A NEW ANALYTICAL METHOD FOR THE QUANTITATIVE DETERMINATION
OF CARBON DIOXIDE IN THE ATMOSPHERE AND BICARBONATE ION IN AQUEOUS SOLUTION

by

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CHAPTER I

INTRODUCTION

The goal of this research has been to find an analytical method of good selectivity and moderate to good sensitivity for the determination of carbon dioxide in the atmosphere and bicarbonate ions in aqueous solutions.

Carbon dioxide has a boiling point of -78.5°C. A carbon dioxide saturated solution of water at 20°C and one atmosphere of pressure is 0.0366 molar in carbonic acid. The dissociation constants of carbonic acid are: $K_1 = 4.3 \times 10^{-7}$, and $K_2 = 5.6 \times 10^{-11}$.

Carbon dioxide is a normal constituent of air and is of vital importance for the flora. Because of its ability to absorb infrared rays from sunlight, carbon dioxide plays a significant role in the heat balance of atmospheric air.

The CO_2-level in unpolluted air is not completely uniform. It has increased from about 290 ppm to about 320 ppm on the average since 1900, due to the consumption of fossil fuels. Heating, traffic, and industry can cause local CO_2-levels which exceed the average level in the open air.

The human respiratory functions are to a large extend independent of variations in the CO_2-level in the atmosphere. In the open atmosphere, hazardous concentrations (5000 ppm) are almost never reached and, consequently, such air is rarely analyzed for its CO_2 content. On the other hand, the CO_2-level of the air, especially in the microclimate, is of interest to the plant physiologist. In enclosed spaces, CO_2 poisoning due to the accumulation of carbon dioxide is possible. As CO_2 is 1.5 times as dense as air, CO_2 accumulates on the floor of

enclosed spaces. Combustion gases can contain up to 20% CO_2, depending upon the O_2-content of the air. In mines, CO_2-rich gas eruptions may cause lethal poisoning. A CO_2-rich atmosphere is usually indicated by the failure of a candle to burn when the CO_2-content exceeds 8%. For concentrations of CO_2 exceeding 2%, a candle flame has a reddish light.

Dangerous levels of CO_2 may also be reached in enclosed spaces due to the presence of a large number of people. An adult person, at rest, exhales about 300 liters of air containing 4 - 5% CO_2 each hour. In living spaces of limited size, for example in submarines or manned satellites, the removal of exhaled CO_2 is important.

In the plant kingdom, CO_2-rich air (less than 1%) is not harmful but leads to increasing assimilation and hence to an increase in growth rate.

CHAPTER II

SURVEY OF ANALYTICAL METHODS FOR CO_2

Present methods of analysis for carbon dioxide can be characterized

by seven classifications: acid-base titration, both aqueous[1-7], and

non-aqueous[8,9]; volumetry[10]; differential conductivity[11]; non-dispersive

infrared spectrophotometry; turbidimetry[12]; and colorimetry[13].

The most accurate of these methods is the acid-base titration, but

this method is far from foolproof. With good technique and about an

hour per determination, the investigator can expect a standard error of

$\pm$ 5%. Also, great care must be exercised to exclude any other acidic

or basic substances.

Volumetric analysis has the advantage of being rapid, simple, and

adaptable to field operations. Again acidic gases may interfere, and

accuracy is not good, usually $\pm$ 15%.

Differential conductivity analysis affords good precision, $\pm$ 1%,

but its accuracy is only about $\pm$ 10%. Also, this method requires an

experienced technician and specialized equipment which requires regular

calibration against a more accurate method. Again, acidic or basic

substances interfere.

Non-dispersive infrared spectroscopy affords ease of operation and

is adaptable to rapid and repetitive analysis. However, this method

requires specialized equipment, and it is not specific for CO_2.

Turbidimetric analysis may be either visual or instrumental, but

neither has good accuracy, $\pm$ 10%. Again, acidic or basic substances

interfere.

The colorometric method involves drawing an air sample through

a tube containing silica gel impregnated with a colorless basic

fuchsine-hydrazine hydrate. A rose color forms in response to CO_2 in the air. The length of the stain in conjunction with the volume of air sampled is a measure of the amount of carbon dioxide present. The accuracy is not good, $\pm$ 15%, and acidic gases interfere.

To avoid interferences from acidic and basic substances, it was decided to base any new method on some chemical property of carbon dioxide or bicarbonate ion other than their acid-base properties. In an attempt to achieve the objectives of simplicity, adaptability, and accuracy, it was decided to attempt to develop a colorometric method of analysis.

The useful chemical properties of the CO_2-bicarbonate-carbonate system are few. Two properties seemed to show some promise. One was the ability of carbonate to precipitate a number of divalent metal ions. The other was the formation of a stable complex with uranyl ion[14], UO_2^{+2}.

CHAPTER III

SURVEY OF LIGAND PROPERTIES

Uranyl was the first choice as an analytical reagent, as its carbonate complexes are soluble. A search for a chromogenic agent for uranyl indicated 1-(2'-pyridylazo)-2-naphthol[15] (o-PAN) as a promising ligand. However, extensive work proved futile in developing a suitable method with these reagents due to the instability of the UO_2^{+2}-PAN complex.

It was then decided to attempt the development of a method based upon the carbonate reaction with divalent metal ions. The very limited solubility of lead carbonate led to the investigation of Pb(II) complexes as analytical reagents. The search for a suitable chromogenic agent to be used with Pb(II) encompassed five likely azo dyes: o-PAN; 2-(4'-hydroxy-6'-methyl-2'-pyrimidylazo)-1-naphthol (HMPmAN); 1-(2'-thiazolylazo)-2-naphthol (TAN); 2-(2'-pyrimidylazo)-1-naphthol (PmAN); and 2-(2'-quinolylazo)-1-naphthol (QAN). 2-(2'-Quinolylazo)-3,4,5,6-tetrachlorophenol was found to display no chromogenic activity with Pb(II). 2-(2'-Pyrimidylazo)-3,4,5,6-tetrachlorophenol was also investigated, but no satisfactory synthetic procedure for this dye was found.

o-PAN, purchased from the Fisher Scientific Company, was found to form a 1:1 complex with Pb(II) in 50% aqueous ethanol and a 4:1 complex in 95% ethanol. The dye in 50% aqueous 2-propanol has an absorbance maximum at 474 nm, and the 1:1 complex has an absorbance maximum at 555 nm ($\varepsilon = 6.06 \times 10^3$), a bathochromic shift of 95 nm. The overall stability constant for the 4:1 complex was found

to be $10^{3.47}$.

$$K_{stab} = \frac{[Pb(Dye)_n]}{[Pb][Dye]^n}$$

The stability constant was calculated from data obtained from isobestic point plots of the complex. The equations used for these calculations may be found in Appendix A. The optimum wavelength for observation of the system was taken as the wavelength at which the dye had an absorbance less than 1% of its absorbance at its absorbance maximum. For the o-PAN - Pb(II):PAN system, this was found to be 565 nm, at which the complex has a molar absorptivity of 6,030 liter mole^{-1}cm^{-1}.

HMPmAN was synthesized by condensing 2-hydrazine-4-hydroxy-6-methyl-pyrimidine with 1,2-naphthalene diquinone. The pyrimidine was purchased from the Aldrich Chemical Company, Inc.. The naphthalene diquinone was prepared from 2-naphthol by the method of Fieser[16]. The dye was found to form a 1:1 complex with Pb(II) in 50% aqueous ethanol and a 2:1 complex in 95% ethanol. The dye has an absorbance maximum at 480 nm, (ϵ = 9,800). The 2:1 complex has an absorbance maximum at 551 nm, (ϵ = 25,200), a bathochromic shift of 71 nm. The stability constant for the 2:1 complex was found to be $10^{5.81}$. The optimum wavelength for this system was found to be 578 nm (ϵ = 20,100).

PmAN was synthesized by condensing 2-hydrazinopyrimidine with 1,2-naphthalene diquinone. 2-Hydrazinopyrimidine was prepared from 2-chloropyrimidine and anhydrous hydrazine by the method of Shirakawa, Ban, and Yoneda[17]. The dye was found to form a 1:1 complex with Pb(II) in 50% aqueous ethanol and a 2:1 complex in 95% ethanol. The dye has absorbance maxima at 352 nm (ϵ = 8,150) and at 472 nm (ϵ = 6,700).

The 2:1 complex has an absorbance maximum at 570 nm (ϵ = 22,600), a bathochromic shift of 98 nm. The optimum wavelength for this system was found to be 610 nm (ϵ = 16,400). The stability constant for the 2:1 complex was found to be $10^{5.88}$.

TAN was synthesized via the diazotization of 2-aminothiazole and coupling with 2-naphthol. The dye was found to form a 1:1 complex with Pb(II) in 50% aqueous ethanol and a 4:1 complex in 95% ethanol. The dye has an absorbance maximum at 483 nm (ϵ = 2,880). The 4:1 complex has an absorbance maximum at 560 nm (ϵ = 11,900), a bathochromic shift of 77 nm. The optimum wavelength for this system was found to be 605 nm (ϵ = 8,650). The stability constant for the 4:1 complex was found to be $10^{4.16}$.

QAN was synthesized by condensing 2-hydrazinoquinoline with 1,2-naphthalene diquinone. 2-Hydrazinoquinoline was prepared from 2-chloroquinoline and anhydrous hydrazine in a manner analogous to the method of Shirakawa[17]. The dye was found to form a 2:1 complex with Pb(II) in both 50% aqueous ethanol and 95% ethanol. The dye has an absorbance maximum at 487 nm (ϵ = 5,730). The complex has an absorbance maximum at 598 nm (ϵ = 17,900), a bathochromic shift of 111 nm. The optimum wavelength for this system was found to be 640 nm. In 95% ethanol, the complex has a molar absorptivity of 17,400 at 640 nm. In 50% aqueous ethanol, the molar absorptivity at 640 nm is 16,400. The stability constant for the complex was found to be $10^{5.92}$.

All of these dyes and complexes exhibit an expected pH dependence. o-PAN has a pK_1 of 1.6 and a pK_2 of 12.2[15] in 50% alcohol. In 50% aqueous ethanol, HMPmAN was found to have a pK of 7.27; PmAN, 10.34;

TAN, 9.59; and QAN, 10.70. All of the complexes displayed the greatest stability in the pH range of 6.5 to 7.5. This is to be expected since the complex is unstable with a protonated naphthol. Also at higher pH values the stability of the complexes is not sufficiently large to compete successfully with the formation of $Pb(OH)_2$ or $[Pb(OH)_4]^{-2}$.

QAN was selected as the best ligand for five reasons. It exhibits the largest stability constant. It exhibits the largest bathochromic shift. It alone exhibits only one stoichiometry for complex formation. It has one of the larger molar absorbtivities at the optimum wavelength. Also, it exhibits the simplest and most symmetrical absorbtivity curve (see Appendix B).

CHAPTER IV

A $Pb(QAN)_2$ METHOD FOR CO_2

' It was expected to use the $Pb(QAN)_2$ complex as a colorometric

agent for the determination of CO_2 or bicarbonate ion by ligand

displacement, the absorbance at 640 nm being inversely proportional

to the amount of bicarbonate or CO_2 added. However, this was found to

be true only over a very narrow concentration range for bicarbonate

ion (see Plate One). Use is made of this property for determining

both CO_2 in the atmosphere and bicarbonate ion in aqueous solution.

To determine bicarbonate ion concentration in an aqueous sample,

the pH of the sample is adjusted to 7.5 with dilute perchloric acid

or potassium hydroxide, the sample is diluted with an equal volume of

95% ethanol and is used to titrate a standard volume of $Pb(QAN)_2$ in

50% ethanol (see Plate Two). The titration must be carried out slowly

under an atmosphere free of CO_2. The end point is indicated by a color

change of blue to reddish orange. However, this end point is slow

in developing. Thus, with the appearance of a violet color, it is

recommended to halt the titration for five minutes and then proceed

at a rate not to exceed one drop every thirty seconds. Admittedly,

this method does not have either good precision or good accuracy.

As an analytical method it does not compete successfully with either

good precision or good accuracy. As an analytical method it does not

compete successfully with either acid-base titration or gravimetric

methods.

To determine CO_2 in the atmosphere, 25 milliliters of 10^{-4} molar

$Pb(QAN)_2$ in 50% ethanol is combined with 0.3 ml of 10^{-2}M bicarbonate

in 50% ethanol. The solution is allowed to equilibrate for 10 to 15

One milliliter aliquots of $NaHCO_3$ solutions of varying concentrations were individually pipeted into a series of 10-ml volumetric flasks. The flasks were then filled to the mark with 1×10^{-4}M $Pb(QAN)_2$ in 50% aqueous ethanol. After 30 minutes for equilibration, the absorbance of each solution was measured at 640 nm and 487 nm.
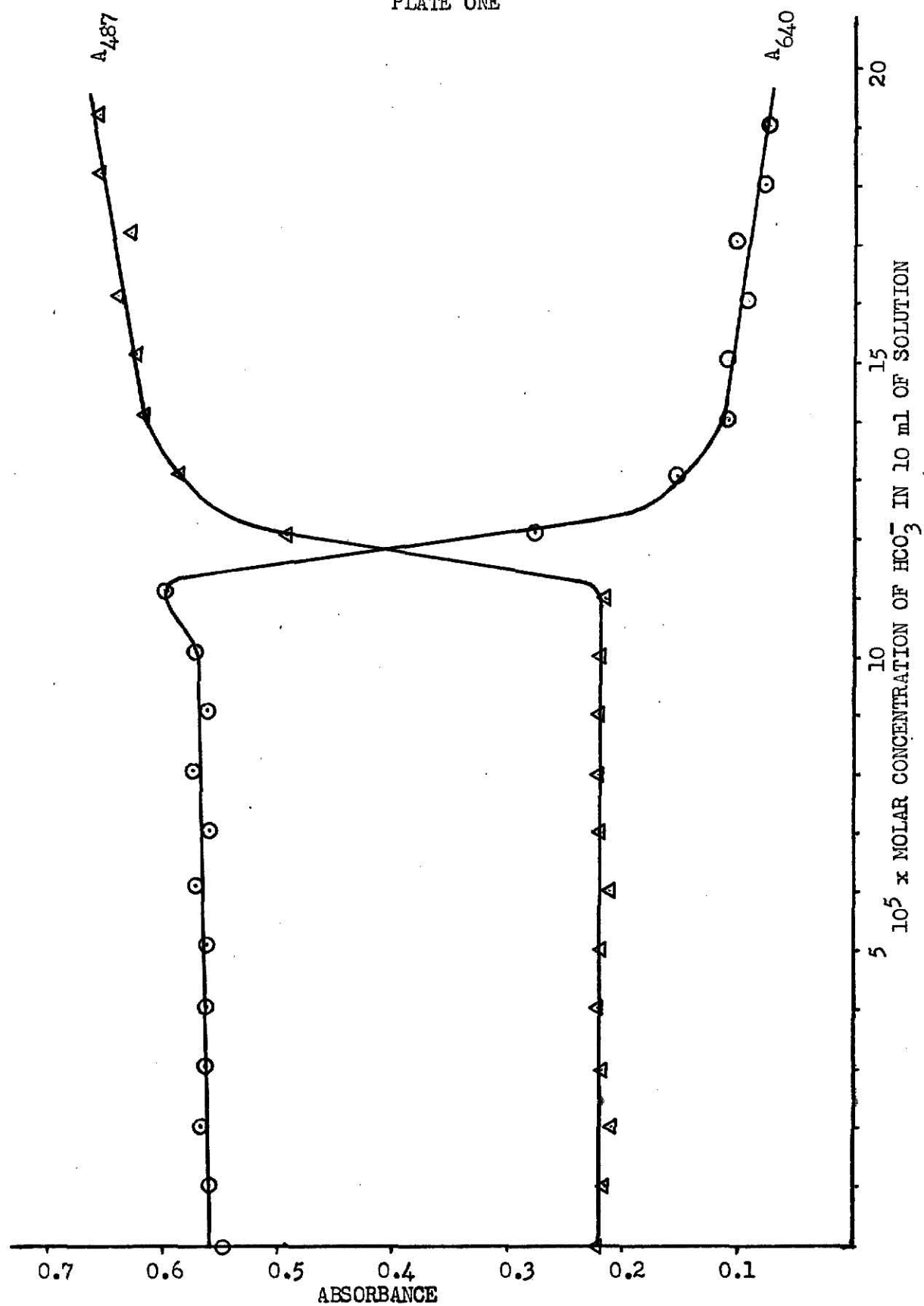
Plate One is a graphical representation of the results of this experiment. It was expected that the absorbance at 640 nm (blue) would decrease linearly and the absorbance at 487 nm (red) would increase linearly with increasing $NaHCO_3$ concentration until equivalence point is reached, at which point both lines should achieve nearly zero slope. The exact slopes of the two lines prior to the equivalence point would depend upon the molar absorbtivities of the colored species present.

The overall reaction is believed to be: $NaHCO_3 + Pb(QAN)_2 \rightarrow [PbHCO_3]^+ + 2QAN^- + Na^+$. The results of the experiment indicate the reaction has a high activation energy requiring a large concentration of $NaHCO_3$ to effect a measurable reaction. Once reaction is started, it proceeds nearly to completion without further addition of $NaHCO_3$.

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE.

THIS IS AS RECEIVED FROM CUSTOMER.

PLATE ONE

Explanation and data for Plate Two

The plate is a graphical representation of the results of 45 titrations with a least-squares fit. Nine different volumes of 1.00 x 10^{-4} M Pb(QAN)$_2$ in 50% aqueous ethanol were used. Five samples at each volume were titrated with 1.0 x 10^{-3} M NaHCO$_3$ in 50% aqueous ethanol.

ml Pb(QAN)$_2$	5.00	10.00	15.00	20.00	25.00	30.00	35.00	40.00	45.00
ml HCO$_3^-$	0.892	1.920	2.234	3.920	5.912	4.350	5.840	6.632	7.954
	0.844	1.786	2.648	3.064	4.080	4.886	5.664	6.860	7.034
	0.756	1.590	2.540	3.178	4.176	4.928	5.760	6.754	7.286
	0.810	1.484	2.480	3.244	4.220	4.966	5.904	6.532	7.496
	0.854	1.540	2.518	3.362	4.316	5.310	5.808	6.198	7.580

Least squares data: slope = 6.085, intercept = -0.524.
Standard deviation of perpendicular distances from least squares line = 5.73.
Results were calculated by a personal program on a Hewlett-Packard model 65 calculator.

PLATE TWO
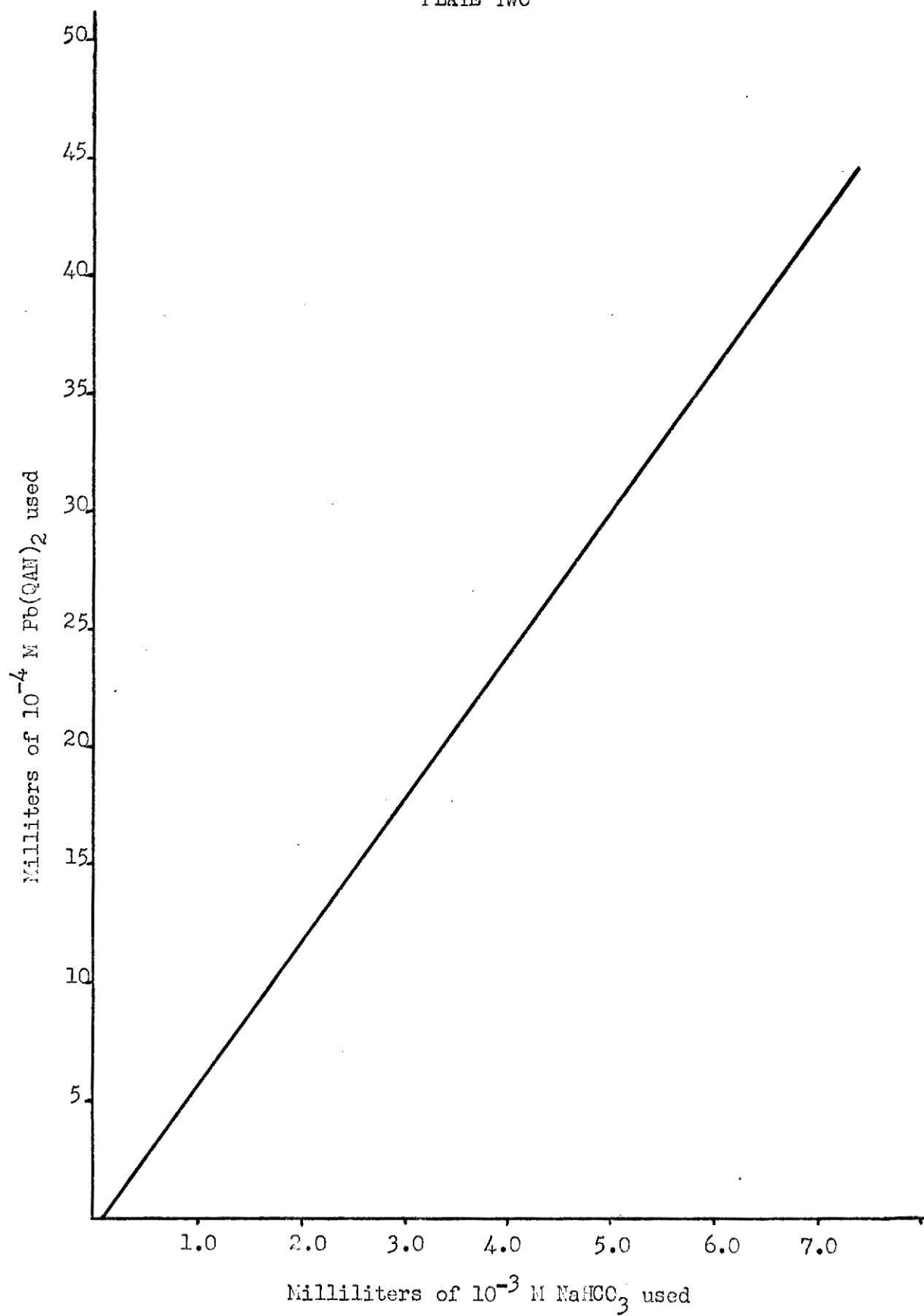
minutes. The absorbance of the solution is measured at 640 nm with a Spectronic 20 spectrophotometer. A known volume of air is then bubbled through the solution at a rate of 20 to 30 milliliters per minute through a fritted glass disc. The absorbance of the solution is again measured at 640 nm. The decrease in absorbance is a measure of the CO_2-content of the air (see plate three). This method is both accurate and precise for an air sample of one liter having a CO_2-content in the range of 100 ppm to 9,000 ppm, which spans the most commonly encountered concentrations. However, if higher concentrations are encountered, the useful range of this method may be extended by either increasing the volume of the liquid reagent used or decreasing the volume of sampled air. The former is recommended as the latter introduces greater uncertainty. The reason for the non-linearity at higher concentrations is that the concentration in solution exceeds the range for which the reagent response is linear. The good agreement between experiments with different concentrations and volumes is good evidence for the complete absorption of the CO_2 from the air stream.

There are few interferences with this method. These include fluoride ion, cyanide ion, and hydroxide ion. However, these are rarely encountered in atmospheric samples. Sulfate in water doesn't interfere.

For these reasons, this method is believed to be an improvement over any previous method. It is simpler, more accurate, and requires no sophisticated equipment.

Much more work is required to determine the exact mechanism of the displacement reaction, to determine the role of solvent participation in the complex formation, and to determine whether the reacting species is H_2CO_3, HCO_3^-, $CO_3^=$ or CO_2.

Explanation and data for Plate Three

The plate is a graphical representation of the results from 25 determinations of CO_2 in a flowing air stream.

Volume of Sample ml	time in seconds	flow rate ml/min	flow rate CO_2 ml/min	ppm CO_2	A_{640} before	A_{640} after	$-\Delta A_{640}$	Volume x ppm x 10^{-6} ml CO_2
1000	2051.2	29.251	.00388	132.6	0.364	0.353	0.011	0.1326
1000	2084.4	28.785	.00388	134.8	0.329	0.318	0.011	0.1348
2000	5139.5	23.349	.00388	166.2	0.320	0.305	0.015	0.3324
3000	6772.1	26.580	.00388	146.0	0.342	0.325	0.017	0.4380
1000	2258.6	26.565	.0097	365.1	0.351	0.337	0.014	0.3651
1100	2258.5	29.223	.0097	331.9	0.372	0.357	0.015	0.3651
1040	2383.3	26.182	.0194	741.0	0.336	0.313	0.023	0.7706
2850	6377.5	26.813	.0194	723.5	0.347	0.299	0.048	2.062
3000	7183.7	25.057	.0194	774.2	0.372	0.320	0.052	2.323
1080	2663.4	24.330	.0388	1595	0.362	0.320	0.042	1.723
1100	2707.6	24.376	.0388	1592	0.340	0.297	0.043	1.755
2500	6210.3	24.153	.0388	1606	0.331	0.244	0.087	4.014
3000	6843.6	26.302	.0388	1475	0.357	0.262	0.095	4.425
1000	2173.7	27.603	.097	3514	0.343	0.266	0.077	3.514
1000	2205.9	27.200	.097	3566	0.324	0.246	0.078	3.566
1500	3752.8	23.982	.097	4045	0.340	0.213	0.127	6.068
2000	5217.4	23.000	.097	4217	0.361	0.187	0.174	8.434
2800	6185.6	27.160	.097	3571	0.341	0.142	0.199	9.999
3000	6493.2	27.731	.097	3499	0.328	0.122	0.206	10.50
1000	2703.8	22.191	.194	8742	0.343	0.163	0.180	8.742
1070	2642.7	24.293	.194	7986	0.317	0.142	0.175	8.545
1580	3959.4	23.943	.194	8103	0.366	0.141	0.225	12.80
1800	4568.5	23.640	.194	8206	0.359	0.127	0.232	14.77
1000	2694.3	22.269	.388	17420	0.314	0.080	0.234	17.42
1050	2721.5	23.149	.388	16760	0.339	0.104	0.235	17.60

Least squares data for values less than 9 ml CO_2; slope = 0.0196, intercept = 0.00794, Standard deviation of perpendicular distances from least squares line = 6.12 x 10^{-6}.

PLATE THREE

MILLILITERS OF CO_2

$-\Delta A_{640}$
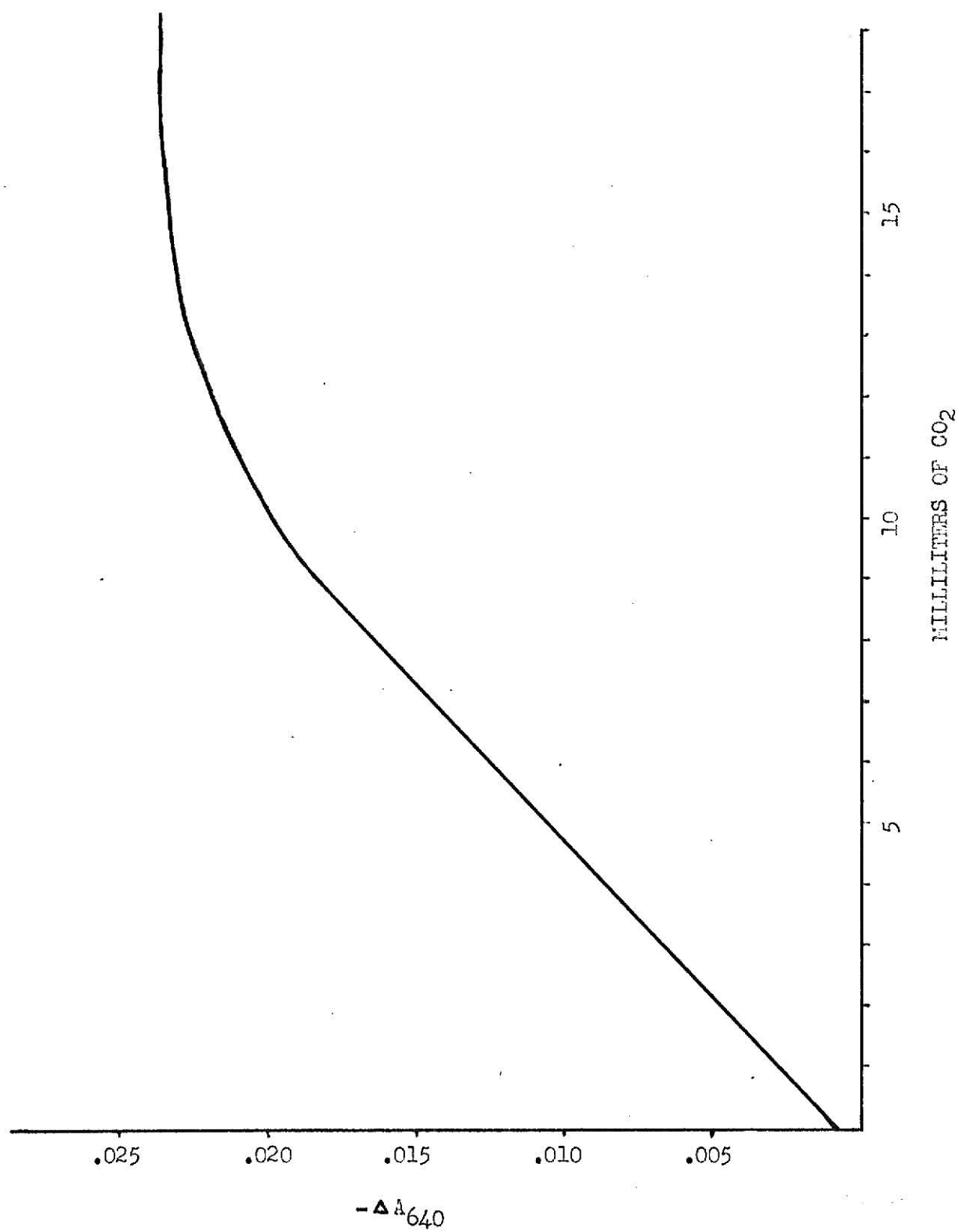
Appendix A

Figure 1 represents the superimposed absorbance curves for three solutions, each containing the same concentration of the azo dye, one containing no metal ion (1), one containing an excess of the metal ion (3), and one containing less than the stoichiometric amount of the metal ion (2). The complex, as presented, represents a bathochromic shift.

The basic equation to be solved is:

$$K_{stab} = \frac{[M(Dye)_n]}{[M][Dye]^n} \tag{1}$$

but: $c_M = [M] + [M(Dye)_n]$

or: $[M] = c_M - [M(Dye)_n]$

also: $c_{dye} = [Dye] + n[M(Dye)_n]$

or: $[Dye] = c_{dye} - n[M(Dye)_n]$

therefore:

$$K_{stab} = \frac{[M(Dye)_n]}{(c_M - [M(Dye)_n])(c_{dye} - n[M(Dye)_n])^n} \tag{2}$$

for a wavelength shorter than that of the isobestic point, such as λ_1, from the law of additive absorbances;

$$A_2 = \varepsilon_{M(Dye)_n} b[M(Dye)_n] + \varepsilon_{dye} b[Dye]$$

but: $\varepsilon_{M(Dye)_n} = n A_3/b\, c_{dye}$

and $\varepsilon_{dye} = A_1/b\, c_{dye}$

substitution and simplification yields:
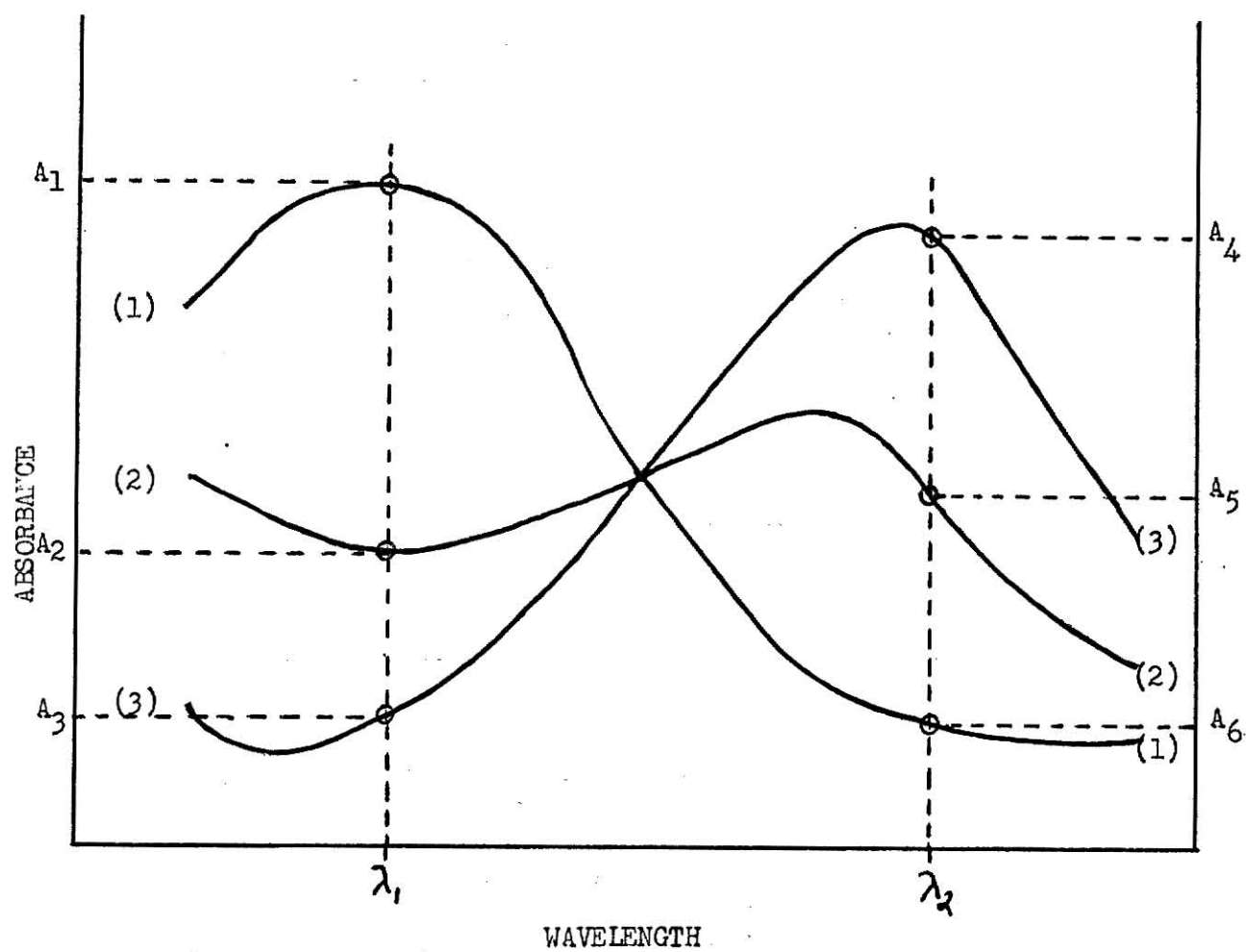
$$[M(Dye)_n] = c_{dye} (A_2 - A_1)/ n (A_3 - A_1) \tag{3}$$

Figure 1. Isobestic point plot

substitution of equation (3 into equation (2 and simplification yields:

$$K_{stab} = \frac{(A_1 - A_2)\,(A_1 - A_3)^n}{c_{dye}^{n-1}\,(A_2 - A_3)^n\,[n\,c_M\,(A_1 - A_3) - c_{dye}\,(A_1 - A_2)]} \qquad (4$$

For a wavelength longer than the isobestic point, such as λ_2, a similar treatment yields:

$$K_{stab} = \frac{(A_5 - A_6)(A_4 - A_6)^n}{c_{dye}^{n-1}\,(A_4 - A_5)^n\,[c_M\,(A_4 - A_6) - c_{dye}\,(A_5 - A_6)]} \qquad (5$$
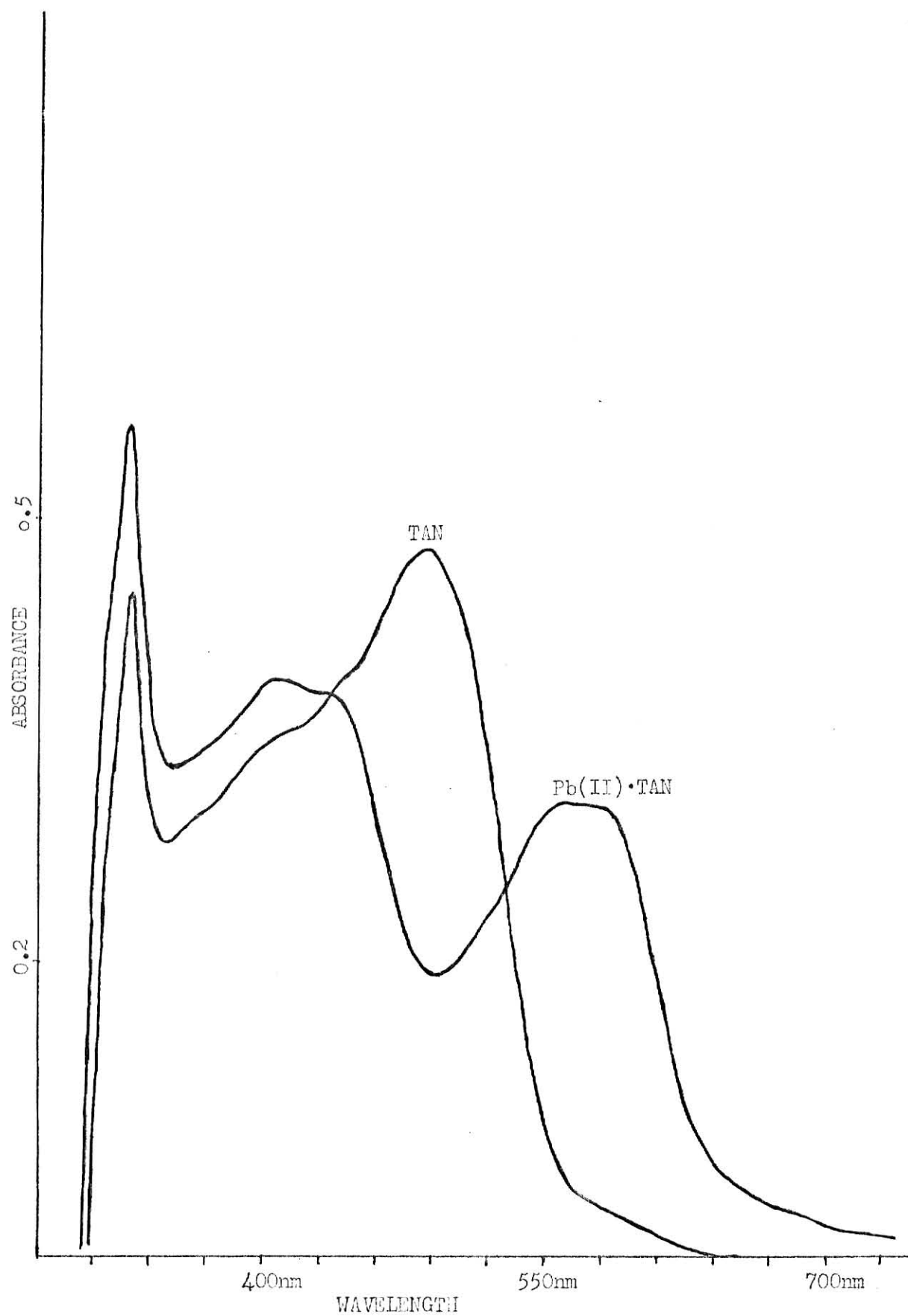
Equations 4 and 5 were used on a series of six solutions for each complex. The arithmetic mean of these results was reported as the stability constant for that complex.
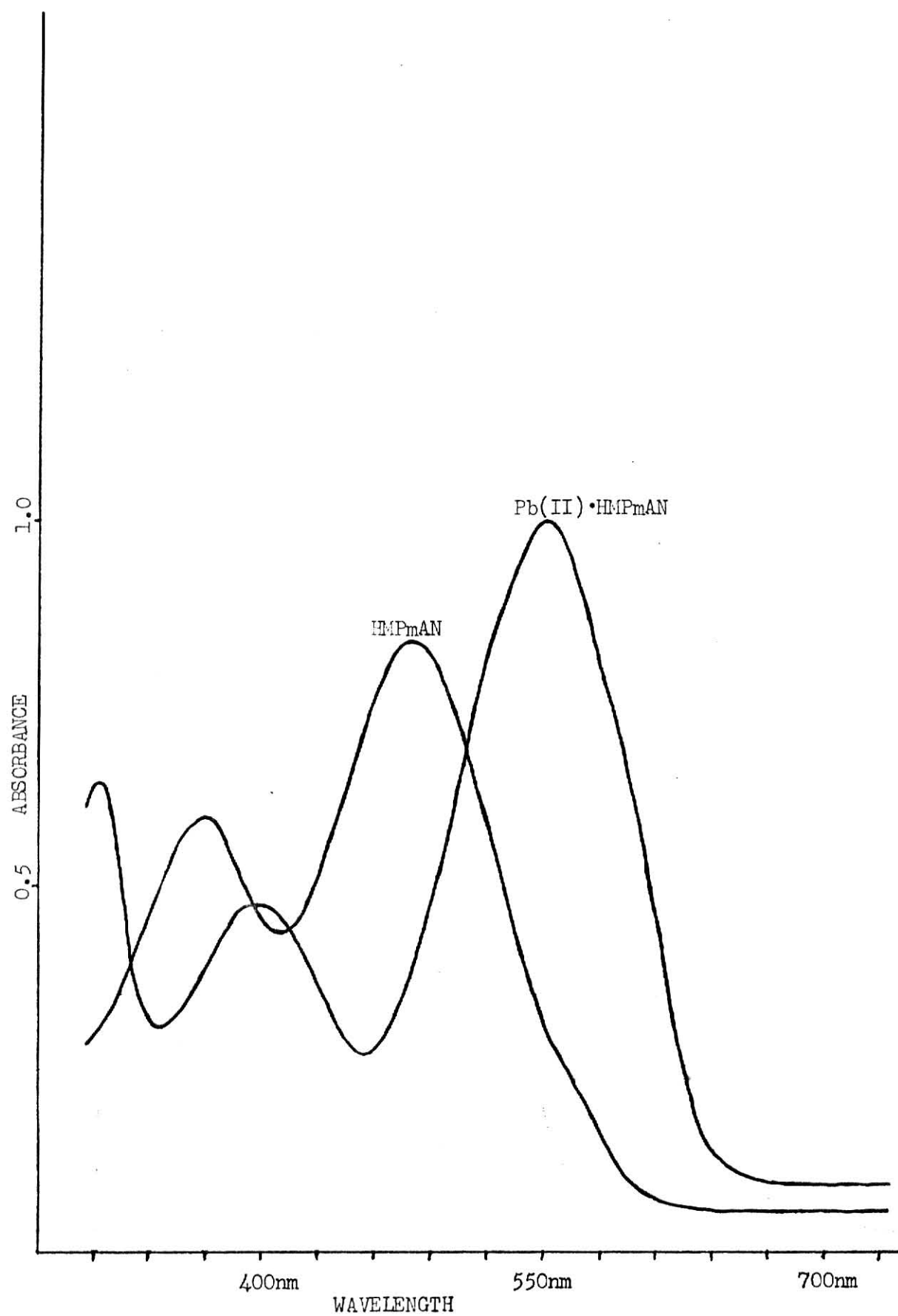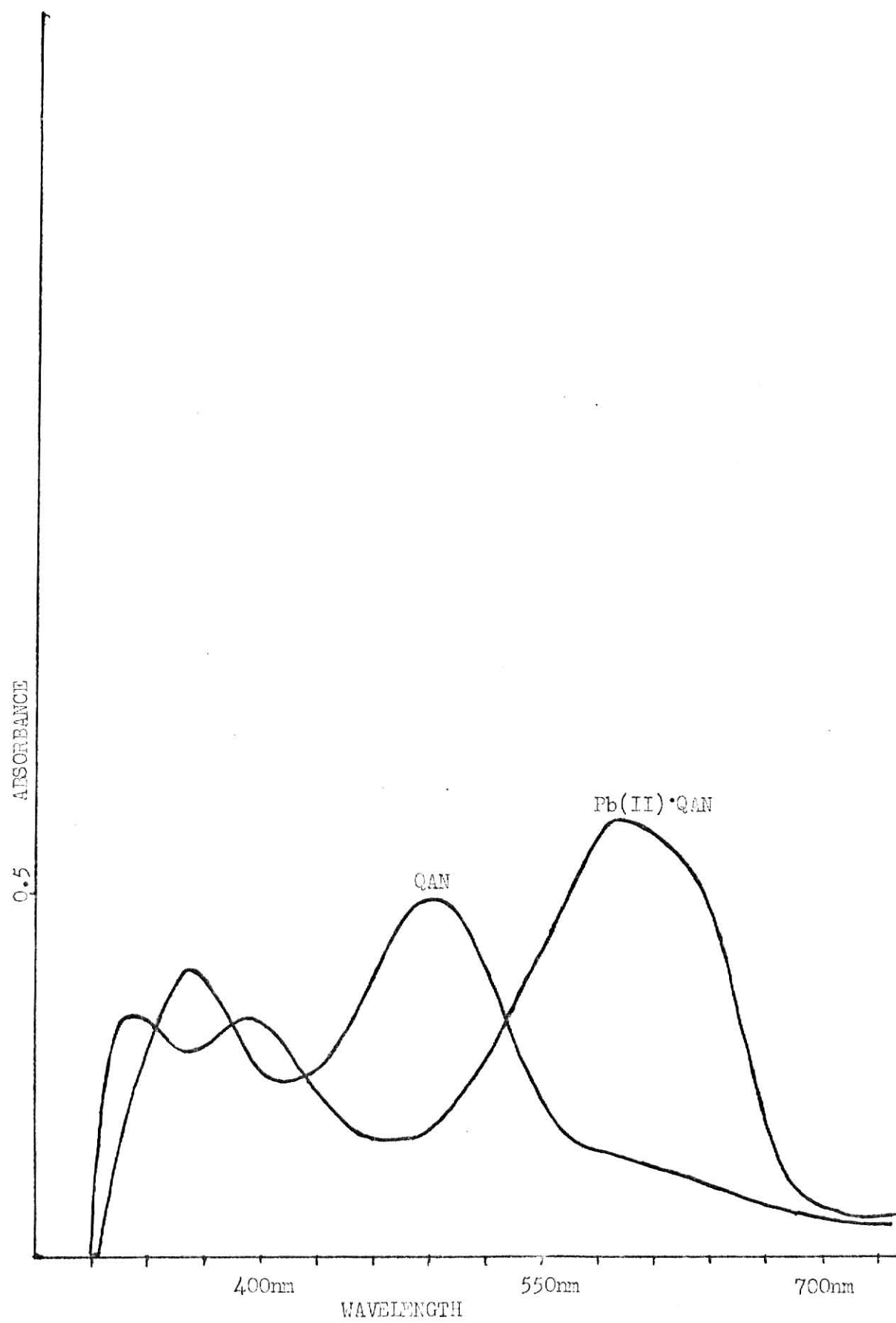
APPENDIX B

The following is a series of absorbance curves for the dyes
and complexes studied. Each is a representation of the absorbing
species in 50% aqueous ethanol at a pH in the range of 6.5 to 7.5.
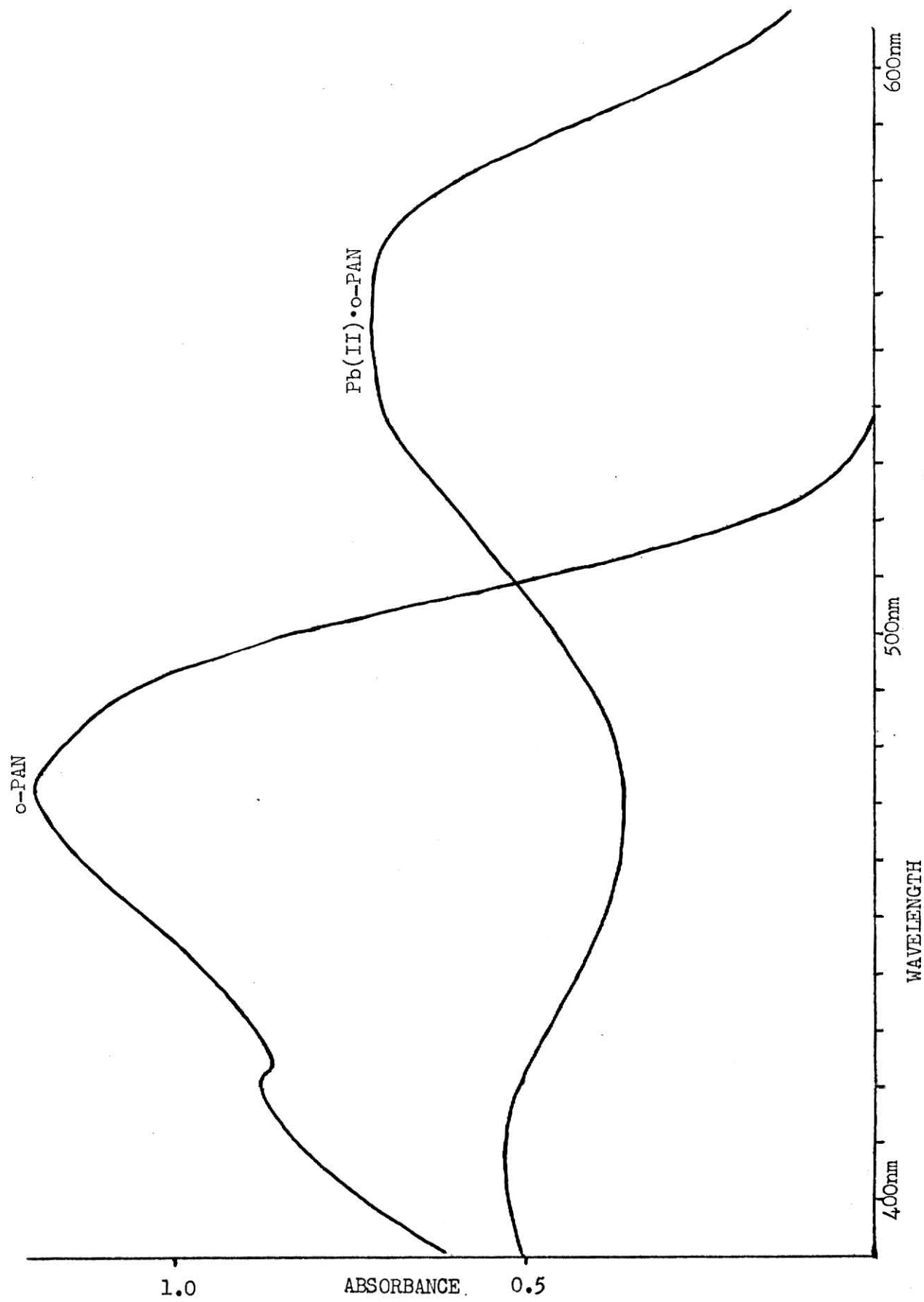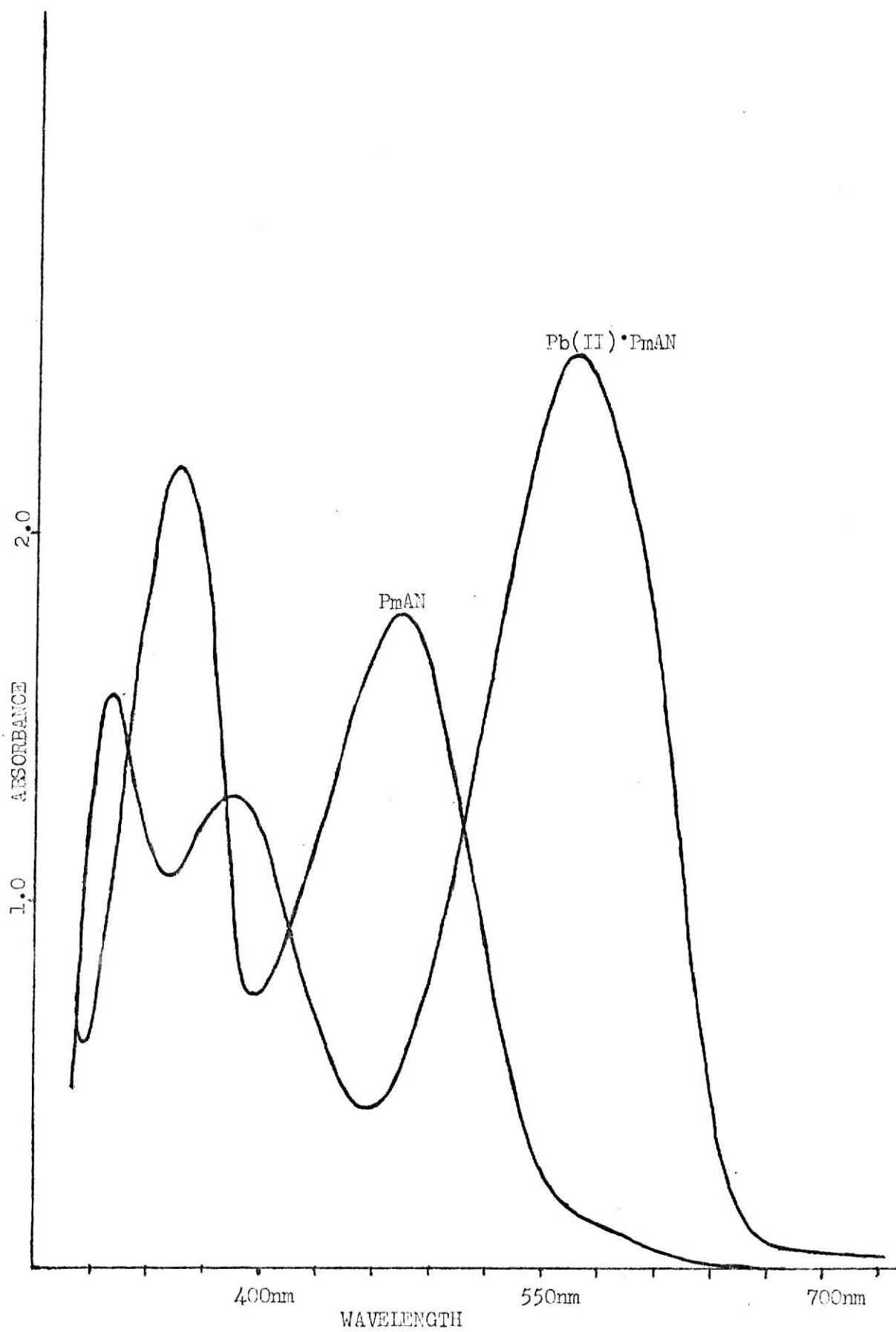
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VITA

Martin David Feist was born November 22, 1945 in Great Bend, Kansas, and lived in rural Claflin, Kansas. He graduated from Maur Hill High School, Atchison, Kansas, in 1963. He is the tenth of eleven children born to Anthony and Eva Feist. He attended Immaculate Conception Seminary, Conception, Missouri for five semesters, and was awarded the B.A. degree in chemistry by the University of Kansas in 1972. He married Patricia Rose Debes on May 22, 1971, to whom was born Martin Joseph Feist on March 16, 1973. He received an Honorable Discharge from the United States Air Force in January, 1971 after four years of service. He entered Kansas State University as a full time graduate student in January, 1973.

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AN ABSTRACT OF A THESIS

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requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1975

Sensitive, new, selective, colorimetric reagents for the quantitative determination of carbon dioxide in the atmosphere are described. Based on o-PAN (1-(2'-pyridylazo)-2-naphthol) as a model, these include the lead complexes in 50% aqueous ethanol of: o-PAN, HMPmAN (2-(4'-hydroxy-6'-methyl-2'-pyrimidylazo)-1-naphthol), PmAN (2-(2'-pyrimidylazo)-1-naphthol), TAN (1-2'-thiazolylazo)-2-naphthol), and QAN (2-(2'-quinolylazo)-1-naphthol). These ligands can be displaced from the lead complex by carbonate or bicarbonate under neutral pH conditions.

Of these ligands, QAN has the largest stability constant and the largest bathochromic shift. For these and other reasons, QAN is the ligand of choice.

A method using $Pb(II)(QAN)_2$ for the determination of atmospheric carbon dioxide is presented and shown to be simple, selective, and accurate.

A method using the same reagent as a titrimetric indicator for aqueous bicarbonate ion is presented. However, this method has little analytical utility.