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STUDIES OF THE ATOMIC FLUORESCENCE OF
ZINC AND BERYLLIUM AND THE SPECTROSCOPIC
STUDIES OF THE CHROMOTROPIC ACID - NITRATE
REACTION.**

**Louisiana State University and Agricultural
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STUDIES OF THE ATOMIC FLUORESCENCE OF
ZINC AND BERYLLIUM AND
THE SPECTROSCOPIC STUDIES OF
THE CHROMOTROPIC ACID - NITRATE REACTION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Chun-Jer Hsu
B.S., Cheng-Kung University, 1960
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ABSTRACT

Atomic fluorescence spectroscopy is a recently developed technique for the determination of several metal elements. Zinc fluorescence has been detected by this method but the parameters controlling the intensity are not understood. A general study of the atomic fluorescence spectroscopy of zinc was undertaken. Important experimental parameters were investigated and are discussed.

The atomic fluorescence of beryllium has been observed for the first time. A high intensity beryllium hollow cathode lamp was used as the radiation source. An oxy-acetylene as well as a nitrous oxide-acetylene flame were studied as atomizers. A newly designed burner assembly is described. This burner enabled nitrous oxide-acetylene flames to be used for atomic fluorescence studies. The analytical sensitivity for beryllium at the resonance line 2349 Å was 10 p.p.m. in oxy-acetylene flame and 0.5 p.p.m. in nitrous oxide-acetylene flame. The analytical calibration curves for both flames are presented. No significant interference was found from the cations studied. Some anionic interferences were removed by the addition of EDTA. The effect of some organic solvents were investigated.

Chromotropic acid is known as a reagent for nitrate spot test in the presence of strong sulfuric acid. The reaction is specific and sensitive. The most sensitive reaction between chromotropic acid and nitrate occurs at about 70% sulfuric acid. The yellow-brown

reaction product is studied by NMR technique and UV method. The NMR spectra indicate that the product is a mononitro derivative of chromotropic acid. The UV spectrum indicates that the product is a quinone compound. It is therefore concluded that the structure of the product is a mononitro-quinone derivative of chromotropic acid in polymer form.

CHAPTER I

ATOMIC FLUORESCENCE SPECTROSCOPY

A. INTRODUCTION

Atomic fluorescence spectroscopy is a new method of chemical analysis. The principle of this method, however, has existed for a number of years. The principle is based upon the following phenomenon: An atom is excited by the absorption of radiant energy at its resonance wavelength. The excited atom formed emits radiant energy at the same or lower frequency thereby generating fluorescence from the atom.

Atomic fluorescence is similar in many respects to molecular ultraviolet fluorescence. It is also related to atomic absorption in the same way that molecular fluorescence is related to molecular ultraviolet absorption. The fluorescent spectra of an atom is simple and corresponds to the transitions of an atom from one energy state to a lower energy state. In this respect it is similar to molecular fluorescence. However, in contrast to molecular fluorescence, the various electronic energy levels are not modified by vibrational and rotational states because simple atoms do not vibrate or rotate in the same sense that molecules do. As a result, the fluorescence consists of a few well-defined fluorescence lines for each

element. The frequency of these lines is the characteristic of each element.

The intensity of atomic fluorescence is proportional to the following parameters: (a) the intensity of the radiation source, (b) the fraction of radiation absorbed by the atoms, (c) the efficiency of conversion of absorbed energy to fluorescence, and (d) the fraction of fluorescence self-absorbed by other sample atoms in the system. The fraction of radiation absorbed by the sample is dependent on the number of atoms in the sample cell. This fact allows the process to be used for analytical purpose.

The attractive features of atomic fluorescence as an analytical tool are as follows: (a) the fluorescence intensity can be increased by increasing the intensity of radiation source, the size of flame cell, and the number of ground state atoms of the sample element, (b) the intensity of fluorescence is linearly related to the concentration of the sample element over a wide concentration range, (c) a radiation source with wide spectral lines can be used, (d) the element may be excited at one wavelength and the fluorescence measured at another wavelength. This eliminates the problem of incident light scattering.

There are several limitations of atomic fluorescence spectroscopy. The chief disadvantage is self-absorption of the fluorescence by the sample. This causes a reversal of the slope of the calibration curve relating the fluorescence intensity and the analysis of the sample at high concentration. However, it can be overcome

by suitable dilution of the sample. If a flame atomizer is used, metals which form refractory oxides will be difficult to detect; and it requires a liquid sample. Only a limited number of metal elements can be studied by the method; most non-metal elements will be excluded at the present instruments available. The scattered radiation by solvent droplets and salt particles in the flame may cause a source of error. Despite these disadvantages, atomic fluorescence capable of being further exploited for analytical purposes is anticipated.

B. HISTORICAL BACKGROUND

Most of the research on the atomic fluorescence of metal vapors enclosed in quartz containers was published between 1900 and 1930. Mitchell and Zemansky (18) and Pringsheim (21) in their books discussed much of this early work. Most of the original work on atomic fluorescence was performed by Wood and Dunoyer (18, 21). However, it was not until 1924 that Nichols and Howes (19) first reported observing atomic fluorescence of lithium, sodium, calcium, strontium, and barium in a Bunsen flame. In 1929, Badger (4) published a paper on the atomic fluorescence of thallium, magnesium, copper, silver, cadmium, mercury, and sodium in a Bunsen flame. Between 1930 and 1960 little research was performed on the atomic fluorescence of metal vapor. In 1961, Robinson (25) noted weak fluorescence of the Mg 2852 Å line in the study of mechanism of elemental spectral excitation in flames. At the 1962 Spectroscopy Colloquium in Maryland, Alkemade (1) described the use of atomic fluorescence as a means of measuring quantum yields for the Na-5890 Å line.

The most serious attempts to use atomic fluorescence as an analytical tool was made in 1964 by Winefordner and co-workers (40, 41). They described atomic fluorescence spectroscopy as a possible means of chemical analysis and developed this method for the determination of zinc, cadmium, and mercury. Since then atomic fluorescence spectroscopy has been demonstrated for at least 26 metallic elements including aluminum, antimony, barium, beryllium, bismuth, calcium, chromium, cobalt, copper, gallium, gold, indium, iron, lead, magnesium, manganese, nickel, palladium, selenium, silver, tellurium, thallium, titanium, and zirconium (3, 5, 6, 8, 9, 10, 12, 13, 17, 20, 29, 31, 37, 42) by several workers. Some of these early works were summarized and reviewed by Robinson (27, 28), West (32, 33) and Winefordner (43, 44). The intensive studies of atomic fluorescence spectroscopy indicate that the method is now under development.

C. TYPES OF ATOMIC FLUORESCENCE

Generally four basic types of atomic fluorescence have been classified (18, 40). These are illustrated in Figure 1.

1. Resonance Fluorescence results when the ground state atom is excited to an excited state and then undergoes radiational deactivation to the ground state re-emitting radiation of the same spectral line which was absorbed. For example, the Zn 2139 Å, Cd 2288 Å, and Be 2349 Å lines belong to this type. Because resonance fluorescence is usually observed and its intensity is generally significantly greater than the intensity of other types of atomic fluorescence, resonance fluorescence has had and will probably have the greatest analytical use.

2. Direct Line Fluorescence results when the ground state atom is excited to a higher excited state and then undergoes a radiational transition to a lower excited state which is not the ground state. In the process it fluoresces. The fluorescence occurs at a longer wavelength than the absorption wavelength. The fluorescent emission of the Tl 5350 Å line after excitation of Tl atoms by the Tl 3776 Å line is the example.

3. Stepwise Line Fluorescence is a process in which the ground state atom is excited to a higher excited state. It then deactivates to a lower excited state without fluorescing, and from this state deactivates back to the ground state. During the final step it fluoresces. An example is the fluorescent emission of the Na 5890 Å line after excitation of Na atoms by the Na 3303 Å line.

4. Sensitized Fluorescence occurs when donor atom is excited by absorption of radiation source, the excited atom collides with the sample atom transferring energy and exciting the sample atom, and then the sample atom undergoes radiation deactivation. For example, if a quartz container has a mixture of mercury and thallium vapor, the mercury atoms may be excited by irradiating the 2537 Å line. Excited mercury atoms collide with the thallium atoms which in turn become excited in the process. Fluorescence of Tl 3776 Å and 5350 Å lines has been observed.

D. THEORY

The mathematical relationships for the atomic fluorescence intensity have been correlated by Windfordner and co-workers (40, 45).

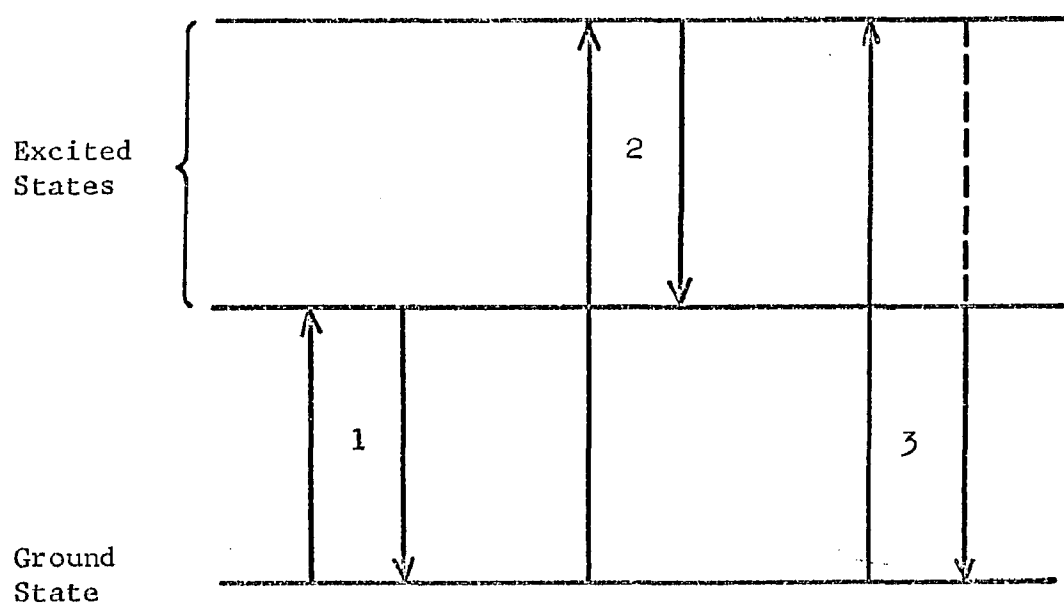


Figure 1

Types of Atomic Fluorescence. (1) Resonance Fluorescence;
(2) Direct Line Fluorescence; (3) Stepwise Line Fluorescence.

Assuming the absorbed and emitted radiation are of the same frequency, i.e., resonance fluorescence, then the intensity of atomic fluorescence is proportional to the quantity of radiant energy absorbed. Therefore

$$P_F = \phi P_A \quad (1)$$

where P_F is the quantity of total fluorescence, P_A is the quantity of radiant energy absorbed, and the proportionality factor, ϕ is the quantum efficiency.

Figure 2 shows an idealized absorption profile of the line, Gaussian in shape, on which a triangle of the same area is superimposed. Because the area of triangle is given by the peak absorption times the half-width of the triangle, the relationship between the absorbed and the incident radiation can be expressed by

$$P_A = P^0 (1 - e^{-K^0 L}) \Delta V \quad (2)$$

where P^0 is the quantity of incident radiation, K^0 the atomic absorption coefficient, L the length of the absorption cell (a flame in this case), and ΔV is half the base-width of the triangle.

An approximation to ΔV can be made using the approach derived by Willis (39). If the absorption profile is Gaussian in shape, it can be approximated to a triangle. Willis has shown the half-width of the triangle, ΔV , is related to the half intensity-width of the Gaussian curve, ΔV_g , by the expression

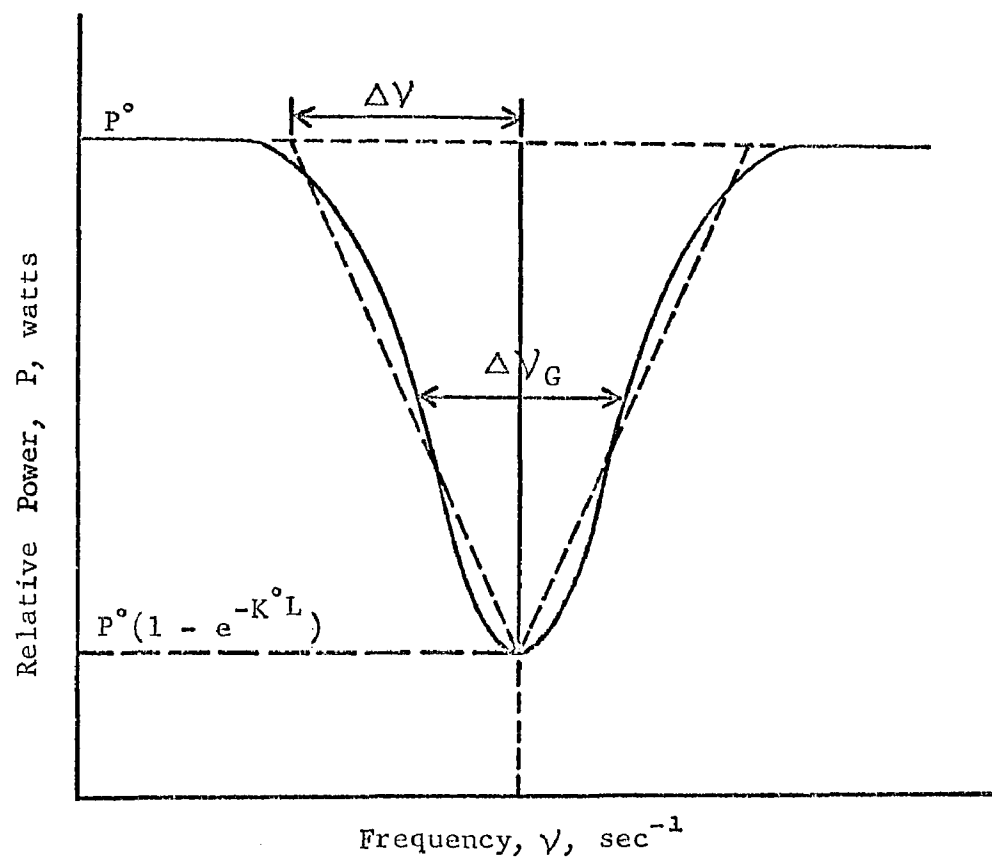


Figure 2

Intensity-frequency Distribution of an Idealized
Absorption Profile of the Line — Gaussian and
Triangular Distribution

$$\Delta\nu = \frac{\pi^{1/2}}{2 (\ln 2)^{1/2}} \Delta\nu_g \quad (3)$$

The value of K° is given by the early work of Mitchell and Zemansky (18):

$$K^\circ = \frac{(\ln 2)^{1/2} \lambda^2 g_1}{4 \pi^{3/2} \Delta\nu_D g_0} N A_t \delta \quad (4)$$

where λ is the wavelength of the absorbing line, g_1/g_0 a priori statistical weights of atoms in states 1 and 0, $\Delta\nu_D$ the Doppler half-width of the absorption line, N the concentration of the absorbing species in the ground state, and A_t the transition probability from 1 to 0. δ is defined as $(\ln 2)^{1/2}$ times the ratio of the Lorents plus Holtsmark plus natural half-widths to the Doppler half-width.

By combining Equation 1 and Equation 2, we have

$$P_F = \phi P^\circ (1 - e^{-K^\circ L}) \Delta\nu e^{-K^\circ L/2} \cosh (K^\circ L/2) \quad (5)$$

where $e^{-K^\circ L/2} \cosh (K^\circ L/2)$ is a correction term for self-absorption by the other atoms of the sample (15). Equation 5 can be rewritten in terms of the intensity I_F by dividing P_F by the area A_F of the flame cell from which the fluorescent radiation is emitted, and by 4π steradians. Then

$$I_F = \frac{\phi P^\circ \Delta\nu}{4 \pi A_F} (1 - e^{-K^\circ L}) e^{-K^\circ L/2} \cosh (K^\circ L/2) \quad (6)$$

From Equation 6 it should be noted that, as in molecular fluorescence, I_F is proportional to N , the number of ground state atoms. But as N increases, the term $(1 - e^{-K^\circ L})$ approaches 1. Therefore, I_F goes through a maximum as N increases; then quenching begins and I_F decreases.

Equation 6 is valid only if the frequency of absorption is equal to the frequency of fluorescence. If this is not the case, Equation 6 is refined to become

$$I_F = \frac{\phi_1}{4\pi A_f} \phi_2 \frac{\nu_1}{\nu_2} \Delta \nu_2 (1 - e^{-K^\circ_1 L}) e^{-K^\circ_2 L/2} \cosh(K^\circ_2 L/2) \quad (7)$$

where subscript 1 refers to the excited state from which the fluorescent transition originates, subscript 2 designates the excited state resulting from the absorption of source radiation, ϕ_1 is the number of atoms which undergo the observed fluorescence transition per unit time divided by the total number of atoms leaving state 1 per unit time, ϕ_2 is the number of atoms which reach excited state 1 per unit time divided by the total number of atoms leaving state 2 per unit time, ν_1 is the frequency of fluoresced radiation, ν_2 is the frequency of absorbed radiation, $\phi_1 \phi_2 \frac{\nu_1}{\nu_2}$ is the energy efficiency of the process, K°_1 is the atomic absorption coefficient for fluoresced radiation (which may be absorbed), and K°_2 is the atomic coefficient for the absorbed radiation. If several lines fluoresce, the term can be expanded further (40).

For the case of low concentration where $K^\circ L$ is small, Equation 6 can be simplified by expanding the $(1 - e^{-K^\circ L})$ term and

noting the self-absorption term approximately equals 1. Then I_F is given by

$$I_F = \frac{\phi P^\circ \Delta V K^\circ L}{4\pi A_f} \quad (8)$$

By substituting Equation 4 into Equation 8, we have

$$I_F = \frac{(\ln 2)^{1/2} \phi \Delta V L \lambda^2 A_t \delta g_1}{16 \pi^{5/2} A_f \Delta V_D g_0} P^\circ N$$

or

$$I_F = C P^\circ N \quad (9)$$

where C is a constant for any particular experimental arrangement. This leads to the relationship that the intensity of fluorescence is proportional to the incident radiation and the number of atoms which can absorb. If the incident radiation is constant, then I_F will be linear with N , the ground state atom concentration.

Since the total solution concentration is to be measured it will be necessary to know the relationship between the ground state atom concentration N and the solution concentration C° . This relationship is given by the expression (44)

$$N = \frac{10^{19} F \epsilon \beta C^\circ}{e_f Q} \quad (10)$$

where F is the flow rate of the aspirated solution in $\text{cm}^3/\text{min.}$, e the aspiration efficiency, β the atomization efficiency, C° the sample concentration in moles/l, e_f the flame expansion factor, and Q the flow rate of gases into the flame in $\text{cm}^3/\text{sec.}$ It is assumed that the fraction of atoms in the excited states is negligible compared to that in the ground state. This assumption is valid for most atoms in which the excited states are widely separated from the ground states (greater than 2 eV.). Walsh (32) calculated the magnitude of the fraction of atoms in the first excited state for resonance lines of various elements at the temperatures ranging from 2000 °K to 5000 °K. His results show that in nearly all cases the number of atoms in the first excited state is only a small fraction of number of atoms in the ground state. However, for transition metal or rare earth atoms with low lying levels, a correction for the ground state atom concentration must be made. According to Boltzman statistics the distribution of atoms in different energy states at temperature T is given by:

$$N_j = \frac{N g_j \exp(-E_j/KT)}{\sum g_j \exp(-E_j/KT)} \quad (11)$$

Here N is the total number of ground state atoms, N_j is the number of atoms in the j th state, g_j is the statistical weight. E_j is the energy of the j th state, and K is the Boltzman constant.

E. EQUIPMENT

Theoretically all models of atomic absorption spectrophotometers can be used for atomic fluorescence work. This can be

done simply by positioning an intense source of radiation at right angle to the entrance slit. The source of radiation falls on the flame atomizer. The sample atoms become excited and fluoresce. The fluorescent radiation is collected at the monochromator entrance slit, and the amplified signal from a multiplier phototube detector is displayed by a meter or recorder. The following diagram in Figure 3 would illustrate the basic components and their arrangement in an atomic fluorescence instrument assembly.

(a) Radiation Sources

The basic and most important component of any atomic fluorescence instrument is the radiation source for excitation. The source need not be a narrow spectral line as required for atomic absorption line to meet the analytical use. A variety of source types have been successfully used in atomic fluorescence studies.

The metal-vapor arc discharge lamps such as Osram and Philips lamps have been used for cadmium, thallium, and zinc excitation sources (5, 17, 41). Although these lamps are available for some other metals, they are either completely self-reversed or extremely weak, and are therefore essentially limited to these three elements.

Microwave-excited electrodeless discharge tubes as sources (7, 8, 9, 10, 17, 42) are currently being extensively investigated. They are easy to construct and they give sharp and intensive spectral lines for many elements. The use of electrodeless discharge tubes as exciting source for atomic fluorescence would seem to be very promising.

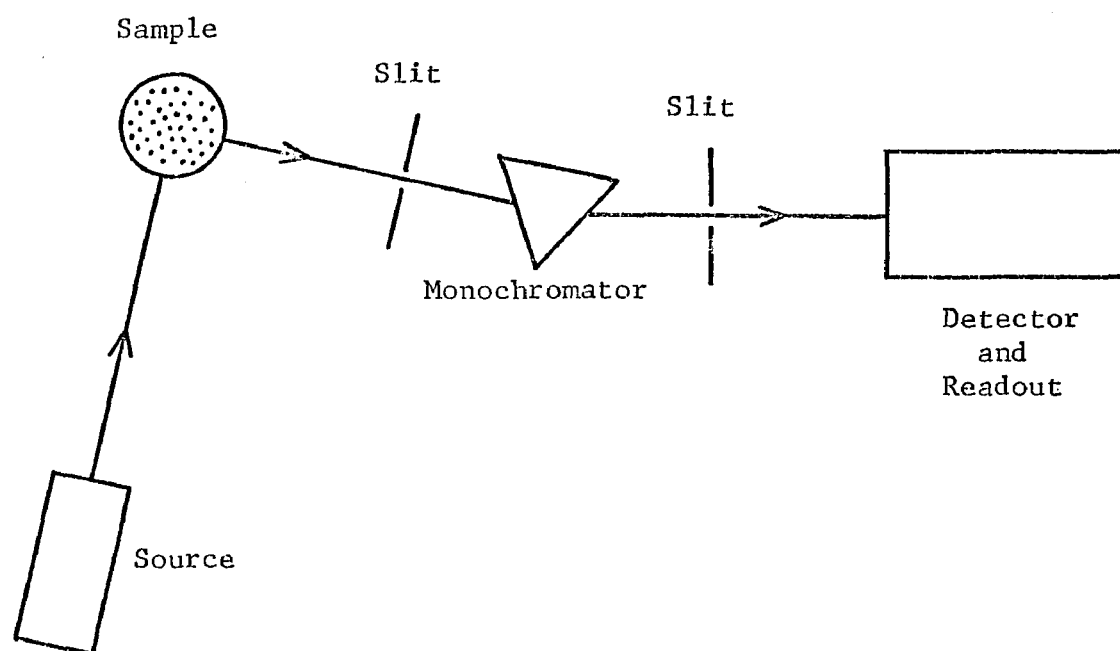


Figure 3

Schematic Diagram of Equipment for
Atomic Fluorescence Measurement

The use of continuous sources such as the xenon arc lamp (6, 13, 31) has demonstrated that a single (continuous) source may be used to excite atomic fluorescence for many elements -- e.g., Ba, Bi, Ca, Cd, Cu, Co, Ga, Au, Fe, Pb, Mg, Mn, Hg, Ni, Ag, Ti, and Zn. More recently a mercury discharge lamp (20) was studied by using its complex high-intensity line source, rather than a continuum, as a general source for exciting the fluorescence of the "overlapping" lines of the other elements -- e.g., Cd, Cr, Cu, Fe, Mn, Mg, Ni, Pd, Tl, and Zn. However, the use of the continuous source requires a high resolution monochromator to reduce the wavelength range of scattered radiation falling on the detector. Also the intensity of a continuous source at any one wavelength, especially in the ultraviolet region, is very low.

The conventional hollow cathode lamps have been used in atomic fluorescence work (25). The intensity of fluorescence was relatively weak mainly due to the low intensity of the hollow cathode light source which was used. Demountable hot hollow cathode lamp as excitation source has proved useful and satisfactory for exciting the fluorescence of at least fourteen elements (11, 12). The high-intensity hollow cathode lamps recently developed by Sullivan and Walsh (30) have been used successfully for excitation source of nickel, silver, and beryllium (3, 29, 37). The method should be tried in other atomic fluorescence investigations. Further, because high-intensity hollow cathode are available for most metals, they would seem the logical choice as a radiation source for this new field.

(b) Modulation

In most instances, thermal excitation of the atoms gives rise to emission of radiation of the same frequency as the absorption line. Also, the flame itself sometimes emits radiation at the same wavelength. This radiation acts as a direct interference to the measurement of the fluorescence intensity. These difficulties can be overcome by modulating the source and tuning the detector. The beam of radiation source is electronically or mechanically modulated at a definite frequency. The amplifier in the readout assembly is tuned to the modulating frequency and therefore, reads only the fluorescence intensity and does not read the emitted radiation since it is not modulated to the tuned frequency of the detector. This is illustrated in Figure 4.

(c) Atomizers

The atomizer is used to reduce the sample element from an ion or a molecule to the neutral atomic state. So far flames have been used exclusively as the atomizers in atomic fluorescence. Hydrogen, acetylene, and propane are the commonly used fuels. Both air and oxygen are often used as supporters of combustion; air mostly in premixed type burners, and oxygen in total consumption burners. West and co-workers(10) used a special type of flame: nitrogen-hydrogen and argon-hydrogen flames for bismuth atomization, because of its low background noise. Very recently Robinson and Hsu (29) introduced a nitrous oxide-acetylene flame which would be useful for refractory

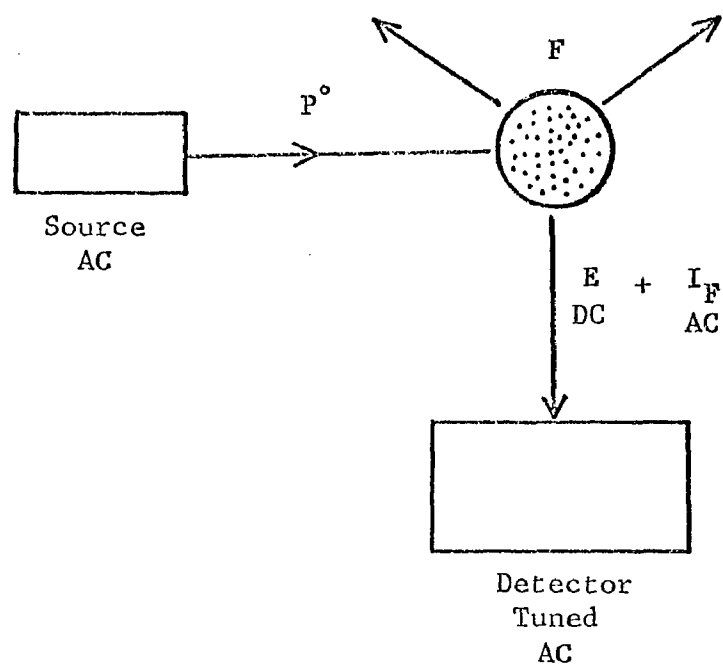


Figure 4

Modulation of Equipment. P° = Source Signal;
F = Flame and Sample; E = Emission from Flame;
and I_F = Intensity of Fluorescence Signal.
Modulation Eliminates Signal E from Readout.

metal atomization. In spite of the low efficiency of reducing the sample element to the atomic state and being subject to numerous sources of error, such as chemical interference, solvent effect, the type of fuel and oxidant used, the ratio of fuel to oxidant, and background noise due to flame emission and scattering of exciting light from small unevaporated solvent droplets and salt particles, flame atomizers are inexpensive, convenient to use, and with little care can provide accurate and reproducible results.

(d) Monochromator

An ordinary ultraviolet-visible monochromator adequate for emission and absorption methods is quite suitable for atomic fluorescence spectroscopy. Either quartz prisms or grating monochromators have been used in these instruments.

(e) Detector

The basic components of this unit are a photomultiplier tube and an amplifier tuned to the modulation frequency. The most commonly used photomultiplier has been an R.C.A. 1P28, E.M.I. - 6255B and 9601B photomultiplier tubes, which are particularly sensitive in the ultraviolet region, where most of the lines used in atomic fluorescence spectroscopy occur, have also been used. However, any of the detectors suitable for atomic absorption would no doubt be suitable for atomic fluorescence.

(f) Optical Systems

As shown in Figure 5 in Chapter II, the radiation source is mounted so that it subtends a right angle to the entrance slit

of the monochromator at the flame. Usually a condensing lens is used to direct the light beam of the source passing through the flame cell. Winefordner and co-workers (17, 31, 41, 42) used a baffle box as flame housing to exclude stray radiation from the entrance slit of the monochromator. Armentrout (3) used a front-surfaced mirror after the flame to reflect the exciting beam back through the flame, and an additional lens between flame and entrance slit to focus the fluorescent emission on the entrance slit. In this study, an additional concave mirror (Figure 5 in Chapter II) was introduced to reflect more fluorescent emission back into the entrance slit.

(g) Commercial Equipment

The Aztec Techtron AA3 and AA4 atomic absorption spectrophotometers with atomic fluorescence attachments are the commercial available instruments. In this study, a modified Techtron AA3 was used throughout.

CHAPTER II

ATOMIC FLUORESCENCE SPECTROSCOPY OF ZINC

A. INTRODUCTION

The atomic fluorescence spectroscopy of zinc has recently been demonstrated by several investigators (6, 13, 17, 31, 41, 42). Most of these studies were undertaken to observe the atomic fluorescence of a series of elements using a single (continuous) xenon arc lamp as exciting source and to observe the effect of various flame atomizers on the limits of detection by the method. A general study of atomic fluorescence spectroscopy of zinc appears to have been neglected.

The work presented here has been carried out to obtain more information concerning the atomic fluorescence spectroscopy of zinc. An optimum condition has been established for the measurement of atomic fluorescence of zinc in aqueous solution by using a Philips zinc vapor discharge lamp as radiation source and an oxy-hydrogen flame as atomizer. Under this optimum condition, the sensitivity limit, calibration curve, chemical interference, and effect of organic solvents have been investigated.

B. EXPERIMENTAL

(a) Apparatus

The apparatus used consisted of a Techtron AA3 atomic absorption spectrophotometer. A Beckman large bore total consumption

burner for oxy-hydrogen flame was used for all studies. The burner was so mounted that it could be adjusted both horizontally and vertically. A Philips zinc vapor discharge lamp was used to excite fluorescence in the flame. The lamp was mounted at right angle to the optical axis of the monochromator and was electronically modulated at 60 cps which tuned to the detector.

Measurements of atomic absorption were made with the same instrument. A zinc hollow cathode lamp (Atomic Spectral Lamps, Australia) provided the necessary radiation at 2139 Å.

(1) Optical System

The experimental setup used is shown in Figure 5. This optical arrangement was similar to the one used by Armentrout (3) except an additional concave mirror was used to focus fluorescence emission onto the entrance slit increasing the detectable fluorescence intensity about two-fold. To obtain the most sensitive results, the lamp source was situated as closely as possible to the flame (about 1 1/2 inch from the lens) with a condensing lens located between the flame and the lamp.

(2) Instrumental Settings

The lamp operated at 0.9 ampere which was delivered through an electronically regulated power supply (Aztec Instruments Inc.). The RCA 1P28 photomultiplier tube operated at 800 volts and the amplifier gain-control was set between positions 9 and 11. The wavelength was set at the zinc resonance line 2139 Å, the only line from which the fluorescent emission was observed. The slit-width was opened to its maximum value of 300 microns without adverse effect on selectivity or stability of the fluorescence signal.

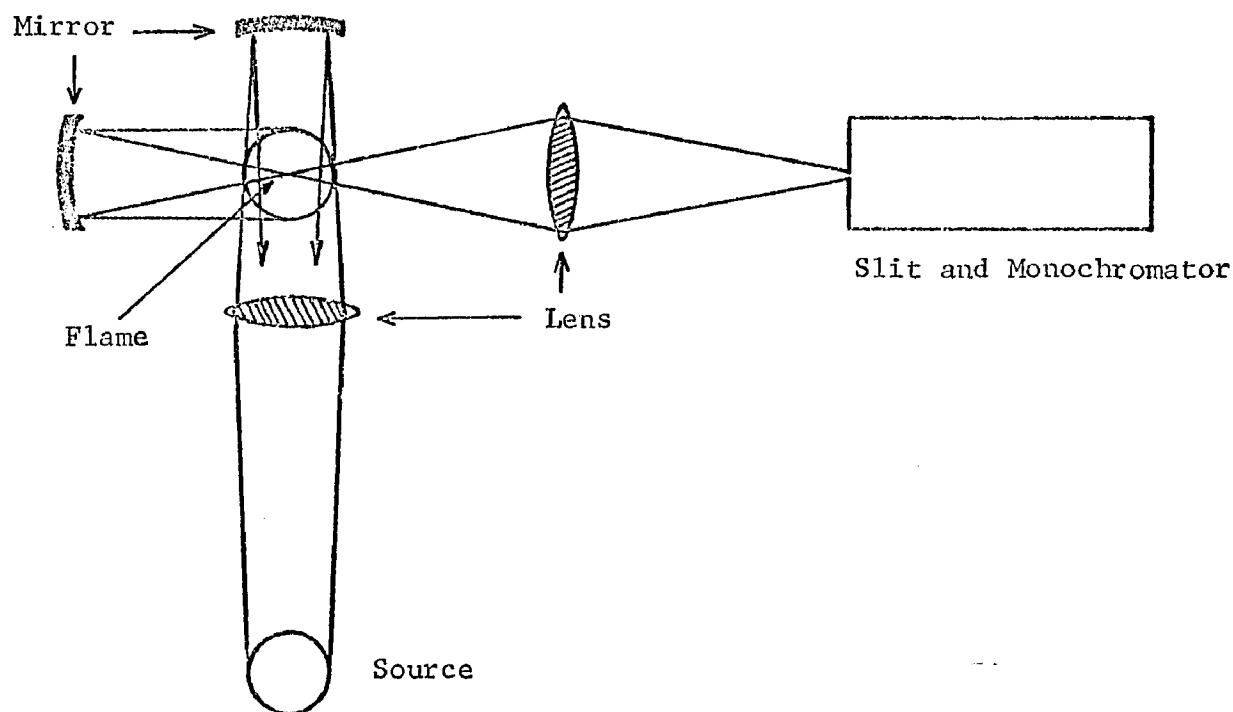


Figure 5

Optical Arrangement for Atomic Fluorescence Studies

(3) Reagents

A stock zinc solution, 1000 mg/l, with respect to zinc, was prepared by dissolving 1.0 g reagent-grade zinc metal in about 4 ml of concentrated hydrochloric acid and diluting to one liter with distilled water. Various other concentrations were prepared by diluting appropriate volumes of the stock solution immediately before measurement.

For the studies of effect of organic solvents, 100 mg/l of zinc in each organic solvent was prepared by dissolving 0.0403 g of zinc acetylacetonate in 100 ml of each organic liquid and then diluting as required.

Other solutions such as those used for interference studies were prepared from analytical-grade chemicals.

(b) Procedure

The zinc vapor discharge lamp is optically aligned to give maximum intensity of radiation on the flame cell. The lamp is turned on and usually requires about 15 minutes to stabilize. While the lamp is warming up, the amplifier circuit and photomultiplier high-voltage power supply are turned on and allowed to warm up. After the burner has been lighted, the distilled water is introduced into the flame and needle on the meter is brought to the zero position by adjusting the zero control. Slight incident light scattering by the water droplets in the flame gases was observed when water was introduced into the flame. The thermal emission due to the zinc sample is negligible at the Zn 2139 Å line for concentration below 1000 p.p.m.

when the experimental setup described is used. When the sample is fed to the flame and if it fluoresces, the needle on the meter is deflected. The relative fluorescence intensity is then read.

Before a series of standard solutions can be run for obtaining a calibration curve, the flame gas composition should be optimized and the flame profile should be measured. These results are discussed in the next section.

C. RESULTS AND DISCUSSION

(a) Effect of Flame Compositions

The fluorescence signal of the 2139 Å line of zinc could be easily observed in oxygen-hydrogen flame. The effect of variation in the ratio of fuel to oxygen in the flame was studied. The flow rates for oxygen and hydrogen were controlled with two stage regulators on gas tanks and a flow meter in the gas lines. In each flame composition, the measurement of fluorescence signal was made by adjusting the flame height until a maximum signal obtained. The aqueous solutions used contained 1 p.p.m. of zinc. The results are shown in Figure 6.

These results show in all cases that the fluorescence intensity is maximum when highly reducing flames are used. The slope of the curve decreases as the optimum flow rate for fuel is reached. For the particular burner used in the experiment, it was found that an oxygen flow rate of 5 l/min. with a hydrogen flow rate of 19 l/min. provided the optimum flame compositions for maximum fluorescence intensity.

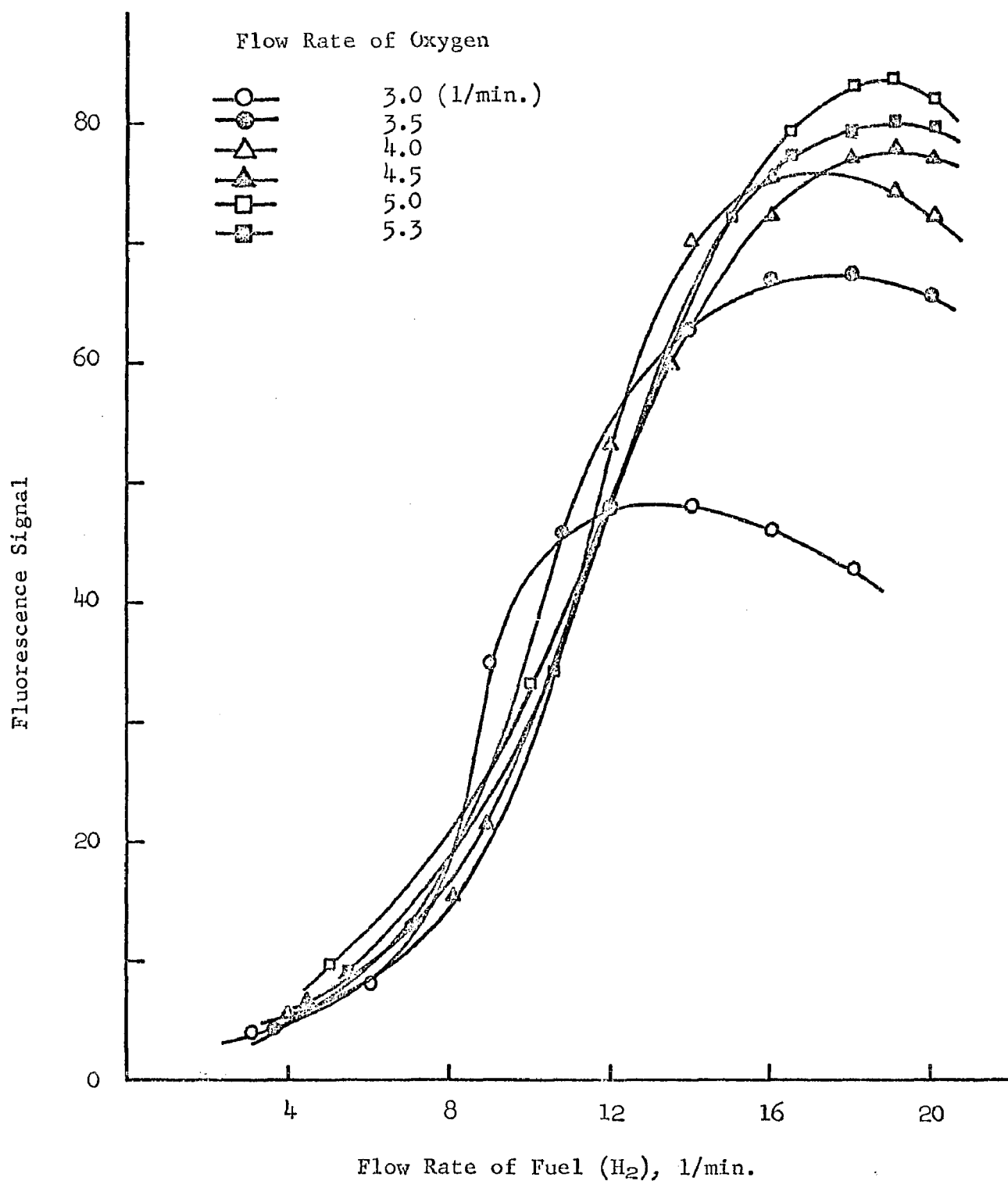


Figure 6

Effect of Flame Compositions on the Fluorescence
Signal of Zinc at 2139 Å. Concentration of Zinc: 1 p.p.m.

(b) Flame Profile

The normal flame from the total consumption burner is about 3 inches high. If the sample is aspirated into the flame, the population of the ground state zinc atoms will not be the same in all parts of the flame. Therefore, if the light beam is passed through the different parts of the flame, the fluorescence intensity will also be different. The relationship between flame height and fluorescence signal or absorption signal is the flame profile.

Various parts of the flame with optimum gas compositions mentioned above were examined. The position of the burner was varied by means of the positioning mechanism. The base of the flame was taken as the zero position. The burner was moved downward in 0.5 cm steps and the fluorescence signal was recorded at each increment. A flame absorption profile for the Zn 2139 Å was also performed for comparison purpose. Results are shown in Figure 7 from which it can be seen that both flame absorption and flame fluorescence profiles are similar. As the height of the light path above the base of the flame is increased, the degrees of absorption and fluorescence first increase, then go through a maximum, and finally decrease at the top of the flame. This change is caused by a change in the number of neutral atoms in different parts of the flame. The profile indicates the relative population of neutral atoms in the various portions of the flame. The slight decrease in the absorption and fluorescence at the top of the flame indicates that a number of zinc atoms become oxidized. It is known that the flame profile in

atomic absorption is controlled directly by the number of free atoms present in that part of the flame. The similarity between the absorption profile and the fluorescence profile indicates that the fluorescence intensity is also proportional to the number of neutral atoms in that part of the flame. It can be deduced from this result that chemiluminescence effects play only a minor role in atomic fluorescence intensity. The maxima for absorption and fluorescence were both located at 5.5 - 6.5 cm from the base of the flame and this was taken as the optimum flame portion for all measurements.

(c) Sensitivity Limit

The limit of detection was chosen as that solution concentration which resulted in a fluorescence signal, the magnitude of which was equal to two thirds of the background noise level. For the experimental setup used, the limit of detection of zinc in aqueous solution under optimum operating conditions (Table 1) was 0.009 p.p.m. This sensitivity limit for zinc is lower than those obtained with a xenon continuous source (6, 13, 31), and comparable with those obtained with the same radiation source, i.e., Philips Zn vapor discharge lamp (17, 20). Although the lowest limit of detection previously reported for zinc was 0.0001 p.p.m., the measurement was made by use of a scale expander (17). A 100-fold sensitivity could thus be obtained.

The sensitivity limit (1% absorption of signal) for zinc by atomic absorption spectroscopy was also investigated using the same instrument and the result was 0.08 p.p.m. The sample feed rate was about 4.5 l/min. for each method. The lower limit of detection by

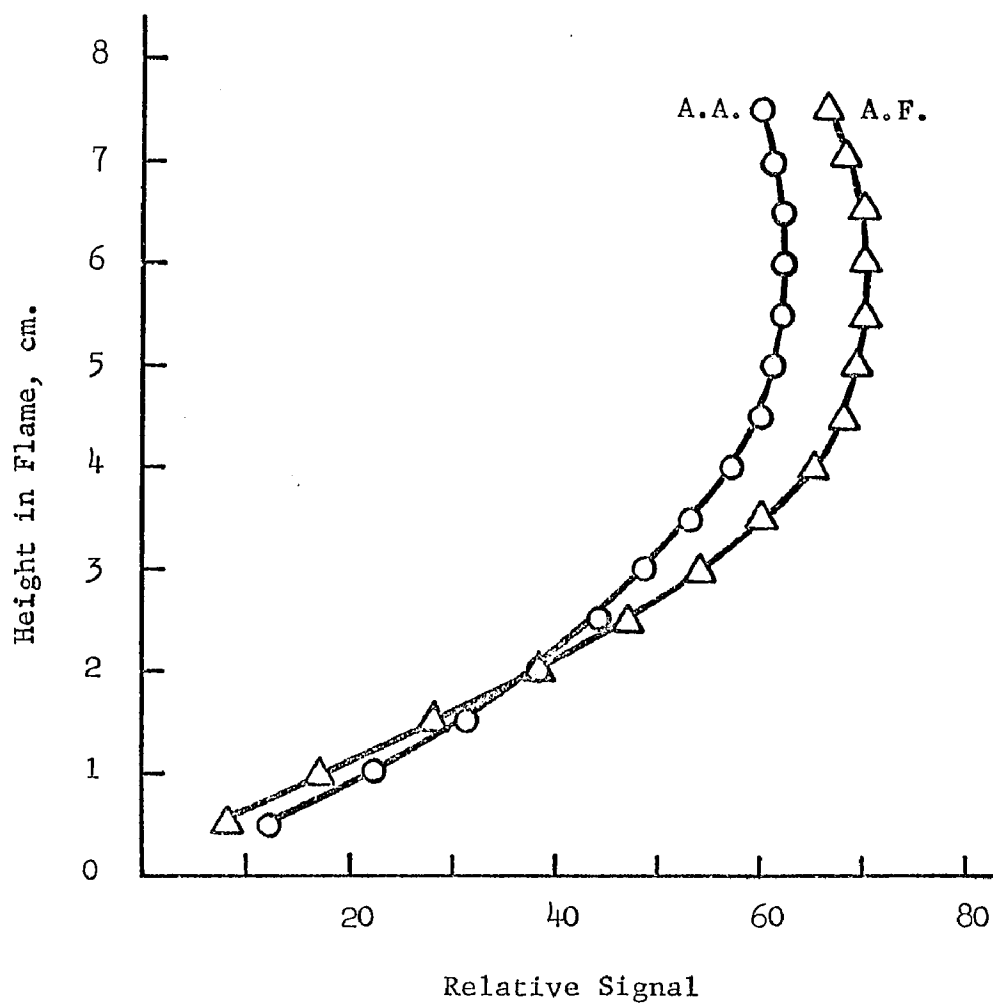


Figure 7

Flame Absorption and Fluorescence Profile for Zn 2139 Å Resonance Line. Concentration of Zn: 10 p.p.m.; Flow Rates: Oxygen 5 l/min., Hydrogen 19 l/min.

TABLE I

OPTIMUM CONDITIONS AND SENSITIVITY LIMITS FOR ZINC

Spectral line (\AA)	Source current		Slit width (mm)	Flow rate (l/min.)		Height in flame (cm)	Sensitivity (p.p.m.)	
	Philips lamp (amp)	Hollow cathode (mA)		O ₂	H ₂		Fluor.	Absor.
2139	0.9	6	0.3	5	19	5.5-6.5	0.009	0.08

atomic fluorescence spectroscopy indicates that under comparable experimental conditions atomic fluorescence method may be more sensitive than atomic absorption method. One of the important reasons for the better sensitivity for atomic fluorescence method is the higher amplifier-gain setting (i.e., 11) of the instrument. For example, if the identical gain-control (i.e., 7) setting for absorption measurement was used for fluorescence measurement, 2 p.p.m. of zinc would be required to emit 1 unit fluorescence signal in contrast to 0.08 p.p.m. of zinc to absorb 1 per cent (or 1 unit) signal.

(d) Calibration Curve

Using the optimum conditions listed in Table I, calibration curve for zinc was determined by measuring the relative fluorescence intensities of a number of standard aqueous solutions varying in concentration from 0.009 p.p.m. to 1000 p.p.m. The calibration curve plot of relative fluorescence intensity against concentration of zinc in aqueous solution for the Zn 2139 Å line when using oxy-hydrogen flame as atomizer is given in Figure 8. The relationship was linear over a wide range of concentration. The maximum on the curve and the subsequent decrease of the slope of the curve indicate a self-absorption of fluorescence signal by other atoms of the sample at high concentration. The reversal of the fluorescence is the main disadvantage of atomic fluorescence spectroscopy. In practice, the upper limit can be extended by diluting the sample solution until the concentration is in a good analytical range. Generally this calibration curve is analytically useful over a 10^3 concentration range which is similar to the range of calibration curves obtained in flame photometric method but greater than

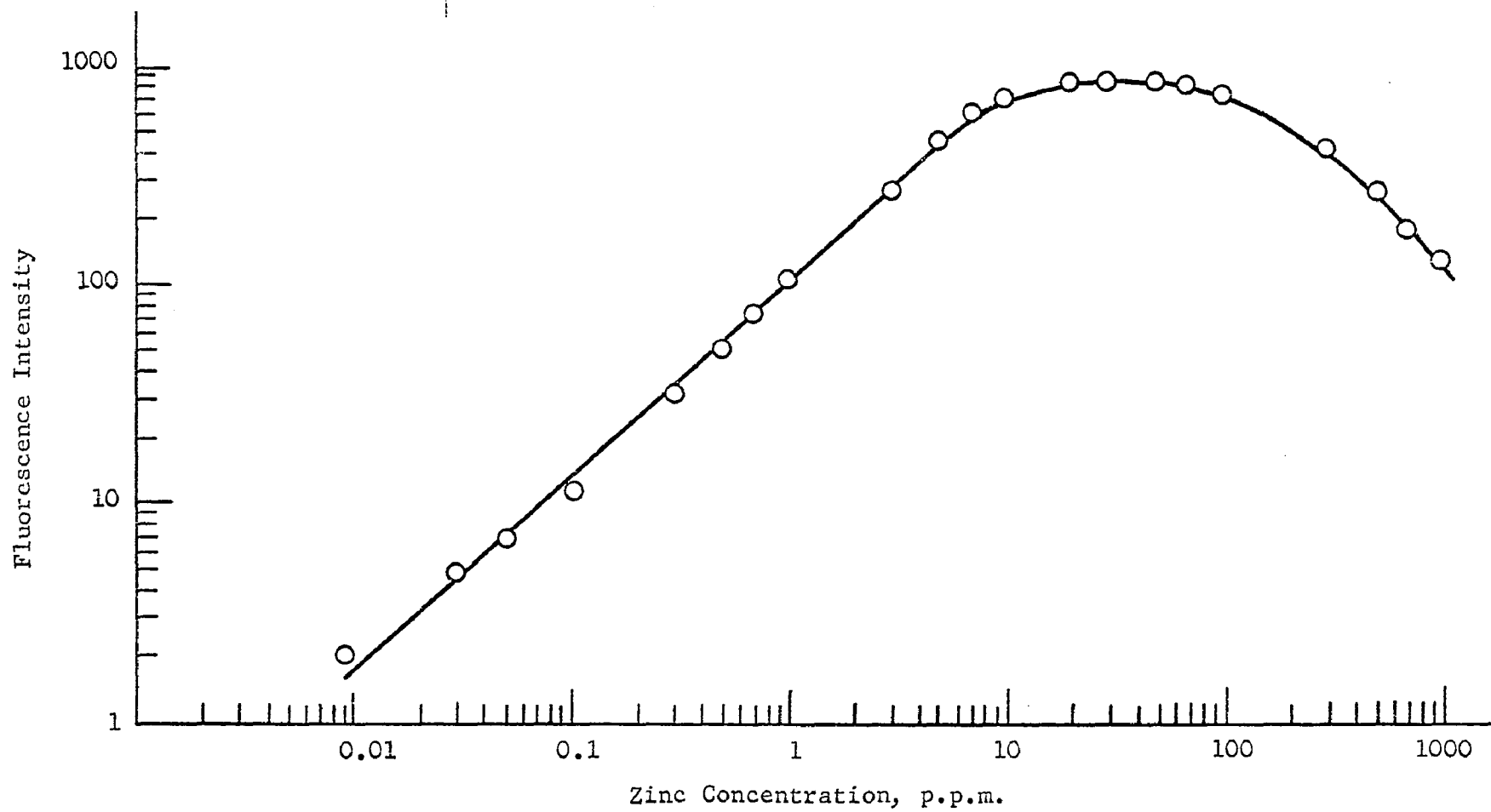


Figure 8

Calibration Curve for Zinc Fluorescence Intensity at 2139 Å

the range normally found in atomic absorption calibration curves.

(e) Chemical Interferences

The effect of 100-fold excess concentration of the following ions and compounds on the spectral fluorescence of zinc were studied:

Cations: NH_4^+ , Al^{3+} , Sb^{3+} , Ba^{2+} , Bi^{2+} , Cd^{2+} ,
 Ca^{2+} , Ce^{4+} , Cs^+ , Co^{2+} , Cu^{2+} , Cr^{3+} , Fe^{2+} , Fe^{3+} ,
 Pb^{2+} , Li^+ , Mg^{2+} , Hg^{2+} , Ni^{2+} , Pd^{2+} , K^+ , Ag^+ , Na^+ ,
 Sr^{2+} , Th^{4+} , Sn^{4+} , Ti^{4+} , Zn^{2+} , Zr^{4+} .

Anions: HAsO_4^{2-} , $\text{B}_4\text{O}_7^{2-}$, Br^- , CO_3^{2-} , HCO_3^- ,
 Cl^- , F^- , I^- , MoO_4^{2-} , NO_3^- , PO_4^{3-} , HPO_4^{2-} ,
 SeO_3^{2-} , SiO_3^{2-} , SO_3^{2-} , SO_4^{2-} , TeO_3^{2-} , SCN^- ,
 WO_4^{2-} , UO_4^{2-} , VO_3^{2-} .

Miscellaneous compounds: Acetate, EDTA,
Citrate, Oxalate, Tartrate, Detergent (Dreft),
HOAc, HCl, HNO₃, HClO₄, H₂SO₄.

The solution tested contained 1 p.p.m. of zinc and 100 p.p.m. of the respective interfering ion. The cations were added as chlorides or nitrates, or in some instances, as sulfates. The anions were introduced as sodium or potassium salts. A solution of "Dreft" was used to study the effect of detergents. The effect of acids was examined by adding 5 ml of concentrated acid to the sample followed by dilution to 100 ml with water. The operation conditions in Table I were used.

No interferences were observed from cations on the fluorescence signal of zinc. Slightly lower fluorescence intensities of zinc were obtained in the presence of certain anions (Table II). This anionic interference can be attributed to chemical interference. The interferences were effectively overcome by the addition of complexing agent EDTA to the solution (Table II). None of the acids interfered in the determination of zinc.

In fact, these results of interference studies are essentially the same as those observed in atomic absorption (23). This is because atomic fluorescence spectroscopy depends on the same basic phenomena as atomic absorption spectroscopy.

(f) Effect of Organic Solvents

The effect of the addition to aqueous solutions of methanol, ethanol, and iso-propanol on the fluorescence signal of zinc was studied in flames of various compositions. These solvents, in general, enhance the fluorescence signal in the following order: methanol > ethanol > iso-propanol. The effect of concentration of these organic solvents on the fluorescence signal was also studied. Results are summarized in Figures 9, 10, and 11, respectively.

The results show that fluorescence was maximum in highly reducing flames and that the fluorescence intensity increased as the concentration of organic solvent increased. At high alcohol percentage of the mixed solution, the flame composition had little effect on the fluorescence intensity.

TABLE II
ANIONIC INTERFERENCES
ON THE ATOMIC FLUORESCENCE OF ZINC

Interfering anion (100 p.p.m.)	Intensity of signal	
	Zn (1 p.p.m.)	Zn (1 p.p.m.) plus EDTA (4000 p.p.m.)
None	66	66
HAsO_4^{2-}	56	66
$\text{B}_4\text{O}_7^{2-}$	50	65.5
CO_3^{2-}	50	66
HC_2O_4^-	42	66
PO_4^{3-}	55	66
HPO_4^{2-}	54	66
SeO_3^{2-}	59	66.5
SiO_3^{2-}	40	66.5

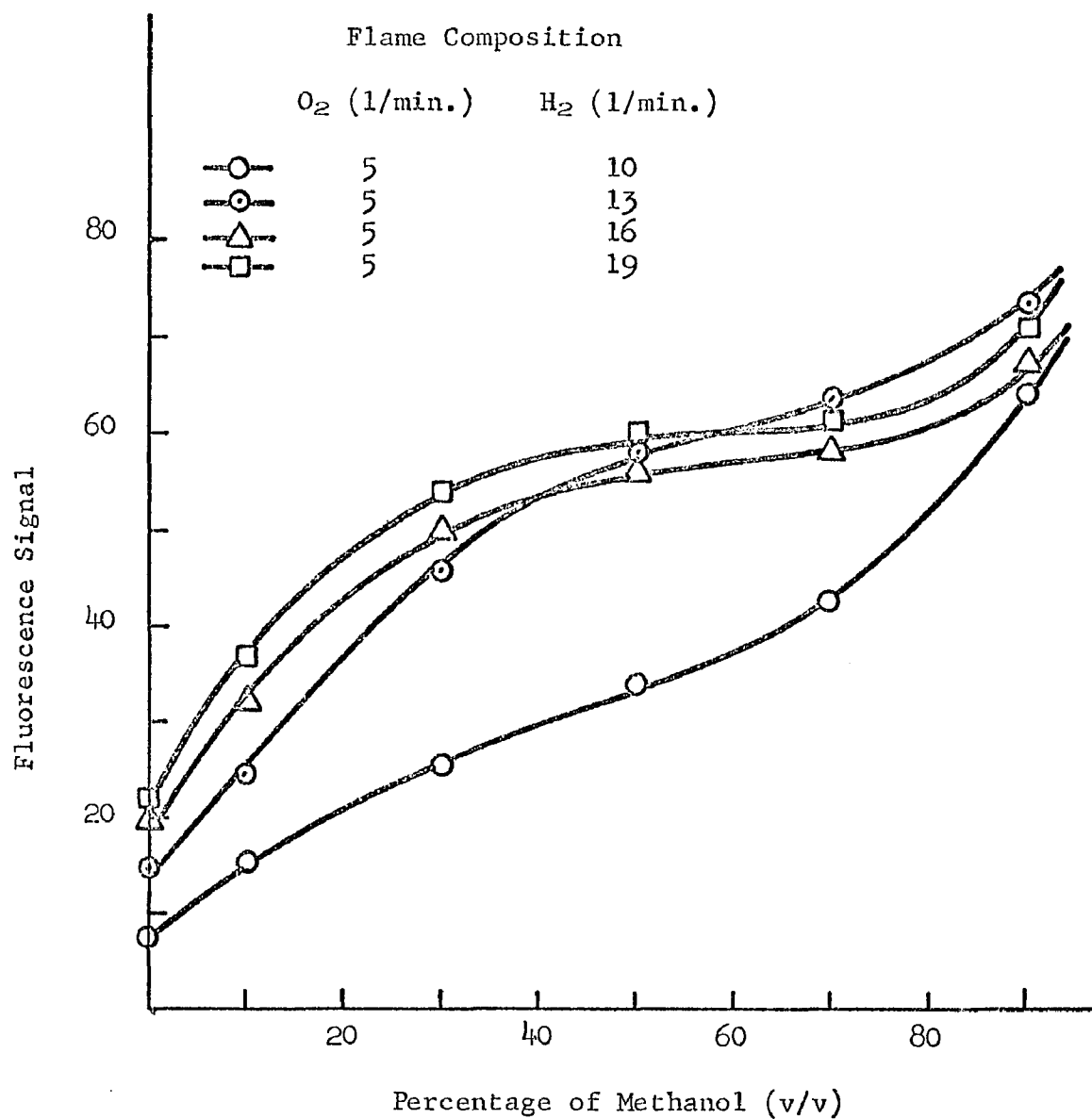


Figure 9

Effect of Methanol on the Fluorescence
of 2139 Å Line of Zinc in
Oxy-hydrogen Flames of Various Compositions

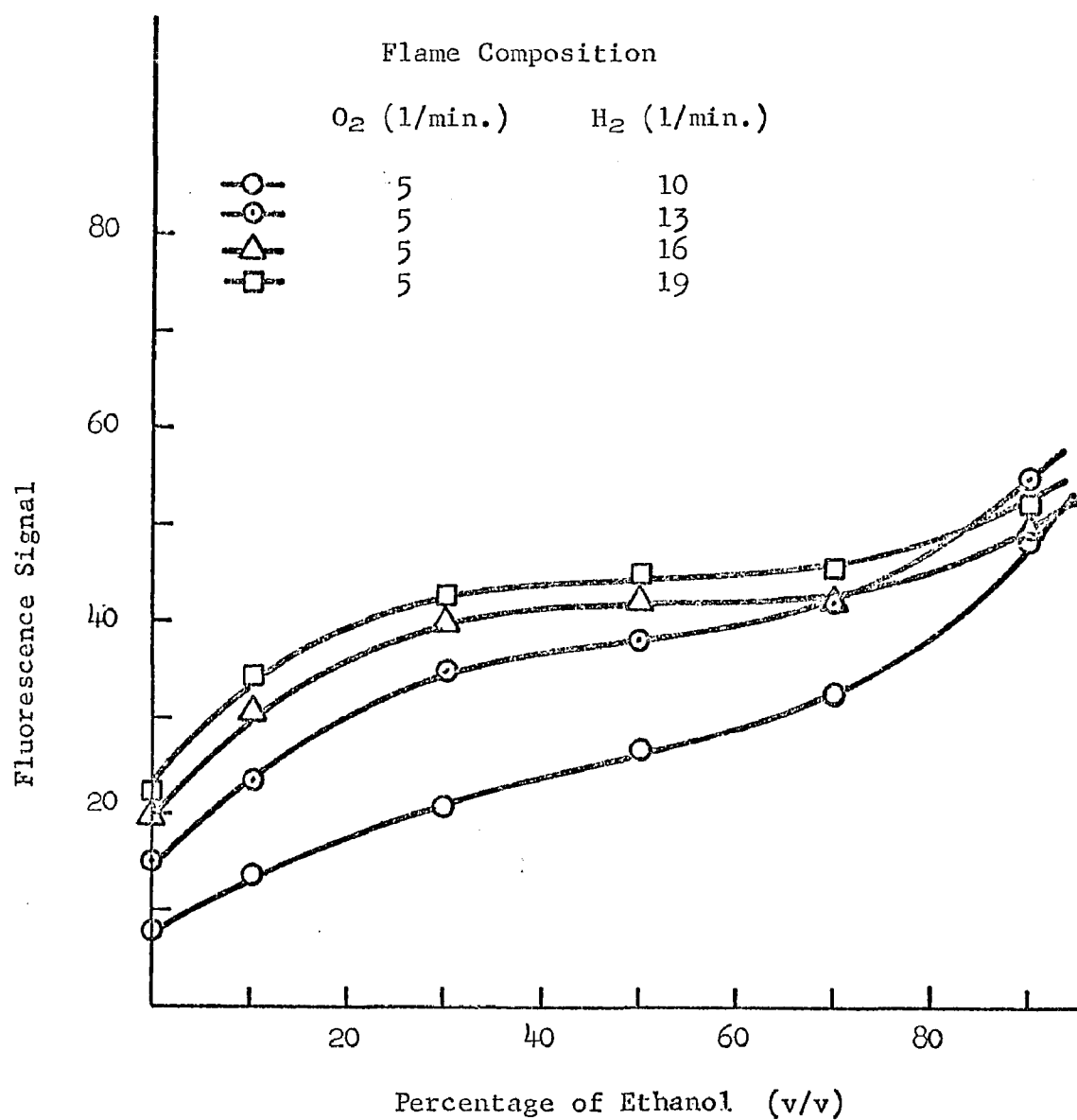


Figure 10

Effect of Ethanol on the Fluorescence
of 2139 Å Line of Zinc in
Oxy-hydrogen Flames of Various Compositions

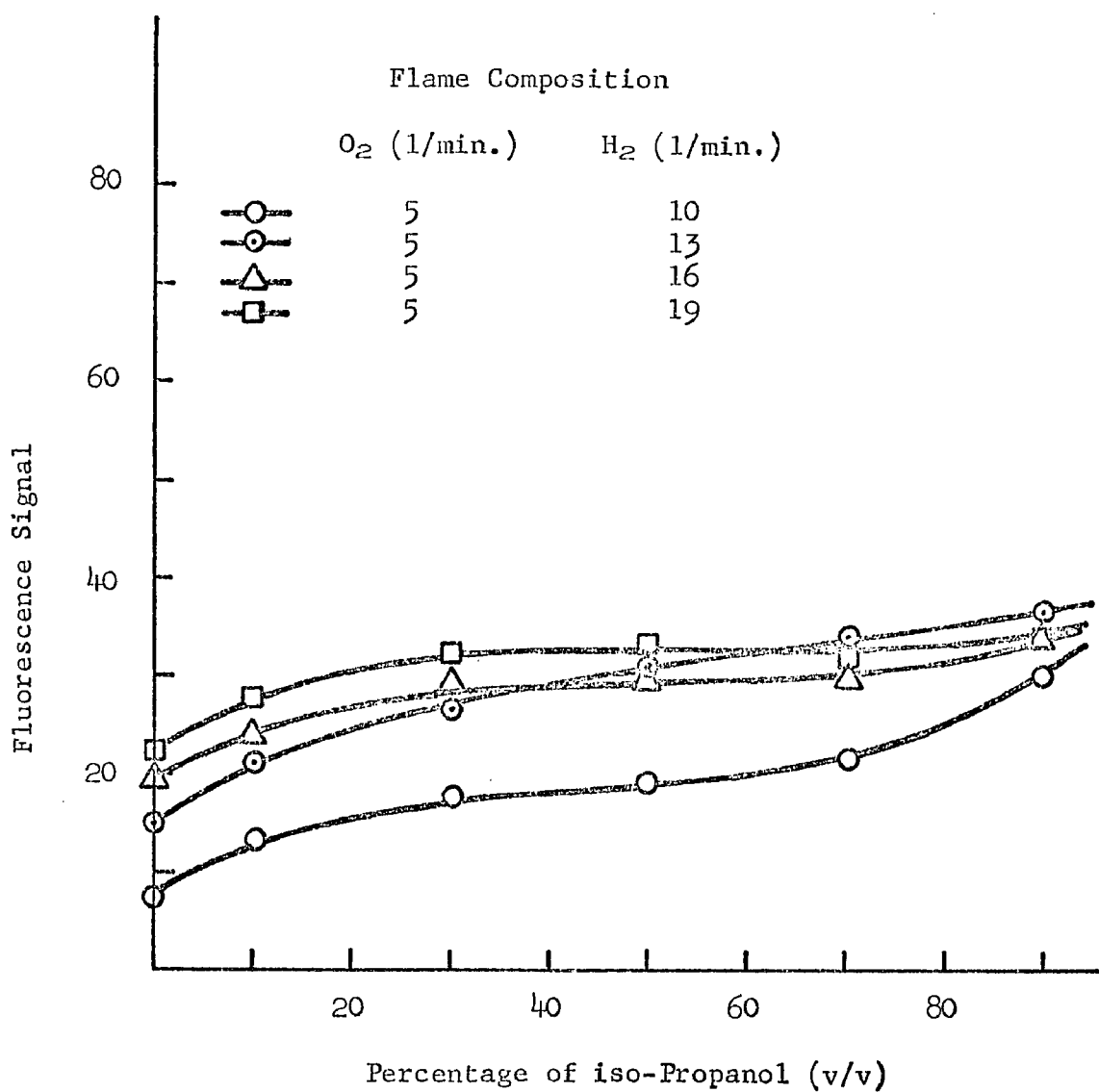


Figure 11

Effect of iso-Propanol on the Fluorescence
of 2139 Å Line of Zinc in
Oxy-hydrogen Flames of Various Compositions

A comparative study of the effect of a series of organic solvents on the fluorescence signal for zinc was made. Results are shown in Table III. Measurements were taken under operation conditions listed in Table I. In most cases, the fluorescence signal was found to be enhanced by the use of organic solvent. The enhancement of the fluorescence signal associated with the use of organic solvents indicates an increased population of ground state metal atoms in the flame. The mechanism for the production of metal atoms (25, 27) and the possible role of organic solvent (2, 14, 16, 25, 27) have been discussed by various authors. The variation in the intensity of fluorescence signal between different organic solvents can be explained by several factors: (a) the effect of solvent on the efficiency of producing atomized species from the sample, (b) the change in sample feed rate with solvents having different viscosities and specific gravities, (c) the effect of surface tension on the droplet size, and (d) reduction of intensity by absorption or quenching by the solvent or its combustion products. Essentially the enhancement of fluorescence signals of zinc by organic solvents is due to high combustibility of organic solvents so that the atom population is increased.

D. CONCLUSION

The present investigation showed that zinc could be determined directly in aqueous samples by atomic fluorescence spectroscopy. The almost complete lack of interference associated with high sensitivity makes this method very attractive for the routine

TABLE III

RELATIVE FLUORESCENCE INTENSITY OF ZINC AT 2139Å
IN DIFFERENT ORGANIC SOLVENTS

Solvent	Feed rate (ml/min.)	Relative intensity (Zn 1 p.p.m.)
Water	4.5	22
Methanol	6.0	79
Ethanol	4.05	57
n-Propanol	2.8	36
iso-Propanol	2.7	38
n-Butylaldehyde	6.3	72
iso-Butylaldehyde	4.2	70
MIBK	6.0	76
Acetic acid	3.6	103
Ethyl acetate	6.65	104
Bis (2-ethoxy-ethyl) ether	3.5	57
n-Butylamine	6.9	76
di-n-Butylamine	4.4	78
tri-ethylamine	8.4	79
Nitropropane-2	5.0	39
Nitrobenzene	2.95	41
Aniline	1.9	34
Pyridine	4.35	82
Dimethyl sulfoxide	2.6	11
Thiophene	4.7	11
tri-n-Butylphosphate	1.6	20
n-Butylchloride	6.6	73
chloroform	5.0	14
Heptane	7.5	21
Heptene-2	7.55	72
Cyclohexane	4.6	14
Cyclohexene	5.55	42
Benzene	6.0	30
Toluene	6.1	30
1-chloronaphthalene	3.45	36

determination of zinc. The effect of large excess of several anions which interfere in the determination of zinc can be readily overcome if the determination is carried out in the presence of EDTA. Zinc in organic liquids can also be measured by atomic fluorescence spectroscopy with considerable enhancement of the fluorescence signal in most cases.

CHAPTER III

ATOMIC FLUORESCENCE SPECTROSCOPY OF BERYLLIUM

A. INTRODUCTION

The technique of atomic fluorescence spectroscopy has provided an elegant means for the determination of several elements at the parts per million and parts per billion levels. Early attempts to obtain atomic fluorescence signal from beryllium were not successful. These employed an air-propane or air-hydrogen flame and irradiation from a 150-W xenon arc lamp (6) also an air-hydrogen flame and irradiation from a hollow cathode lamp (12).

In the present work a study was made using a high intensity beryllium hollow cathode lamp as a radiation source and oxy-acetylene or nitrous oxide-acetylene flame as atomizer. Atomic fluorescence from beryllium at the resonance line 2349 \AA was observed with the sensitivities of 10 p.p.m. in oxy-acetylene flame and 0.5 p.p.m. in nitrous oxide-acetylene flame.

A newly designed atomizer burner was constructed for nitrous oxide-acetylene flame for use in atomic fluorescence studies. The calibration curve for beryllium determination in this flame was linear over the range 0.5 p.p.m. to 10 p.p.m. The intensity reversed and approached zero at higher concentrations of beryllium. In the oxy-acetylene flame the linear range was 10 p.p.m. to 1000 p.p.m.

B. EXPERIMENTAL

(a) Apparatus

A Techtron AA3 atomic absorption spectrophotometer was used for fluorescence intensity measurements. For oxy-acetylene flame studies a large bore Beckman total consumption burner was used and for nitrous oxide-acetylene flame a newly designed burner (as described in the following section) was used. A high intensity beryllium hollow cathode lamp (Atomic Spectral Lamps, Australia) was used as radiation source. The lamp and detector were modulated at 60 cps.

(1) Burner Assembly Construction

A burner with a cylindrical burner head with multiple slots was built for use with the nitrous oxide-acetylene flame. It is illustrated in Figure 12. The burner head was water cooled to prevent flash-back which may occur when the acetylene flow rate was reduced. It was found that nitrous oxide-acetylene mixture could be safely burned with multiple slots as wide as 0.020 in. in a burner made of 1/2 in. thick stainless steel. A stainless steel spray-chamber was used because of its rigidity, and because the high thermal conductivity which further helped to prevent flash-back. The burner was carried in a support which could be moved in the vertical or both horizontal planes. This enabled easy optical alignment of the burner and also enabled studies to be made of intensity of fluorescence signal from various portions of the flame.

Five slots were cut in the burner head. It was positioned so that the slots were parallel to the optical axis of the monochromator. The maximum fluorescence signal was obtained using

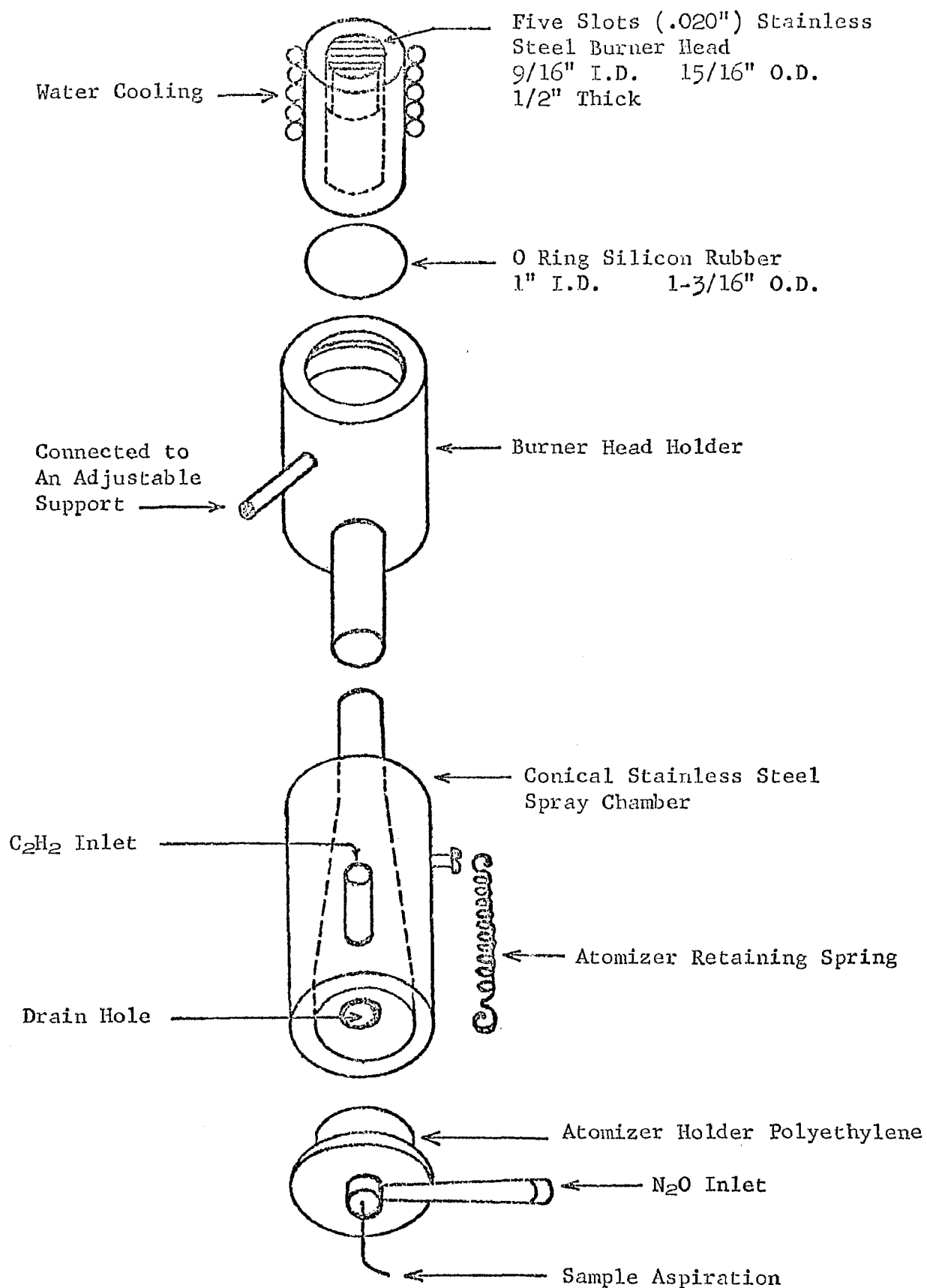


Figure 12

Schematic Diagram of Atomizer Burner Assembly for N₂O/C₂H₂ Flame

this alignment. If the slots were perpendicular to the optical axis of the monochromator the intensity of the fluorescence emission was about 70% that of the former case, and if it was positioned at 45° angle to both entrance slit and source the signal intensity about 85%.

The burner produced a stable rose-red inner cone in the nitrous oxide-acetylene flame. The burner should be useful for atomic fluorescence studies of refractory metals such as aluminium, beryllium, silicon, titanium, tungsten and vanadium which are not appreciably atomized with other flames.

(2) Optical System

The experimental setup used is as described in the previous chapter.

(3) Reagents

A stock solution containing 1.0 g/l beryllium was prepared by dissolving 19.7 g of analytical grade $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in 1 liter of distilled water. Standard solutions were made by appropriate dilution of stock solution immediately before measurement.

For the studies of effect of organic solvents, 100 p.p.m. of beryllium in each organic solvent was prepared by dissolving 0.691 g of beryllium acetylacetonate in 100 ml of each organic liquid and then diluted as required.

In the interference studies, sodium or potassium salts were used for anionic interference and chlorides, nitrates or sulfates for cationic interference studies. Concentrated acids were used to study the effect of the addition of acids.

(b) Procedure

With aqueous solutions containing 500 p.p.m. of beryllium for oxy-acetylene flame and 5 p.p.m. of beryllium for nitrous oxide-acetylene flame, the optimum operating conditions listed in Table IV for each flame were established, while adjusting the burner height and fuel ratio to obtain maximum fluorescence intensity. Fluorescence measurement were made at 3 cm above the burner top for oxy-acetylene flame and at the rose-red inner cone of the flame about 1 1/2 cm from the burner head for the nitrous oxide-acetylene flame. Under these conditions, the sample feed rates were about 1.15 l/min. and 4.8 l/min. for oxy-acetylene and nitrous oxide-acetylene flame respectively.

Using the above conditions, calibration curves for beryllium at 2349 Å in oxy-acetylene and nitrous oxide-acetylene flames were determined by measuring the relative fluorescence intensities of a number of standard aqueous solutions varying in concentration from 1000 to 0.5 p.p.m.

C. RESULTS AND DISCUSSION

(a) Atomization Profile

The position of the burner was varied by means of the positioning mechanism. The operating conditions were as listed in the procedure and the concentration of beryllium in the oxy-acetylene flame was 700 p.p.m. and 10 p.p.m. in the nitrous oxide-acetylene flame. The base of the flame was taken as the zero position. The burner was moved downward in 0.5 cm steps and the fluorescence signal

TABLE IV
OPERATION CONDITIONS FOR BERYLLIUM

Spectral line (Å)	Current (mA)		Slit width (mm)	Flow rate (l/min)			Height in flame (cm)	Sensitivity (p.p.m.)
	Lamp	Booster		O ₂	C ₂ H ₂	N ₂ O		
2349	25	400	0.3	2.3	3.5		2.5-3.0	10
					5.3	29	1.5-2.0	0.5

was recorded at each increment. The fluorescence signal was maximum about 2.5-3.0 cm from the base of the flame in oxy-acetylene flame and 1.5-2.0 cm from the flame base in the nitrous oxide-acetylene flame (Figure 12). In the nitrous oxide-acetylene flame, the fluorescence signal was observed only in the rose-red cone of the flame. Apparently the sharp maximum in both flames indicated that beryllium oxide was formed very rapidly even though a fuel-rich reducing flame was used.

(b) Sensitivity

The limits of detection are listed in Table IV together with the optimum operating conditions. The sensitivities for beryllium were 10 p.p.m. with oxy-acetylene flame and 0.5 p.p.m. with nitrous oxide-acetylene flame and these are comparable with the best atomic absorption sensitivity data reported for this element with the same flames (23). In the latter paper, a 10% diethylene glycol diethyl ether in water was recommended to enhance the sensitivity of beryllium and a 5-fold enhancement of absorption by beryllium was reported. A similar solvent containing 10% diethylene glycol diethyl ether in water was studied for comparison. It was found that the sensitivity was 4 p.p.m. in oxy-acetylene flame, but no significant sensitivity enhancement was detected in nitrous oxide-acetylene flame. It should be noted that the sample feed rate (4.8 l/min.) using nitrous oxide-acetylene flame was four times larger than the feed rate (1.15 l/min.) when oxy-acetylene flame.

(c) Calibration Curve

Figure 14 illustrates the relationship between fluorescence intensity and the concentration of beryllium in aqueous solution.

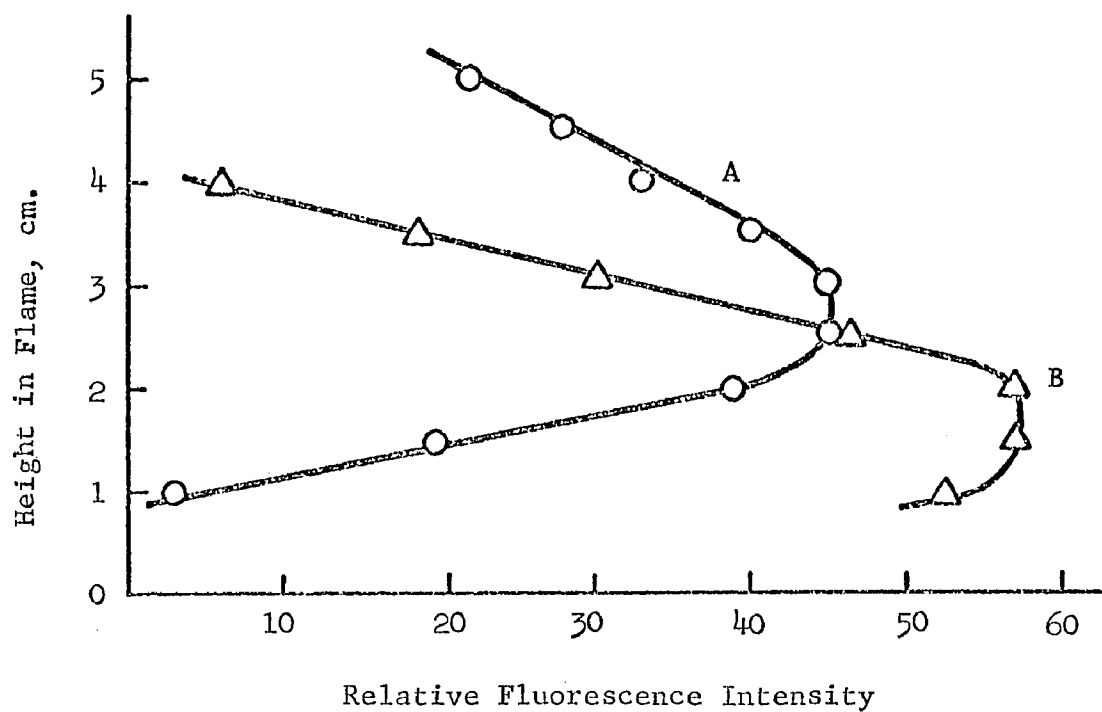


Figure 13

Flame Profile of Atomic Fluorescence for Beryllium at Wavelength of 2349\AA
 (A) in Oxy-acetylene Flame; (B) in Nitrous Oxide-acetylene Flame

The 2349 Å line was studied using oxy-acetylene and nitrous oxide-acetylene flames for sample atomization. The shape of calibration curves had already been discussed by Winefordner and Vickers (40). The relationship is linear at low metal concentrations and curved at high concentrations. It can be seen from Figure 4 that this type of relationship was also obtained when an oxy-acetylene flame was used. But when a nitrous oxide-acetylene flame was used the beryllium fluorescence signal went through a maximum and approached zero. This relationship is markedly similar to that observed in molecular fluorescence and may be caused by the same phenomena, i.e. self absorption or quenching. This may present an important problem to the determination of this metal by atomic fluorescence spectroscopy.

(d) Effect of Flame Composition

It was thought the shape of the fluorescence/concentration working curve for beryllium in nitrous oxide-acetylene flame might be varied by changing the flame composition. Therefore, a change in fuel ratio from optimized condition was made. The flame was optimized at a flow rate of 5.3 l/min. producing a red inner cone. The inner cone disappeared when the acetylene was decreased to 4.8 l/min. and the flame turned to light yellow when the acetylene flow rate was increased to 5.8 l/min. The relative fluorescence intensities and working curves were illustrated in Figure 15. It can be seen that the fluorescence intensity was very sensitive to flame composition but the general shape of working curve remained the same.

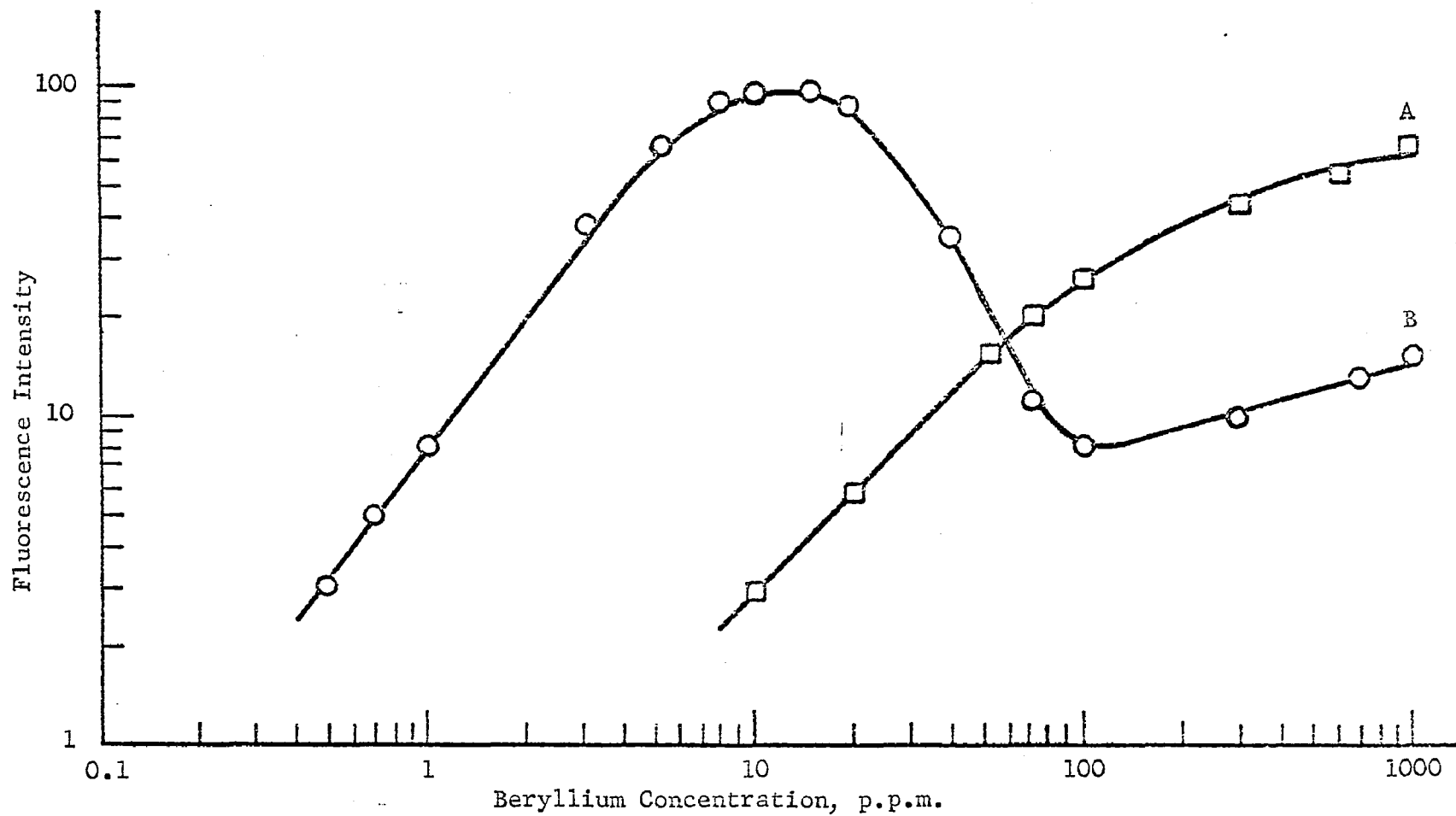


Figure 14
Calibration Curves for Beryllium Fluorescence Intensities at 2349 \AA
(A) in Oxy-acetylene Flame; (B) in Nitrous Oxide-acetylene Flame

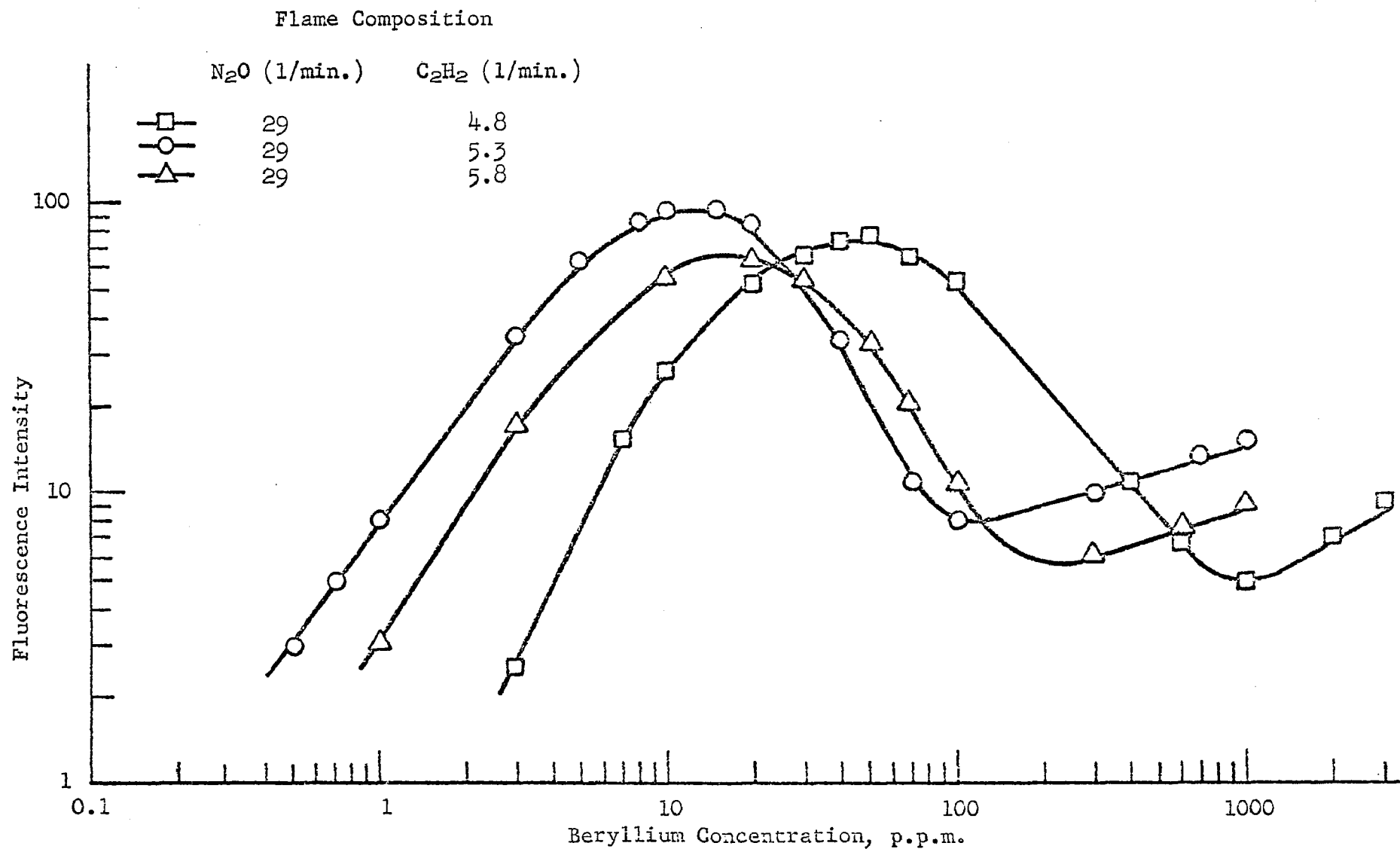


Figure 15
Calibration Curves for Beryllium Fluorescence Intensities
with Varying Fuel Ratio in Nitrous Oxide-acetylene Flame

(e) Study of Interferences

The interfering effect of foreign ions on the fluorescence signal of beryllium was examined using the conditions indicated in Table IV. The results are shown in Table V. The concentrations of beryllium were 300 p.p.m. for oxy-acetylene flame and 5 p.p.m. for nitrous oxide-acetylene flame, and that of interfering ion, 300 p.p.m. for both flames. Hydrolysis of the interference salt was prevented where necessary by the addition of sufficient acid to maintain a clear solution. The effect of various acids was examined by making a 5% acid solution.

In general, it was noted that the signal interference by the interferents is larger in the oxy-acetylene flame than in the nitrous oxide-acetylene flame. No significant interference ($\pm 5\%$) was observed from ions and compounds studied in the nitrous oxide-acetylene flame except acetic acid and sulfuric acid. Both Al^{3+} and Co^{2+} ions caused more suppression of the beryllium signal than any other cations in both flames. In oxy-acetylene flame, cations such as Cu^{2+} and Ti^{4+} enhanced the signal to 6 and 8% respectively, while anions such as Br^- , Cl^- , PO_4^{3-} , HPO_4^{2-} , SO_3^{2-} , and SO_4^{2-} produced an interference greater than 5%. The interference from anions were eliminated by adding EDTA to the solution (Table VI).

When an oxy-acetylene flame was used all acids enhanced the fluorescence intensities for beryllium about the same extent. When a nitrous oxide-acetylene flame was used no similar enhancement was observed. However, in the latter flame acetic acid slightly enhanced the signal but sulfuric acid slightly reduced the fluorescence intensity.

TABLE V

INTERFERENCE EFFECTS OF OTHER IONS AND COMPOUNDS ON
THE ATOMIC FLUORESCENCE OF BERYLLIUM

Interferent	Intensity of signal		Difference, %	
	O_2/C_2H_2	N_2O/C_2H_2	O_2/C_2H_2	N_2O/C_2H_2
None	36	52	—	—
Al^{3+}	34	50	-6	-4
Co^{2+}	34	50.5	-6	-3
Cu^{2+}	38	53	+6	+2
Mn^{2+}	34.5	51	-4	-2
Hg^{2+}	34.5	52	-4	0
Ti^{4+}	39	53	+8	+2
Zr^{4+}	37.5	53	+4	+2
$B_4O_7^{2-}$	38	51	+6	-2
Br^-	33	52	-8	0
Cl^-	32	52	-11	0
PO_4^{3-}	34	51	-6	-2
HPO_4^{2-}	32	51	-11	-2
SO_3^{2-}	32	52.5	-11	+1
SO_4^{2-}	34	52.5	-6	+1
HAc	41	55	+14	+6
HCl	41	50	+14	-4
HNO_3	42	51	+17	-2
$HClO_4$	41	52	+14	0
H_2SO_4	42.5	48	+18	-8

No significant interference was found from the following ions and compounds: Sb^{3+} , Ba^{2+} , Bi^{2+} , Cd^{2+} , Ca^{2+} , Ce^{4+} , Cs^+ , Cr^{3+} , Fe^{2+} , Fe^{3+} , Pb^{2+} , Li^+ , Mg^{2+} , Ni^{2+} , Pd^{2+} , K^+ , Ag^+ , Na^+ , Sr^{2+} , Th^{4+} , Sn^{4+} , Zn^{2+} , NH_4^+ , $HAsO_4^{2-}$, Co_3^{2-} , HCO_3^- , F^- , I^- , MoO_4^{2-} , NO_3^- , SeO_3^{2-} , SiO_3^{2-} , TeO_3^{2-} , SCN^- , WO_4^{2-} , UO_4^{2-} , VO_3^{2-} , Acetate, EDTA, Citrate, Oxalate, Tartrate, and Detergent (Dreft).

TABLE VI
ANIONIC INTERFERENCES
ON THE ATOMIC FLUORESCENCE OF BERYLLIUM

Interfering anion (300 p.p.m.)	Intensity of signal	
	Be (300 p.p.m.)	Be (300 p.p.m.) plus EDTA (4000 p.p.m.)
None	36	37
Br ⁻	33	37
Cl ⁻	32	37
PO ₄ ³⁻	34	37
HPO ₄ ²⁻	32	36.5
SO ₃ ²⁻	32	37
SO ₄ ²⁻	34	37.5

(f) The Effect of Organic Solvents

The relative fluorescence intensities of the beryllium 2349 Å line were investigated in a series of different organic liquids. The results are listed in Table VII. It was observed that different organic solvents affect the intensity of beryllium fluorescence signal differently. As already known and discussed in the previous chapter, organic solvents in many cases enhance the intensity of flame emission, absorption, and fluorescence for a given metal as compared to aqueous solution. This was also found to be true of some of the solvents studied for beryllium fluorescence. However, more than half of the solvents studied reduced the signal intensity as compared to aqueous solution. It is interesting to note that solvents which enhanced the fluorescence intensities of beryllium in nitrous oxide-acetylene flame also enhanced the fluorescence signal in oxy-acetylene flame. It has been explained that the enhancement of fluorescence signal of zinc by organic solvents is mainly due to high combustibility of organic solvents in the flame. However, with a nitrous oxide-supported flame, the number of solvents that can be successfully burnt is limited. When most of organic solvents particularly high carbon compounds were sprayed into the nitrous oxide-acetylene flame, a deposit of incompletely burnt material was formed on the burner top and an unstable "dirty" flame resulted. There was not so much a problem in oxy-acetylene flame. Further studies are necessary to elucidate fully the role played by organic solvents in the detection process.

TABLE VII

RELATIVE FLUORESCENCE INTENSITY OF BERYLLIUM AT 2349Å IN DIFFERENT
ORGANIC SOLVENTS

Solvent	Oxy-acetylene flame		Nitrous oxide-acetylene flame	
	Feed rate (ml/min.)	Fluorescence intensity (Be 50 p.p.m.)	Feed rate (ml/min.)	Fluorescence intensity (Be 3 p.p.m.)
Water	1.15	25	4.8	26
Methanol	1.8	49	5.1	58
Ethanol	1.0	42	4.6	47
n-Propanol	0.55	39	4.1	47
iso-Propanol	0.5	40	4.0	42
n-Butylaldehyde	1.75	24	5.05	17
iso-Butylaldehyde	0.85	33	4.5	27
MIBK	1.7	22	5.05	34
Acetic acid	0.9	36	3.6	54
Ethyl Acetate	2.3	24	5.2	20
Bis (2-ethoxy-ethyl) ether	0.8	34	4.2	40
n-Butylamine	2.0	23	5.0	7
di-n-Butylamine	1.05	29	4.75	40
tri-Ethylamine	3.35	12	5.6	2
Nitropropane-2	1.25	27	4.9	50
Nitrobenzene	0.55	22	3.7	25
Aniline	0.3	27	3.35	18
Pyridine	1.05	23	4.5	24
Dimethyl sulfoxide	0.5	30	3.85	27
Thiophene	1.5	10	4.9	12
tri-n-Butylphosphate	0.25	36	3.3	25
n-Butylchloride	2.25	15	5.2	3
Chloroform	1.25	2	4.8	2
Heptane	3.1	14	5.45	3
Heptene-2	3.1	8	5.45	2
Cyclohexane	1.15	20	4.8	2
Cyclohexene	1.65	14	4.9	5
Benzene	1.7	8	5.0	10
Toluene	1.85	9	5.1	18
1-Chloronaphthalene	0.35	13	3.5	21

(g) Studies on the Other Atomic Lines and Other Flames

No detectable fluorescence was observed for the beryllium lines at 2495, 2651, 3131, and 3321 Å using a beryllium solution of 100 p.p.m. concentration. Oxy-hydrogen, air-hydrogen, and air-acetylene flames were also tested at the resonance line 2349 Å but yielded no fluorescence signal.

D. CONCLUSION

An investigation of the atomic fluorescence signal of beryllium has shown that beryllium can be determined using a high intensity beryllium hollow cathode lamp as source and a oxy-acetylene or nitrous oxide-acetylene flame as atomizer, and the sensitivity is 10 p.p.m. in oxy-acetylene flame while 0.5 p.p.m. in nitrous oxide-acetylene flame. No significant interference was found in the presence of 300 p.p.m. of certain cations and some anions. The interference from several anions were effectively overcome by adding EDTA to the sample solutions.

CHAPTER IV

GENERAL DISCUSSION

A. ADVANTAGES

The inherent advantages of atomic fluorescence spectroscopy as an analytical tool compared to other comparative procedures are as follows:

(a) Sensitivity

The procedure is capable of high sensitivity. Many elements can be determined in the p.p.m. and p.p.b. range. In Table VIII, limiting detectable concentrations of various elements introduced into flames as salts (nitrates, chlorides, in most cases) and measured by atomic fluorescence method are listed. The results obtained using line sources are as low or lower than the lowest limits of detection obtained by atomic absorption and flame photometric methods. Since the intensity of atomic fluorescence is proportional to the intensity of radiation source, it can be expected that considerable better sensitivity can be obtained as soon as many time more intense source can be developed.

(b) Interferences

The freedom from interference from other components in a sample, characteristic of atomic absorption spectroscopy, should be almost as in atomic fluorescence spectroscopy. In the preliminary experiments, it has been found that both zinc and beryllium suffer

TABLE VIII

SENSITIVITY LIMITS REPORTED FOR VARIOUS ELEMENTS
BY ATOMIC FLUORESCENCE SPECTROSCOPY

Element-Line(\AA)	Radiation source*	Limit of detection (p.p.m)	Reference
Al 3870	HHC	25	(12)
Sb 2176	EDT	0.05	(9)
Be 2349	HHHC	0.5	(29)
Bi 3025	EDT	0.05	(10)
3968	HHC	0.1	(12)
Cd 2288	Ph	0.002	(17)
	Os	0.01	(5)
	Xe	0.1	(31)
Ca 4227	Xe	0.1	(13)
Co 2407	Xe	0.5	(13)
	HHC	0.5	(12)
Cu 3248	Xe	0.35	(31)
	HHC	0.001	(12)
Cr 3579	HHC	100	(12)
Ga 4172	EDT	10	(17)
	HHC	0.05	(12)
Au 2676	Xe	3.5	(31)
	HHC	0.05	(12)
In 4105	EDT	10	(17)
	HHC	50	(12)
Fe 2483	Xe	5	(6)
	HHC	5	(12)
	Ph.Hg	1	(20)
Pb 4058	Xe	7.5	(31)
	HHC	1	(12)
Mg 2852	Xe	0.01	(13)

Continuation of Table VIII

Element-Line(\AA)	Radiation source*	Limit of detection (p.p.m.)	Reference
Mn 2794	Xe	0.15	(6)
	HHC	5	(12)
Hg 2537	EDT	0.1	(17)
Ni 2320	HIHC	0.3	(3)
	HHC	0.5	(12)
Pd 2500	HHC	0.5	(12)
Se 2040	EDT	0.15	(18)
Ag 3281	Xe	0.001	(13)
	HHC	0.001	(12)
	HIHC	0.004	(37)
Te 2143	EDT	0.15	(8)
Tl 3776	Ph	0.04	(17)
	HHC	0.1	(12)
Ti 3895	HHC	5	(12)
Zn 2139	Ph	0.0001	(17)
	Os	0.1	(41)
	Xe	0.03	(13)
Zr 3890	HHC	10	(12)

* HHC, hot hollow cathode lamp; EDT, electrodeless discharge tube; HIHC, high intensity hollow cathode lamp; Ph, Philips metal vapor discharge lamp; Os, Osram metal vapor discharge lamp; Xe, xe arc continuum; Ph.Hg, Philips mercury lamp.

no significant interferences from cations tested. Anionic interferences have been observed for both elements but they are readily eliminated by adding complexing agent such as EDTA. In other reported interference studies for other elements, no interference was encountered in most cases (5, 6, 8, 9, 10, 37). This chemical interference, of course, is very prevalent in flame photometry and emission spectrography. It is not so much of a problem in activation analysis and X-ray fluorescence.

(c) Simplicity and Low Cost

In some respects the instrumental demands of atomic fluorescence spectroscopy are simpler than those of atomic absorption spectroscopy. Radiation source of very narrow spectral profile is required for atomic-absorbance measurements because of the narrow band-width of absorption bands. This is best obtained from a hollow cathode lamp, with cathode made from the metal being analyzed or one of its alloys. On the other hand, for atomic fluorescence spectroscopy, much cheaper and more readily obtained non-reversed sources such as spectral-discharge lamps may be used. Compared to emission spectrography, X-ray fluorescence, and activation analysis, the equipment for atomic fluorescence spectroscopy is comparatively simple and low cost. Certainly, flame photometry is somewhat cheaper, but generally as an analytical process it is not as versatile as atomic fluorescence.

B. DISADVANTAGES

(a) Not All Elements

Like atomic absorption spectroscopy, all elements in the periodic table cannot be determined by atomic fluorescence spectroscopy.

Only 26 elements so far have demonstrated their fluorescence characteristics. It can be expected that the number of elements which can be determined by atomic fluorescence spectroscopy should eventually be comparable to those measured by atomic absorption and flame photometry.

(b) Flame Atomizers Require Liquid Samples

Only liquid samples have been used to date. When solid or gaseous samples are to be analyzed, conversion to a liquid sometimes necessitates considerable sample preparation.

(c) Simultaneous Analysis

Simultaneous analysis of several elements would be difficult so long as flame atomizers are used.

(d) Radiation Interference

Background emission and thermal emission should be eliminated by modulation of the system. However, the flame background emission (though often negligible) is a form of interference in atomic fluorescence spectroscopy, and it is never wholly eliminated by modulation, since the emission has a noise component at the frequency of modulation. Incident light scattering by solvent droplets and salt particles in the flame gases which is generally negligible in atomic absorption spectroscopy and non-existence in flame photometry could be significant in atomic fluorescence spectroscopy, particularly when a continuous source is used.

(e) Self-absorption

Quenching effect, which is not observed in atomic absorption spectroscopy, can take place at high concentration in atomic fluorescence

spectroscopy. As shown in Figures 8 and 14, a reversal calibration curve occurs and this limits the detectability at upper parts.

C. PROBLEMS AND FUTURE DEVELOPMENTS

(a) Means of Atomization

Thermal atomization in flames is an inefficient process. The relationship between ground state atoms and total concentration of copper sample has been calculated (28). It turned out to be only one copper atom in 10^5 is reduced to the atomic state for the sensitivity 0.1 p.p.m. of copper. This indicates that sensitivities a thousand times better than those attained to date should be available with better atomizer. Therefore, a development of better methods of atomization would be very important problem for atomic fluorescence spectroscopy.

(b) Lack of Radiation Sources

The intense radiation sources capable of exciting fluorescence of elements are still limited. The elements which fluoresce from using a continuous source are limited and the sensitivities are generally poorer than those obtained by using a line source. To broaden its applications and the number of elements which can be determined by atomic fluorescence method, an increase in a large number of stable high-intensity sources commercially available are highly desirable.

D. ANALYTICAL APPLICATIONS

It is anticipated that atomic fluorescence spectroscopy should

be applied to actual analyses similar to those now using atomic absorption spectroscopy and flame photometry. The fields for analytical applications should include wines, body fluids, water, air, metals, cements, soils, tissue, fertilizer, ores, isotopes, etc. Undoubtly this technique will prove to be invaluable for inorganic trace analysis in the nanogram range in the near future.

CHAPTER V

THE SPECTROSCOPIC STUDIES OF THE CHROMOTROPIC ACID - NITRATE REACTION

A. INTRODUCTION

The spectrophotometric determination of nitrate using chromotropic acid has been known for several years (22, 34). The reaction provides a specific and sensitive spot test for nitrate (33) based on its reaction with a solution of chromotropic acid (1,8 - dihydroxy-3,6-naphthalenedisulfonic acid) in strong sulfuric acid. In the presence of 70% sulfuric acid, as little as a microgram amount of nitrate ion produces the immediate appearance of a yellow color with chromotropic acid at room temperature. The reaction between chromotropic acid and nitrate is markedly influenced by the amount of sulfuric acid present in solution. Spectrophotometric studies (22, 34) indicated that the yellow coloration obtained with chromotropic acid and nitrate was most intense in aqueous media containing 69-73% sulfuric acid. It was also indicated that one mole of nitrate reacted with one mole of chromotropic acid. But the exact chemical nature of the reaction was not clearly understood.

A further investigation of the reaction between chromotropic acid and nitrate at optimum concentration (i.e. about 70%) of sulfuric acid using NMR method has been carried out. Interpretation

of the NMR spectra indicates that one mole of chromotropic acid reacts with one mole of nitrate in 70% sulfuric acid. The UV spectrum indicated the formation of a quinone compound during the reaction. It was concluded that a polymerized mononitro derivative of chromotropic acid was the chromophoric agent in the reaction.

B. EXPERIMENTAL

(a) Reagents

(1) Purified Chromotropic Acid A saturated solution of disodium salt of 1,8-dihydroxy-3,6-naphthalenedisulfonic acid (Eastman Organic Chemicals, technical grade) was processed twice using decolorizing charcoal. The purified reagent was crystallized from the filtered solution by cooling and adding concentrated sulfuric acid. The white product was filtered under suction, washed several times with ethanol, and dried in a vacuum oven.

(2) Standard Nitrate Solution A stock nitrate solution was prepared by dissolving 0.825 g of analytical grade sodium nitrate in 1 ml of distilled water to give a 0.602 mg nitrate/ μ l solution.

(3) Sulfuric Acid Concentrated sulfuric acid (du Pont Company) was found to be free from nitrate by testing with chromotropic acid.

(b) Equipment

A Varian HA-60 MHz spectrometer was used to obtain NMR spectra. A Beckman model DB spectrophotometer equipped with a Sargent recorder was used in the study of absorption spectrum.

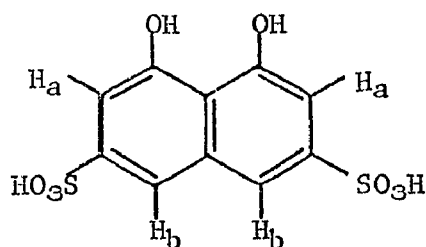
(c) Procedure

The optimum concentration (70%) of sulfuric acid which gave the most sensitive result for the chromotropic acid-nitrate reaction was chosen as the reaction media. 25 mg of chromotropic acid was dissolved in 0.5 ml of 70% (v/v) sulfuric acid. The NMR spectra of the chromotropic acid-nitrate system were taken at various ratios of the two compounds. This was achieved by keeping the amount of chromotropic acid constant and varying the amount of standard nitrate solution. Increasing concentrations of nitrate were added until the proton peaks of the naphthalene ring disappeared from the NMR spectrum.

C. RESULTS AND DISCUSSION

(a) NMR Spectra of Chromotropic Acid

(1) In Water and Deuterium Oxide The structure of chromotropic acid is illustrated as follows:



The NMR spectrum is shown in Figure 16. The assignments of the ring protons are indicated. The protons in phenolic group and sulfonic acid group are not evident in the spectrum because they exchange rapidly with water molecules in the solvent. In benzene the ring proton is usually located at 7.26 p.p.m. The location of the H_a peak which is

upfield at 7.13 p.p.m. compared to benzene because of diamagnetic shifts caused by: (a) the -OH group, (b) the -SO₃H group. The location of H_b peak is downfield at 7.83 p.p.m. due to three effects: (a) the -OH group in para position has about the same effect as in ortho position, (b) the -SO₃H group causes a slight diamagnetic shift, and (c) the neighboring phenyl group causes a strong paramagnetic shift. The distance between these two peaks is 0.7 p.p.m. The splitting of each peak into a doublet is due to coupling between the ring protons. The equal area of the two peaks by integration indicates that each peak contains the same number of protons.

For a comparison purpose, the NMR spectrum of chromotropic acid in deuterium oxide was also recorded. Figure 17 shows the result which is essentially the same as in the water.

(2) In Dimethyl Sulfoxide - D₆ In order to identify the phenolic proton peak, deuterated dimethyl sulfoxide was used as a solvent for chromotropic acid. The results are given in Figure 18 and the assignment for the peaks is labeled. The broad peak at 10.88 p.p.m. is due to phenolic proton resonance. Integration of the three peaks for -OH, H_a, and H_b, showed that all three peaks have the same area. It can be concluded from this that each peak represents two protons.

(3) In 70% Sulfuric Acid The reaction of the chromotropic acid-nitrate system was studied under condition of optimum concentration of sulfuric acid. The NMR spectrum of chromotropic

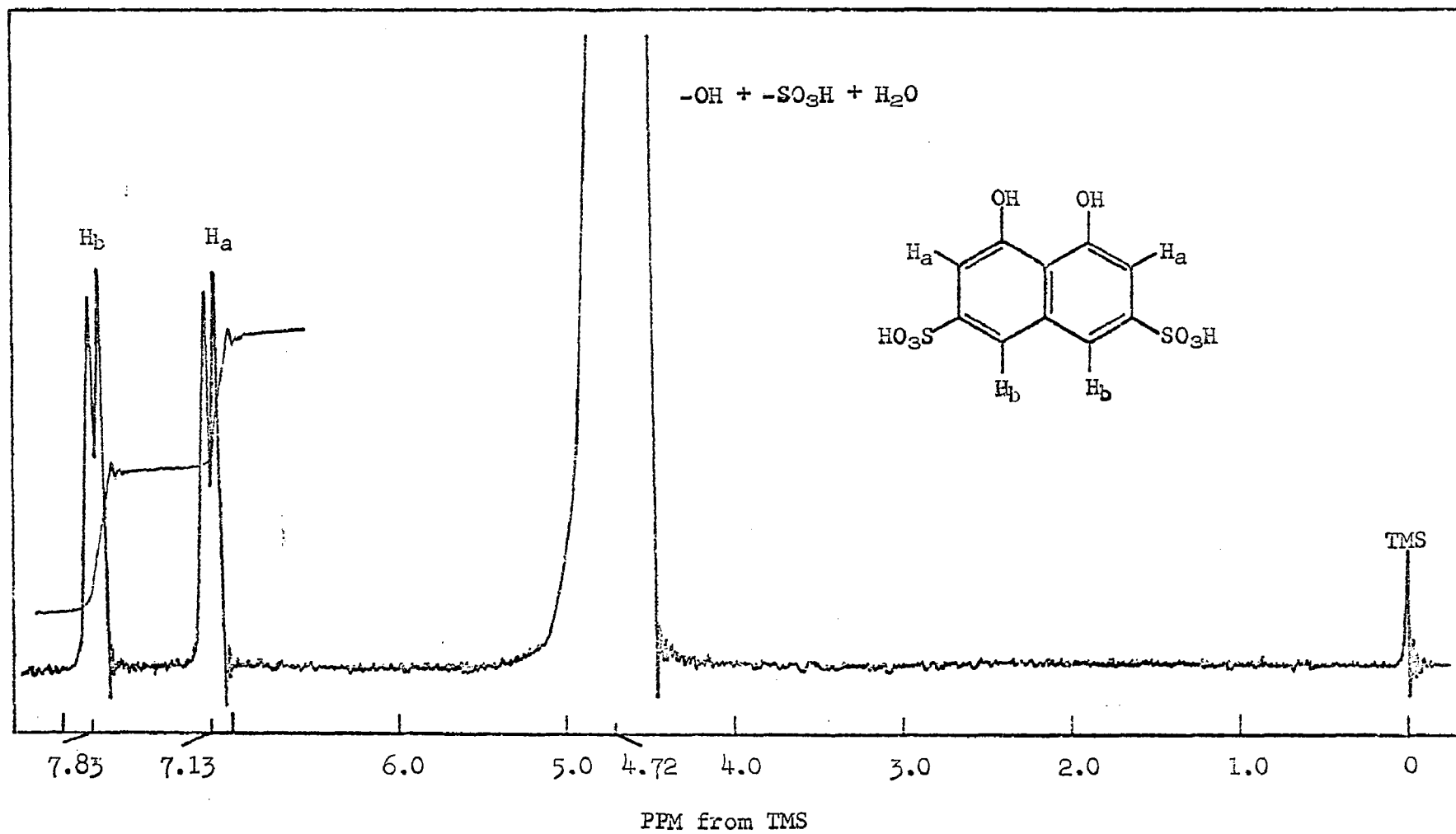


Figure 16

NMR Spectrum of Chromotropic Acid, 10% (w/v) in Water

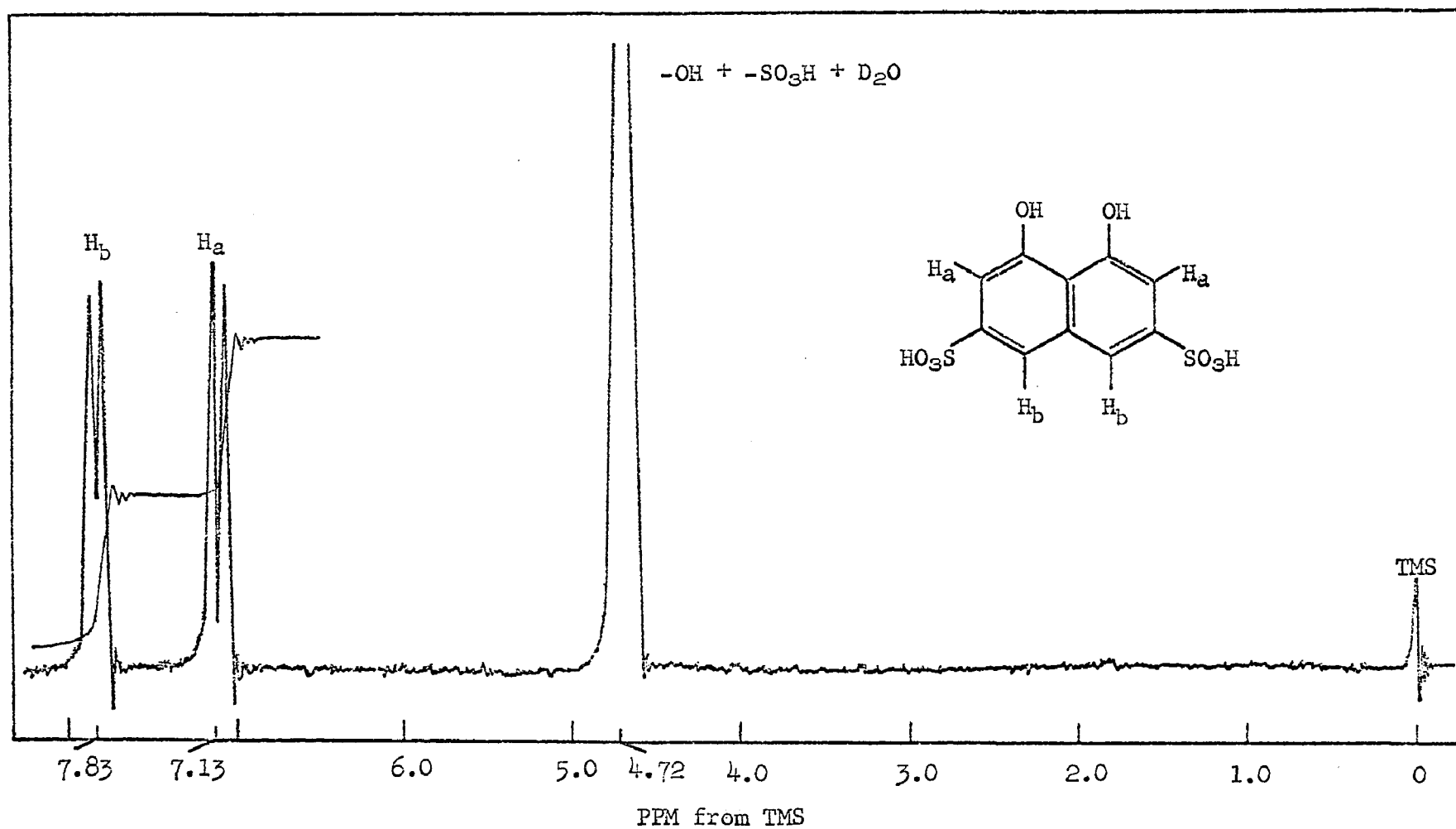


Figure 17
NMR Spectrum of Chromotropic Acid, 10% (w/v) in Deuterium Oxide

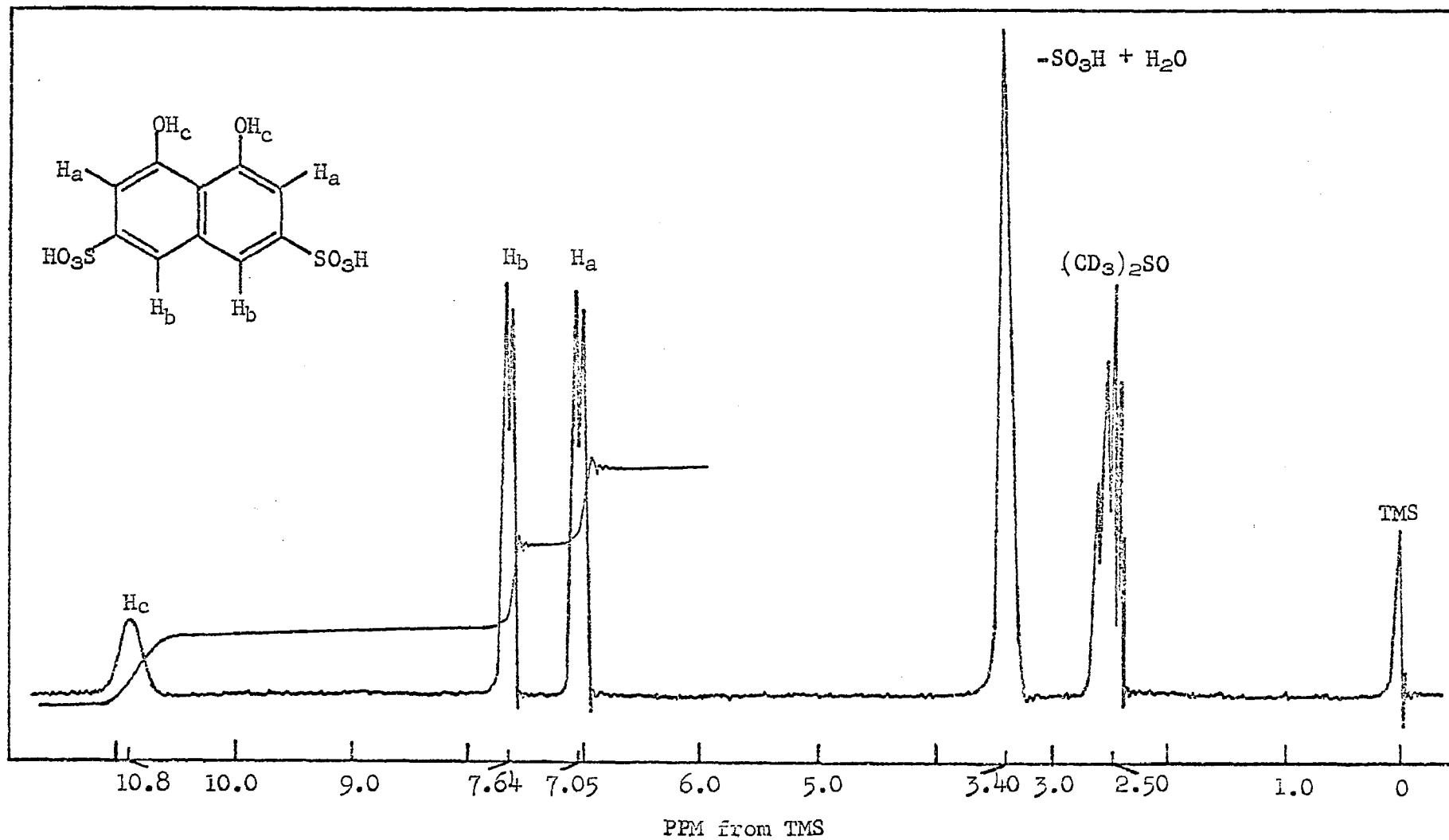


Figure 18
NMR Spectrum of Chromotropic Acid, 8% (w/v) in Dimethyl Sulfoxide - D_6

acid was observed in 70% (v/v) sulfuric acid. It is shown in Figure 19. The water peak shifted downfield in the strong acid media. The chemical shift of the ring hydrogens remained the same, but the spin-spin splitting was lost. Apparently the coupling between the protons decreased in the strongly acidic solution.

(b) NMR Spectra of the Chromotropic Acid-Nitrate System in 70% Sulfuric Acid

(1) Solution Prepared by the Addition of Standard Nitrate Solution The spectrum of the chromotropic acid in 70% sulfuric acid was first obtained. Without changing the instrumental settings, the spectrum of the chromotropic acid in 70% sulfuric acid was recorded after the addition of standard nitrate solution. The process was repeated with increased nitrate addition. The results are shown in Figure 20. Both H_a and H_b peaks are equally affected by the addition of nitrate solution. Further extra peaks became evident. These were attributed to the formation of the disodium salt of the chromotropic acid causing a different chemical shift from the free acid. The presence of the disodium salt and the free acid resulted in four peaks instead of two. At mole ratio 1 : 1, the H_a and H_b peaks disappeared. Obviously both H_a and H_b protons in chromotropic acid are attacked simultaneously during the addition of nitrate solution. This indicated that the product was a mononitration compound.

(2) Solution Prepared by the Addition of Concentrated Nitric Acid It was suggested that the appearance of the extra peaks in Figure 20 was the result of the formation of disodium salt of the chromotropic acid. Therefore a study was made using nitric acid instead of

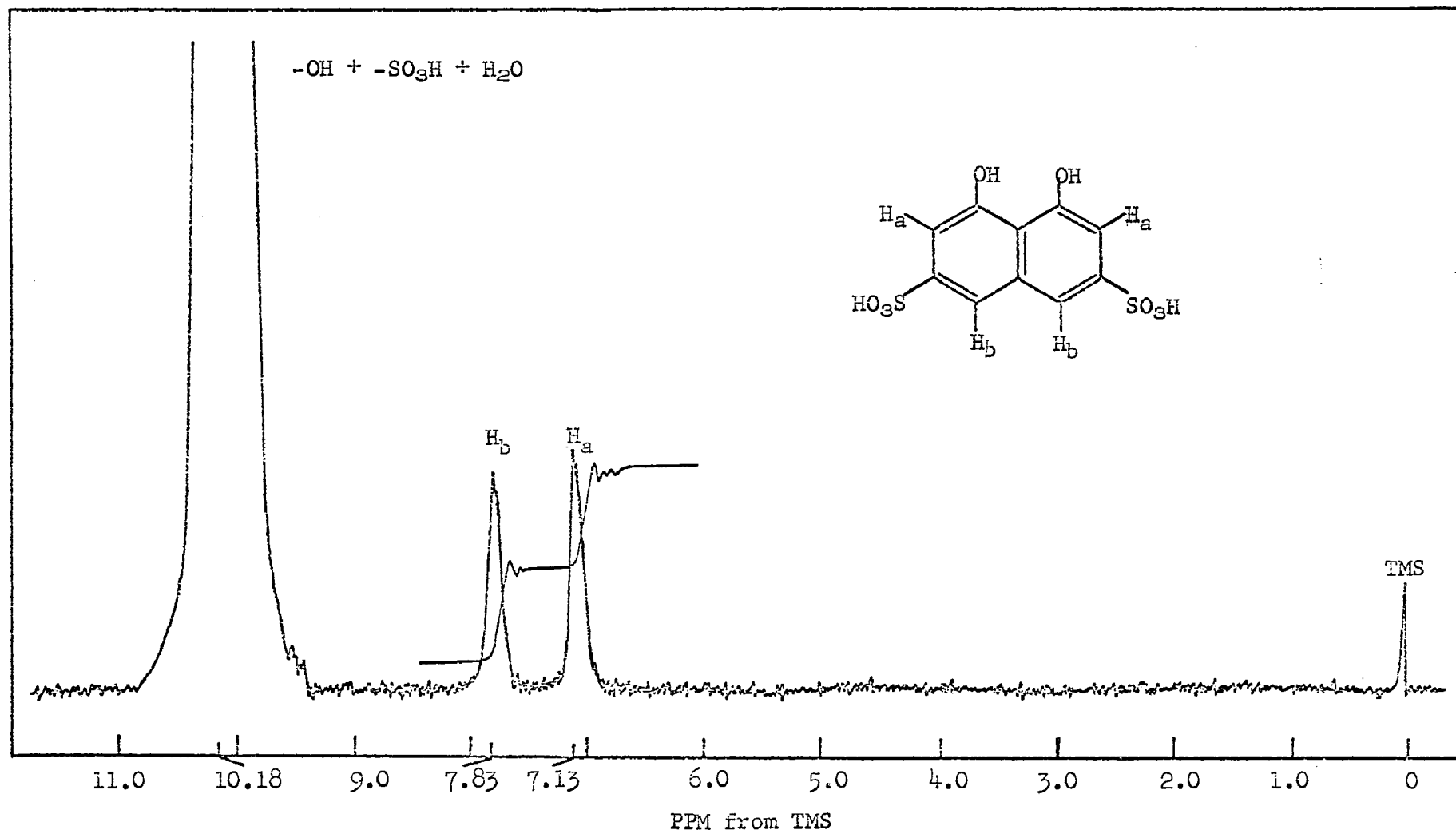


Figure 19

NMR Spectrum of Chromotropic Acid, 5% (w/v) in 70% Sulfuric Acid

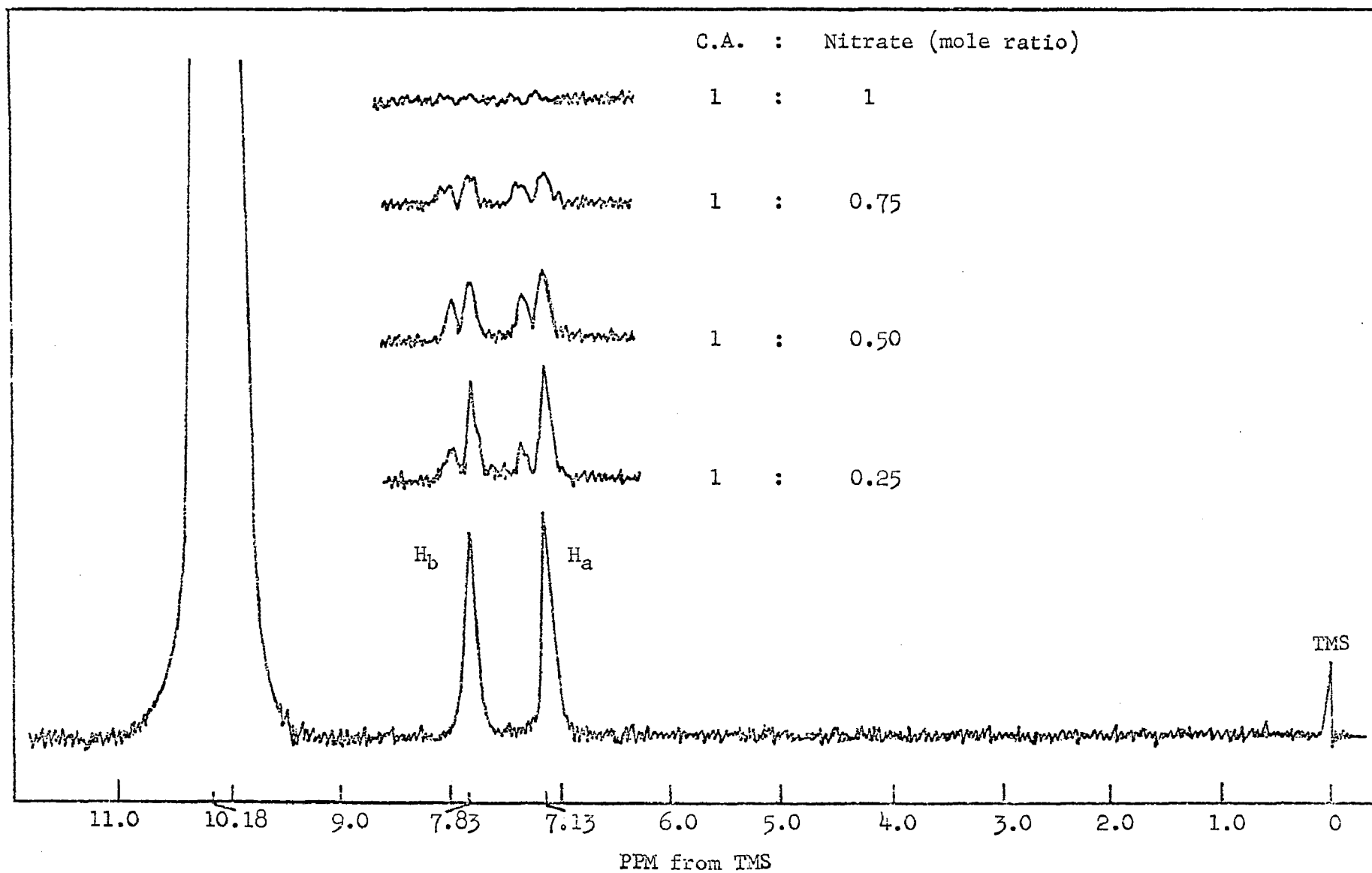


Figure 20

NMR Spectra of the Chromotropic Acid - Nitrate System in 70% Sulfuric Acid:
By the Addition of Sodium Nitrate Solution

sodium nitrate solution as a means of adding nitrate ion to the solution. The results are shown in Figure 21. The extra small peaks seen in Figure 20 did not appear under these conditions. However as before both H_a and H_b peaks disappeared at an equimole of nitrate to chromotropic acid.

(c) NMR Spectrum of the Chromotropic Acid-Nitrate System in 10% Sulfuric Acid

As already mentioned the reaction between chromotropic acid and nitrate is markedly influenced by the amount of sulfuric acid present in the solution and the most sensitive reaction takes place at about 70% of sulfuric acid. For the purpose of comparison, a 10% sulfuric acid used as reaction media was also investigated. The results are shown in Figure 22. It was observed that when nitrate solution was increased to large excess, a slight decrease in the H_a and H_b peak intensities followed. At the mole ratio 1 : 3 (chromotropic acid/nitrate) two small extra peaks started to appear. At mole ratio 1 : 5, both H_a and H_b peaks disappeared. This indicates reduced attack by the addition of nitrate solution on chromotropic acid at this low acidity.

(d) UV Spectrum of the Chromotropic Acid-Nitrate System in 70% Sulfuric Acid

In order to identify the product of the chromotropic acid-nitrate reaction at the mole ratio 1 : 1 in the presence of 70% sulfuric acid, an absorption spectrum for this yellow-brown color solution was taken. The result is shown in Figure 23. It has been known that p-Benzoquinone has a high intensity band near 245 $m\mu$, a medium intensity band near 285 $m\mu$, and a low intensity band near

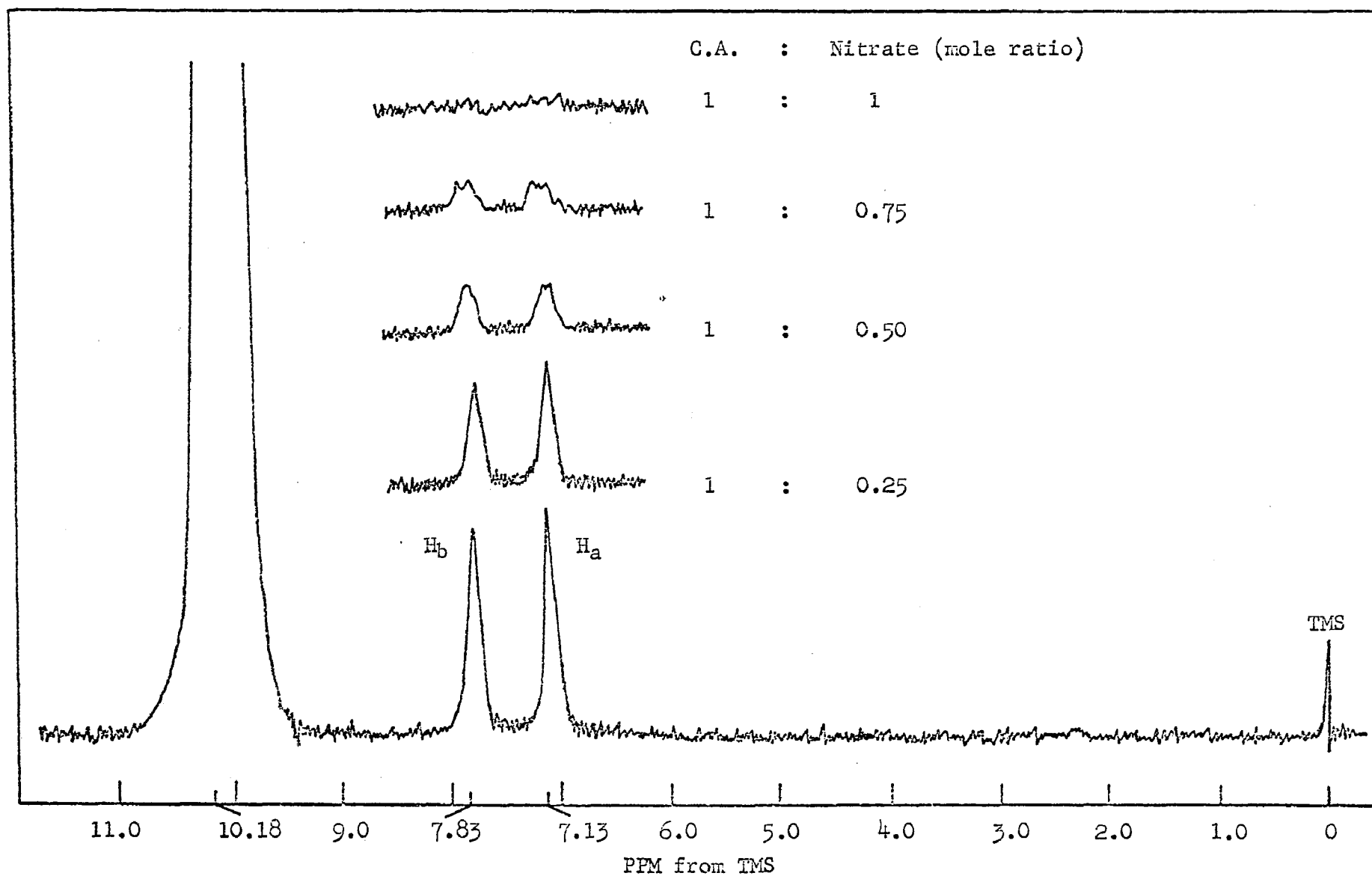


Figure 21
NMR Spectra of the Chromotropic Acid - Nitrate System in 70% Sulfuric Acid:
By the Addition of Concentrated Nitric Acid

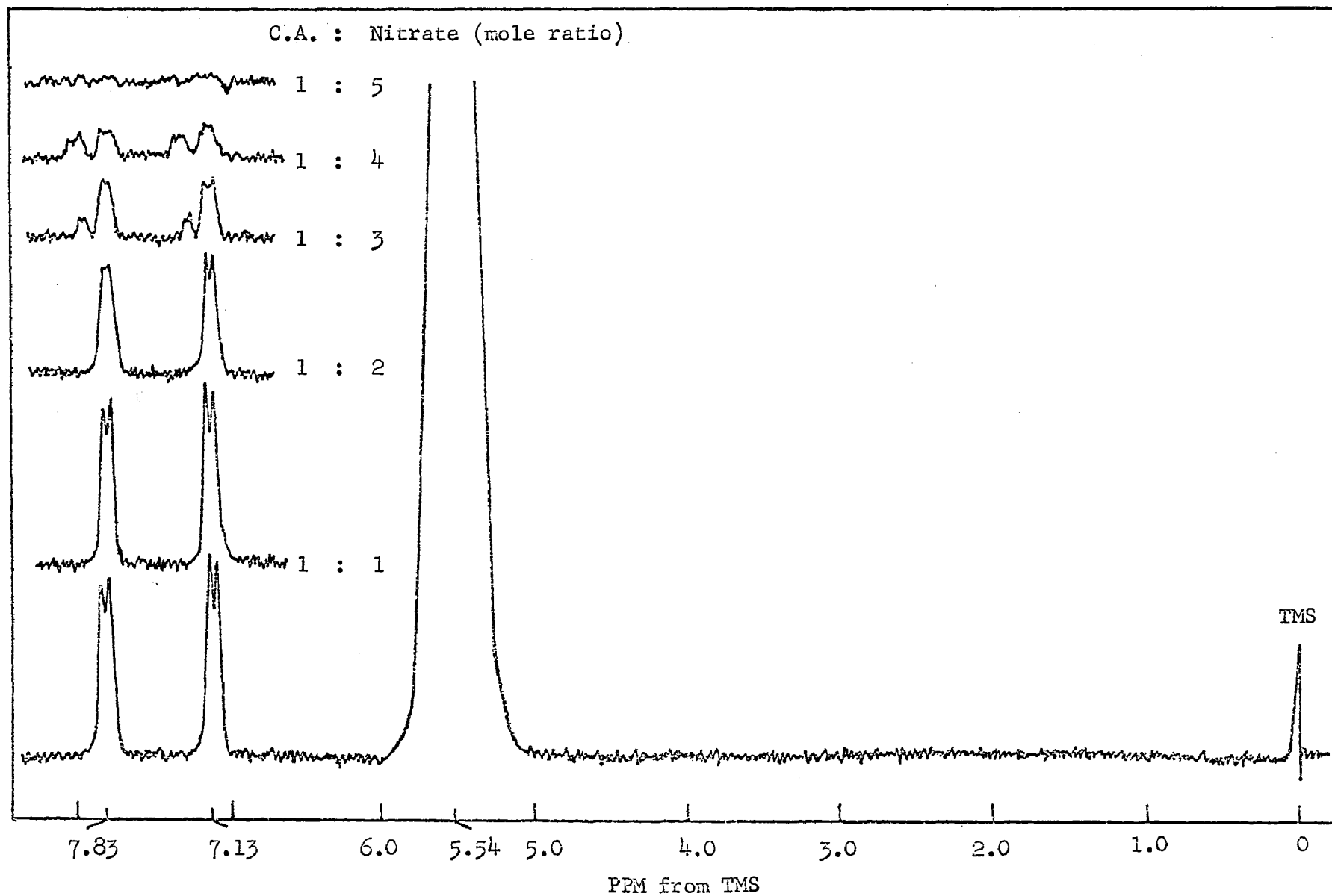


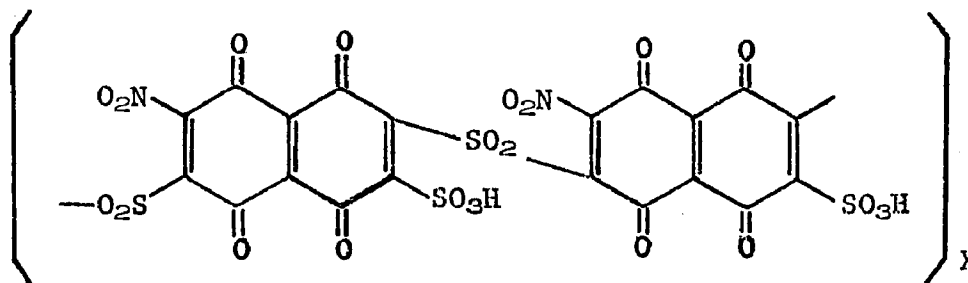
Figure 22

NMR Spectra of the Chromotropic Acid - Nitrate System in 10% Sulfuric Acid

435 $m\mu$ (38). The spectrum obtained shows that the color product has a high intensity band near 221 $m\mu$, a medium intensity band near 259 $m\mu$, and a low intensity band near 435 $m\mu$. Since these three absorption bands of the product closely resemble those of p-Benzoquinone, it can be concluded that the color product is a quinone compound.

D. CONCLUSION

The NMR spectra indicate that the product of the chromotropic acid-nitrate reaction in 70% sulfuric acid is a mononitration compound, while the UV spectrum indicates that the product is a quinone compound. Since the nitrate solution present in strong sulfuric acid produced a nitronium ion (NO_2^+), the product would be a mononitro derivative of chromotropic acid. Furthermore, since both H_a and H_b proton peaks of chromotropic acid in NMR spectrum disappeared, the structure for the product of the chromotropic acid-nitrate reaction in 70% sulfuric acid may be represented as below:



The compound is a mononitro-quinone derivative of chromotropic acid in polymer form.

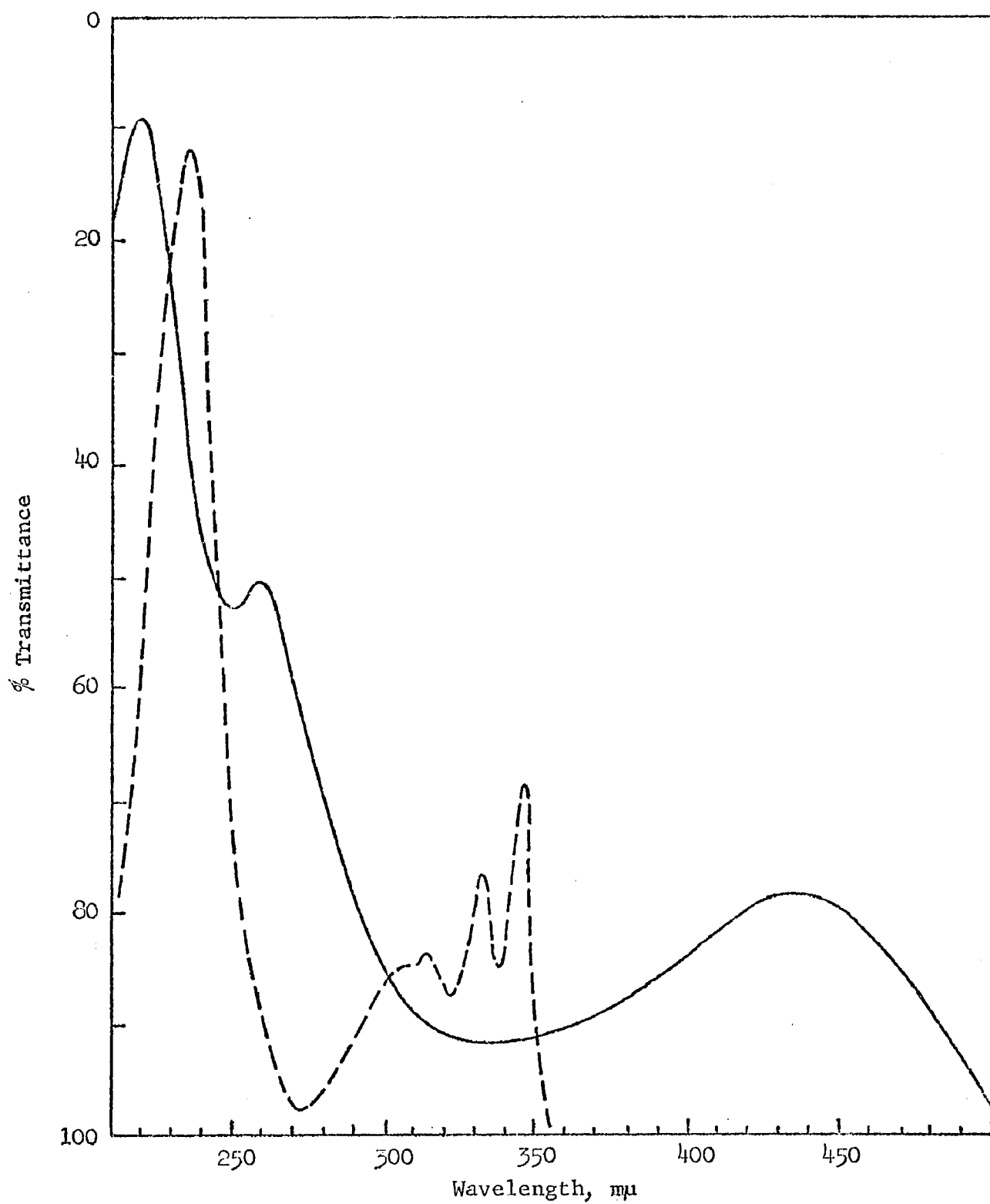


Figure 23

UV Absorption Spectra
----- Absorption Spectrum of Chromotropic Acid in 70% Sulfuric Acid
——— Absorption Spectrum of the Chromotropic Acid - Nitrate System
at Mole Ratio 1 : 1 in 70% Sulfuric Acid

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VITA

Chun-Jer Hsu was born on January 7, 1936, in Taiwan, China. He graduated from Tainan Second High School, Taiwan in 1955. He attended Cheng-Kung University, Taiwan from which he received his B.S. in Chemical Engineering in 1960. He then began one year of military service in the Chinese army. From 1961 to 1963 he worked as a chemical engineer at Taiwan Alkali Company. In September 1963, he entered the Graduate School of Louisiana State University, and is presently a candidate for the degree of Doctor of Philosophy in Chemistry.

He is married to the former Hso-Hwi Su and has one child, Kelly.

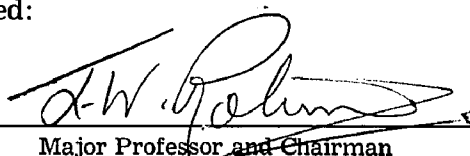
EXAMINATION AND THESIS REPORT


Candidate: Chun-jer Hsu

Major Field: Chemistry

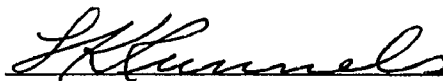
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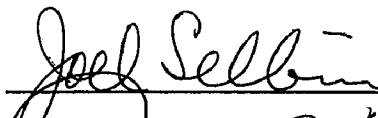
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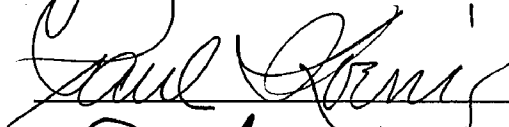

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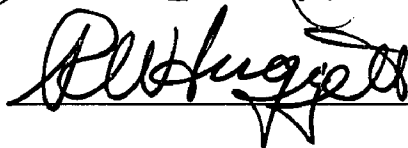

Dean of the Graduate School

EXAMINING COMMITTEE:









Date of Examination:

July 2, 1968