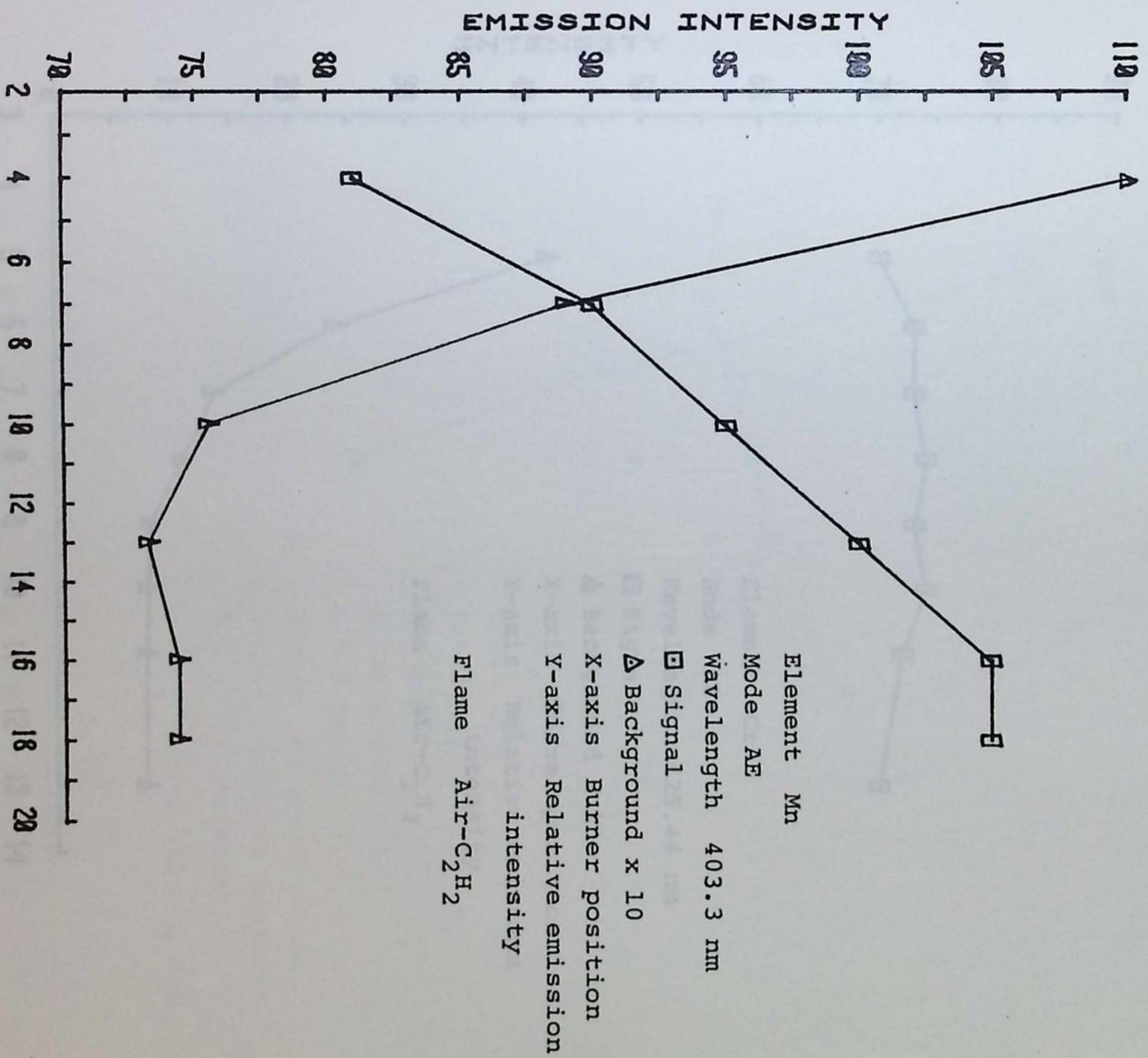


Figure 38

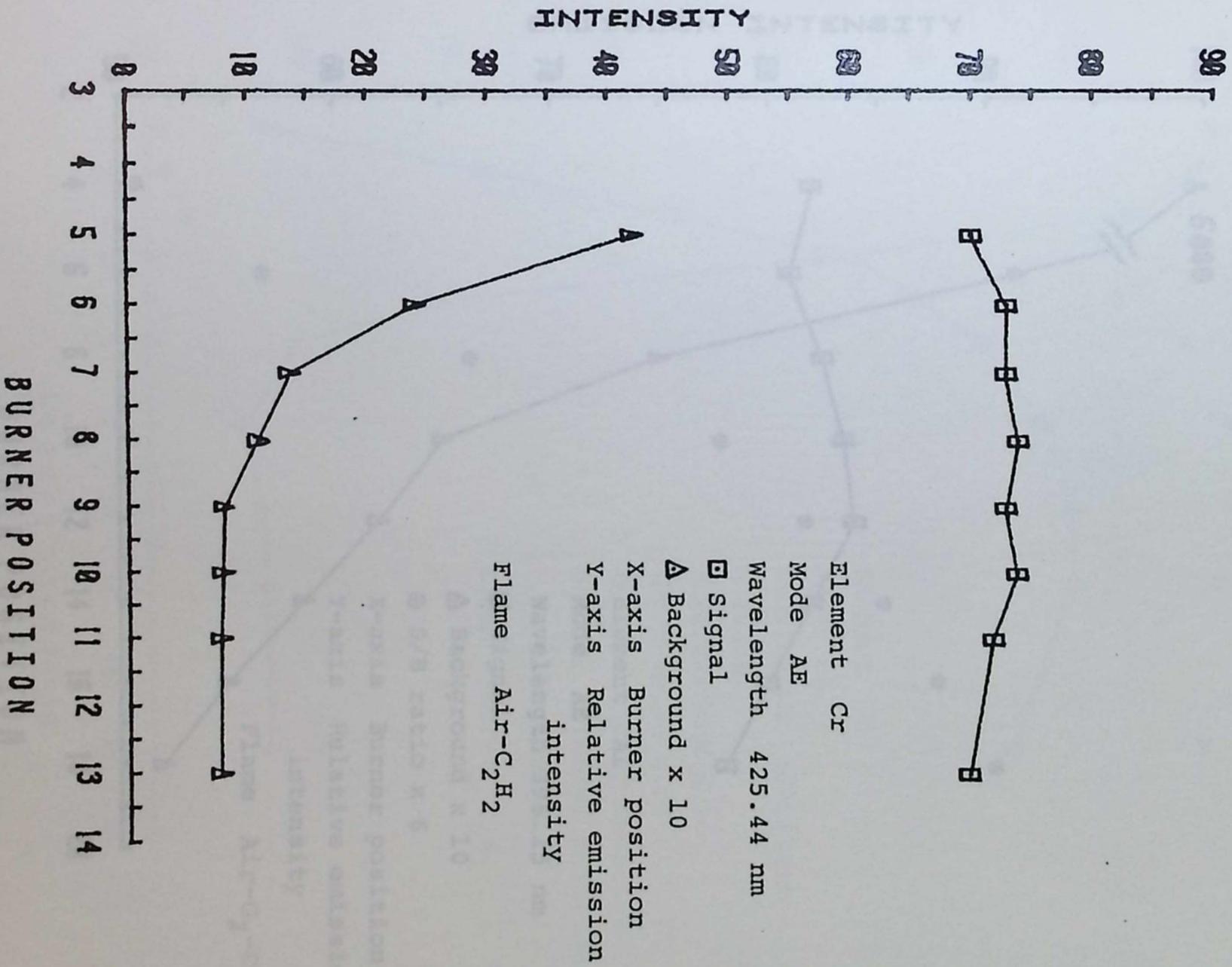


Figure 39

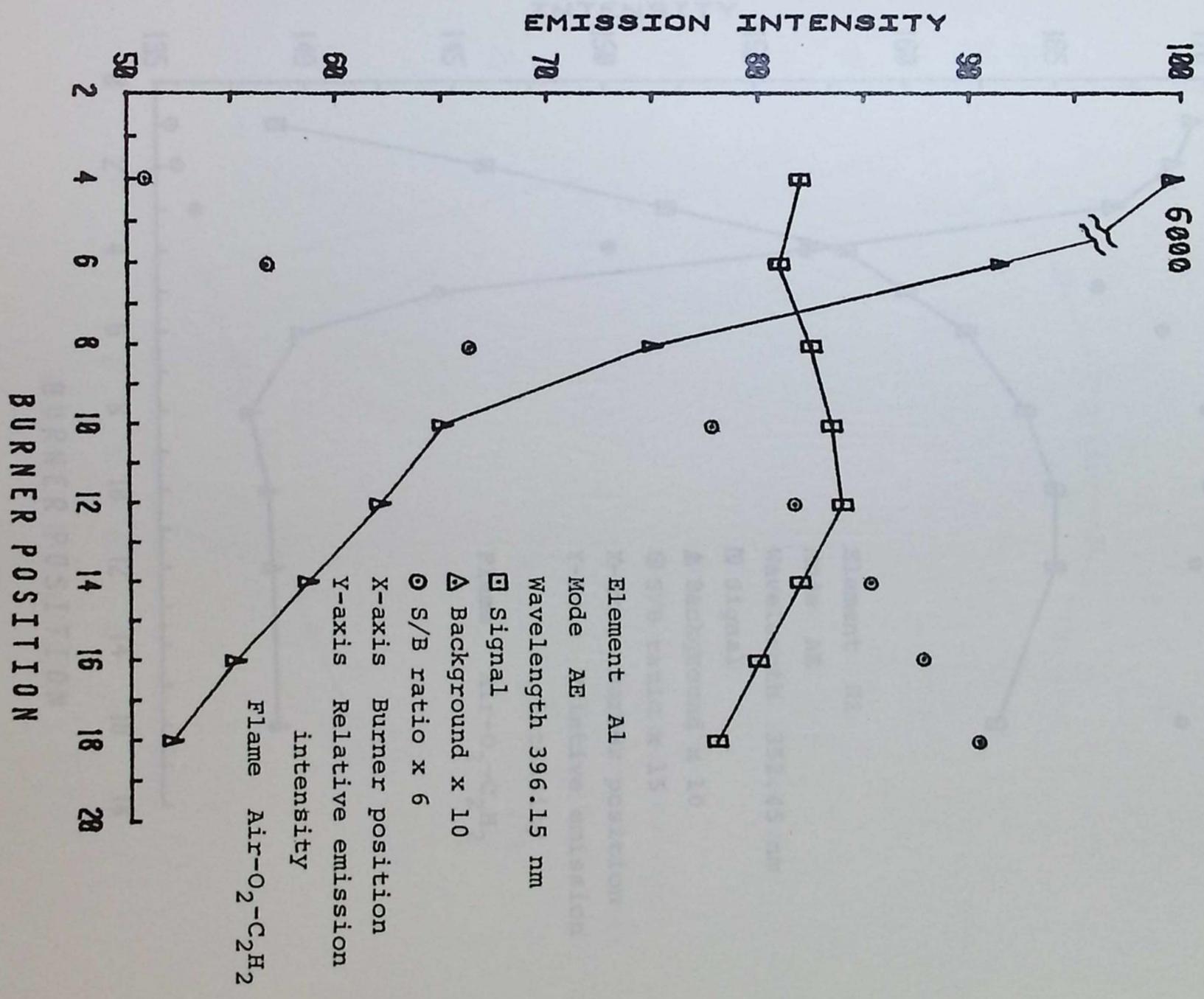


Figure 40

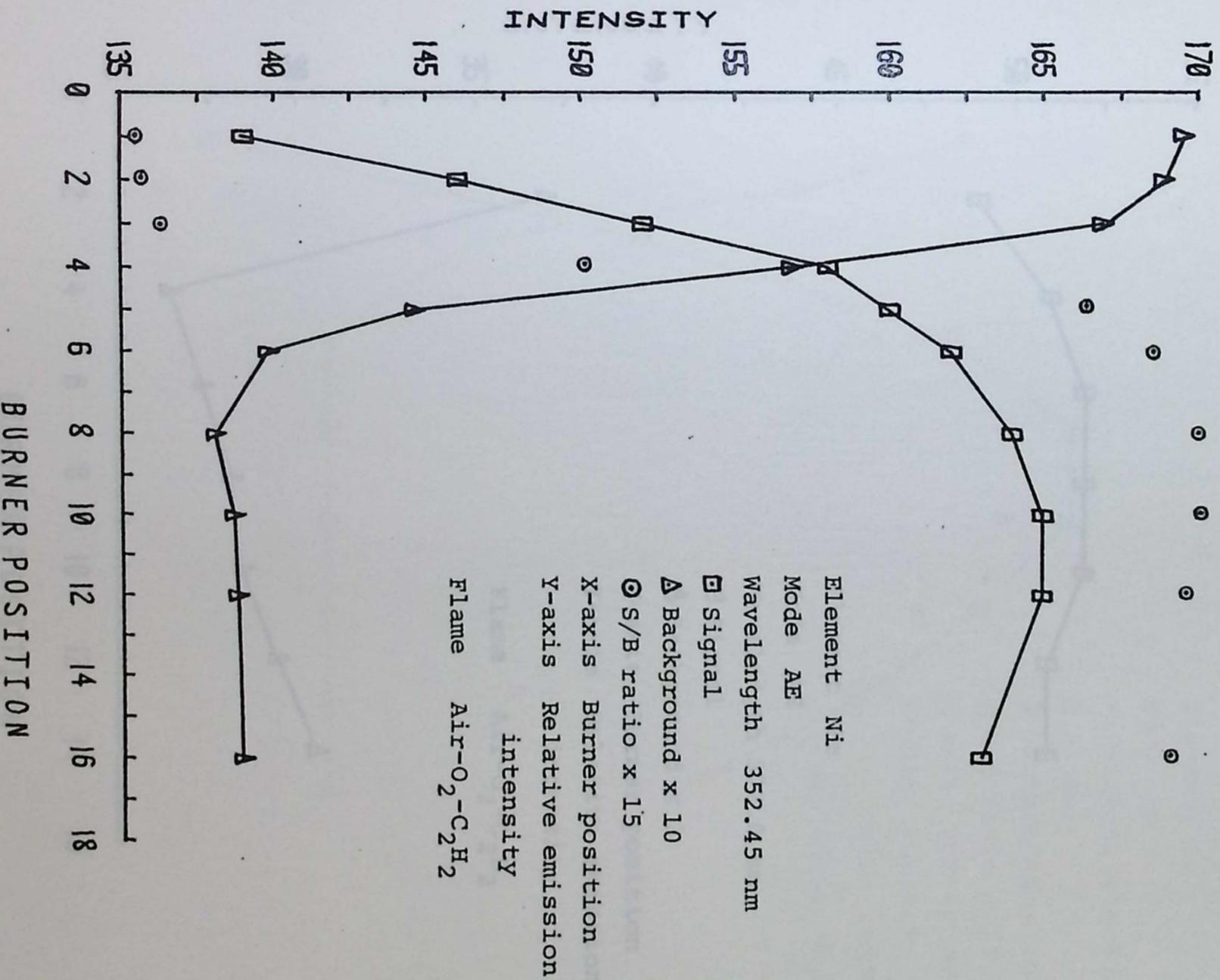


Figure 41

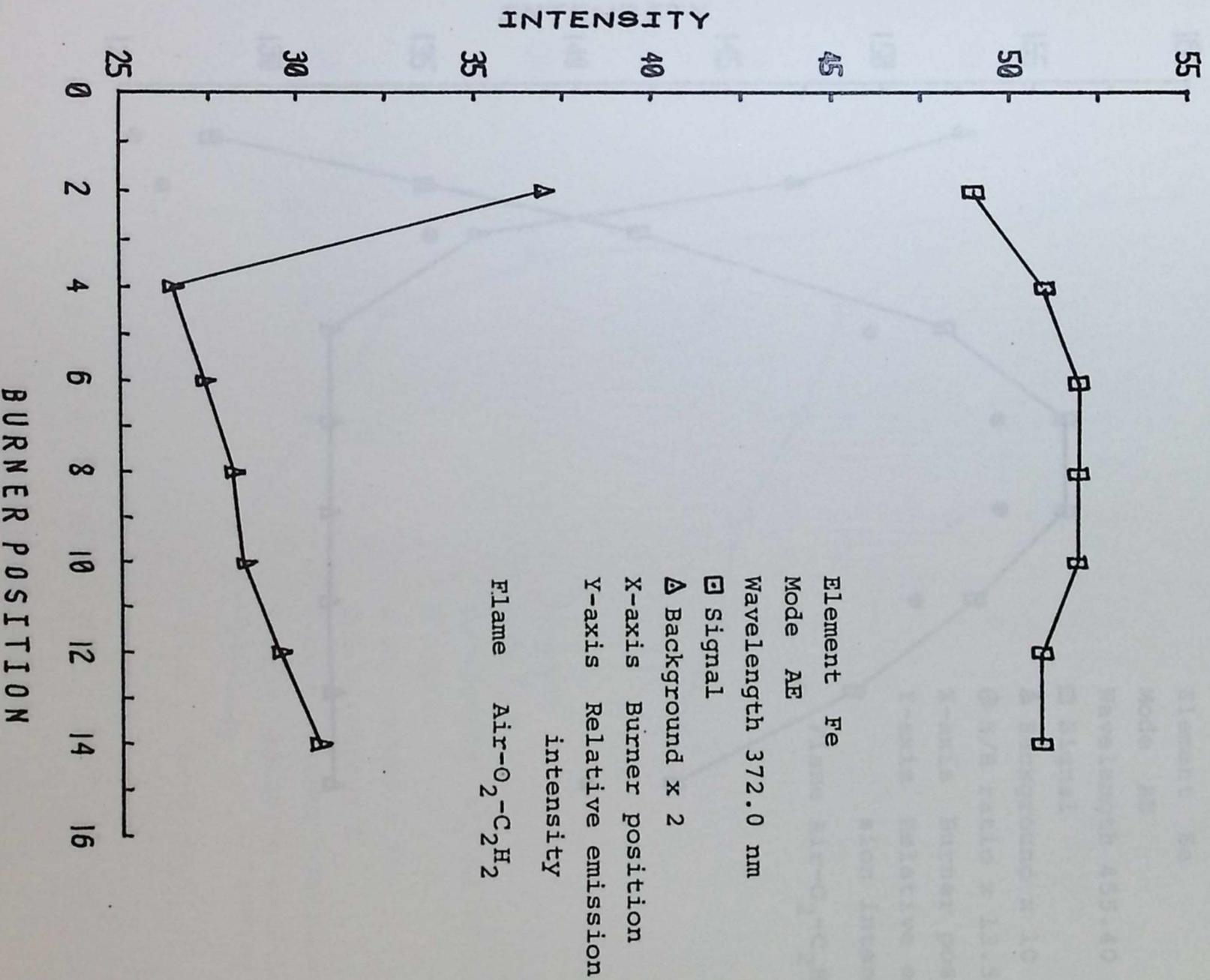


Figure 42

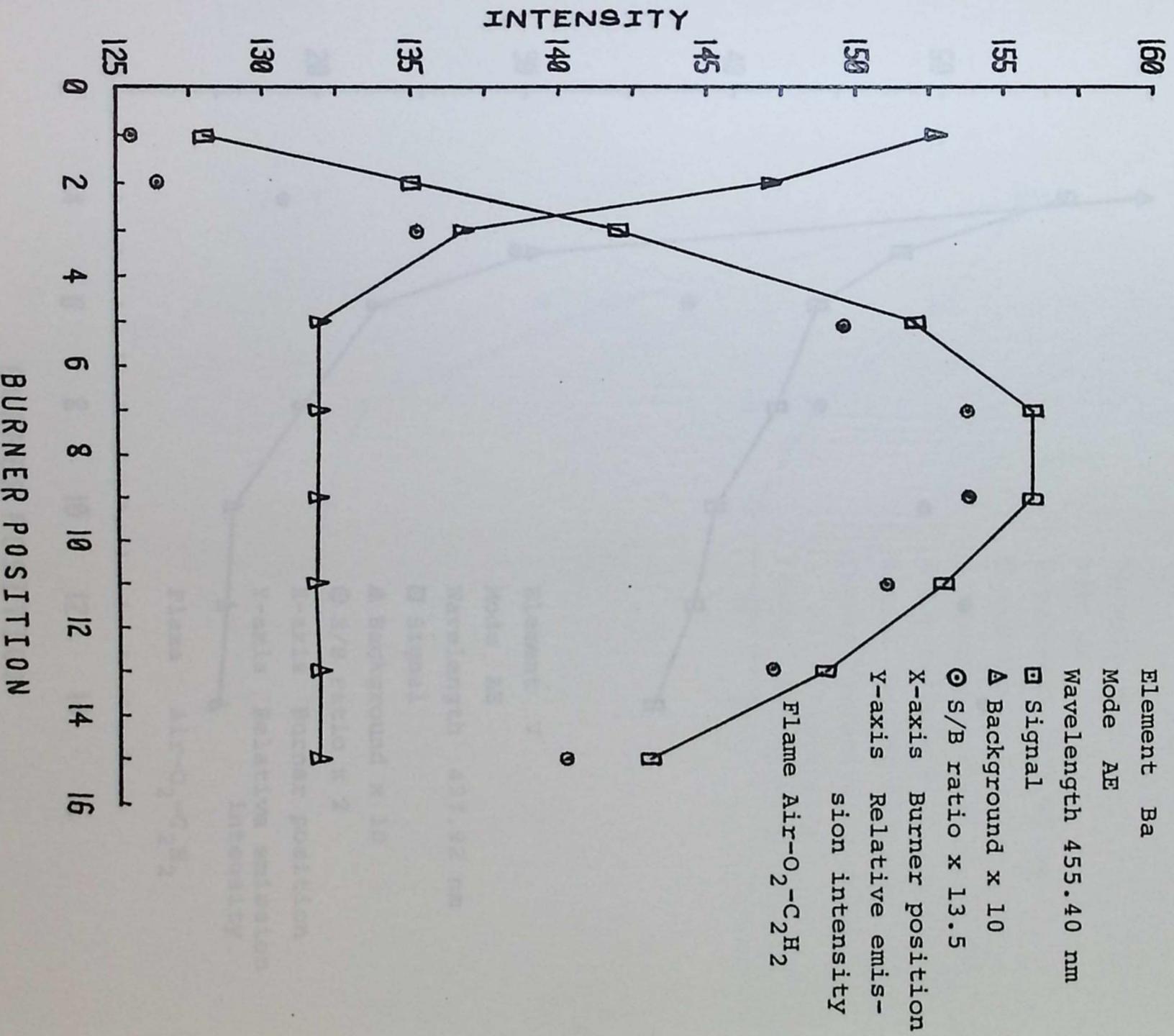


Figure 43

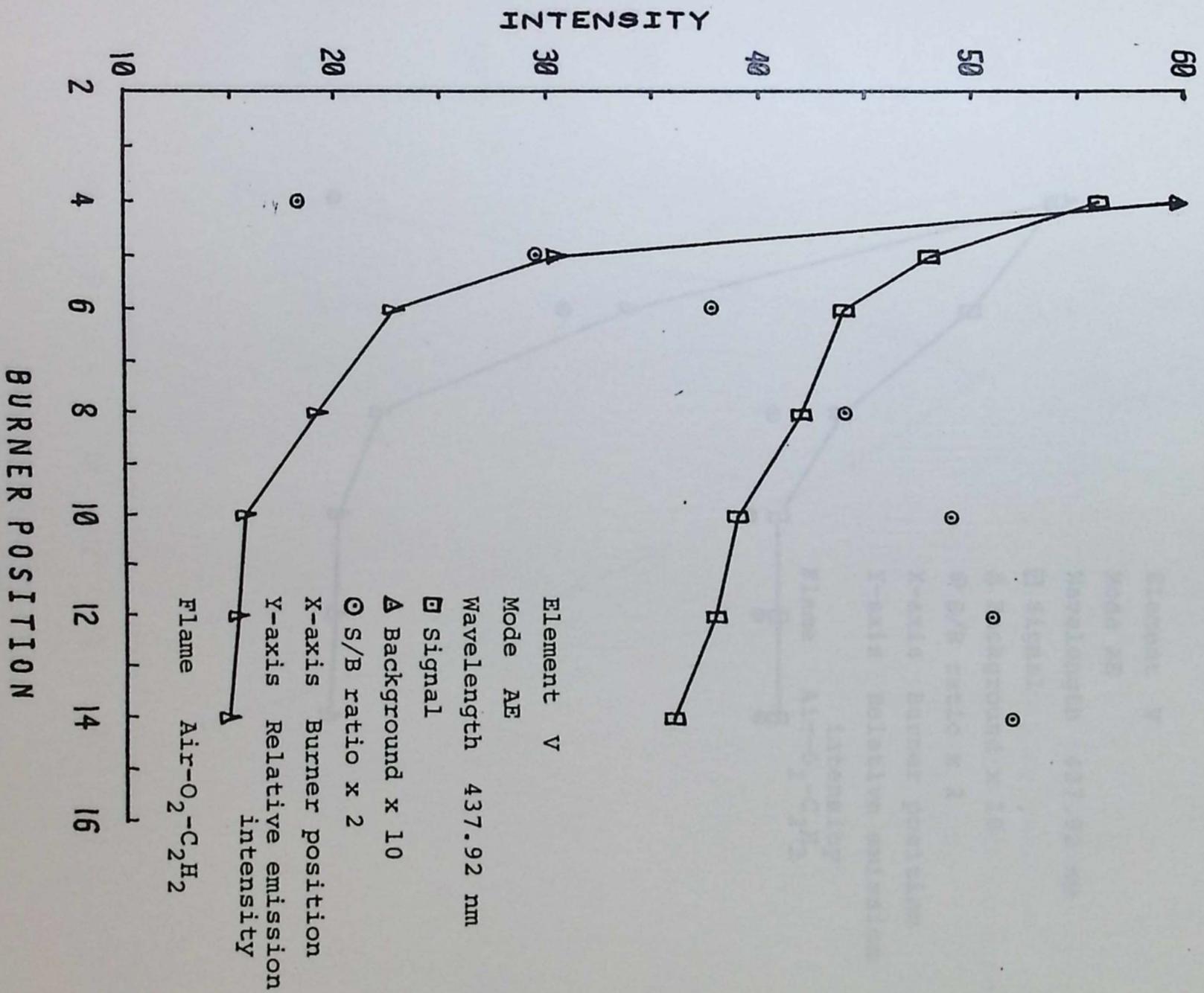


Figure 44

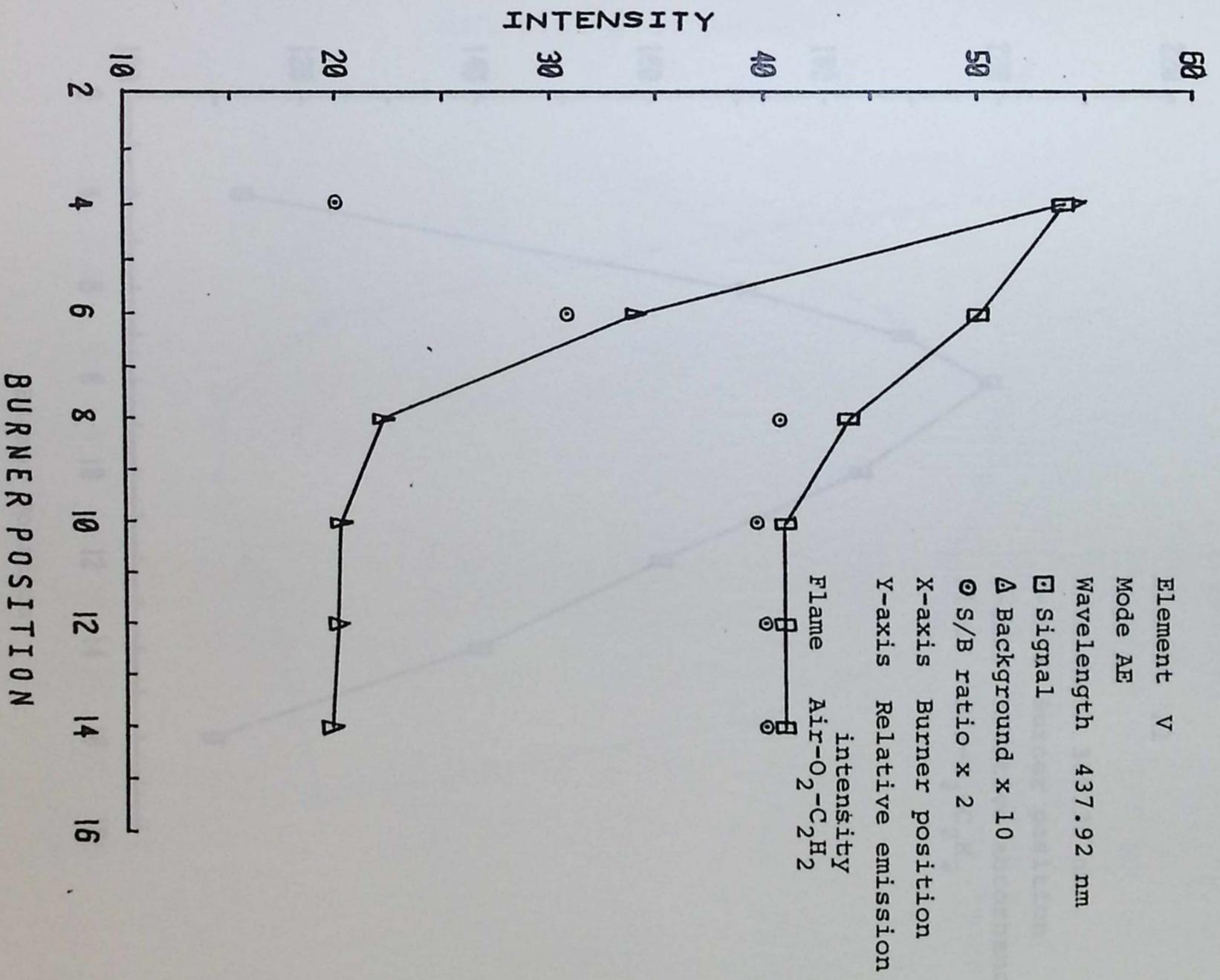


Figure 45

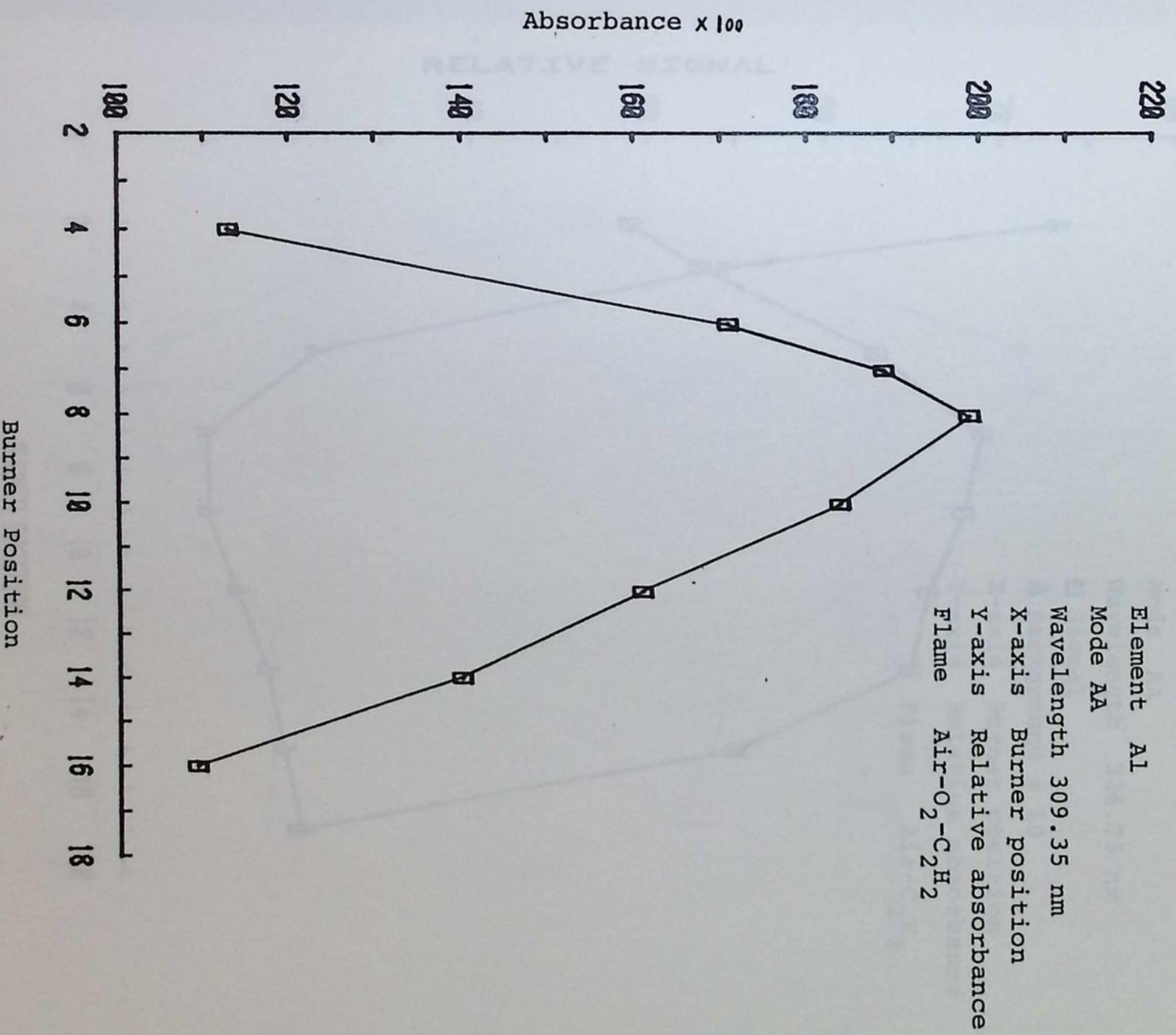
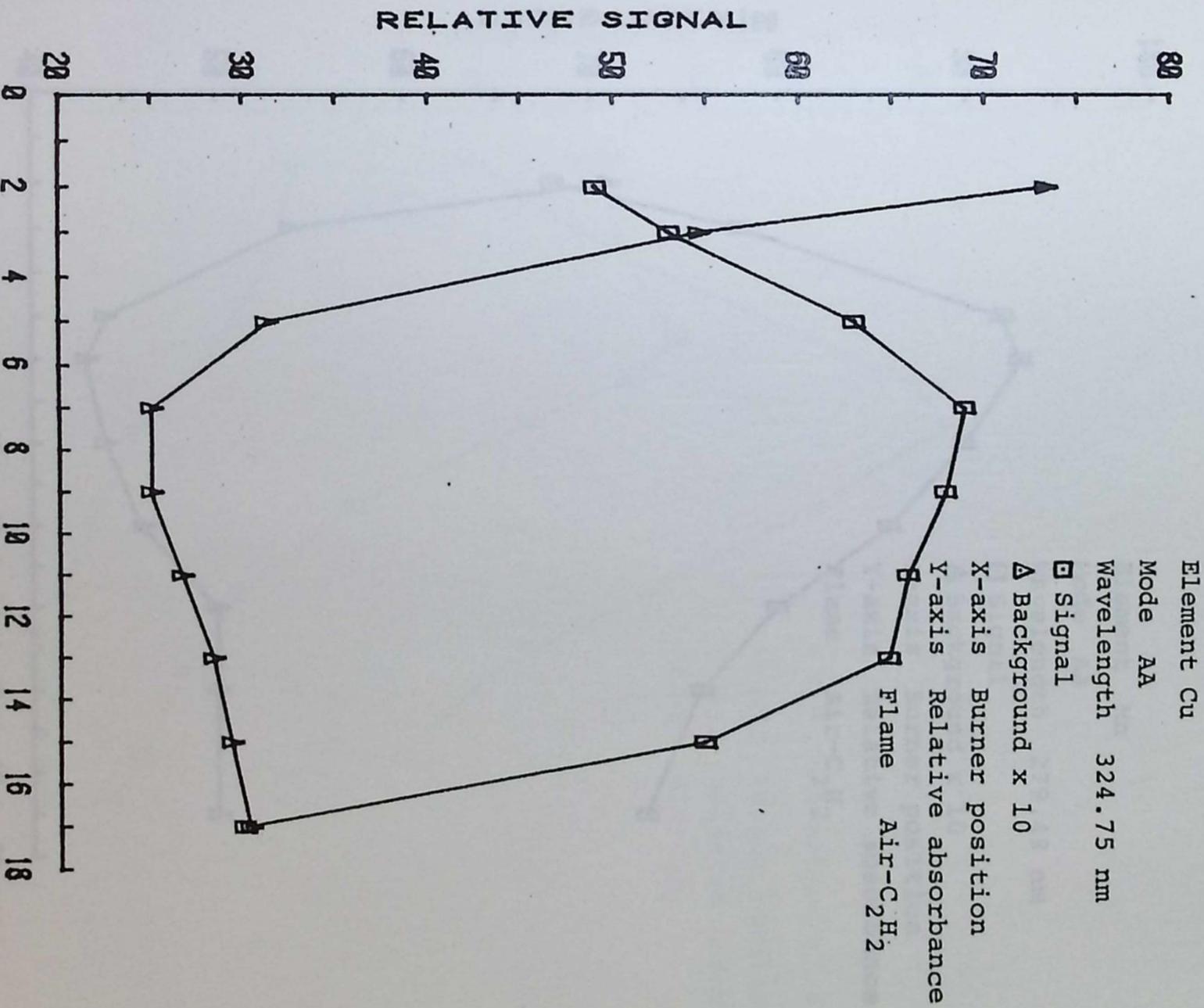


Figure 46



BURNER POSITION

Figure 47

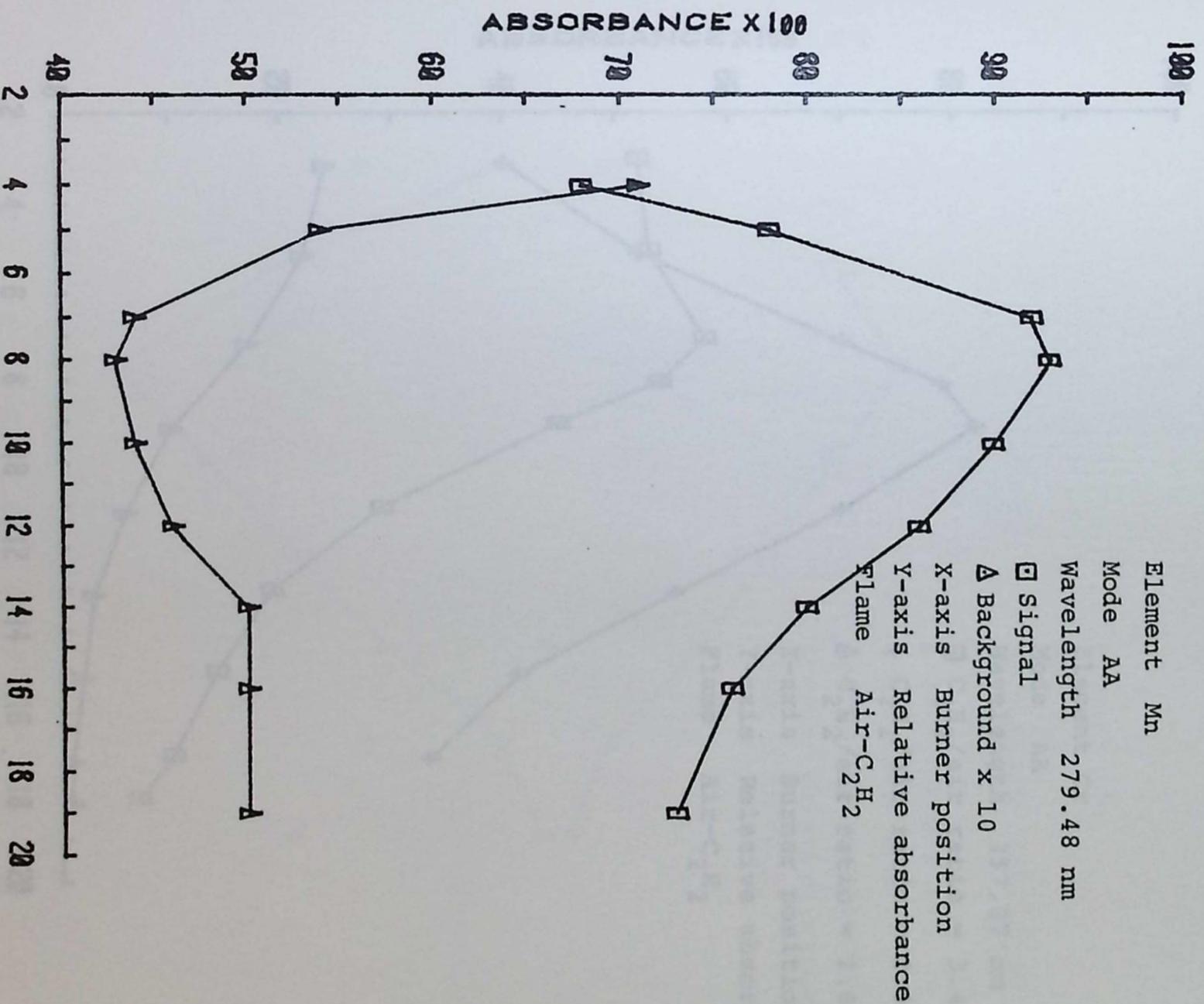


Figure 48

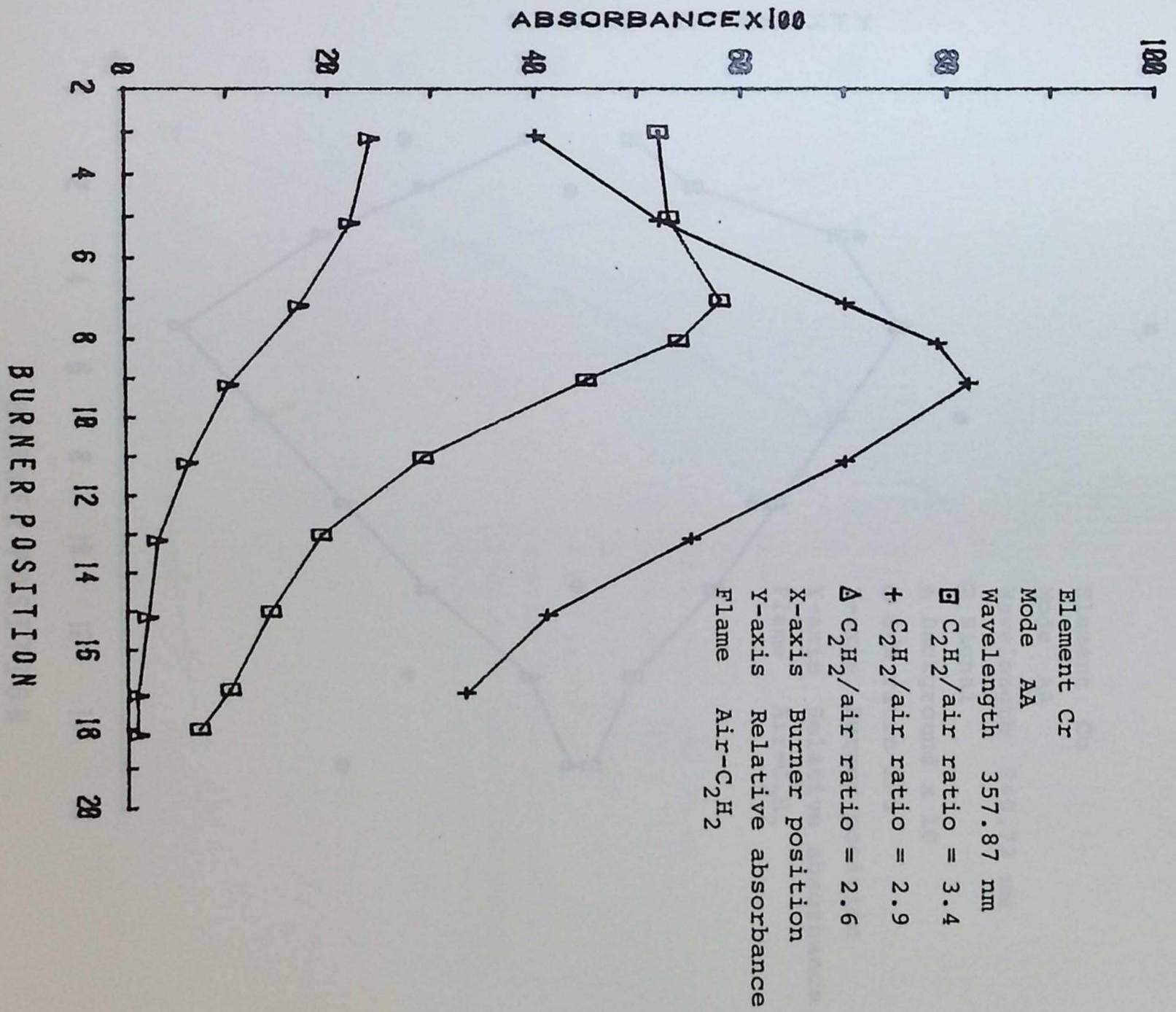


Figure 49

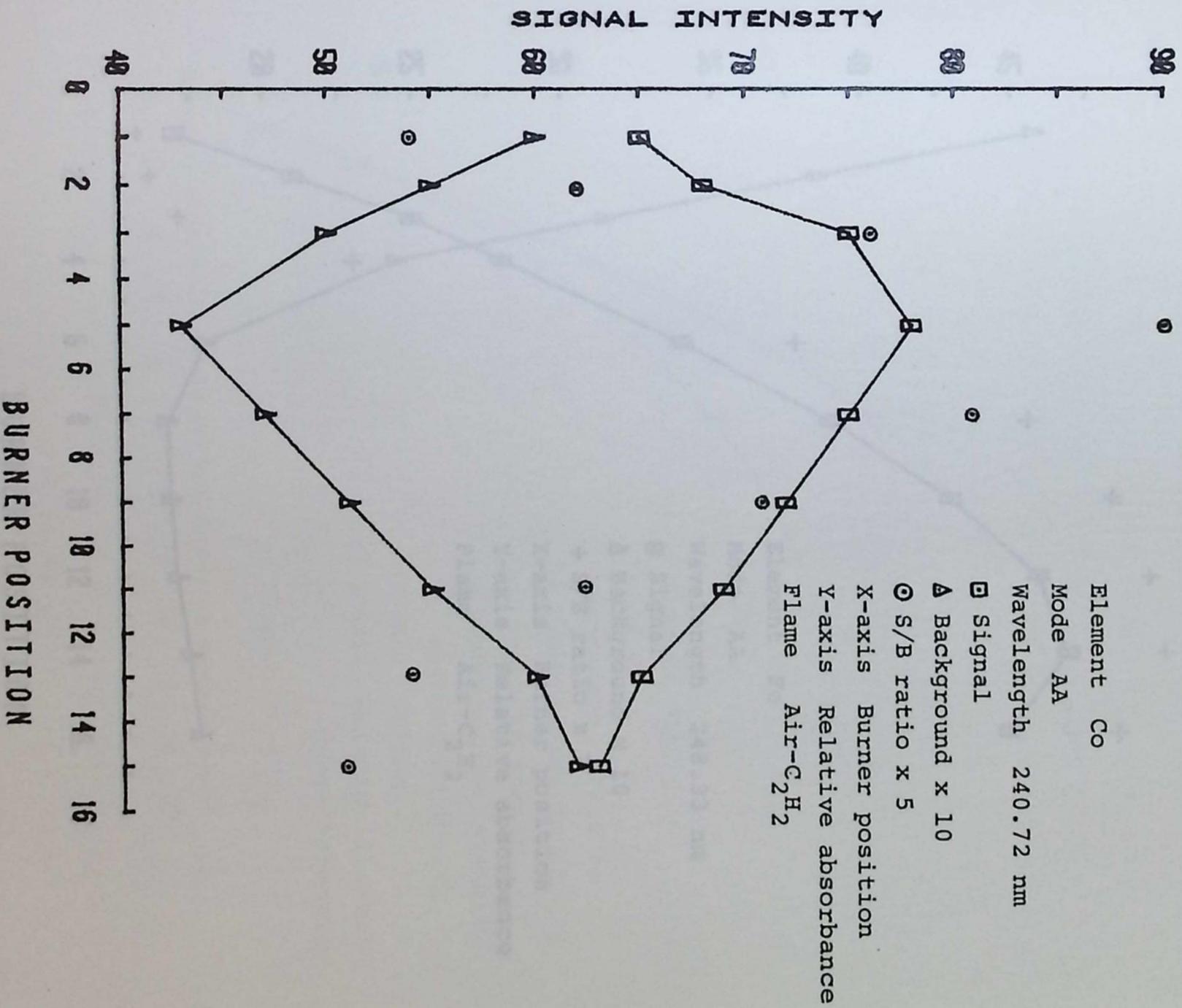


Figure 50

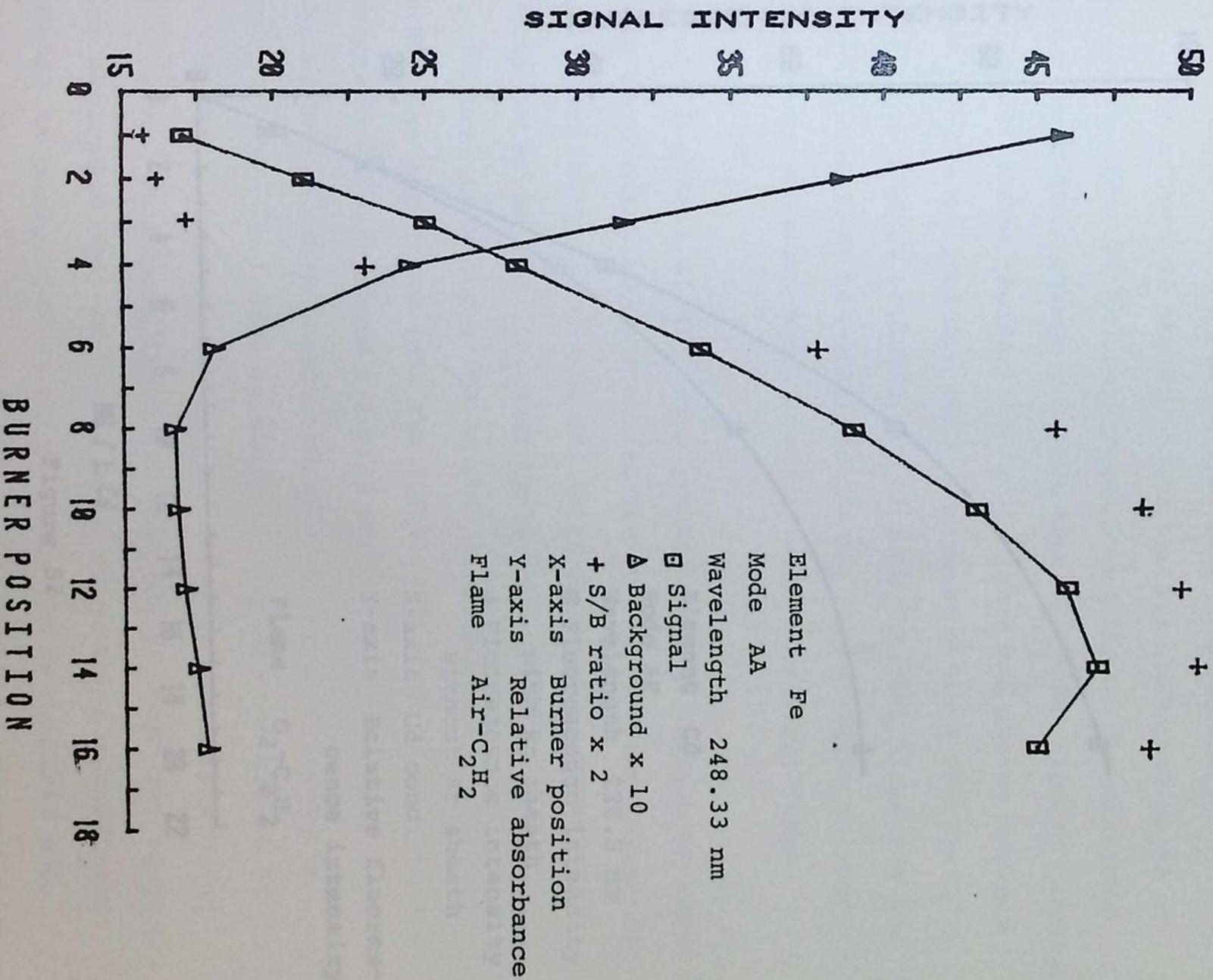


Figure 51

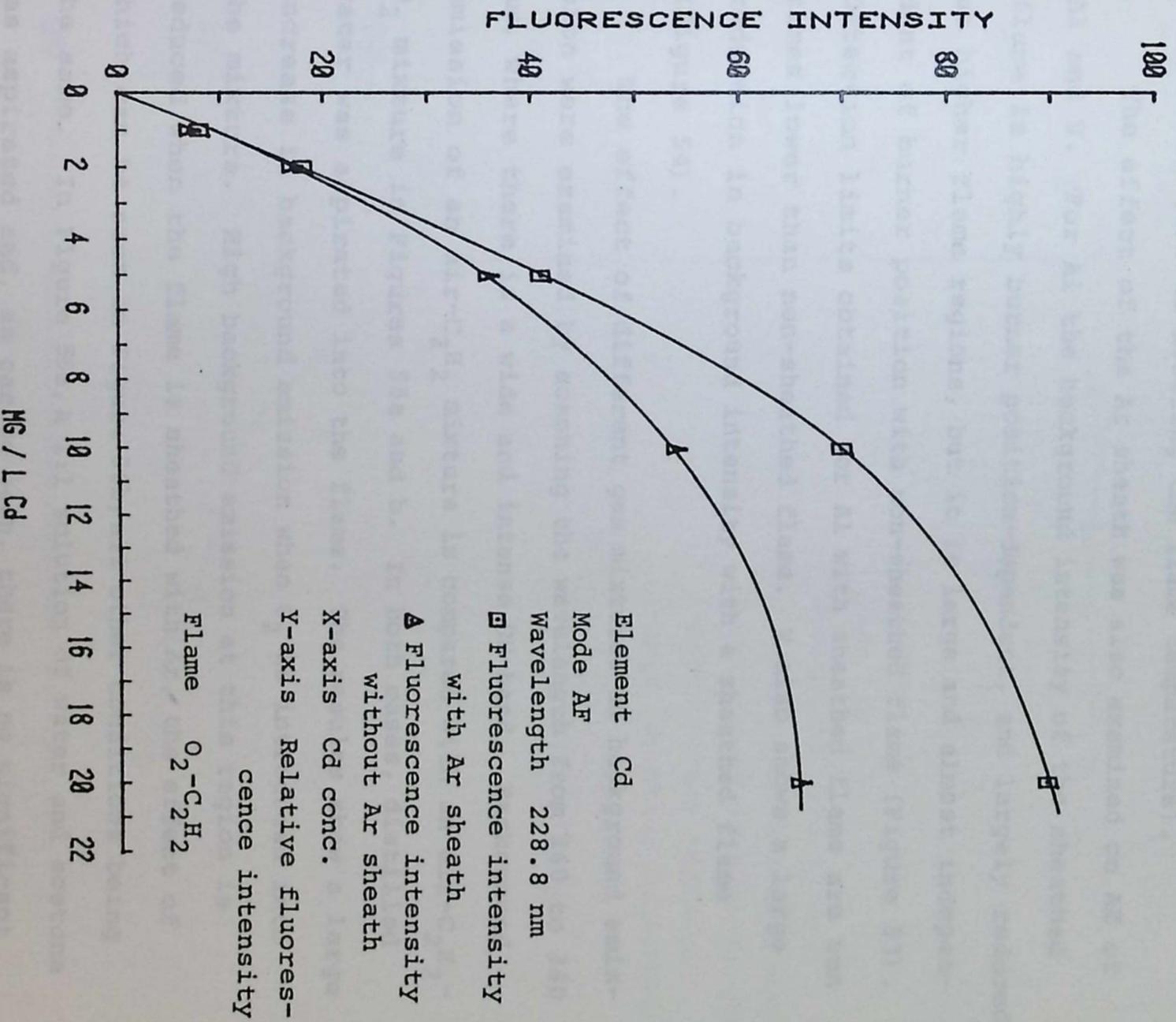


Figure 52

increase in the population of excited atoms due to decrease in concentration of quenchers and/or a decrease in thermal excitation (due to lowering the flame temperature).

The effect of the Ar sheath was also examined on AE of Al and V. For Al the background intensity of the sheathed flame is highly burner position-dependent, and largely reduced at higher flame regions, but it is large and almost independent of burner position with non-sheathed flame (Figure 53). Detection limits obtained for Al with sheathed flame are ten times lower than non-sheathed flame. V also shows a large reduction in background intensity with a sheathed flame (Figure 54).

The effect of different gas mixtures on background emission were examined by scanning the wavelength from 260 to 360 nm, where there is a wide and intense OH band. Background emission of an air-C<sub>2</sub>H<sub>2</sub> mixture is compared with an air-C<sub>2</sub>H<sub>2</sub>-O<sub>2</sub> mixture in Figures 55a and b. In both cases, distilled water was aspirated into the flame. The results show a large increase in background emission when O<sub>2</sub> is introduced into the mixture. High background emission at this region is reduced when the flame is sheathed with Ar, the effect of which can be seen in Figure 56b, all other conditions being the same. In Figure 56a, a 1:1 solution of water and acetone was aspirated and, as can be seen, there is no significant change in background emission. This can be compared with Figure 57b, where the Ar sheath was eliminated. A comparison

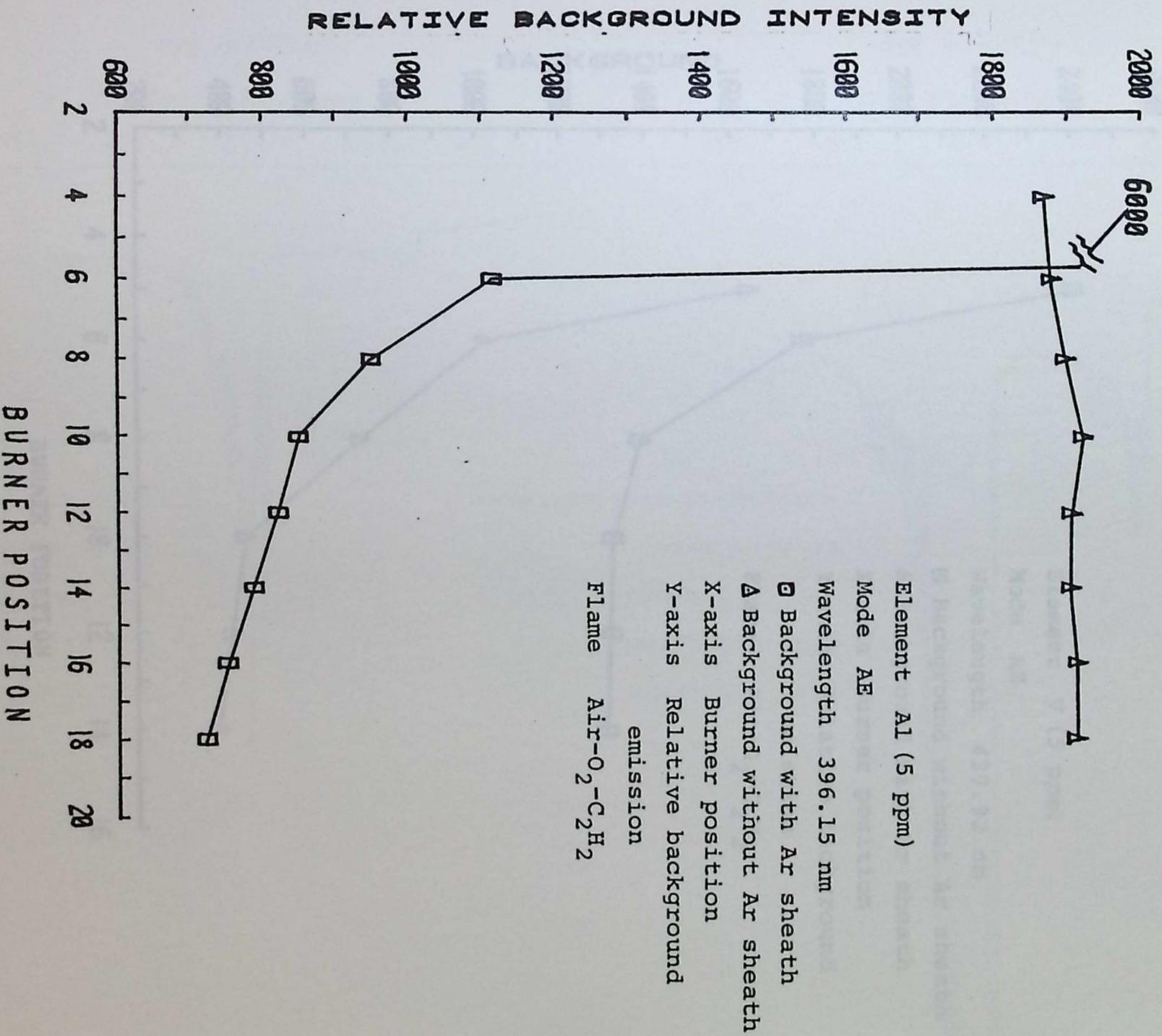


Figure 53

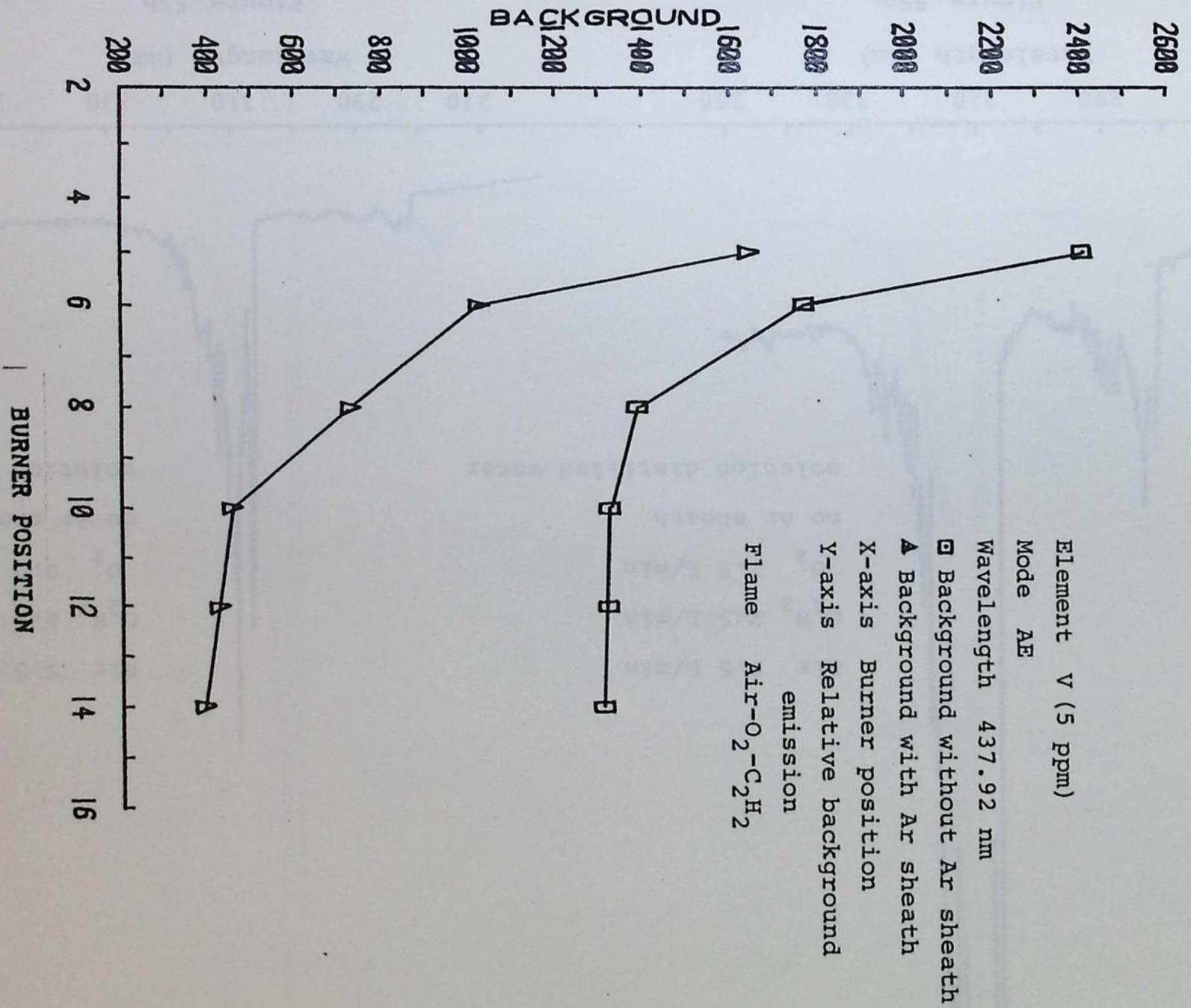


Figure 54

Background Emission

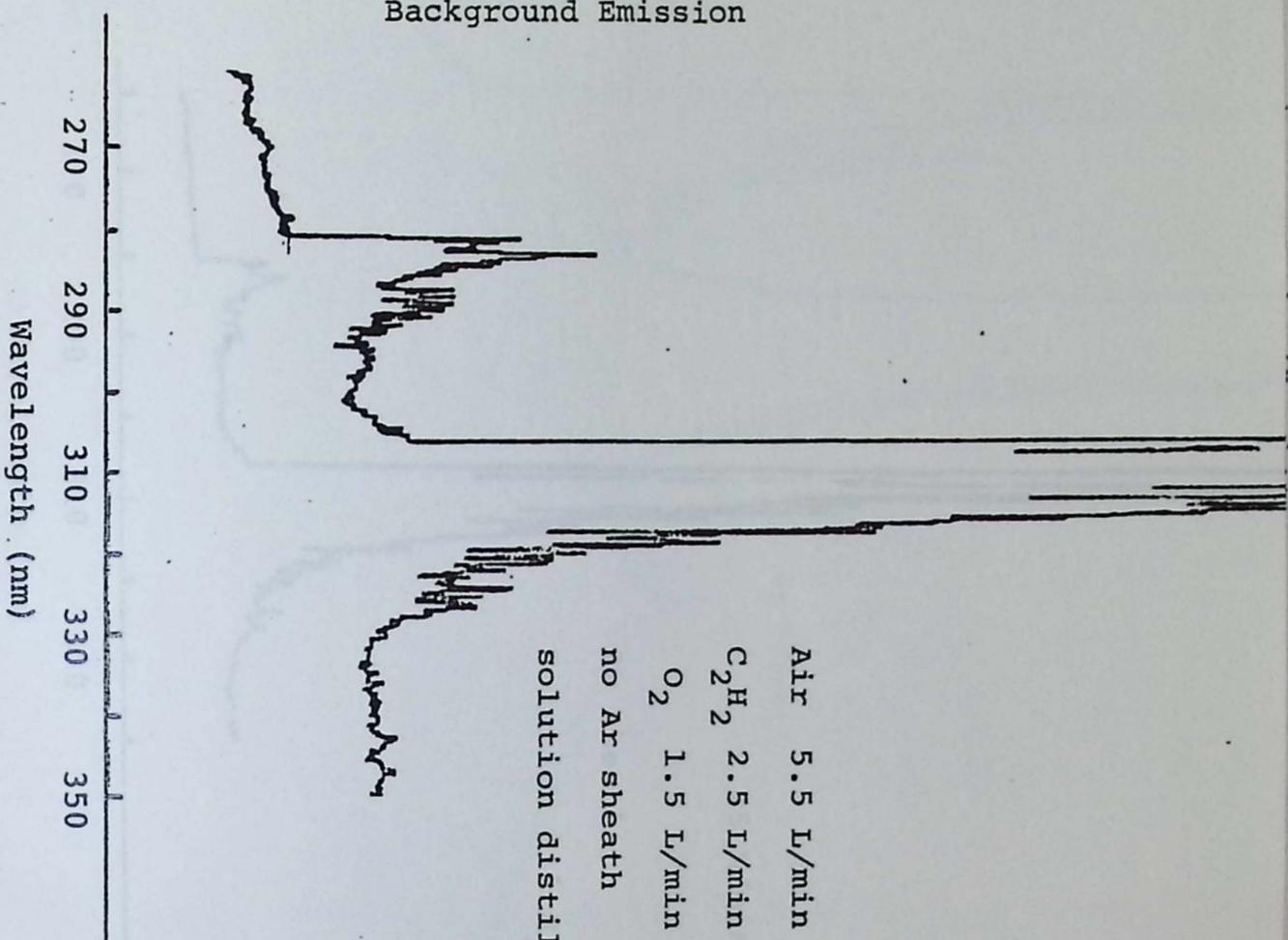


Figure 55a

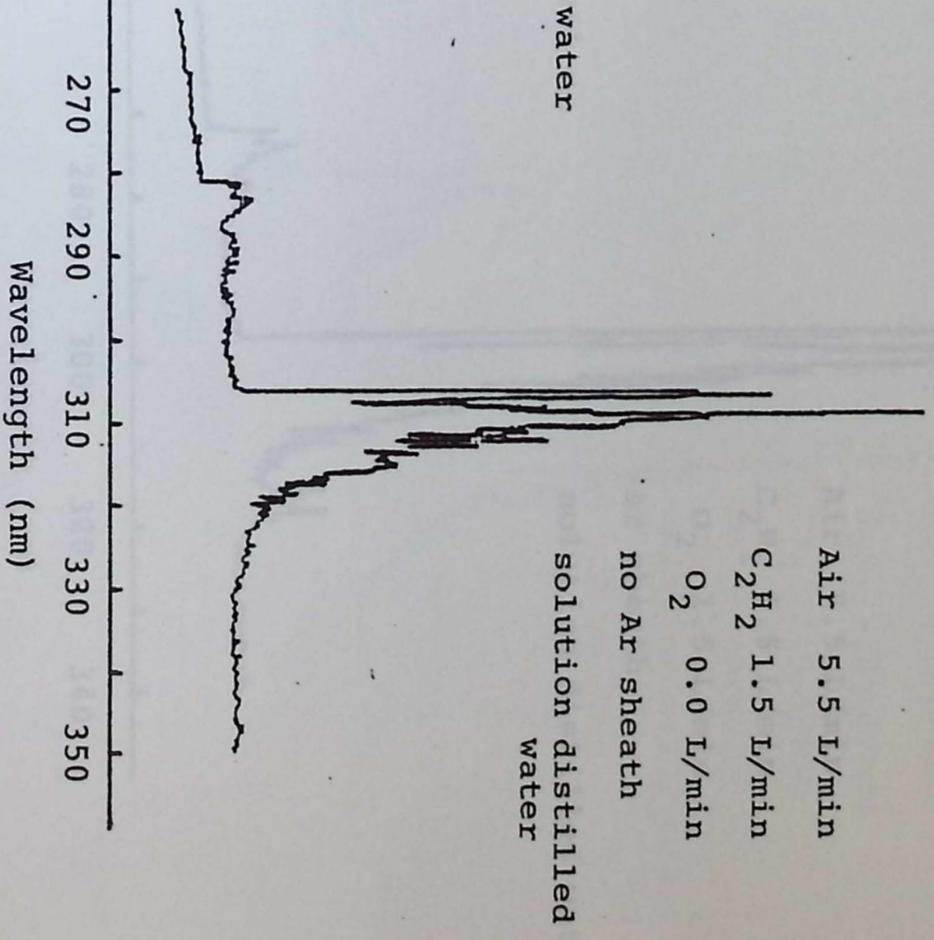


Figure 55b

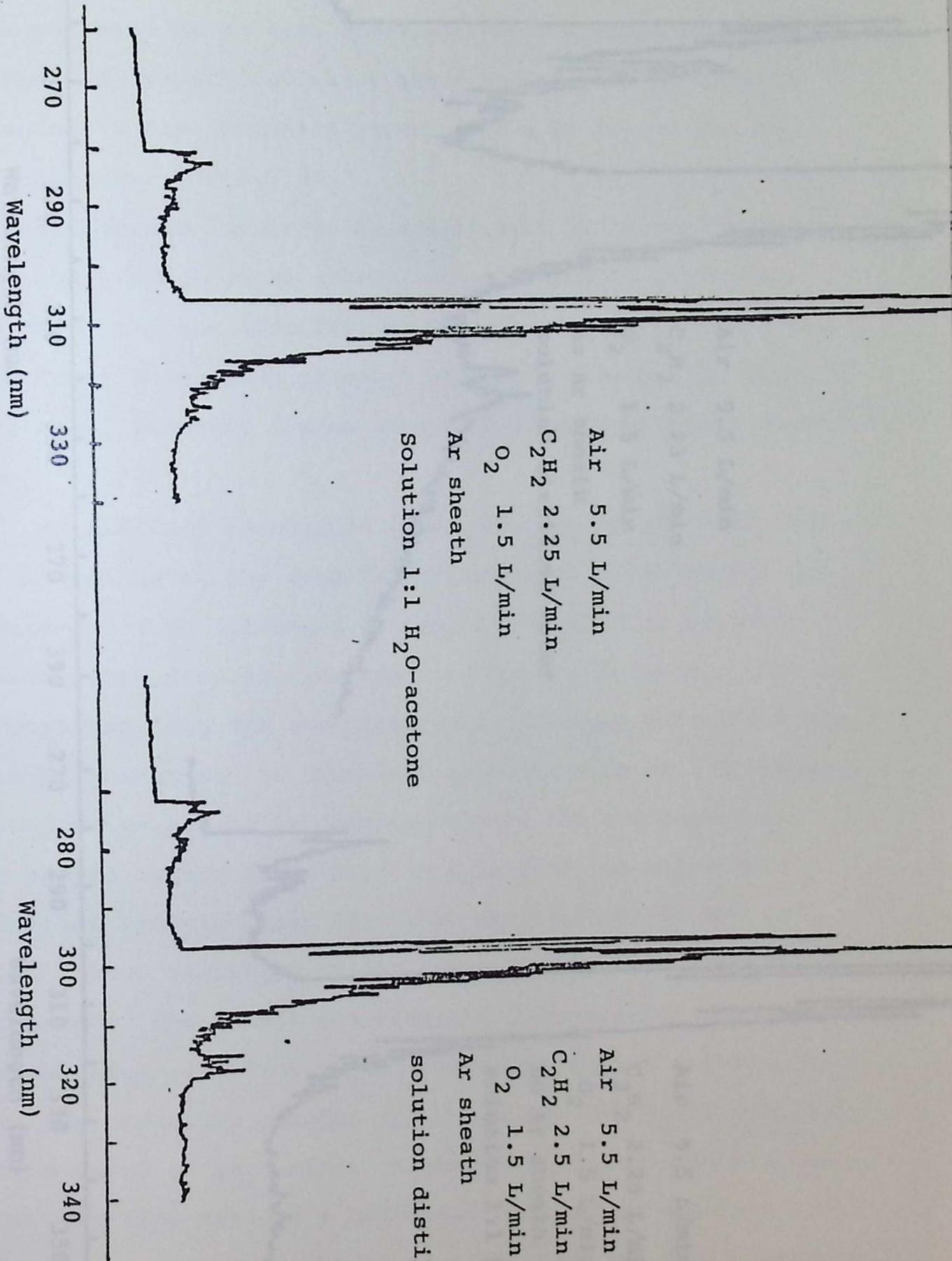


Figure 56a

Figure 56b

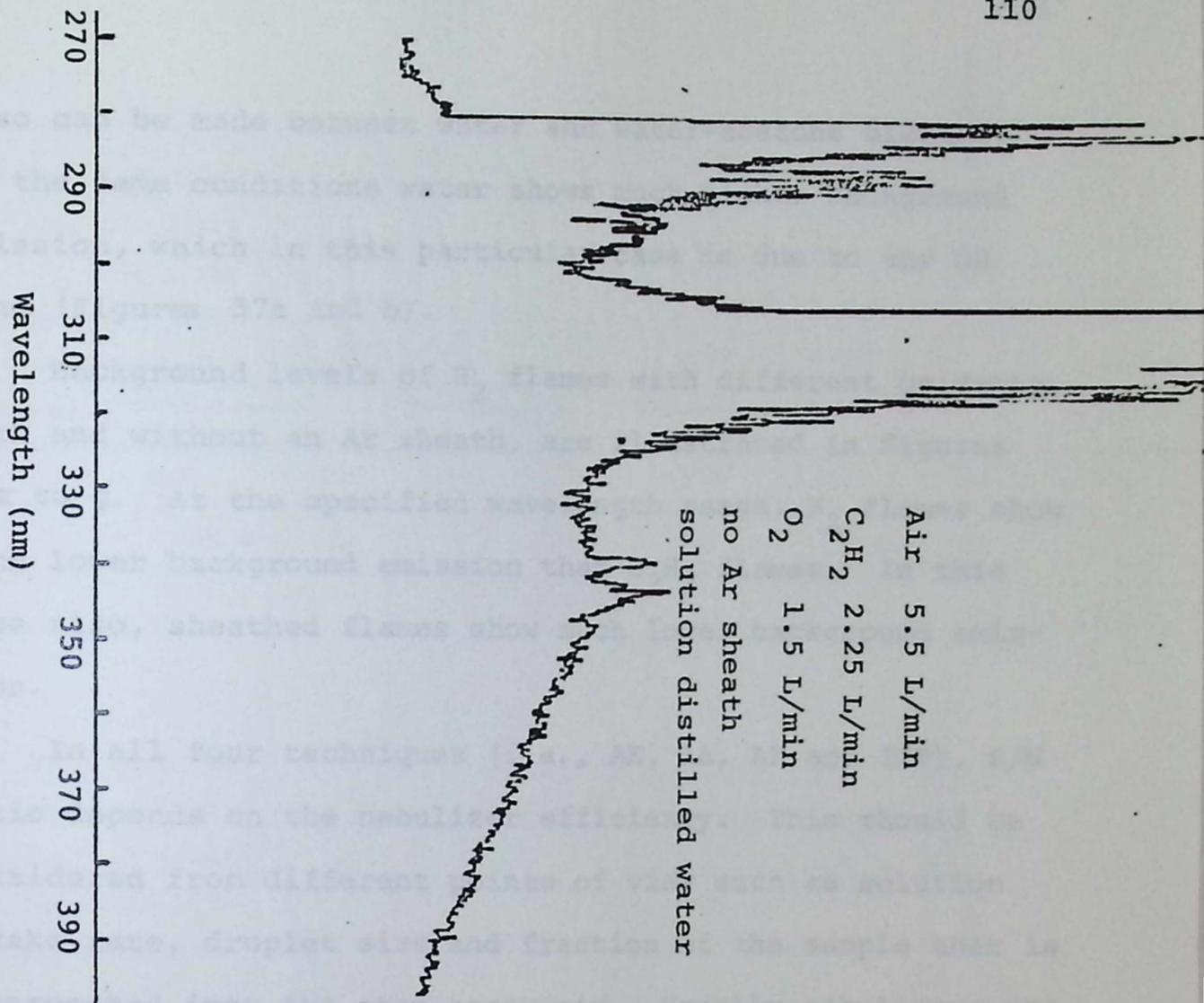


Figure 57a

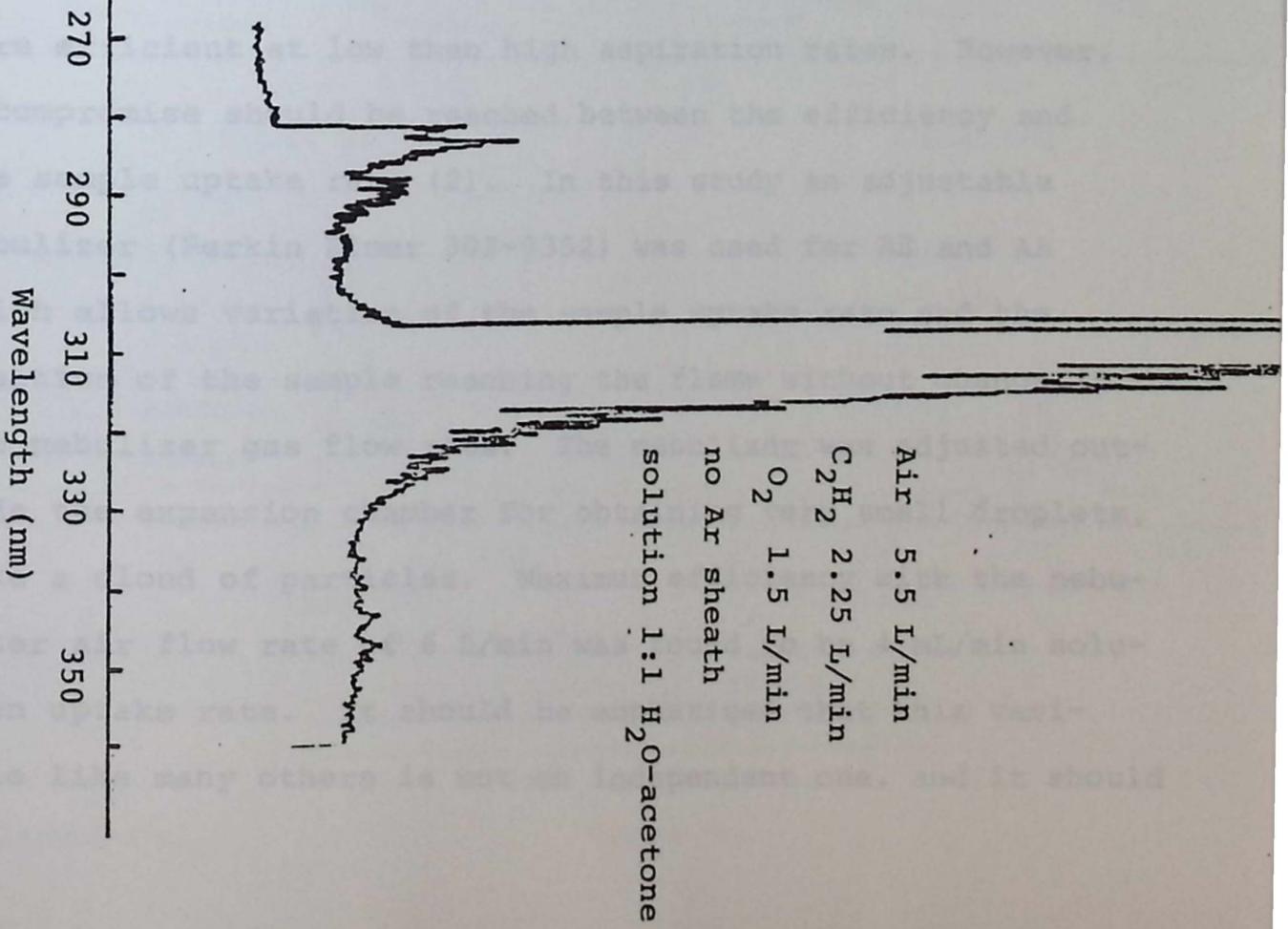


Figure 57b

also can be made between water and water-acetone mixture; at the same conditions water shows much higher background emission, which in this particular case is due to the OH band (Figures 57a and b).

Background levels of  $H_2$  flames with different oxidants, with and without an Ar sheath, are illustrated in Figures 58a to g. At the specified wavelength range,  $H_2$  flames show much lower background emission than  $C_2H_2$  flames. In this case also, sheathed flames show much lower background emission.

In all four techniques (*i.e.*, AE, AA, AF and ICP), S/N ratio depends on the nebulizer efficiency. This should be considered from different points of view such as solution uptake rate, droplet size and fraction of the sample that is transported into the atom reservoir. Usually nebulizers are more efficient at low than high aspiration rates. However, a compromise should be reached between the efficiency and the sample uptake rate (2). In this study an adjustable nebulizer (Perkin Elmer 303-0352) was used for AE and AA which allows variation of the sample uptake rate and the fraction of the sample reaching the flame without change in the nebulizer gas flow rate. The nebulizer was adjusted outside the expansion chamber for obtaining very small droplets, like a cloud of particles. Maximum efficiency with the nebulizer air flow rate of 6 L/min was found to be 4 mL/min solution uptake rate. It should be emphasized that this variable like many others is not an independent one, and it should

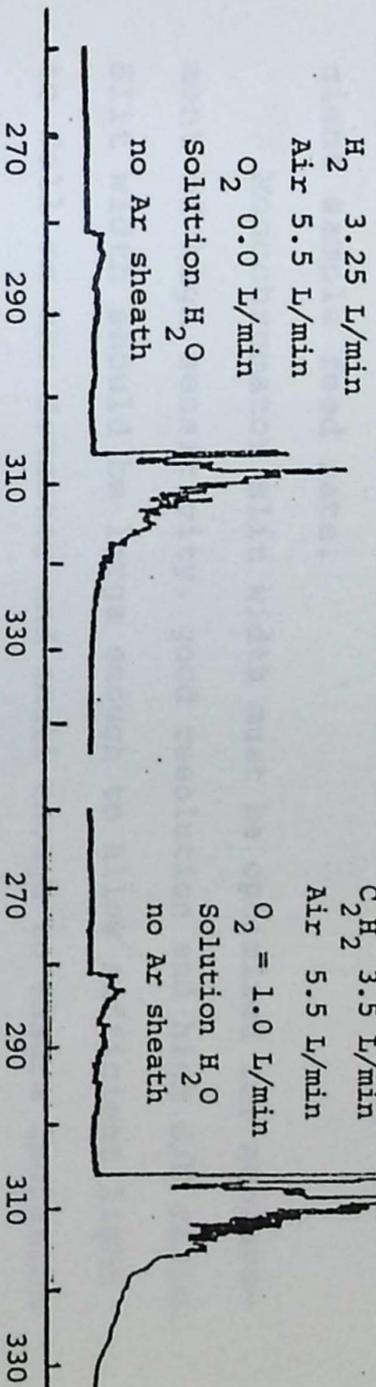


Figure 58a

Figure 58b

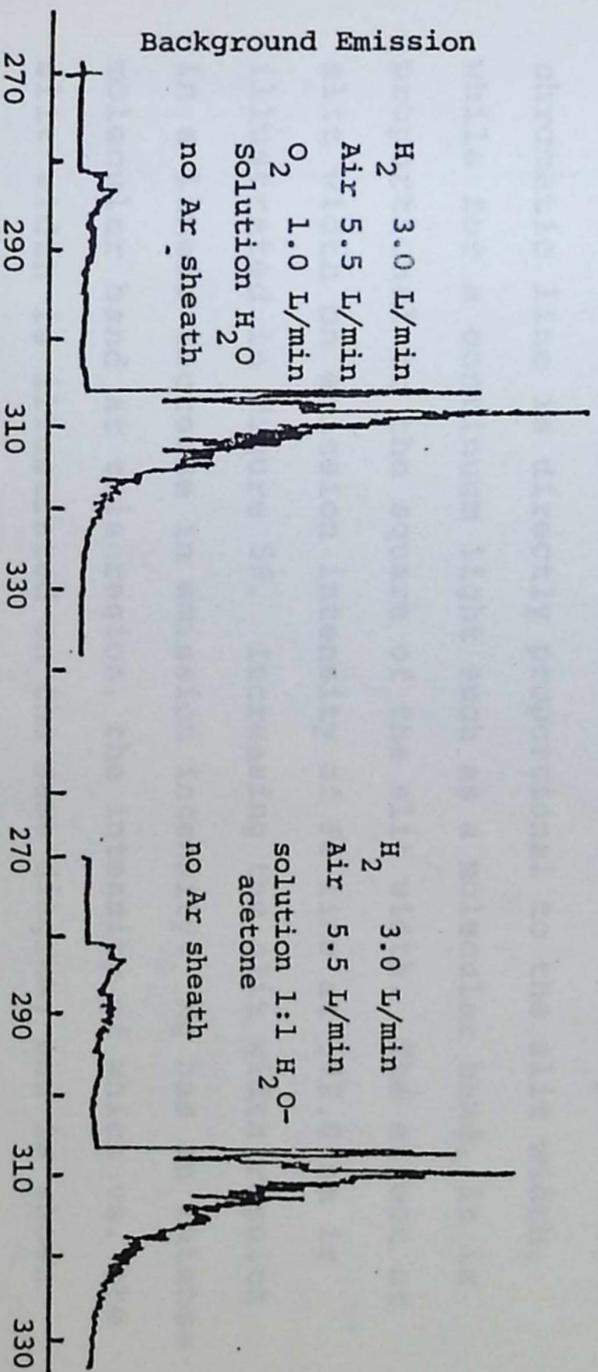


Figure 58c

Figure 58d

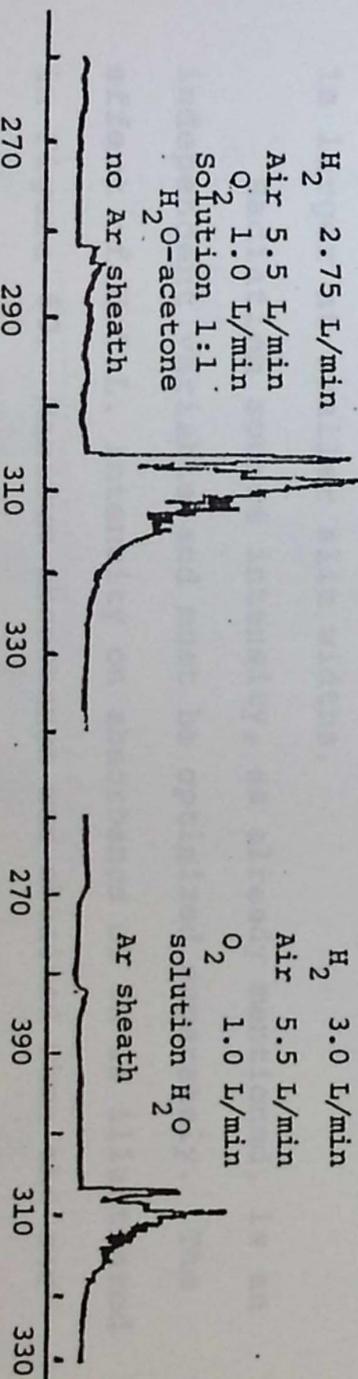


Figure 58e

Figure 58f

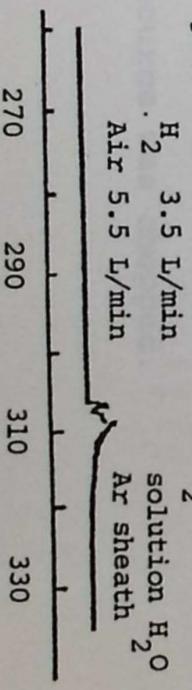


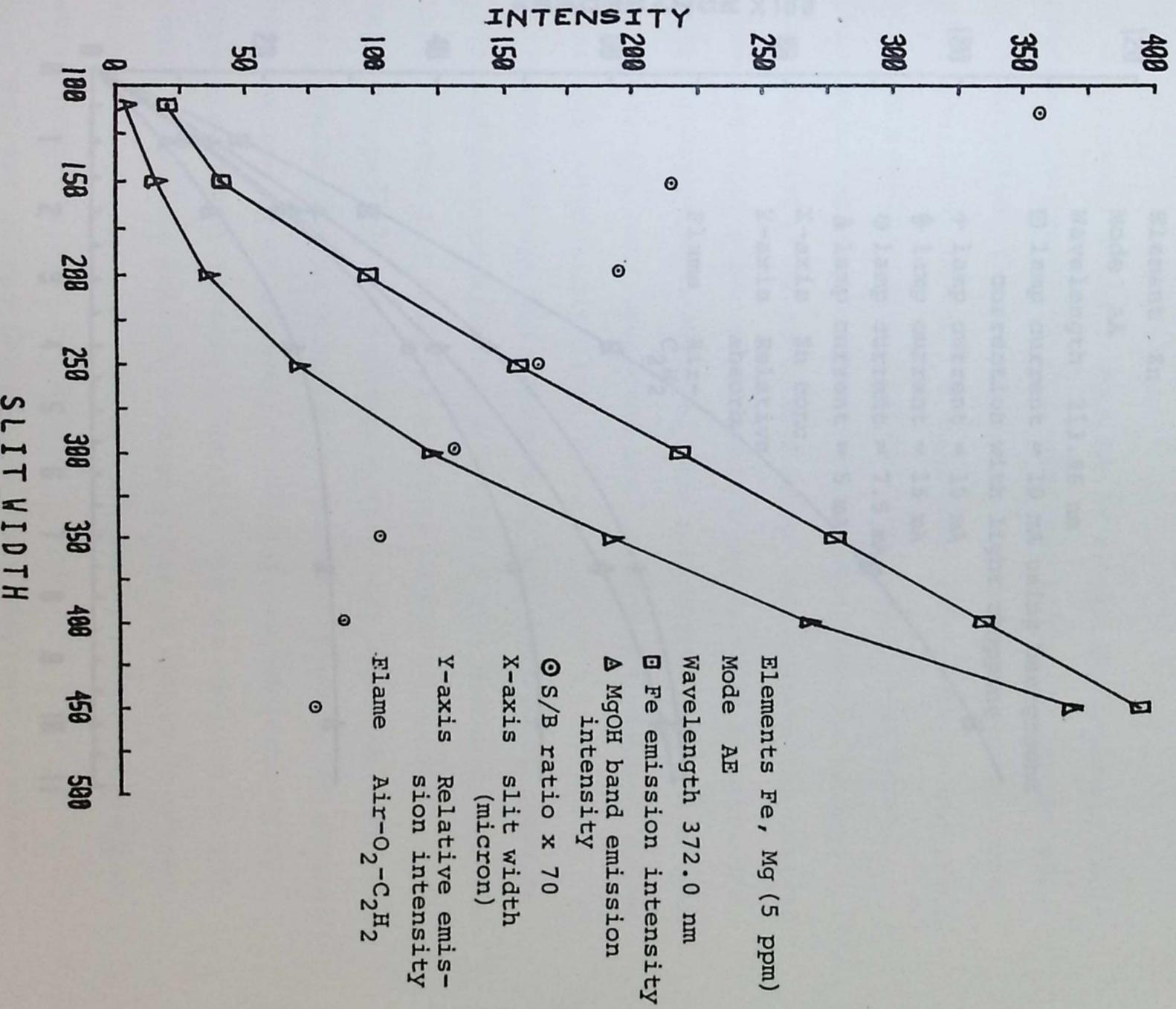
Figure 58g

Wavelength (nm)

be made to obtain small and uniform droplets with an efficient sample feed rate.

Monochromator slit width must be optimized for achievement of high sensitivity, good resolution and high S/N ratio. Slit width should be large enough to allow sufficient light to fall on the detector and small enough to ensure isolation of the spectral line of interest from other lines or bands which are considered interferences. The intensity of a monochromatic line is directly proportional to the slit width, while for a continuum light such as a molecular band, it is proportional to the square of the slit width. The effect of slit width on emission intensity of Fe line at 372.0 nm is illustrated in Figure 59. Increasing the slit width results in a linear increase in emission intensity. Mg has an intense molecular band at this region, the intensity of which vs. the slit width is illustrated on the same diagram, and is shown to be proportional to the square of the slit width. The S/N ratio (Fe/MgOH emission intensity) is also illustrated, which is larger at smaller slit widths.

Radiation source intensity, as already mentioned, is an independent variable and must be optimized separately. The effect of H.C.L. intensity on absorbance of Zn is illustrated in Figure 60. Maximum absorbance was obtained when the current through the lamp was 10 mA. Sensitivity was even higher when the light source was chopped.



SLIT WIDTH  
Figure 59

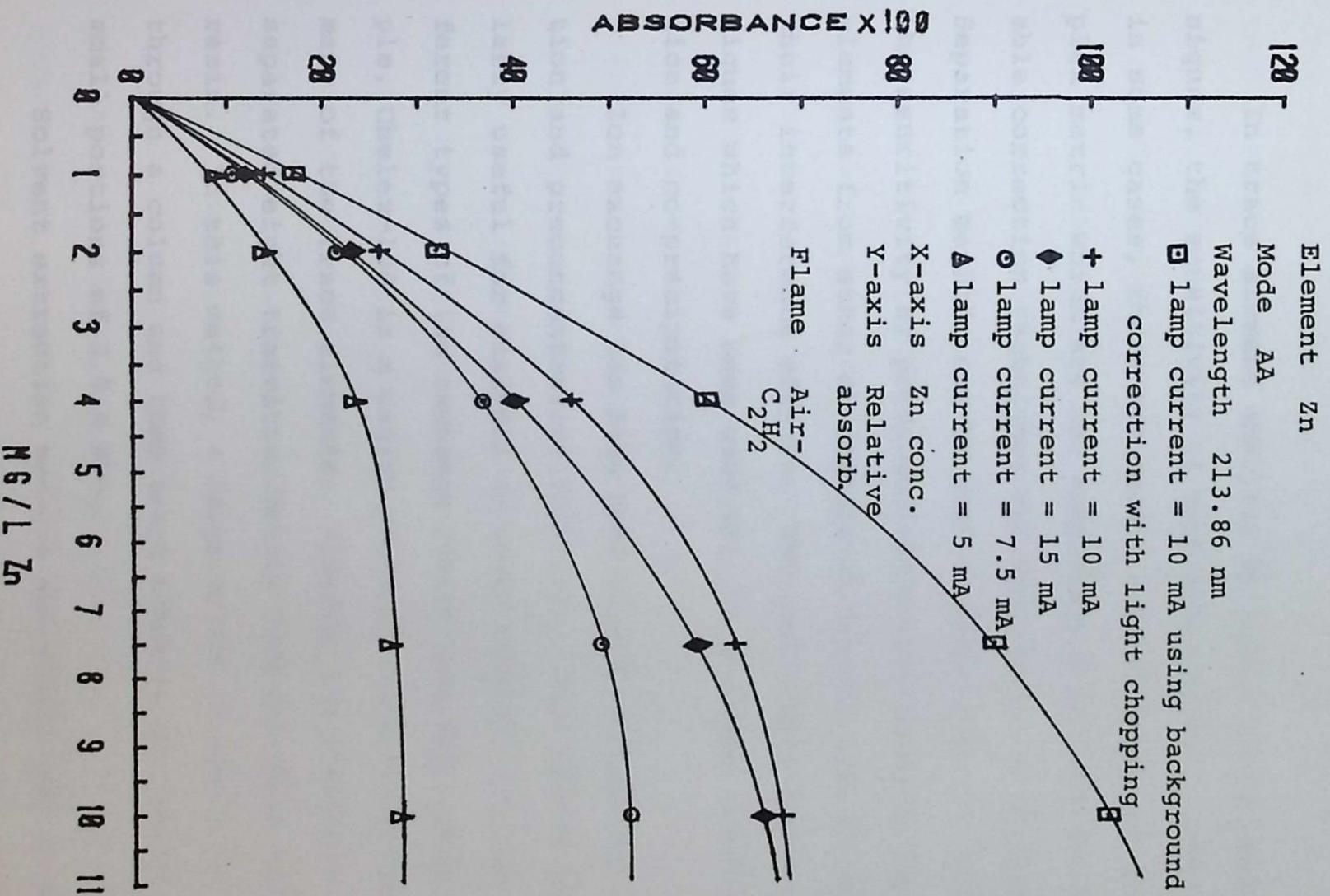


Figure 60

## Chapter VI.

## Solvent Extraction in Trace Element Analysis

In trace element analysis by atomic spectroscopic techniques, the sensitivity is very poor for many elements or, in some cases, there are severe interferences due to a complex matrix which are not completely eliminated by the available correction techniques and thus result in an error. Separation methods can be used in these cases to enhance the sensitivity by preconcentration and separate the desired elements from other components of the solution to eliminate their interference effects. The most common separation techniques which have been used are ion exchange, solvent extraction and co-precipitation.

Ion exchange has been used by many workers for separation and preconcentration (111-113). This method is particularly useful for analysis of water samples (114,115). Different types of ion exchange resins have been used; for example, Chelex-100 is a cation exchange resin which can chelate many of the trace elements. Kingston and coworkers (116) separated eight transition metals from sea water using this resin. In this method, a large volume of sample is passed through a column and then trace elements are eluted with small portions of 2.5 M  $\text{HNO}_3$ .

Solvent extraction methods are widely used in atomic spectroscopic techniques, especially AA and AF. Extraction

is usually carried out from aqueous into organic solvent.

An organic complexing agent is added to the sample to produce extractable metal complexes and then the complex is easily extracted into a relatively small volume of organic solvent. Some of the well-known complexing agents are:

8-hydroxyquinoline (oxine)

acetylacetone

1,10-phenanthroline

diphenylthiocarbazone (dithizone)

sodium diethyldithiocarbamate (NADDC)

diethylammoniumdiethyldithiocarbamate (DDDC)

ammonium pyrrolidine dithiocarbamate (APDC)

cupferron

Organic solvents which are usually used to extract metal complexes are: chloroform, acetylacetone, ethylacetate, methylisobutylketone (MIBK), amyl alcohol, ether and benzene.

Among these solvent, MIBK has been used extensively for the extraction of different metal complexes prior to atomic spectroscopic measurements. It is more suitable than many other solvents due to its relatively high solubility in water, higher chemical stability after extraction and good combustion in flames.

All of the above chelating agents are able to complex several metal ions, and their selectivity depends on various factors such as pH, temperature and concentration of different species in the solution. Thus, by adjusting the pH of

the solution and addition of masking agents, selective separation for one or a group of elements is possible. The extraction efficiency in an important factor in all extraction systems and at a given set of conditions it is expressed as percent of extraction.

$$\% \text{ extraction} = \frac{100 D}{D + \frac{V_{aq}}{V_o}}$$

$D$  = Distribution ratio

$V_{aq}$  = volume of aqueous solution

$V_o$  = volume of organic solvent

The most usual type of solvent extraction procedure is the batch extraction. In this method, after adjusting separation conditions, such as pH, and addition of a masking agent (if necessary), a suitable complexing agent is added, then the solution is shaken in a separatory funnel with a suitable organic solvent, and finally the layers are separated from each other. In some cases, where the efficiency of extraction is not enough, the process can be repeated several times.

There is an enormous amount of literature about solvent extraction of metal ions, only a few of these will be discussed here. 8-Hydroxyquinoline (oxine) readily forms extractable complexes with many elements (117,118). The complex can be readily extracted into chloroform or MIBK. Pitt (119) used this compound for extraction of Al prior to measurement

with FAE. Fe, Mo and Ga form complexes with oxine, which then can be extracted into MIBK (120). Oxine also has been employed for chelation of Pb, Ni, Co, Zn, Ag, Al, Be, Fe and Cd, and then extraction into MIBK (121).

NADDC chelates many elements extractable into MIBK and chloroform. Cu and Bi have been separated from blood samples with NADDC and MIBK with 100% efficiency (122). The same extraction system was used by Hannaker and Hughes (120), who separated 16 metal ions from geological samples for FAA measurement. They found their procedure quantitative, if complex-forming elements, when present in large excess (such as Fe and Mn in many geological samples), were removed.

APDC-MIBK is a widely used extraction system in atomic spectroscopy. A wide range of metals can be extracted by this mixture. Advantages of this system are its capability to complex many trace elements over a wide pH range and its stability in acid solutions. Brooks and coworkers

used APDC-MIBK for extraction of Co, Cu, Fe, Pb, Ni and Zn from saline waters at pH 3.5 prior to FAA determination (124). Kinrade *et al.* (125) have described the use of APDC-DDDC-MIBK for simultaneous extraction of Cd, Co, Cu, Fe, Pb, Ni, Ag and Zn. In their extraction system pH was adjusted to 5 with citrate buffer and after extraction the measurement was carried out on the organic phase by FAA. As already mentioned, APDC can be used in strongly acid solutions. Allan (126) has reported extraction of Cu from 6 N HCl, 9 N H<sub>2</sub>SO<sub>4</sub>

and up to 10%  $\text{HClO}_4$  ( $\text{HNO}_3$  cannot be used because it decomposes the reagent) with APDC and ethyl acetate. Debbeka (127) has extracted Pb and Cd by APDC-MIBK system from  $\text{HNO}_3$ - $\text{HClO}_4$  digest, at pH 1.4-1.8 and then stripped into  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ . He has reported good precision and accuracy, very few interferences and no need for extraction of standards. Extraction of many other elements has been carried out using APDC-MIBK system (115,128-130).

Other extraction systems have also been used prior to flame or non-flame atomic spectroscopic techniques. 1,10-Phenanthroline is a well-known complexing agent for a variety of trace elements (131). Schilt and coworkers (132) applied this reagent for extraction of metal ions and determined distribution ratios and extraction efficiencies of 19 elements. They have extracted metal complexes from aqueous solutions of  $\text{NaClO}_4$  and  $\text{CH}_3\text{COONH}_4$  at pH 7 into nitrobenzene prior to measurement. Reported values of the extraction efficiencies for  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are 100%. For  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ag}^+$  the efficiencies have been reported as 96, 99 and 95 percent, respectively. Viets (133) used tricaprylmethylammonium chloride and MIBK (Aliquot 336-MIBK) to extract several metal ions (Ag, Bi, Cd, Cu, Pb and Zn) in geological materials after  $\text{KClO}_3$ -HCl digestion. He has reported selective extraction of these metal ions in the presence of ascorbic acid and KI. The measurements were carried out by FAA. For more information about the theory

and different extraction systems, the following references may be consulted:

1. Importance of extraction parameters (125)
2. Solubility product of some divalent metal ions with APDC (134)
3. A complete review of extraction systems (135)
4. Selective extraction of Al with cupferron and MIBK or chloroform (136,137)
5. Application of solvent extraction in atomic spectroscopy (138)
6. Quantitative extraction of Fe, Mo, Tl and Sn with cupferron-MIBK (122)
- Cu and Bi with DDDC-MIBK (122)
- Co and Ni with APDC-MIBK (122)
- Mn with oxine-MIBK (122)
- Li, Sr, Ca, Mg with thenoyltrifluoro-acetone-MIBK (122)
7. Extraction of Cd, Fe, Zn, Cu, Mn and Pb by NADDc-isoamyl alcohol (139)
8. Extraction of 32 elements by K-ethyl-xanthate and  $\text{CHCl}_3$  (140)

Most of the organic solvents which are used in extraction of trace elements when directly aspirated into the flame result in very large background levels and thus decrease the S/N ratio. Organic solvents also change the flame characteristics, including flame temperature, flame shape and position

of the interconal zone. These problems can be eliminated by back extraction of elements into aqueous phase or evaporation of the organic solvent. Interferences from organic solvents are much lower with furnace or other thermal atomization devices because the samples are desolvated first and then vaporized, so almost all of the solvent is removed from the atom reservoir.

Separation by co-precipitation has not been used as widely in atomic spectroscopic techniques as solvent extraction or ion exchange. Only two examples will be mentioned here. Hudnik *et al.* (141) have determined Cd, Co, Cr, Cu, Ni and Pb in mineral waters by flameless AA. Their procedure is briefly as follows: mix the samples with  $\text{Fe}^{3+}$  as collector, remove  $\text{CO}_2$ , add APDC and filter the precipitate. The precipitate is then dissolved in dilute  $\text{HNO}_3$ , evaporated to dryness and dissolved in a small volume of dilute  $\text{H}_2\text{SO}_4$ . Krishnamurty *et al.* (142) have used  $\text{Co}^{2+}$  instead of  $\text{Fe}^{3+}$  and carried out the preconcentration of Pb and several other metals by coprecipitation with cobalt-PDC (pyrrolidinedithiocarbamate)cobalt(III).

## Chapter VII.

## The Analysis of Hydrocarbon-Rich Shales

## A. History and Nature of Oil Shales

Oil shale is an intimate mixture of mineral matter and solid organic matter. It was generated in the distant past by simultaneous deposition of organic remains and mineral silts upon the beds of ancient lakes and seas. Over the interim ages, heat and pressure from the accumulated burden solidified the material and altered its chemical composition to that of the potential energy resources which are called "oil shales" (143). Deposits of oil shales with different compositions are found in many parts of the world. Inorganic material consists mainly of clay, dolomite, calcite and iron compounds (144).

The organic material in oil shale decomposes upon heating to form hydrocarbon gases and petroleum liquids, which are readily isolated from the mineral constituents. Attempts to extract oil from oil shale on a large scale have utilized two approaches, either heating the shale in a retort and collecting oil and gases, or *in situ* processing, which consists of underground treatment with steam and oxygen (145).

Oil shale technology has a long history and it has been known for over 100 years. Research on the production of oil from oil shale has been conducted since the discovery of this resource. However, a commercial production of these types of fuels in amounts and at a price compatible with

traditional sources of fuels has never been accomplished. Because of the energy and mineral shortage, the development of this type of fuel now appears favorable (146). There are some interesting statistics regarding oil shales in the literature. It is estimated that the world shale oil resources are about 2.1 quadrillion barrels, which is sufficient for several lifetimes of space heating and illumination (145). The total oil shale deposits in the United States contain a 42,000 year supply of petroleum equivalent (145). It is estimated that the oil production from oil shale will be 750,000 barrels a day by 1990, and the most optimistic projection postulates a production of 2.5 million barrels a day by 1990 (147). The recoverable shale oil may vary from 10-80 gallons per ton of oil shale. Oil shales from some areas of Kansas have about 15 gallons of oil per ton of shale.

Before this source of energy comes into consideration as a major fuel source, there are other aspects that need to be considered. Factors such as environmental considerations, the maximum recovery of fuel products and, probably, recovery of some associated minerals. Some oil shales have a high concentration of otherwise minor and trace elements, some of which have potential economic value. Concentrations of Mo, Sr, B, Li, Zn, Cd, As, Pb, U, Se and some other elements are much larger than the average abundance in the earth's crust (148-150). Thus, it may be valuable to extract some of these elements from the spent shale. Extraction of U and Al has

been achieved by some workers (144,145). Some oil shales in Kansas contain nodules high in phosphate and they also may have a significant uranium content.

Environmental effects including air, water, and solid waste pollution are very important and must be considered very carefully, because of the very large volume of material that will have to be processed. When oil shales are processed at high temperature by retorting, there is a high possibility that some of the toxic elements will be volatilized into the atmosphere or leached into the ground waters (151). Therefore, it is necessary to measure the elemental concentration of oil shale before any process has been performed.

Different techniques have been used for major, minor and trace elements in oil shales. Most work is done using atomic absorption, x-ray fluorescence, neutron activation analysis or optical emission spectroscopy.

In this study five different Kansas shales were used for the analysis. These samples were obtained from Dr. Hathaway of the Kansas Geological Survey and include Ninnescah (red shale), Heebner (black shale), Heumader (gray shale), Eudora (black shale) and Heebner (black shale No. 2, obtained as large pieces). Among these shales only Eudora black shale and Heebner black shales have a considerable amount of organic matter and may be considered as hydrocarbon-rich black shales. The Ninnescah shale is a shale from an oxidizing environment, whereas the others represent varying degrees of reducing environments. To get a rough estimate of the

percentage of organic matter, the loss on ignition in the ash-ing process (see next section) may be considered. This also incorporates loss of  $\text{CO}_2$  from  $\text{CaCO}_3$ ,  $\text{H}_2\text{O}$  from shales, etc. The ignition loss when samples are heated up to  $500^\circ\text{C}$  is shown in Table 4. The Eudora and Heebner shales show relatively large values, indicating a high concentration of organic matter.

Table 4

Sample No.	Sample name and type	% Loss (approx. values)
1	Ninnescah red	3
2	Heebner black	21
3	Heumader gray	5.5
4	Eudora black	30
5	Heebner black No. 2	22

#### B. Sample Preparation Methods

Atomic spectroscopic methods usually require the sample to be in the form of a solution. There are different ways to solubilize the sample. Selection of a particular method of dissolution and decomposition depends on various factors such as type of sample, species of interest, and method of analysis. Some samples such as oil shales have an appreciable amount of organic matter which should be decomposed before any other treatment. This facilitates the dissolution and reduces

interferences. The technique usually employed is heating the sample gradually up to 500° C in a platinum or silica dish for at least 10 hours in open air. However, in the determination of volatile elements such as As, Sb, Hg and Se, there is the danger of loss of the analyte upon heating. In this case the organic matter can be decomposed by treating the samples with strong oxidizing agents. If the decomposition procedure is performed at relatively low temperature under carefully controlled conditions, loss of volatile elements can be minimized. An effective way of dissolution is the use of the teflon bomb technique, which prevents the loss of volatile elements. This method is based on decomposition of the sample with HF under pressure (152).

Usually dissolution of samples containing silicon as a major constituent has been achieved either by fusion with a flux or by acid digestion. In the fusion methods different fluxes have been used. Alkali fluxes such as  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{B}_4\text{O}_7$  have been used extensively in decomposition of silicates. The disadvantage of these fluxes is contamination of the samples with large excesses of Na and K which usually require determination themselves. Introducing these elements in high concentration into the sample may cause interferences in determination of some elements. Lithium tetraborate has been suggested as a flux for decomposition of samples (153). Ingamells (154) has proposed decomposition with lithium metaborate ( $\text{LiBO}_2$ ). Fusions with  $\text{LiBO}_2$  are

carried out in platinum or graphite vessels. This method has been used extensively in atomic spectroscopy by different workers (155-157). Biskupsky (158) has proposed a combination of boric acid and lithium fluoride for decomposition of silicates. This is a good way of removing Si in some cases when it interferes with other elements. In general,  $\text{LiBO}_2$  seems to be superior to the other alkali fluxes because of its ability to decompose resistant minerals, prevention of contamination of the samples with elements such as Na and K, and reduction of contamination of the sample with the crucible and the crucible with the sample materials. Fusion methods, in spite of several advantages, have a limitation in the determination of volatile trace elements which are lost in total or in part during the fusion process. This limitation can be severe for samples of high organic content such as oil shales.

Acid digestions are effective in dissolution of the oil shales. For complete dissolution of samples, HF is necessary because of high silica content. Oxidizing conditions must be maintained to remove the organic matrix and prevent loss of some elements.  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  are usually used.

Two different methods were used for the dissolution of the samples in this analysis, fusion and acid digestion. Ashed samples were obtained by heating carbonaceous shales up to  $500^\circ\text{C}$  for about 10 hrs. in open air. Ashed samples can be used for the determination of non-volatile elements

such as Fe, Al, Ca, Mg, Na, K, Si, Mn, Co, Ni, Cu, Mo, Sr, Ba and V. For volatile elements such as As, Sb, Se and Hg, raw samples should be used and the method of choice for dissolution is acid digestion at low temperatures.

0.2-0.3 g of ashed sample was weighed exactly and transferred into a platinum dish for acid digestion. 10 mL 1:1  $\text{HNO}_3$  and 4 mL HF were added to the sample and it was allowed to stand overnight. Then 4 mL of  $\text{HClO}_4$  was added and the solution was fumed to near dryness. 2 mL of  $\text{HClO}_4$  was added and again the acid was fumed off to near dryness. The residue was dissolved in about 10 mL of distilled water containing 2 mL of conc. HCl and digested for 1/2 hr. on a hot plate. The sample was then transferred into a 100 mL volumetric flask and diluted with distilled water.

Fusion of the samples was carried out using  $\text{LiBO}_2$ . 0.2-0.3 g of the finely ground sample (dried at  $105^\circ\text{C}$ ) was weighed out and mixed with 1 g  $\text{LiBO}_2$  in a graphite crucible (platinum crucibles also can be used). The mixture was fused in a furnace at  $900^\circ\text{C}$  for about 20 minutes. The crucible was swirled gently to bring the melt from the walls to the bottom of the crucible and then it was fused for 10 more minutes. The melt was transferred into a beaker containing 50 mL of distilled water into which 5 mL of conc. HCl had been added. The solution was stirred with a magnetic stirrer until all the material dissolved and then it was diluted to 100 mL in a volumetric flask. The procedure was carried out for all the samples and also a blank sample was prepared by fusion of

1 g  $\text{LiBO}_2$  following the same procedure.

Preparation of Stock Solutions:

Methods for preparation of 1000 mg/L stock solutions are described in Table 5. These solutions were stored in polyethylene containers. All the standard solutions used for AE and AA measurements were made by appropriate dilutions of these solutions. For ICP analysis standard solutions were made from reagent grade 1000 ppm standard solutions which are commercially available (Fisher Scientific Company).

Table 5.

Aluminum

Dissolve 1 g of Al metal foil in 25 mL conc. HCl to which a few drops of conc.  $\text{HNO}_3$  have been added. Dilute to 1 liter.

Arsenic

Dissolve 1.320 g  $\text{As}_2\text{O}_3$  in 50 mL conc. HCl. Dilute to 1 liter.

Barium

Dissolve 1.779 g  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  in deionized water, add a few drops of conc. HCl and dilute to 1 liter.

Calcium

Dry  $\text{CaCO}_3$  24 hours at  $85^\circ \text{C}$ . Put 2.498 g into 300 mL  $\text{H}_2\text{O}$ . Add 10 mL conc. HCl dropwise. Dilute to 1 liter.

Cadmium

Dissolve 1 g Cd metal in 10 mL conc.  $\text{HNO}_3$ . Dilute to 1 liter.

Chromium

Dissolve 2.8290 g  $K_2Cr_2O_7$  in deionized water. Dilute to 1 liter.

Copper

Dissolve 1 g Cu metal in a minimum volume (1:1)  $HNO_3$ . Dilute to 1 liter.

Iron

Dissolve 1 g Fe metal in 10 mL conc.

HCl with gentle heat. Dilute to 1 liter.

Magnesium

Dissolve 1 g Mg ribbon in a minimum volume (1:1) HCl. Dilute to 1 liter.

Manganese

Dissolve 1 g Mn metal in 10 mL conc. HCl. Dilute to 1 liter.

Nickel

Dissolve 1 g Ni metal in 10 mL conc.  $HNO_3$  with gentle heat. Dilute to 1 liter.

Lead

Dissolve 1.5985 g  $Pb(NO_3)_2$  in deionized water, add a few drops of  $HNO_3$ . Dilute to 1 liter.

Strontium

Dissolve 2.4155 g  $Sr(NO_3)_2$  in deionized water, add a few drops of  $HNO_3$ . Dilute to 1 liter.

Vanadium

Dissolve 1 g V metal in a minimum volume of  $HNO_3$ . Dilute to 1 liter.

Zinc

Dissolve 1 g Zn metal in 10 mL conc. HCl. Dilute to 1 liter.

All chemical compounds used in making these standard solutions were reagent grade. However, the concentrations of

some of these standards may be slightly less than 1000 ppm due to the impurity of the metals, especially Mg, Zn and Al.

### C. Elemental Analysis and Necessary Pretreatments

Atomic spectroscopic techniques have found rapid acceptance in the analysis of geochemical materials. It is possible to analyze the most important components of these materials directly or indirectly with sufficient sensitivity and very good precision. There are many problems that must be taken into consideration prior to analysis. The purpose of this section is to deal with the difficulties in the analysis of geochemical materials, especially shales, in terms of possible matrix interferences and methods that should be utilized to eliminate some of these problems.

#### 1. Possible Interferences

Typical mineralogical analysis of shales has shown that the inorganic material is composed mainly of clay, silica, calcite, dolomite and iron compounds. Thus there are high concentrations of Si, Al, Ca, Mg, and Fe and it is to be expected that sulfur and phosphorous may also reach appreciable concentration levels in some shales. These constituents can cause severe interferences in the analysis. In Chapter IV different types of interferences were discussed and here only the effect of the sample matrix on the elements to be measured is discussed.

Sulfate, phosphate, silicate and aluminum (aluminate)

interfere with the measurement of alkaline earth elements. This has been verified by many workers (see Chapter IV). Different methods are used for the elimination of these interferences, the most important of which include addition of a large amount of La (80,159,160), addition of EDTA (159) and addition of other alkaline earth elements such as Sr in the determination of Ca and Mg. The extent of these interferences depends on atomization conditions, high temperature flames reducing the interferences. However, ionization interference increases in hot flames, but can be minimized by addition of ionization buffers.

The high concentration of Fe in shales can cause interferences on many elements because of its great number of spectral lines between 340 to 440 nm. In the AE measurement of Al at 396.2 nm, there is a possible spectral interference from Fe which has an emission line at 396.8 nm. Fe also affects Cr emission at some wavelengths, reduces Cr absorption, and at high concentrations causes chemical interferences on some of the alkaline earth elements. Interferences on Fe are not as frequent as those of Fe on other elements. However, there are some interferences such as the effect of Si (161) or the effects of Co, Cu and Ni on Fe absorption (162), which depend on flame conditions. Most of these elements will not affect the emission or absorption of Fe in shale samples because of their low concentrations relative to Fe.

Other major interferences related to the matrix can be

the effect of Si on the absorption of Mn, phosphate and sulfate interferences on Pb absorption (163), and the effect of Ca and Si on Al (164).

## 2. Sample Pretreatments

One of the most important requirements in the analysis is that the samples be similar in all respects to the standards. Matrix-free standard solutions do not correspond to the samples having a complex matrix. Consequently, the measured concentration of the elements (especially trace elements) is either higher than the true value, due to enhancement by the matrix, or lower, due to suppression, if the comparison is made with matrix-free standards.

There are several methods by which these problems can be dealt with, such as standard addition, matrix matching, extraction techniques, and matrix modification. Among these methods matrix matching, which means to make standards with the same composition as the samples, is inconvenient and sometimes impossible because of a very complex matrix. The standard addition method is helpful in many cases, especially when there are physical interferences. However, most chemical interferences are concentration-dependent, *i.e.*, the effect of the matrix on added standards may not be the same as it is on the sample. Thus, the standard addition method cannot be used in measurement of many elements, except when some type of pretreatment is utilized.

Matrix modification includes addition of compounds to the sample solution either to react with one or a group of

elements to form more volatile compounds, or to react with interfering components and release the elements of interest. An example of the first modification type is addition of complexing agents such as EDTA to chelate the metal ions and form more volatile compounds, and an example of the second type is addition of La to release the alkaline earth metals. Selective extraction is an effective method for matrix elimination (see Chapter VI).

For measurement of alkaline earth metals, all samples and standards were made 1000 ppm in La to minimize the effect of phosphate, sulfate, aluminum and silicate. For the measurement of Ba in addition to La, all the solutions and standards were made 1% in KCl because the selected wavelength is an ionic line (455.40 nm) and some of the elements in the sample can suppress the ionization. By making all the samples and standards highly concentrated in an element such as potassium, it is possible to have the same rate of ionization in both samples and standards. Ba and Sr were measured with an  $O_2-C_2H_2$ -air flame which is expected to have a temperature of about 3000° C, close to that of  $N_2O-C_2H_2$ . The reason for using this flame was that these two elements have relatively low concentrations in the samples. However, there are high concentrations of interfering compounds which should be eliminated and high temperature flames have proven to be a good way to eliminate these interferences. On the other hand, a high temperature was necessary for ionization of Ba. The same type of flame was used for Al and V because they are

refractory elements.

The concentration of Fe is great enough that its determination can be carried out either on the original solution without any pretreatment, or after extraction of its chloro complex into *n*-butyl acetate to eliminate the effect of the matrix.

The extraction method that was used in this study has been developed by Hannaker and Hughes (120). In this procedure Fe is eliminated from the solution. Elimination of Fe has two advantages. First, the interference effect of Fe on trace elements is prevented and, second, extraction of trace elements is improved because the presence of Fe effectively reduces the partitioning of trace elements into the MIBK phase.

Reagents:

Buffer. Dissolve 10.2 g potassium biphthalate in 50 mL water. Extract once with 15 mL MIBK.

NaDDC. Dissolve 6 g NaDDC in 100 mL water. Filter the solution and extract three times, each time with 15 mL MIBK to purify the reagent.

APDC. Dissolve 1 g APDC in 50 mL water. Extract with 10 mL MIBK to purify the reagent.

Standard Solutions. Dilute an appropriate volume of 1000 ppm stock solutions.

Procedure:

Evaporate 100 mL of the solution obtained from acid digestion ( $\text{HF}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ) to near dryness, and then take up the residue into 100 mL of 8 M HCl. Extract this solution two times with 10 mL portions of *n*-butyl acetate. The organic phase contains Fe, Mo and some other metals. The aqueous solution contains most of the trace elements. Evaporate the aqueous phase to near dryness. Make up the residue to about 100 mL with distilled water. Add 3 mL buffer solution. Adjust the pH to 2.0 by addition of HCl and  $\text{NH}_3$ . Add 5 mL NADDC solution and extract two times with 20 mL portions of MIBK. Evaporate the organic phase at very low temperature and take up the residue in 50 mL of 1 M HCl. Digest the solution for 1 hr. on a hot plate and then dilute to 100 mL with distilled water. These solutions were used for the determination of Mn, Cu, Ni, Co, Cr, Pb, Zn and Cd by AA and AE.

Another extraction procedure was employed for Pb which was based upon the APDC-MIBK system.

Procedure:

Dilute 50 mL of the acid-digested samples to 100 mL. Adjust the pH to 1.6. Add 5 mL of APDC solution and extract into 20 mL of MIBK. For standard solutions, 10 mL of 2, 5, 7.5 and 10 ppm Pb solutions are each diluted to 50 mL. Adjust the pH to 1.6 and extract into 10 mL MIBK. The organic phases

after extraction were directly aspirated into the flame for AE measurement of Pb.

### 3. Experimental Conditions

The following conditions were used for AE measurements with GCA/McPherson (EU 703-D) spectrometer and the premixed capillary burner head.

<u>Element</u>	<u>Wavelength (nm)</u>	<u>Nebulizer gas flow rate</u>	<u>Fuel flow rate</u>	<u>Oxidant flow rate</u>
Al	396.15	Air = 6	Ace = 4.5	O <sub>2</sub> = 3.25
Ba	455.40	Air = 5.5	Ace = 4.5	O <sub>2</sub> = 4.25
Ca	422.68	Air = 4.5	Ace = 1.0	----
Co	345.35	Air = 5.5	Ace = 2.0	Air = 5
Cr	425.44	Air = 5.75	Ace = 1.5	----
Cu	324.75	Air = 5.75	Ace = 1.5	Air = 7.0
Fe	372.0	Air = 5.5	Ace = 2.75	O <sub>2</sub> = 2
Mg	285.22	Air = 4.5	Ace = 1.0	----
Mn	403.3	Air = 6.0	Ace = 1.25	----
Ni	352.45	Air = 6.0	Ace = 2.5	O <sub>2</sub> = 2.0
Pb	405.8			
Sr	460.73	Air = 5.75	Ace = 2.25	O <sub>2</sub> = 2.0
V	437.92	Air = 6.0	Ace = 5.0	O <sub>2</sub> = 3.5

Experimental conditions used in AA measurement with GCA/McPherson (EU 703-D) spectrometer with the Varian burner head were as follows:

<u>Element</u>	<u>Wavelength (nm)</u>	<u>Nebulizer gas flow rate</u>	<u>Fuel flow rate</u>	<u>Oxidant flow rate</u>
Al	309.35	Air = 5.5	Ace = 6.75	O <sub>2</sub> = 4.25
Ca	422.67	Air = 5.5	Ace = 3.75	Air = 9
Co	240.72	Air = 5.75	Ace = 2.25	Air = 2
Cr	357.87	Air = 5.75	Ace = 2.5	Air = 3.5
Cu	324.75	Air = 5.75	Ace = 2.5	Air = 4.75
Cd	228.80	Air = 6.25	Ace = 1.25	----
Fe	248.33	Air = 5.3	Ace = 2.25	----
Mg	285.22	Air = 4.25	Ace = 2.0	Air = 4
Mn	279.48	Air = 5.75	Ace = 1.75	----
Pb	283.30	Air = 5.75	Ace = 2.5	Air = 4
Zn	213.86	Air = 5.75	Ace = 1.5	Air = 6

#### 4. Measurements with ICP

The same dissolution procedure using acid digestion was used for samples to be analyzed with ICP. However, there is the possibility that HF remaining in the solution from the acid digestion could damage the torch, and it should be removed from the solution. This was done by digestion of the solutions with HClO<sub>4</sub> after dissolution and evaporation to near dryness. The residue was then dissolved in distilled

water and diluted in volumetric flasks.

Standardization of the ICP was carried out with a blank and the following set of standards:

Standard No. 1 Ni, Mo, Ti (1 ppm); Al, Sr, Ba, Fe (10 ppm)  
Standard No. 2 Co, Zn, Pb, Mn, Cu, Cd (1 ppm); Ca, Mg (10 ppm)  
Standard No. 3 As, Cr (1 ppm); P (10 ppm)  
Standard No. 4 V (1 ppm); Ca (100 ppm)

Two point standardization with blank and a high standard was used for each element.

After standardization of the plasma, all the standard solutions were run as samples. This was repeated also at the end of the measurement of samples. The recoveries of elements were 100±2%.

Instrumental parameters and operating conditions of the Jarrell-Ash Model 975 ICAP Atom Comp. were:

Gas flows: Cooling gas, 17 L/min  
Nebulizer gas, 1 L/min  
Solution uptake rate, 0.7 mL/min  
Observation height: 17 mm above load coil  
Optimized vertically and horizontally on  
cadmium line while aspirating 1 ppm cadmium.

Exposure time: 10 sec on line. No background correction.

##### 5. Determination of Mercury

Flameless Atomic Absorption has been used as a very sensitive method for the determination of mercury in

different types of samples. This method was first described by Hatch and Ott (165). In this method the sample is taken into solution by an oxidizing acid attack. Mercury in the solution is reduced to the elemental state by a stannous chloride or stannous sulphate solution, and then aerated from the solution. Mercury vapor passes through an absorption tube located in the light beam and its absorbance is measured. For more sensitive measurements, or when there are some interferences, a preconcentration step is necessary. Different methods have been used for preconcentration of mercury. Ure and Shand (166) used acidic  $KMnO_4$  to collect the mercury from the reduction aeration step followed by its determination. Vapor phase amalgamation is another method of preconcentration in which the mercury evolved from heating of the solid sample is deposited onto a "metal base" such as gold, silver or copper. Mercury is then released from the metal base upon heating and then passed through the absorption cell (167,168). Several modifications have been made to these methods by different workers. Ure (169) reviewed the analytical aspects of non-flame AA and AF methods for determination of mercury.

One of the most important aspects in mercury determination is sample dissolution prior to measurement. Huffman *et al.* (170) have reported methods for dissolution of different types of samples, especially those having a considerable content of organic matter such as coals and shales. They have used flameless AA for measurement of submicrogram quantities

of mercury in rocks, soils, shales and coals. Donnell *et al.* (147) have used a modification of this method for the analysis of oil shales.

In this study the method of dissolution is based on the Huffman *et al.* report. The measurement was carried out without preconcentration. A Perkin Elmer mercury analysis system (303-0832) equipped with a Dessiccant Kit containing  $Mg(ClO_4)_2$  to absorb water vapor, and a Mercury Scrubber Kit to prevent contamination of the laboratory with the mercury vapor released from the sample, was employed.

#### Reagents

All chemicals were reagent grade.

Mercury standard stock solution. Dissolve 1.3535 g

$HgCl_2$  in 100 mL 1 N  $H_2SO_4$ . Dilute to 1 liter.

Stannous chloride solution. Dissolve 10 g  $SnCl_2 \cdot 2 H_2O$

in 10 mL hot conc. HCl. Dilute to 100 mL.

Potassium permanganate. Make a 5% solution in distilled water, allow the solution to stand for a few days and decant the clear solution into a dark bottle.

Hydroxylamine hydrochloride. Dissolve 10 g of the reagent in 100 mL distilled water.

#### Apparatus

Spectrophotometer. GCA/McPherson (EU-703-D)

Light source. Mercury H.C.L., Perkin Elmer

Mercury Analyzer. Perkin Elmer (Model 303-0832)

Glassware. All were pyrex and were cleaned with Chromerge solution.

#### Digestion Procedure:

0.2-0.3 g of powdered shale sample was digested with 10 mL conc.  $H_2SO_4$  for 10 minutes on the hot plate (about  $150^\circ C$ ). The sample was cooled and after addition of 5 mL conc.  $HNO_3$  it was digested for about 30 minutes. Then the solution of 5%  $KMnO_4$  was added slowly until the solution turned to a purple color (about 30 mL was used). The solution was digested on the hot plate for about 1 hr. During digestion the purple color disappeared, so about 5 more mL of  $KMnO_4$  solution was added and digestion was continued for another 30 minutes. Then the solution was cooled and transferred into the aeration bottle. 15 mL hydroxylamine hydrochloride was added to the bottle, and the sides of the bottle were rinsed down with distilled water. The volume of the solution was adjusted to about 100 mL with distilled water.

Blank solutions were made by addition of the same volume of reagents, following the above digestion procedure. To each bottle of the sample or blank, 5 mL of  $SnCl_2$  solution was added and the aeration process was started.

#### Standardization and Measurement:

Two different methods were used, the standard addition and the calibration curve methods. In the standard addition method three samples of about the same weight (0.2-0.3 g) were used. To samples number two and three, after digestion, 1 and 2 mL of 0.5 ppm mercury standard solution were added, respectively. The concentration of mercury then was obtained

from a plot of absorbance vs. concentration.

The calibration curve method was carried out by putting 1, 2, 3 and 4 mL of standard mercury solution into the aeration bottles, followed by addition of 10 mL conc.  $H_2SO_4$ , 5 mL conc.  $HNO_3$  and 15 mL hydroxylamine hydrochloride solution to each bottle. All the solutions were diluted to about 100 mL and the reduction and aeration were then carried out.

In both methods, the baseline of the recorder was adjusted by running the blank solution. This was done before measurement of each sample and standard to ensure the complete removal of mercury from the cycle. The analytical wavelength was 253.65 nm, the resonance line of mercury. At the beginning of the aeration process, absorbance increased and after about 2 minutes it began to decrease. The reason for this behavior is that at the beginning mercury is not completely vaporized. As the vaporization goes to completion, the absorbance will increase. Finally, the decrease is due to loss of the mercury from the cycle to the tubes and partially to the atmosphere.

#### D. Results and Discussion

Before going into the discussion of the analytical results, it is necessary to discuss two important performance characteristics of the measurements, i.e., detection limits and quantifiable limits.

Detection limit is defined in various ways, but in general all definitions represent the minimum concentration of

the analyte which can be detected. The most common definition of the detection limit is the analyte concentration required to produce a S/N ratio of 2. To find the detection limits, one can find the standard deviation of at least ten blank readings and then calculate the analyte concentration, which is equal to two times the standard deviation.

Quantifiable limit is the minimum concentration at which a precise measurement can be carried out for a satisfactory quantitative estimate of the analyte (171). Quantifiable limit is usually taken as five times the detection limit.

Detection limits of elements obtained in this work are presented in Table 6. Most of the trace element concentrations of samples in solution were close to quantifiable limits; this resulted in relatively high standard deviation in some cases.

Concentration of some major, minor and trace elements converted to a raw shale weight basis are presented in Tables 7 to 12. The reported concentrations of Mn, Cu, Pb, Cr, Co, Zn, Cd and Ni by AE and AA are obtained after extraction into NaDDC-MIBK. For other elements the measurements were carried out on the original solutions after necessary pretreatments.

A series of experiments were run on several elements with AE and AA before pretreatment of the samples. The resultant concentrations for most elements, especially trace elements, were much different than those obtained after pretreatments. Trace elements show a large positive error without pretreatment and this is much more severe in AE than in AA.

This behavior may be discussed in terms of chemical interferences in both AA and AE, which have an enhancing or depressing effect on the analyte, and spectral interferences especially in AE, due to coexistence of nearby spectral lines or bands.

Results obtained with ICP are in most cases in agreement with AA and AE results. However, Cu and Pb show a higher concentration by ICP. For Cu the 324.75 nm atomic line was used, which is located in the OH band region (85), so there is a possible spectral interference resulting in a positive error. This interference can be minimized or eliminated by doing the measurement in a background-corrected mode. In the case of Pb, the signal was noisy and, in fact, it showed relatively high standard deviations. This is not only true in the case of ICP, but for FAA and FAE, where high deviations were also observed.

The precision of all three methods was good for most elements. However, the best precision on the measurements was obtained by ICP with a RSD of less than  $\pm 2\%$  for most elements. This good characteristic of ICP can be related to the stability of the plasma, reproducibility of the nebulizer, and much less severe chemical interferences as compared to FAA and FAE. Precision in FAE and FAA measurements depends largely on the element to be measured and its concentration. For major elements precision is better than 1%, but some trace elements show a relatively high RSD; this is due to relatively low S/B ratios at low concentrations.

In general, it was found that FAE and, in some cases, FAA, employed for the analysis of complex matrices such as shales by direct analysis of the samples after dissolution, were unsatisfactory and all of the possible types of interferences should be considered and compensated for if possible.

Results of the analysis of Hg by cold vapor AA technique are presented in Table 13. The Heebner and Eudora shales contain relatively high concentrations of Hg.

The Heebner and Eudora black shales, which have a high concentration of organic matter as heavy hydrocarbons, represent higher concentrations of some trace elements such as Cu, Cr, Zn, Ni and V, as compared to two other shale samples. This characteristic of hydrocarbon-rich shales may be related to the high organic matter content which has the capability of complexing certain metal species.

Table 6

## Detection Limits (ppm)

Element	AE		AA		ICP	
	Wavelength (nm)	D.L.	Wavelength (nm)	D.L.	Wavelength (nm)	D.L.
Ca	422.68	0.03	422.67	0.05	396.8	0.06
Mg	285.22	0.07	285.22	0.02	383.23	0.03
Fe	372.0	0.04	248.33	0.04	259.9	0.008
Al	396.15	0.03	309.35	0.05	308.22	0.02
Mn	403.30	0.02	279.48	0.03	257.6	0.0008
Cu	324.75	0.06	324.75	0.02	324.7	0.002
Pb	405.8	0.2	283.30	0.10	220.3	0.03
Cr	425.44	0.04	357.87	0.01	267.7	0.004
Co	345.35	0.05	240.72	0.03	228.6	0.003
Zn	--	--	213.86	0.006	213.8	0.002
Cd	--	--	228.80	0.007	228.8 x 2	0.005
Ni	352.45	0.07	--	--	231.6 x 2	0.01
Sr	460.73	0.003	--	--	421.5	0.001
Ba	455.40	0.04	--	--	493.4	0.002
V	437.92	0.30	--	--	292.4	0.003
Hg	--	--	253.65	0.0003	--	--
As	--	--	--	--	197.20	0.07
Mo	--	--	--	--	202.0	0.01
Tl	--	--	--	--	334.9	0.001
PO <sub>4</sub>	--	--	--	--	214.9 x 2	0.3

Table 7

## Elemental Concentrations of Ninnescah Shale

Element	FAE		FAA		ICP	
	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD
Ca	4.40	0.6	4.76	0.5	4.60	0.5
Mg	3.04	1.2	3.27	0.9	3.28	1.3
Fe	2.36	0.8	2.32	0.8	2.38	0.7
Al	4.66	1.0	4.70	2.7	4.83	0.94
Mn	0.103	3.1	0.099	1.3	0.10	0.9
Cu	0.0068	6.9	0.0065	6.7	0.019	1.5
Pb	0.0083	4.3	0.0073	11.0	0.014	2.5
Cr	0.011	3.5	0.0064	0.5	0.0063	2.7
Co	0.0042	4.2	0.0031	4.5	0.0026	0.6
Zn	----	----	0.019	2.0	0.022	1.0
Cd	----	----	0.0087	3.4	0.010	1.8
Ni	0.0054	3.3	----	----	0.0048	1.4
Sr	0.019	2.6	----	----	0.015	0.43
Ba	0.028	0.8	----	----	0.026	0.5
V	0.0083	6.0	----	----	0.0064	2.0

Table 8

## Elemental Concentration of Heebner Shale

Element	FAE		FAA		ICP	
	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD
Ca	0.45	1.0	0.43	0.4	0.45	1.6
Mg	1.06	2.4	1.0	0.9	1.05	1.6
Fe	3.59	0.3	3.58	0.5	3.68	1.7
Al	7.08	1.2	6.90	1.0	7.26	1.9
Mn	0.024	3.2	0.020	5.0	0.019	2.0
Cu	0.011	7.0	0.012	4.0	0.031	2.1
Pb	0.015	4.5	0.012	4.3	0.025	3.5
Cr	0.041	1.8	0.039	0.7	0.038	1.8
Co	0.0046	4.7	0.0030	7.5	0.0033	2.7
Zn	----	----	0.102	0.6	0.10	0.6
Cd	----	----	0.0049	3.3	0.0059	2.0
Ni	0.026	1.0	----	----	0.022	2.5
Sr	0.0087	2.8	----	----	0.008	1.6
Ba	0.042	2.1	----	----	0.053	1.3
V	0.098	2.0	----	----	0.085	1.8

Table 9

## Elemental Concentration of Heumader Shale

Element	FAE		FAA		ICP	
	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD
Ca	0.338	1.5	0.345	3.0	0.365	1.4
Mg	1.146	0.8	1.09	1.0	1.06	1.3
Fe	3.55	0.3	3.49	0.5	3.71	0.7
Al	8.98	0.5	9.13	1.3	9.24	1.5
Mn	0.045	1.6	0.033	1.8	0.034	0.6
Cu	0.0050	7.8	0.0078	5.1	0.013	0.8
Pb	0.0084	7.0	0.0098	4.7	0.023	3.0
Cr	0.0061	1.0	0.0057	4.0	0.0060	1.6
Co	0.0048	6.2	0.0041	3.7	0.0045	1.6
Zn	----	----	0.013	3.5	0.015	1.8
Cd	----	----	0.0025	6.0	0.0022	4.2
Ni	0.0073	2.3	----	----	0.0066	4.9
Sr	0.024	3.2	----	----	0.021	2.0
Ba	0.052	1.33	----	----	0.057	2.2
V	0.028	7.5	----	----	0.015	1.5

Table 10

## Elemental Concentration of Eudora Shale

Element	FAE		FAA		ICP	
	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD
Ca	1.58	2.4	1.70	0.6	1.72	0.9
Mg	1.30	0.9	1.24	0.8	1.20	1.5
Fe	2.42	0.5	2.42	1.0	2.32	0.6
Al	5.50	0.5	5.46	1.8	5.30	1.6
Mn	0.021	4.3	0.013	2.9	0.014	0.45
Cu	0.012	4.5	0.011	3.1	0.014	1.7
Pb	0.0082	4.5	0.0075	8.7	0.037	1.7
Cr	0.075	0.7	0.067	0.5	0.065	0.45
Co	0.0044	5.0	0.0032	3.3	0.0025	1.7
Zn	----	----	0.102	0.75	0.091	1.5
Cd	----	----	0.0039	4.2	0.0042	2.4
Ni	0.035	1.0	----	----	0.031	0.9
Sr	0.026	2.4	----	----	0.022	0.8
Ba	0.030	1.7	----	----	0.035	1.0
V	0.0605	2.0	----	----	0.037	0.4

Table 11

## Elemental Concentration of Heebner Shale No. 2

Element	FAE		FAA		ICP	
	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD
Ca	0.68	1.4	0.65	1.2	0.65	1.7
Mg	1.096	1.8	1.02	0.4	0.97	1.9
Fe	3.12	0.5	3.09	0.8	3.11	2.2
Al	6.57	0.5	7.0	1.3	6.8	2.5
Mn	0.023	2.4	0.016	4.2	0.017	2.2
Cu	0.012	5.5	0.012	2.7	0.018	2.5
Pb	0.013	5.0	0.012	5.6	0.019	5.4
Cr	0.029	1.8	0.027	1.3	0.023	2.8
Co	0.0038	6.0	0.0034	8.6	0.0030	1.2
Zn	----	----	0.145	0.5	0.136	0.7
Cd	----	----	0.123	2.9	0.013	0.3
Ni	0.030	2.0	----	----	0.022	1.9
Str	0.009	3.5	----	----	0.008	1.8
Ba	0.032	1.0	----	----	0.039	1.2
V	0.081	3.0	----	----	0.067	2.2

Table 12

Concentrations of As, Mo, Ti and PO<sub>4</sub> Measured only with ICP

Element	Ninnescah Shale		Heebner Shale		Heumader Shale		Eudora Shale		Heebner Shale No. 2	
	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD	% Conc.	% RSD
As	0.027	2.9	0.042	5.6	0.053	0.008	0.033	3.5	0.046	2.0
Mo	0.0037	0.8	0.014	2.2	0.008	4.6	0.0073	2.9	0.010	2.4
Ti	0.42	0.5	0.36	1.5	0.50	2.0	0.25	0.9	0.313	2.7
PO <sub>4</sub>	0.23	3.8	0.37	3.2	0.38	1.9	1.90	1.2	0.65	0.7

Table 13

Concentration of Mercury  
(ppm)

Sample No.	Run 1	Run 2	Run 3	Run 4	Average	% RSD
1 (Ninnescah)	0.81	0.85	0.83	---	0.83	2.4
2 (Heebner) <sup>a</sup>	2.51	2.76	2.66	---	2.64	4.8
3 (Heumader)	1.04	1.12	0.99	---	1.05	6.2
4 (Eudora)	2.41	2.33	2.51	---	2.42	3.7
5 (Heebner) <sup>b</sup>	2.43	2.55	2.60	2.65	2.56	3.7

<sup>a</sup>This sample was obtained as a powder from the Kansas Geological Survey

<sup>b</sup>This sample was obtained as a piece of rock from the Kansas Geological Survey.

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