

A SELF-RELIANT APPROACH
TO CHEMICAL INSTRUMENTATION

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A SELF-RELIANT APPROACH TO
CHEMICAL INSTRUMENTATION

A Thesis
Submitted to the
Faculty of the College of Science
Florida Atlantic University

in Partial Fulfillment
of the Requirements for the Degree of
Master of Science in Teaching

by
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December, 1974

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This thesis was prepared under the direction of the candidate's thesis advisor, Dr. Franklin A. Schultz, Department of Chemistry, and has been approved by the members of his supervisory committee. It was submitted to the faculty of the College of Science and was accepted in partial fulfillment of the requirements for the degree of Master of Science in Teaching.

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ACKNOWLEDGMENT

Grateful acknowledgment is hereby expressed to those who have helped to make this study possible. Indebtedness is recognized to Dr. Franklin A. Schultz, my advisor, for his sincere interest and helpful guidance, and to Dr. Samuel F. Clark, Chairman of the Chemistry Department.

The writer expresses appreciation and acknowledgment to Mr. William Ott for critical technical advice and assistance at various stages of this study.

To my family, I express grateful thanks for inspiration and encouragement to go forward.

n'D. n'G.

ABSTRACT

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Title: A Self-Reliant Approach to Chemical
Instrumentation
Institution: Florida Atlantic University
Degree: Master of Science in Teaching
Year: 1974

This thesis was planned to aid teachers in introducing chemical instrumentation in upper secondary or undergraduate chemistry courses. The problems encountered and solved in the construction of a single beam visible range spectrophotometer, conductance bridge, and polarimeter are described. Experiments were carried out with each instrument to demonstrate their efficiency as compared to commercial models. Pertinent theory on the operation of the instruments is included that can be easily understood by students on this educational level. Construction of the instruments is simple and inexpensive, which allows schools with limited budgets to introduce topics on instrumentation into the chemistry curriculum.

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I. INTRODUCTION

Chemists must be equipped with the knowledge sufficient to design and use instruments for problems of various types. The present occupation of the author is that of teaching chemistry on the continent of Africa, where instrumentation is seldom afforded the teacher on the job. This situation has served as a major source of inspiration for this work. There is great need for young scientists the world over to be able to interpret and use instrumental measurements in order to keep pace with the development of chemical science.

The purpose of this thesis is to provide a workable guide to the construction of several instruments that are of interest to chemists. Teachers are often required to provide ideas for science demonstrations and to aid industrious pupils. This body of work can guide the teacher as well as students in the construction of three basic instruments: a single beam visible range spectrophotometer, an audio conductance bridge, and a polarimeter. These instruments are designed to serve as an instructional aid to the teaching of chemistry on the upper secondary and undergraduate levels.

In the teaching of chemistry, these instruments will be an asset to the instructor in demonstrating the principles of the Beer-Lambert law, Ohm's law, and the phenomenon of optical activity. On this basis, a series of experiments was selected that clearly demonstrates the success of the instruments. The experiments also provide interesting

material for helping the teacher explain the basic concepts underlying these theories and laws. The experiments are interesting, yet simple enough to be executed by the student concerned on this educational level.

The approach taken in this thesis is one of self reliance, meaning that construction of instruments is possible in circumstances where material and funds are limited. This situation frequently prevails in secondary schools and small colleges. The three instruments described in this work will enable an instructor to introduce the topic of instrumental analysis into the chemistry curriculum without undue expense. The following sections present a brief discussion of relevant theory, details of design and construction, and an evaluation of the performance of the instruments.

II. THEORY

A. Beer-Lambert Law

Absorption spectroscopy is based on the interaction of electromagnetic radiation (light) with molecules. When a sample is irradiated with monochromatic light of the proper wavelength, absorption of light occurs and the change in light intensity is measured by a photodetection system. The visible range is generally regarded as light of wavelengths between 380 and 780nm. Electronic excitation of the sample molecules occurs within this region of the spectrum.

The absorption of light by ions and molecules supports many qualitative analytical procedures, such as formula and structure determinations, chemical reaction kinetics, and stability of ions in solution. The Beer-Lambert law is the basis of quantitative analysis associated with all types of light absorption spectroscopy. The law states that "successive increments in the number of identical absorbing molecules in the path of a beam of monochromatic radiation absorb equal fractions of the radiant energy traversing them" (1). Mathematically, this may be stated as:

$$dI = -kI db \quad (1)$$

where I is the intensity of transmitted light after absorption by the sample, I₀ is the intensity of incident radiation, and db is the incremental pathlength through the sample material (usually expressed in

cm). The negative sign in equation 1 results from the fact that \underline{I} decreases as the pathlength, \underline{b} , increases. Rearrangement of equation 1 gives:

$$dI/I = -kb \quad (2)$$

Integration between the limits $\underline{I_0}$ and \underline{I} :

$$\int_{I_0}^I dI/I = -k \int_0^b db \quad (3)$$

and conversion to Briggsian logarithms (base $_{10}$) gives:

$$\log_{10} I/I_0 = -kb/2.303 \quad (4)$$

If the cross sectional area of the beam is one cm^2 , then the number of moles of sample absorbing radiation is \underline{bc} , where \underline{c} is the concentration in moles per liter. Thus the Beer-Lambert law becomes:

$$-\log_{10} I/I_0 = \epsilon bc = A \quad (5)$$

In equation 5, $\underline{k}/2.303$ is replaced by $\underline{\epsilon}$, which is a constant of proportionality characteristic of the solute. If concentration is expressed in moles per liter and path length in centimeters, $\underline{\epsilon}$ is the molar extinction or molar absorptivity coefficient. \underline{A} is the absorbance and is sometimes incorrectly referred to as O. D. (optical density).

Many spectrophotometers read only percent transmittance, $\underline{\%T}$,

because this quantity is linearly related to light intensity. Transmittance is defined as the intensity of radiation after absorption by the sample divided by the intensity of the incident radiation:

$$T = I/I_0 \quad (6)$$

and

$$\%T = I(100)/I_0 \quad (7)$$

Absorbance and transmittance are inversely related. As absorbance increases, transmittance decreases, therefore:

$$A = -\log T \quad (8)$$

or

$$A = 2 - \log \%T \quad (9)$$

Both A and $\log \%T$ are directly proportional to concentration.

If a sample obeys the Beer-Lambert law, a straight line is observed when absorbance is plotted against concentration; the slope of the line is ϵ . If a sample is sufficiently dilute, equation 5 is usually obeyed. However, as concentration increases one may observe a deviation towards either the ordinate or abscissa. Non-monochromatic light is the most frequent reason for deviation from the Beer-Lambert law and always causes the absorbance versus concentration curve to bend toward the concentration axis (2). Other factors responsible for

deviation from the Beer-Lambert law are temperature changes, fluorescence effects, reflection, light scattering, convergence, and non-homogeneity of the incident radiation. Shifts in chemical equilibrium also may give rise to chemical deviations. For example, the dichromate ion ($\text{Cr}_2\text{O}_7^{=}$) dissociates in water, and one observes a negative deviation from the Beer-Lambert law due to the equilibrium established between this ion and hydrogen chromate ion (HCrO_4^-). One may also observe deviation due to non-parallel incident radiation, especially from cylindrical absorption cells. Square cuvettes are much more reliable for spectrometric measurements.

B. Ohm's Law

In 1828, Ohm enunciated his well-known law of electrical conductance, which states that the magnitude of the electric current flowing in a conductor is directly proportional to the difference in potential between the ends of the conductor, and inversely proportional to the resistance of the circuit (3). Mathematically, this law is states as:

$$i = E/R \quad (10)$$

where i represents current in amperes, E the difference in potential (also called electromotive force) in volts, and R the resistance in ohms. In this paper, discussion is restricted to Ohm's law as applied to electrolytic conductance of solutions, omitting its application to metallic conductors. The current passing through a sample solution under

given conditions is inversely proportional to the resistance of the solution. The quantity known as conductance, which is expressed in ohm⁻¹ or mhos, is defined as:

$$\text{Conductance} = 1/\text{Resistance} \quad (11)$$

Ohm's law is obeyed in electrolytic solutions as well as in metallic conductors.

The apparatus generally used for measurement of specific conductance is the Wheatstone bridge. The bridge consists of an alternating current source, a detector, and various precision resistors---- both variable and non-variable. Alternating current is needed to prevent decomposition of the solvent at the electrodes and the production of gas bubbles, which is typical in the electrolysis of solutions by direct current. Platinization of the electrodes also is helpful in reducing the polarization effect.

The detector may be a "magic-eye" tube, earphone, oscilloscope, or galvanometer. Any of these devices can detect a null or balance point when there is no current flow through the bridge. At the null point, the potential drop, \underline{E} , across the different parts of the bridge is such that:

$$E_c = E_R \quad (12)$$

and

$$E_{ad} = E_{bd} \quad (13)$$

subscript c refers to the resistance of the unknown conductivity cell which is in contact with the solution under investigation. Subscript R refers to the variable resistance (called the multiplier), and subscript ad and bd establish the resistance ratio (variable resistance coil). The location of d along the slide-wire enables the operator to determine the null point. Since $\underline{E} = \underline{iR}$, it can be shown that the resistance ratio of the bridge at null is:

$$C/R = ad/db \quad (14)$$

By properly positioning d along slide wire ab, the null point is located and the resistance of the unknown solution is obtained.

Determination of a factor called the cell constant, k, is helpful in the measurement of solution conductance. The cell constant is determined experimentally for a given cell with a standard solution of known conductance. A 0.02M KCl solution, which has specific conductances of $L_{18^\circ} = 0.002394$ and $L_{25^\circ} = 0.002768 \text{ ohm}^{-1} \text{ cm}^{-1}$ (4), may be used as a standard.

Specific conductance, L, is the reciprocal of specific resistance:

$$L = 1/\rho \quad (15)$$

The specific resistance, ρ , of an electrolyte is the resistance of a solution in a cell having electrodes exactly 1 cm^2 in area and 1 cm apart. The units of specific conductivity are mho cm^{-1} or $\text{ohm}^{-1} \text{ cm}^{-1}$.

The cell constant, \underline{k} , is determined from the relationship:

$$k = LR \quad (16)$$

Once the cell constant has been measured, one may obtain from the measured resistance the specific conductance of any solution in that cell.

Equivalent conductance, $\underline{\Lambda}$, is obtained by multiplying the specific conductance by the volume, \underline{V} , in milliliters. For a solution with a concentration, \underline{c} , in gram-equivalents per liter:

$$\Lambda = VL = 1000L/c \quad (17)$$

A related term is the molar conductance, Λ_M , which is defined as in equation 17, with the exception that concentration is given in moles per liter.

The speed of migration and conductance of ions is influenced by several factors. Temperature is important, because conductance increases by about 1.5 - 2% per degree C (5). Conductance depends significantly on the size and charge of the ions. Viscosity and attractive forces operate between the solute and solvent also affect the ionic conductance. In a highly concentrated solution, the solute is surrounded by many ions and its rate of movement is diminished. In dilute solutions the attractive forces decrease progressively and vanish at infinite dilution.

Conductimetry is particularly useful in measuring changes in ionic content and in determining the equivalence point of acid-base titrations. It is a method that can be utilized when solutions are naturally colored and the use of an indicator is not feasible. Since conductance depends on the number and charge of ions in solution, it is a measurement that can be used to determine the number of ions in a metal complex.

C. Optical Activity

Light is composed of electric and magnetic vectors oriented at 90° to one another. These vibrations occur at right angles to the direction of propagation, and are generated in all directions from a light source. If light is passed through an appropriate polarizing lens, such as a Nicol prism or tourmaline crystal, it emerges along a single plane of propagation. Such light is said to be polarized.

A polarimeter is used for measuring optical activity. The instrument contains two polarizing lenses. One lens polarizes the light; the second lens, called the analyzing prism, is rotated such that its crystal axis is at 90° to the light vector giving a minimum transmission of light.

Stereochemistry got its impetus from the study of the action of plane polarized light on molecular isomers. Isomers are compounds with the same molecular formula, but with different positional, structural, geometric, or configurational arrangement of atoms. Polarimetry is concerned with configurational isomers known as enantiomers. Enantiomers have the same molecular formula with atoms joined in the same

way. Their chemical and physical properties are identical except in their ability to rotate the plane of polarized light. This is the phenomena of optical activity. Substances showing optical activity have a right-handed or left-handed nature in their structure, which leads to a difference between the right-handed and left-handed polarizability or index of refraction (6). Enantiomers are therefore mirror images of one another and rotate the plane of polarized light in opposite directions by equal magnitudes. The direction and magnitude of this rotation is characteristic of the substance under investigation. When the direction of polarization is to the right (+) the isomer is called dextrorotatory. When the rotation is to the left (-), the isomer is levorotatory. If a compound does not rotate the plane of polarized light, it is optically inactive.

Optical activity is measured in terms of observed rotation, α . The specific rotation, $[\alpha]$, is the degrees of rotation of the plane of polarized light at the wavelength of the sodium D line (5893 Å) when passed through a solution containing one gram per hundred ml of solute in a 1 decimeter tube. Mathematically, specific rotation is defined as:

$$[\alpha]_{\lambda}^t = 100/\ell c \quad (18)$$

where the superscript, t , represents the temperature in $^{\circ}\text{C}$, and subscript, λ , the wavelength of the light source. In equation 18, ℓ is the path length in decimeters, and c is the concentration of solute in grams per 100 ml. It also may be desirable to calculate molar rotation, M , from the expression:

$$\underline{M} = [\alpha](\text{gfw})/100 \quad (19)$$

where gfw is the gram-formula weight of the solute.

Polarimetry is applicable to optically active substances, which may be organic or inorganic in nature. Carbohydrates have received the greatest amount of attention and study, so much so that the analytical procedure is often called saccharimetry. Carbohydrates frequently show a change in optical activity with time, usually upon denaturization. This phenomenon is known as mutarotation. Inorganic substances also may show optical activity depending on their coordination geometry.

III. CONSTRUCTION OF THE INSTRUMENTS

A. Visible Range Spectrophotometer

In construction of a spectrophotometer one must consider not only design, but the cost and source of materials. It was decided to construct a single beam instrument using a grating monochromator, a cadmium sulfide photocell, and an intense light source. This design involves simple construction and is relatively inexpensive.

A quartz halogen bulb was chosen as the light source because it offered a greater intensity than a tungsten filament. The source is powered by a 12-volt battery. The source output extends into the ultra-violet, which is a desirable property. The bulb's filament produces a narrow beam of light which can be focused through a small pin-hole to minimize white light intrusion within the monochromator. The filament life is somewhat limited, therefore it is wise to purchase several replacement parts that will not require a change in design or specifications.

The block diagram and optical path of the spectrophotometer beam are shown in Figures 1 and 2. An optical bench was used to determine the most favorable location of the components. Three lenses were chosen on a trial-and-error basis to give the highest quality spectrum obtainable from the light source and grating used. The achromatic lens (L_3 , Figure 2) gives less aberration when placed after the grating. The spectrum must be as free as possible from white light intrusion and intense enough to penetrate a colored sample through a narrow slit

Figure 1

Block Diagram of Spectrophotometer

Scale: 2.16 x diagram = actual size

A = Quartz Halogen Source

B = Grating

B' = Monochromator

C = Sample Compartment

D = Detector

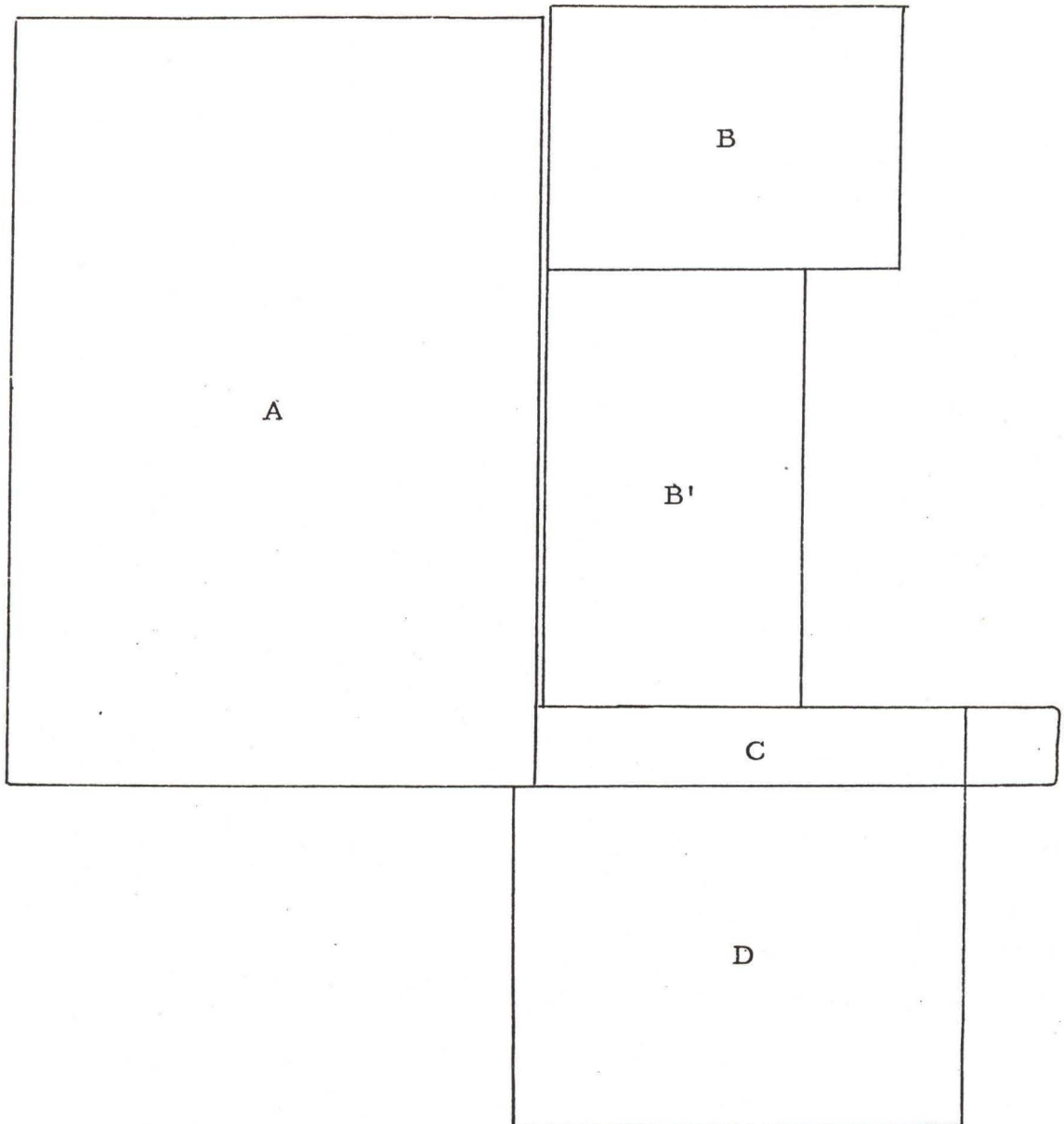


Figure 2

Optical Path of Spectrophotometer

M = Concave Mirror

B = Quartz Halogen Bulb

P₁ = Pin Hole

L₁ = Double Convex Lens

P₂ = Pin Hole

L₂ = Plano Convex Lens

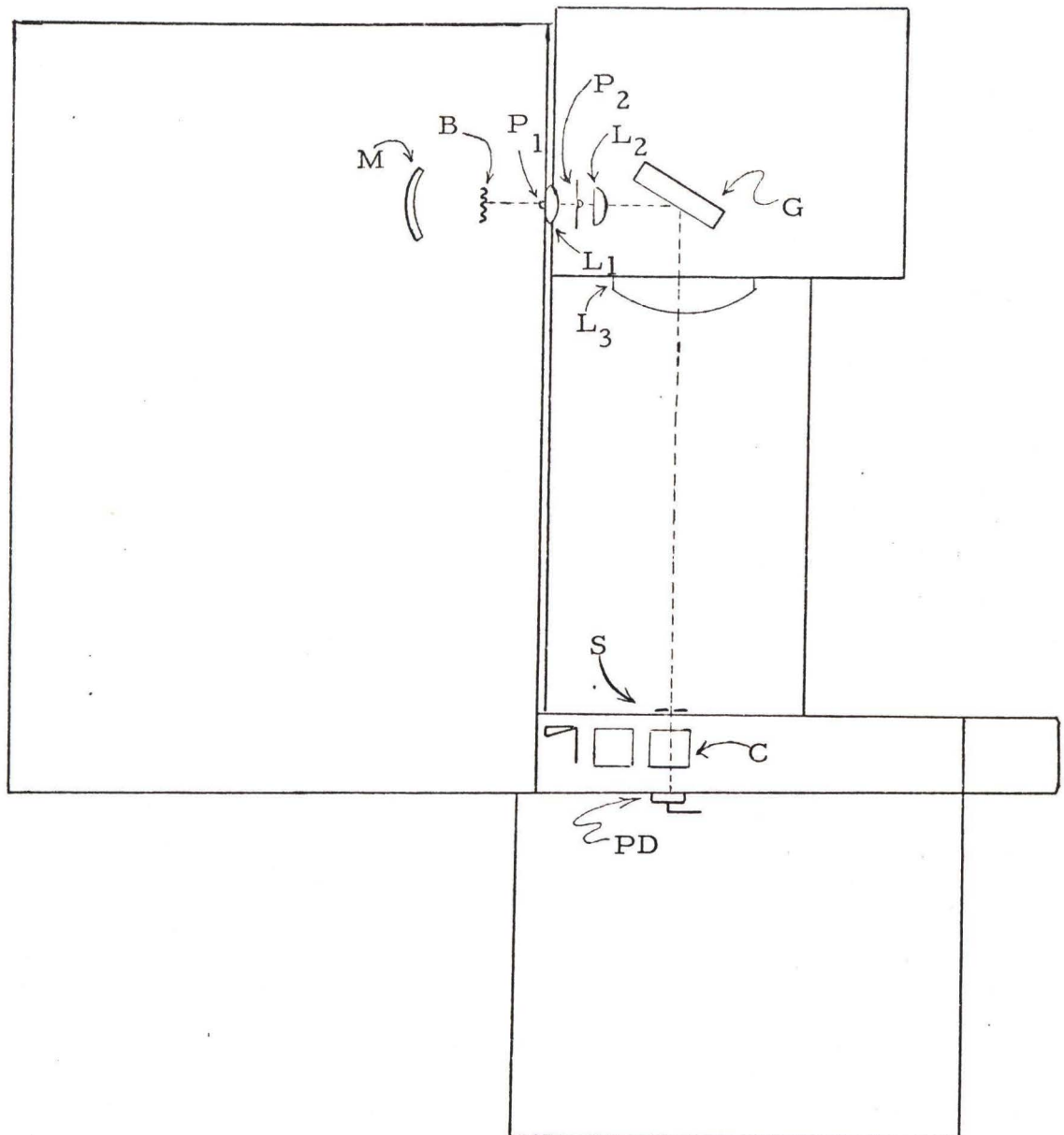
G = Diffraction Grating

L₃ = Achromatic Lens

S = Slit

C = Sample Cell

PD = Photodetector



opening. Once the exact focal lengths, the angle of the diffraction grating, and the positioning of the lenses were determined, the height of beam was adjusted to coincide with the sample cell and photodetector.

The diffraction grating was assembled on a circular stage that could be positioned at various heights and angles by the adjustment of a set screw. The stage hung from a perpendicular shaft that fitted into a double vernier linkage. This mechanical linkage allowed the 1:8 ratio of the verniers to be geared down to a 1:16 ratio. This tolerance was sensitive enough to control and focus a narrow bandwidth across the slit. One hundred positions can be read on the vernier, each position corresponding to 4 nanometers. One can accurately estimate wavelength to within 2 nanometers by reading the mid-points of these positions.

An adjustable slit with controls on the outside of the monochromator was constructed from aluminum plate. Its range of adjustment is from 0.35mm to a fully closed position. In order to allow for full scale expansion of the detector meter the minimum slit-width for this design is 0.13mm. Another important specification is the size of the entrance ports along the light path. In Figure 2 pin-hole one is 2.78mm in diameter and pin-hole two is 1.93mm in diameter. A small collar, $\frac{1}{2}$ cm long and 2.78mm in diameter, is placed between lens 1 and pin-hole 2 to help collimate the light beam.

The sample compartment was constructed from an aluminum chassis to hold rectangular cuvettes. The sample compartment was designed to contain the reference solution, sample solution, and a shutter

for the zero percent transmittance setting. A notched slide attached to the base of the compartment was used to indicate the element in the light path.

The detector consists of a cadmium sulfide photocell, a 50-microampere meter, controls to adjust both zero and maximum scale readings, and a power source. Many wiring diagrams were constructed and improved upon, within an effort to obtain maximum response from the photocell in the violet region of the spectrum. A major obstacle is that the spectral response of the photocell (Figure 3) and the intensity of the light source (Figure 4) fall off sharply as the ultraviolet region of the spectrum is approached. Consequently, the sensitivity of the instrument is low in this region. Adequate response was obtained by using a 54-volt battery to power the photocell. The schematic diagram of the detector is shown in Figure 5.

The components of the spectrophotometer were housed in aluminum boxes. These boxes are ideal, because they can be dismantled easily and reassembled without the loss of alignment. A photograph of the assembled spectrophotometer is shown in Figure 6.

After construction, the wavelength scale of the spectrophotometer must be calibrated. Three narrow band-pass filters of 4400 Å, 4900 Å, and 5500 Å, obtained from the components of a Welch Chem Anal system, were used for calibration. Three calibration points were obtained by placing the filters in the optical path and reading the vernier setting of maximum transmittance. The plot of vernier setting versus wavelength

Figure 3

Spectral Response of CdS Photocell

Figure 4

Typical Spectral Irradiance of Quartz Halogen Bulb, 100 watts, 12 V

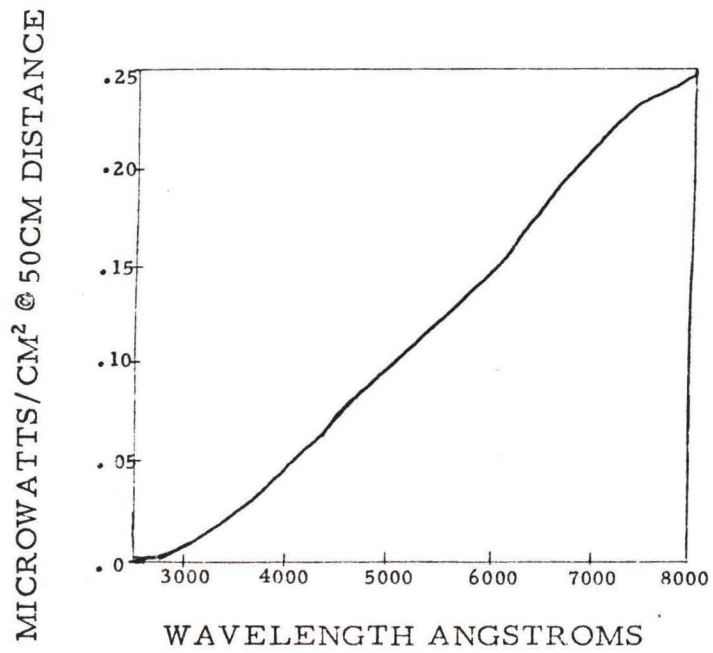
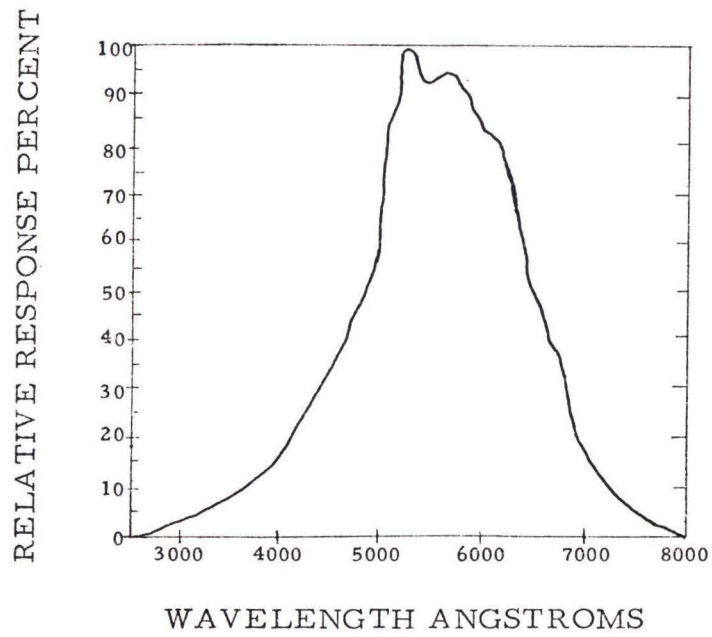


Figure 5
Schematic Diagram of
Detector and Light Source

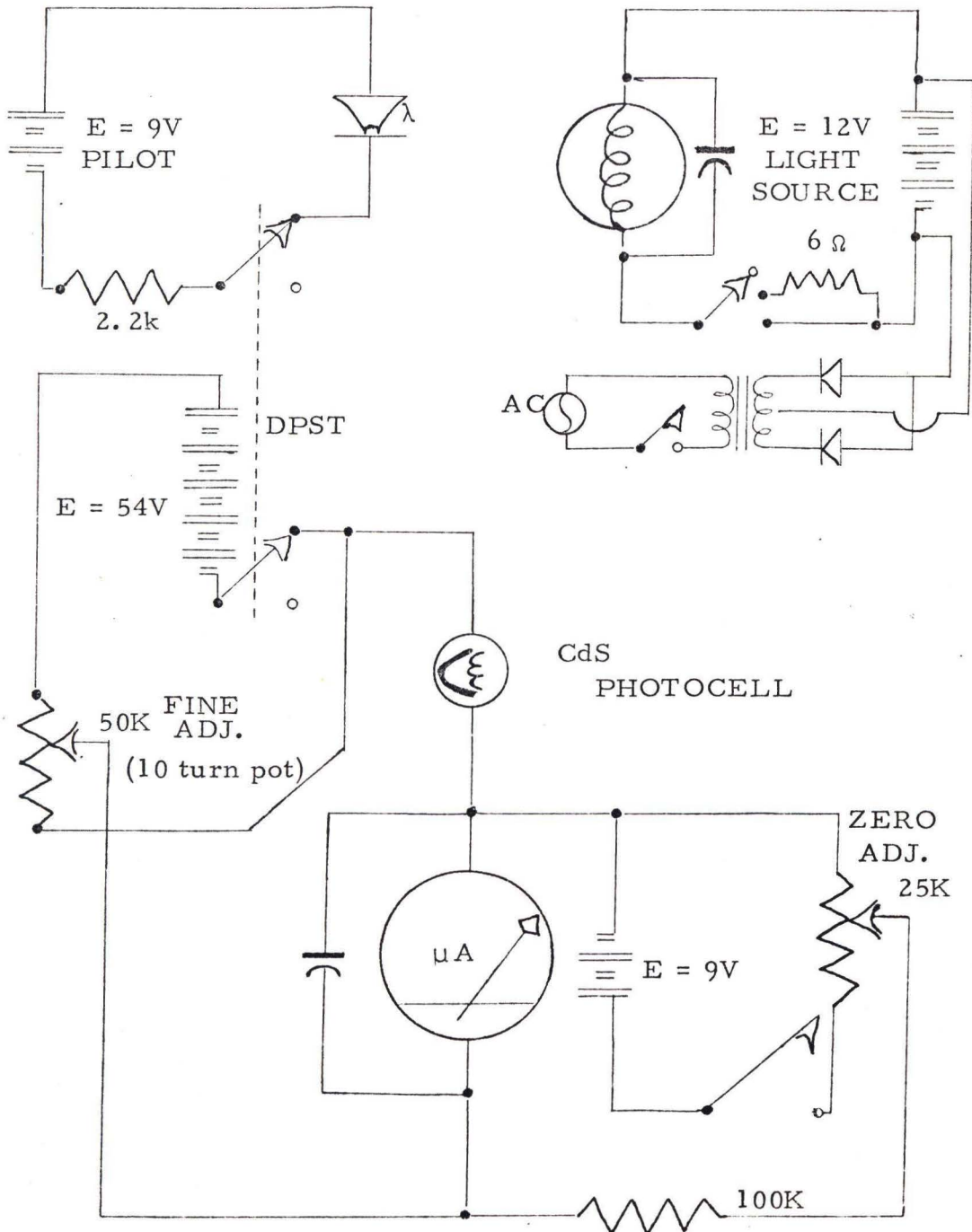


Figure 6

Visible Range Spectrophotometer

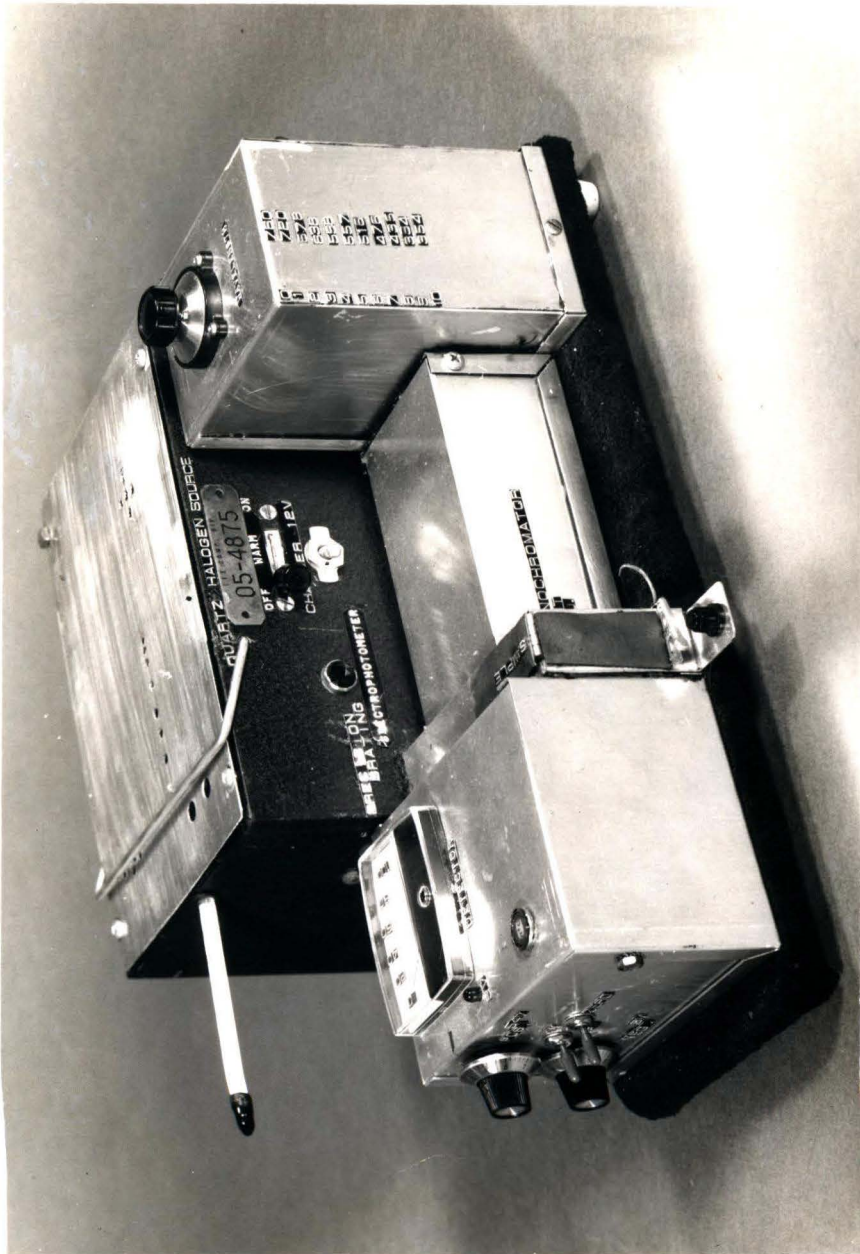


Table 1

Cost and Source of Materials for Visible Range Spectrophotometer

<u>Quantity</u>	<u>Description</u>	<u>Company</u>	<u>Stock No.</u>	<u>Size</u>	<u>Retail Price</u>
1	Diffraction Grating	Edmund Scientific	41048	$\frac{1}{2} \times 1''$	\$30.00
1	Motorcycle Battery	Yamaha Gold Coast		12V	16.95
1	0-50 Microammeter	Radio Shack	22-051		7.95
1	Quartz Halogen Bulb	Aid Auto Stores Pompano Bch, Fla.		12V, 55W	6.99
1	Battery Charger	Aid Auto Stores		2amp/hr	9.95
2	Vernier Dials	Radio Shack	274605	$1\frac{1}{2}''$	1.69 ea.
1	Double Convex Lens F. L. 20mm	Edmund Scientific	94342	18mm dia.	1.20
1	Plano Convex Lens F. L. 29mm	Edmund Scientific	94693	15mm dia.	.65
1	Achromatic Lens F. L. 133mm	Edmund Scientific	6324	43mm dia.	3.00
1	CdS Photocell	Radio Shack	276-116	$\frac{1}{2} \times \frac{1}{4}''$.79
8	Transistor Batteries	Radio Shack	23-553	9V	1.39
1	Potentiometer, 5-turn	F.A.U. Chem. Dept.		50K	6.00 est.
2	Tuning Knobs	Radio Shack	274-413		1.98
4	Switches	Radio Shack			6.22 est.
4	Aluminum Circuit Boxes	Radio Shack			7.00 est.

was linear and allowed the vernier control to be calibrated into wavelengths. According to the final calibration curve, the range of the instrument is from 354 to 760nm. This range is more than adequate to obtain spectral results in the visible range, and it even extends into the near ultraviolet. A change of photocell, rearrangement of lenses, light source replacement, or virtually any readjustment (with exception of slit-width) requires recalibration.

Table 1 gives a detailed account of the cost and source of materials for the spectrophotometer. The total cost of the self-designed instrument is approximately \$115. This price is low compared to that of commercial spectrophotometers. The Bausch and Lomb Spectronic 20 and Welch Chem Anal spectrophotometers cost approximately \$400 to \$500. The Perkin-Elmer Model 202 spectrophotometer, which scans both visible and ultraviolet regions, costs about \$6,000. The performance of the self-designed spectrophotometer is compared to that of commercial instruments in all experiments.

B. Conductance Bridge

Construction of the conductance bridge relies heavily on an understanding of basic electronics. The self-designed instrument is a direct reading electrolytic ohm meter based on a Wheatstone bridge circuit. A typical circuit for a Wheatstone bridge is shown in Figure 7. Recalling the null condition for the bridge given in equation 14, the unknown cell resistance, R_x , is:

Figure 7

Block Diagram of Wheatstone Bridge

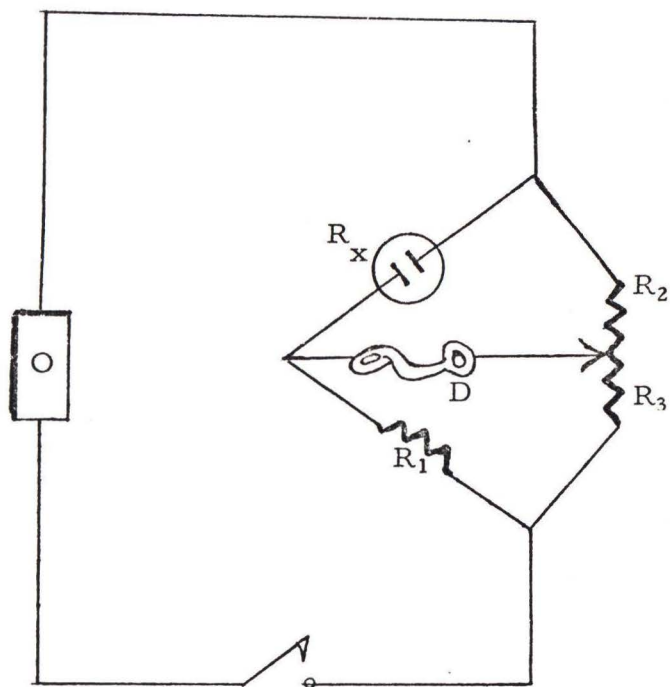
O = Audio Oscillator

R_x = Unknown Cell

R_1 = Multiplier

R_2 and R_3 = Variable Resistor

D = Detector (earphone)



$$R_x = R_1(R_2)/R_3 \quad (20)$$

by substituting equation 16 into this equation, the specific conductance becomes:

$$L = R_3(k)/R_1(R_2) \quad (21)$$

The electronic components except for the cell and earphone were assembled in a $5'' \times 2\frac{1}{4}'' \times 2\frac{1}{4}''$ aluminum box. The multiplier (resistor R_1) is controlled by a miniature switch, which inserts different resistors into the circuitry. Precision resistors of 10, 100, 1000, 10K, and 100K ohms cover the entire range of signals that can be detected with the present design. The variable resistors (R_2 , R_3 , Figure 7) consist of a 500 ohm, 10-turn potentiometer in series with a 500 ohm resistor. The specific conductance of electrolyte solutions varies between 10^{-2} and 10^{-7} ohm $^{-1}$ cm $^{-1}$ (5). For a cell constant of 1, the range of resistances covered is 10 to 10^6 ohms. This range is sufficient for measurement of most electrolyte solutions.

The complete circuit diagram of the conductance bridge is shown in Figure 8. The alternating signal required to detect the null point is supplied by a square-wave oscillator which delivers 3000 cycles per second of bridge current. The oscillator is a 16-pin, 12-transistor integrated circuit chip which converts a 9-volt direct current source to an alternating output. The oscillator is a relaxation type, complementary Metal Oxide Semiconductor (CMOS) hex inverter integrated

Figure 8

Circuit Diagram for Conductance Bridge

R_1 = Multiplier (10, 100, 1000, 10K, and 100K ohms, 1%)

R_2 = 500 ohm 10-Turn Helipot

R_3 = 500 ohm (1%)

R_x = Unknown Cell Resistance

I = Inverter

IC - Integrated Circuit (Audio Oscillator)

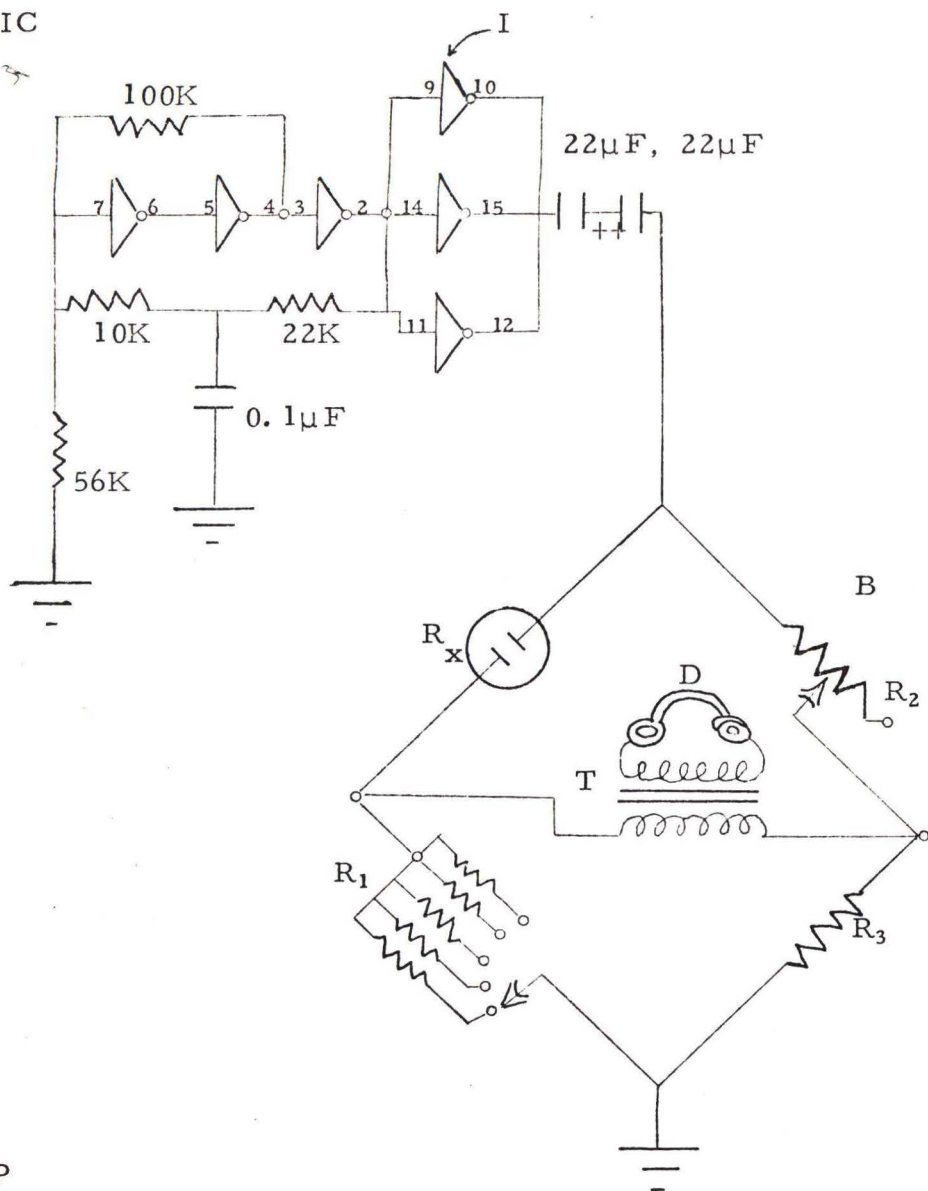
B = Bridge

D = Detector (Earphone)

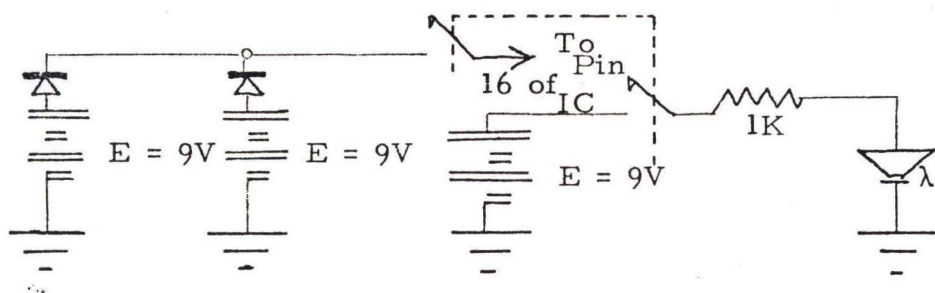
P = Power Supply and Pilot Lamp

T = Audio Transformer

IC



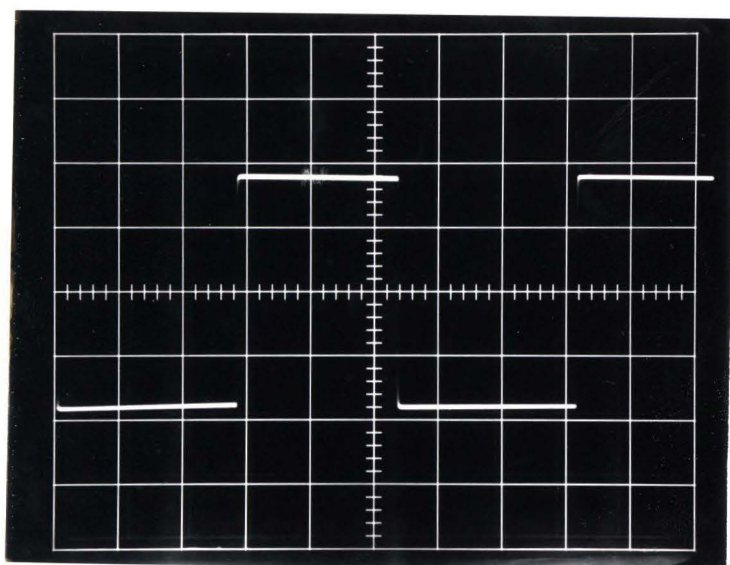
P



circuit (RCA catalog # CD 4009 A). The characteristics of the inverters are such that as the input goes positive and passes the threshold (half the supply voltage), the output goes negative to ground. Likewise, as the input goes negative passing the threshold the output goes positive. As pin 7 of the integrated circuit (IC-7) travels past the threshold, IC-6 and IC-5 go to ground. This causes IC-4 and IC-3 to assume a positive voltage, and IC-2 to go to ground. The $0.1\mu\text{F}$ capacitor discharges some time after the threshold is passed. This causes IC-6 and IC-5 to move to a positive voltage, and IC-4 and IC-3 to return to ground; IC-2 then assumes a positive voltage. Some time after this threshold is passed the $0.1\mu\text{F}$ capacitor charges, causing IC-6 and IC-5 to return to ground. This operation continues at a frequency dependent on the charge-discharge time of the $0.1\mu\text{F}$ capacitor, and the 22K ohm resistor. IC-9 and 10, IC-14 and 15, and IC-11 and 12 serve as buffers to isolate the bridge from the oscillator. The 100K and 10K ohm resistors provide hysteresis. The 56K ohm resistor serves to balance the oscillation to 50% duty cycle. The two $22\mu\text{F}$ capacitors isolate the d. c. bias of the oscillator from the bridge, thereby providing a 4.5 V, 3000Hz square-wave voltage. The square-wave output of the oscillator is shown in Figure 9. The conductance bridge is modified by an audio transformer (T, Figure 8), which serves the purpose of matching impedance to give a better power transfer. It is suggested that further reference to the construction of astable and monostable oscillators be made in texts on electronic circuitry (7).

Figure 9

Oscillogram of the Squarewave Produced by
Audio Oscillator



An earphone from a small transistor radio or tape recorder, having a sensitivity of 200 microvolts, was used for detecting the null point. This arrangement is superior to an elaborate and expensive headphone, because it offers a low resistance of 10 ohms. The output transformer greatly improved the ability to hear bridge equilibrium in the region of the 100K ohm multiplier.

Two dip-type electrode assemblies having cell constants 1 and 0.1 were used for all measurements. Each cell contained two platinum electrodes attached to wire leads. Each wire was drawn through glass tubing and heat-sealed, close to the electrode plane, to prevent solution leakage. The electrodes were inserted into a two-hole rubber stopper. A plexiglass cylinder of proper diameter was fitted over the electrodes onto the stopper to provide a shield. The electrodes work best if coated with platinum black to minimize capacity effects. In this way a sharp null point is observed. A photograph of the complete conductance bridge is shown in Figure 10.

The cost of the conductance bridge is approximately \$50 as itemized in Table 2. Commercial models, such as the Yellow Springs Instruments (YSI) Model 31 and Industrial Instruments Model RC 16B-2 bridges, cost approximately \$300. The performance of the self-designed instrument is compared to these commercial bridges in later experiments.

C. The Polarimeter

A block diagram of the polarimeter is shown in Figure 11. Pola-

Figure 10

Conductance Bridge

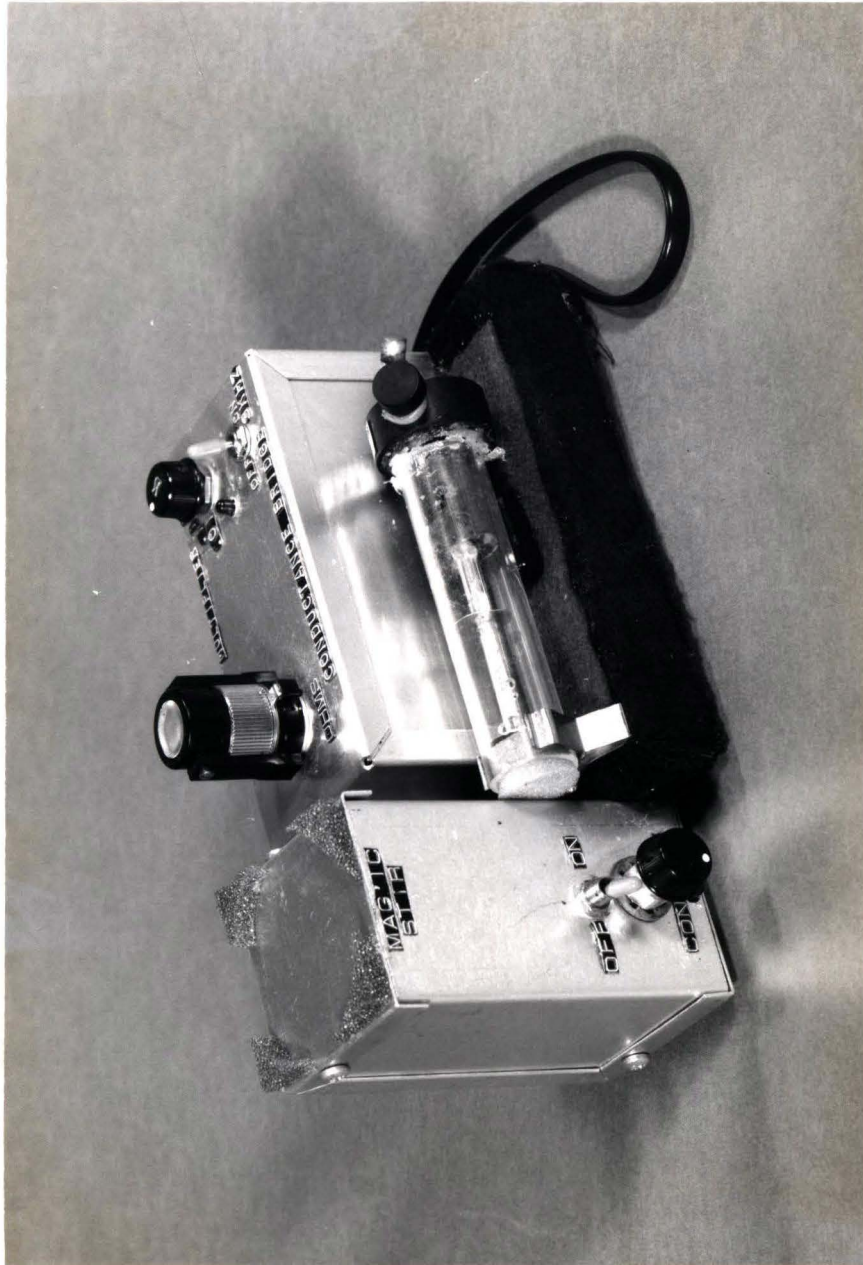


Table 2

Cost and Source of Materials for Conductance Bridge

<u>Quantity</u>	<u>Description</u>	<u>Company</u>	<u>Stock No.</u>	<u>Size</u>	<u>Retail Price</u>
1	Aluminum Chassis Box	Radio Shack		5 x $2\frac{1}{4}$ x $2\frac{1}{4}$ "	\$1.90
1	10-Turn Potentiometer	Allied Electronics		500 ohm (1%)	6.45
1	Digital Counting Dial	Allied Electronics	5301071	1 x $1\frac{7}{16}$ "	11.19
1	IC (CMOS) Chip	RCA	CD4009A	16 pin	3.60
11	Resistors (1%)	Allied Electronics			8.00 est.
3	Capacitors	Allied Electronics			3.00 est.
1	Rotary Switch	Radio Shack	275-1385	$\frac{1}{4}$ " diam.	0.99
1	Miniature Knob	Radio Shack			0.40
1	Earphone	Radio Shack	33-174	$\frac{1}{32}$ " plug	1.39
1	Audio Transformer	Radio Shack	273-1380		1.39
1	Light Emitting Diode	Radio Shack	276-026		0.89

roid plastic sheet was found to be a suitable polarizing material which was inexpensive and easily workable. This choice was superior to Nicol prisms, which retail at \$123 each. The film was cut to the desired shape with scissors. Additional lenses aided in focusing the image and recognizing the angle of minimum transmittance. The function of the vernier and dial is to measure the angle of rotation in degrees that takes place when an optically active sample is placed in the path of the light beam.

A tungsten filament bulb delivering a high and low intensity was chosen as the light source. The bulb was taken from a Roxter high intensity lamp and used as shown in Figure 12. The bulb was powered by a step down transformer taken from an electronic calculator. Light was focused on the filter by a mirror placed at a 45° angle to the path of the beam. Since a white light source was used, a narrow band-pass filter was needed to select light of 5893 \AA to enter the sample cell. This wavelength was chosen because polarimetry data are conventionally measured with the Sodium D line. The sample cell used was a typical 1-decimeter polarimeter tube, which can be readily removed from its housing through a curtain on the side of the instrument. A photograph of the assembled polarimeter is shown in Figure 13.

The total cost of the self-designed polarimeter is \$51, an improvement over commercial instruments, such as the Steeg and Reuter Type SR6 polarimeter, which costs \$750 and the classic Rudolph model, which retails for \$3,600. A list of cost and source of construction materials may be found in Table 3.

Figure 11

Block Diagram of Polarimeter

B = Tungsten Bulb

M = Front Surface Mirror

F = 5893 Å Filter

L₁ = Polarizing Lens

C = Sample Cell

L₂ = Analyzing Lens

L₃ and L₄ = Focusing Lenses

V and D = Vernier and Dial

(Drawing is actual size)

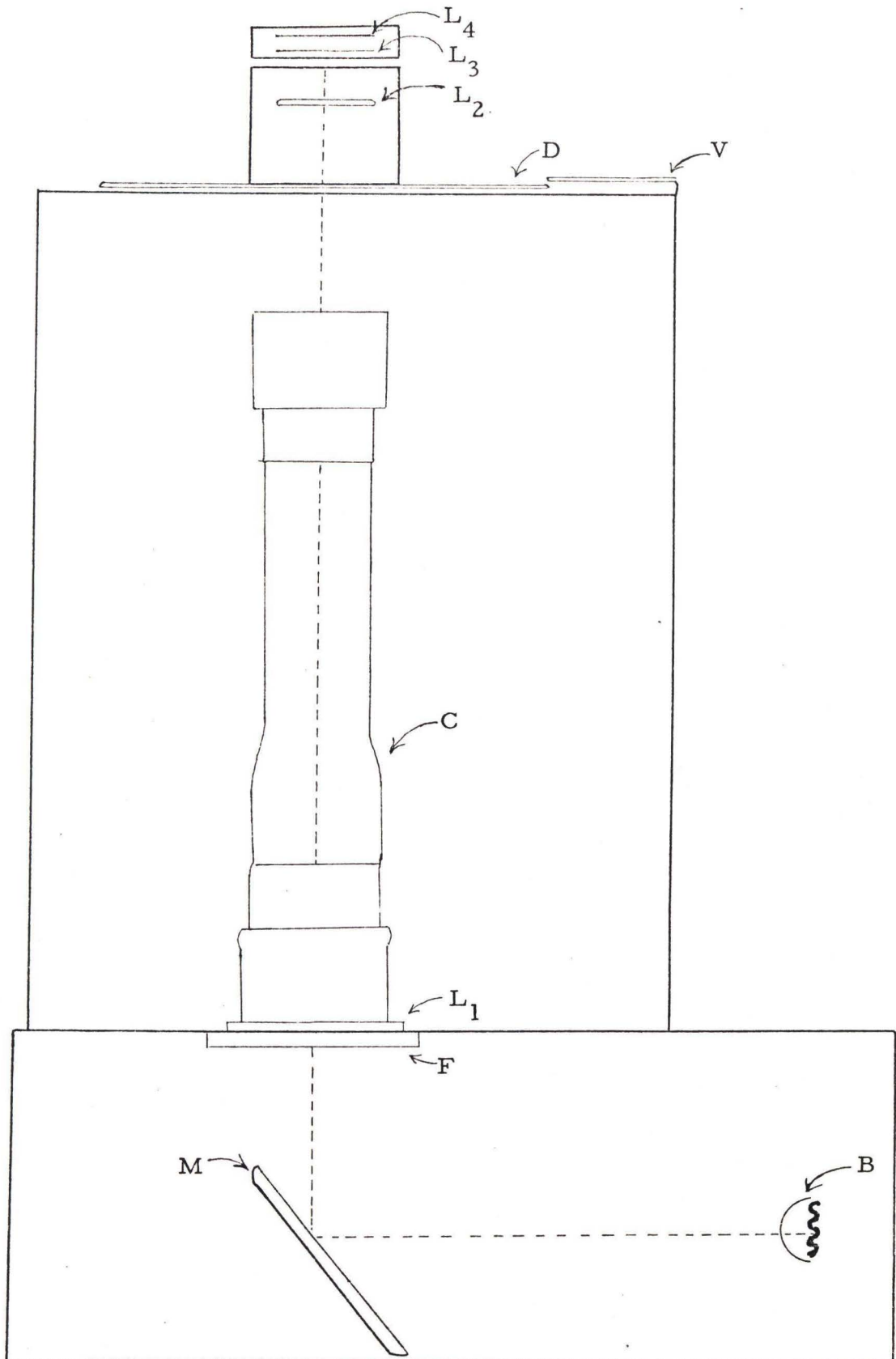


Figure 12

Wiring Diagram for Polarimeter Light Source

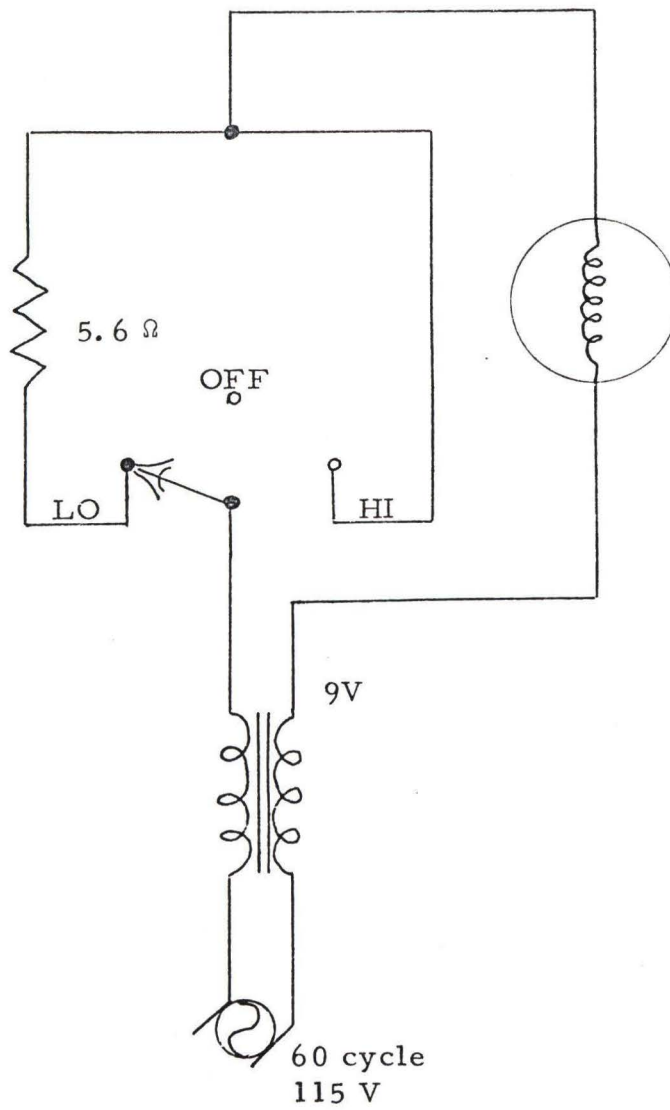


Figure 13

Polarimeter



Table 3

Cost and Source of Materials for Polarimeter

<u>Quantity</u>	<u>Description</u>	<u>Source</u>	<u>Size</u>	<u>Retail Price</u>
1	Tungsten Bulb	F.A.U. Electronics Shop	9V	\$0.50 approx.
1	Front Surface Mirror	Edmund Scientific	30mm diam.	1.20
1	Polaroid Sheet	Boca Optics	4 sq. "	4.00
2	Focusing Lens	Removed from Camera	20mm diam.	2.00 est.
1	Polarimeter Tube	F.A.U. Chemistry Dept.	1 dm	
1	Yellow Sodium 565- 630nm Filter	Arthur H. Thomas Co. Filter #59	5 x 5 x 0.8 cm	29.78
1	Vernier and Dial	Pic Design Corp.		15.00

IV. EXPERIMENTAL RESULTS

This section is devoted to a comparison of results obtained with the self-designed models and established commercial instruments. Discussion is made of any differences in results that may be observed. The experiments selected for evaluation of the instruments underline the principles of visible range spectrophotometry, conductimetry, and polarimetry.

A. Visible Range Spectrophotometer

1. Beer-Lambert Law Behavior

Beer-Lambert law behavior and determination of molar absorptivity are typical challenges to instruments capable of measuring spectral absorption phenomena. The self-designed instrument is compared to the Welch Chem Anal and Perkin-Elmer Model 202 spectrometers.

A 0.05M stock solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and dilutions of 0.04, 0.03, 0.02, and 0.01M were prepared in accordance with standard laboratory directions (8). Spectra of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions are shown in Figures 14, 15, and 16 for the three instruments. The wavelengths of maximum absorption are located at 410 and 580 nm for each instrument. It may be observed that the absorbance of the 410nm band is less on the self designed model than on the other two instruments. This is due to the limitation of instrument sensitivity in the shorter wavelength regions as described in the chapter on construction. Nevertheless, the spectrum obtained with the self-designed model is in good agreement with the

Figure 14

Absorption Spectra of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Solutions Obtained with Self-Designed Spectrophotometer.

Solvent: Distilled H_2O

Concentrations: 0.01, 0.02, 0.03, 0.04, and 0.05M

Cell Path: 10mm

Reference: Distilled H_2O

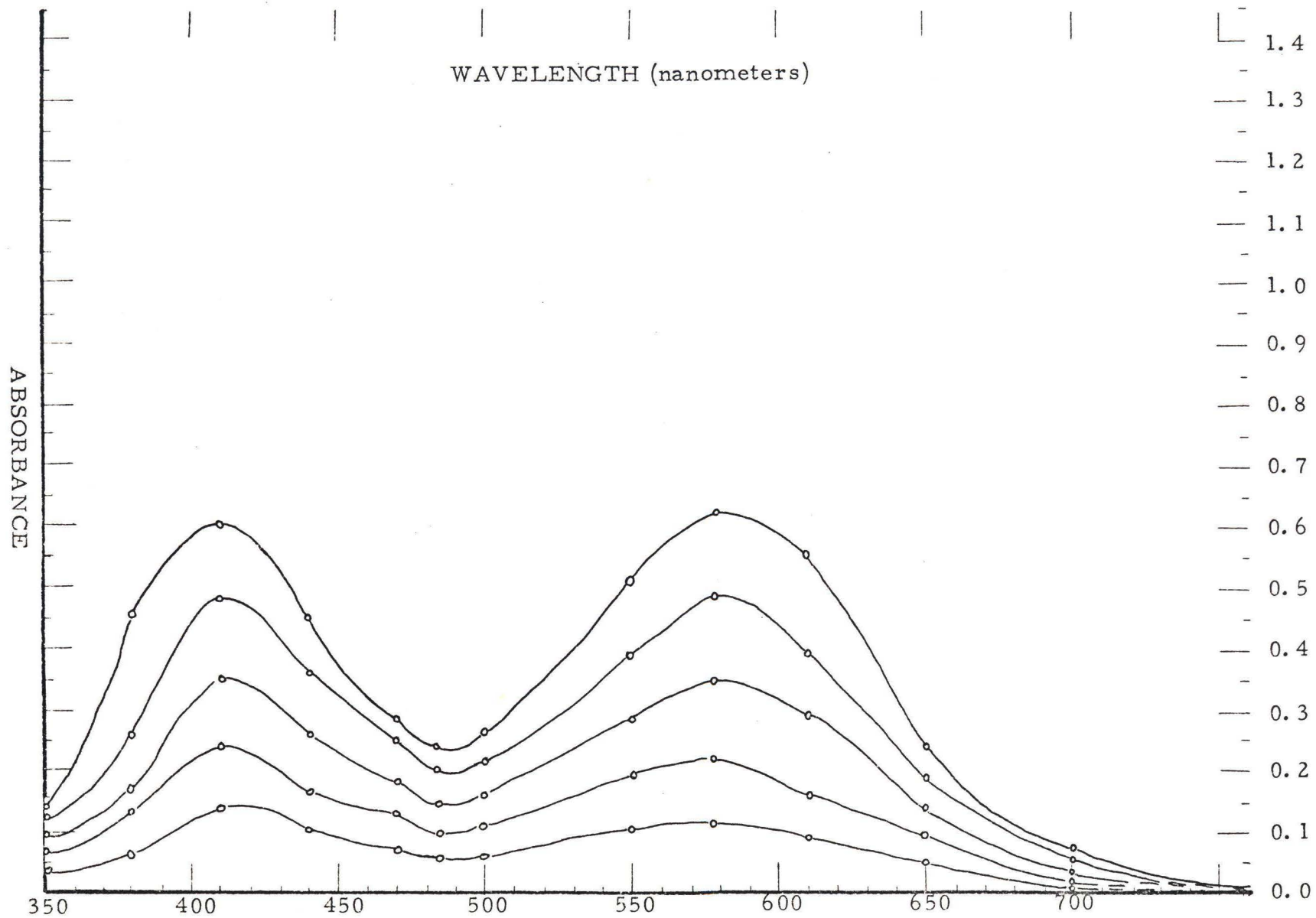


Figure 15

Absorption Spectra of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Solutions Obtained with Welch Chem Anal Spectrophotometer.

Solvent: Distilled H_2O

Concentrations: 0.01, 0.02, 0.03, 0.04, and 0.05M

Cell Path: 10mm

Reference: Distilled H_2O

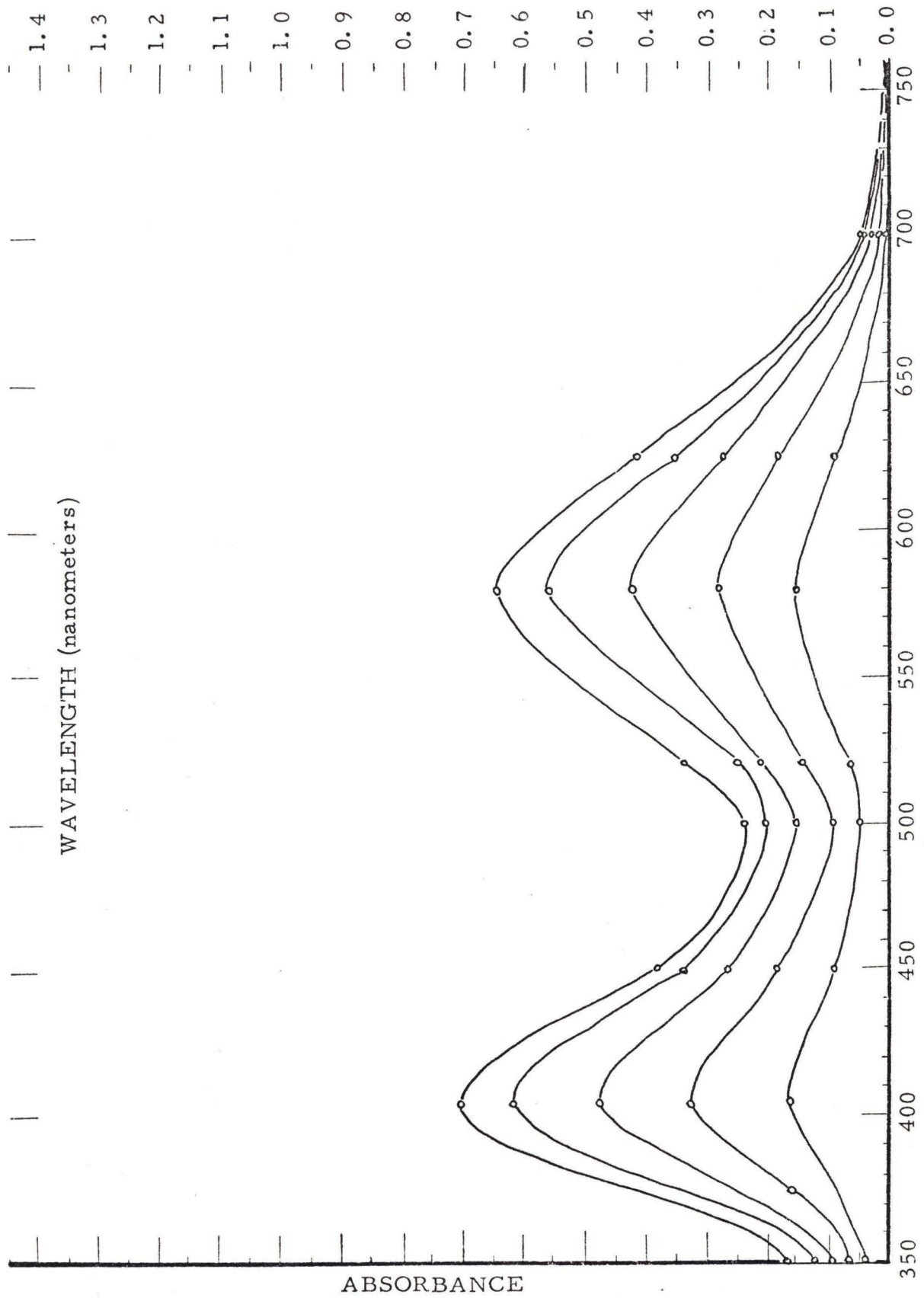


Figure 16

Absorption Spectra of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Solutions Obtained with Perkin-Elmer Model 202 Spectrophotometer.

Solvent: Distilled H_2O

Concentration: 0.01, 0.02, 0.03, 0.04, and 0.05M

Cell Path: 10mm

Reference: Distilled H_2O

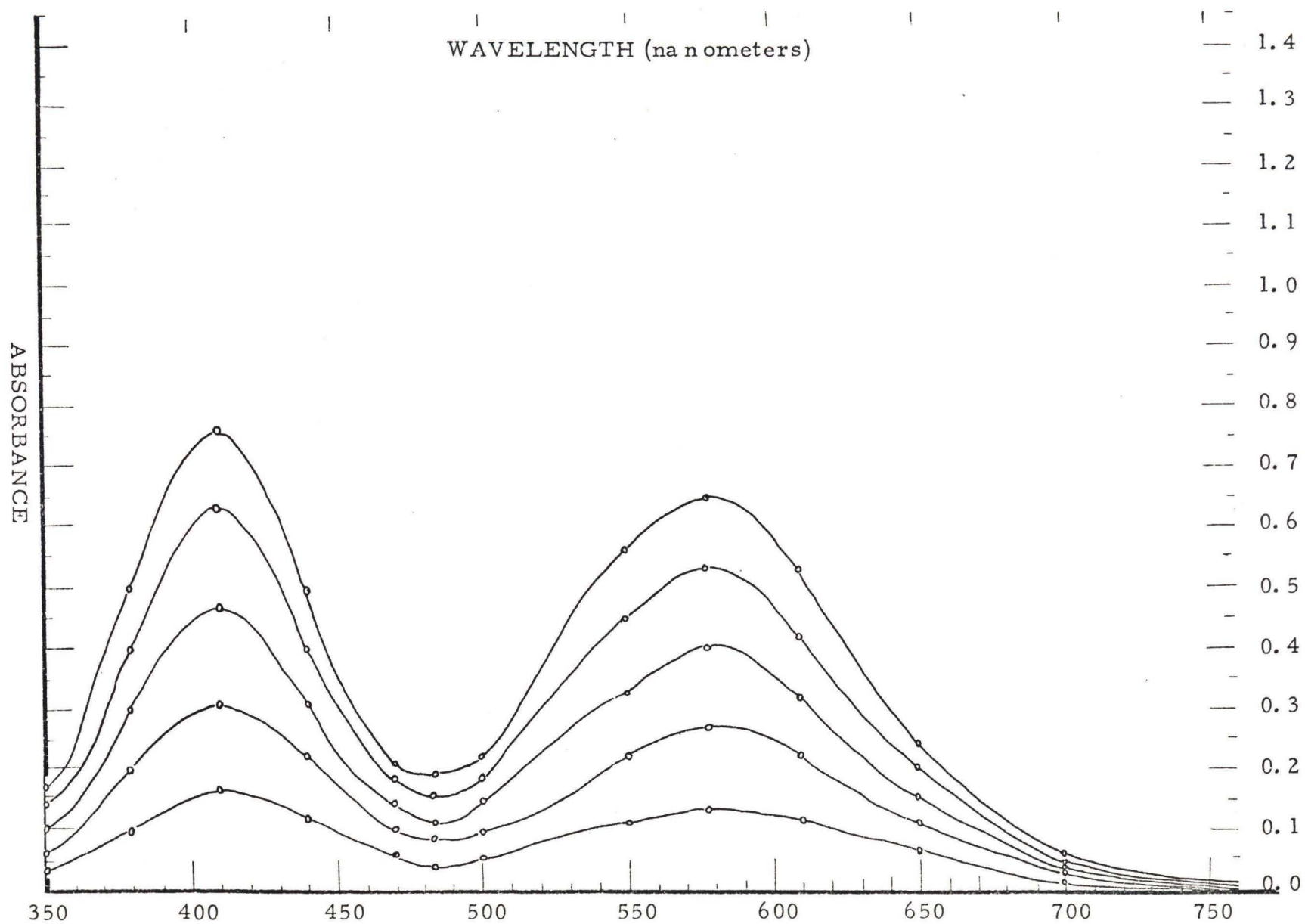


Figure 17

Beer-Lambert Law Plots at $410(\lambda_1)$ and $580(\lambda_2)$ nm Obtained with Self-Designed Spectrophotometer.

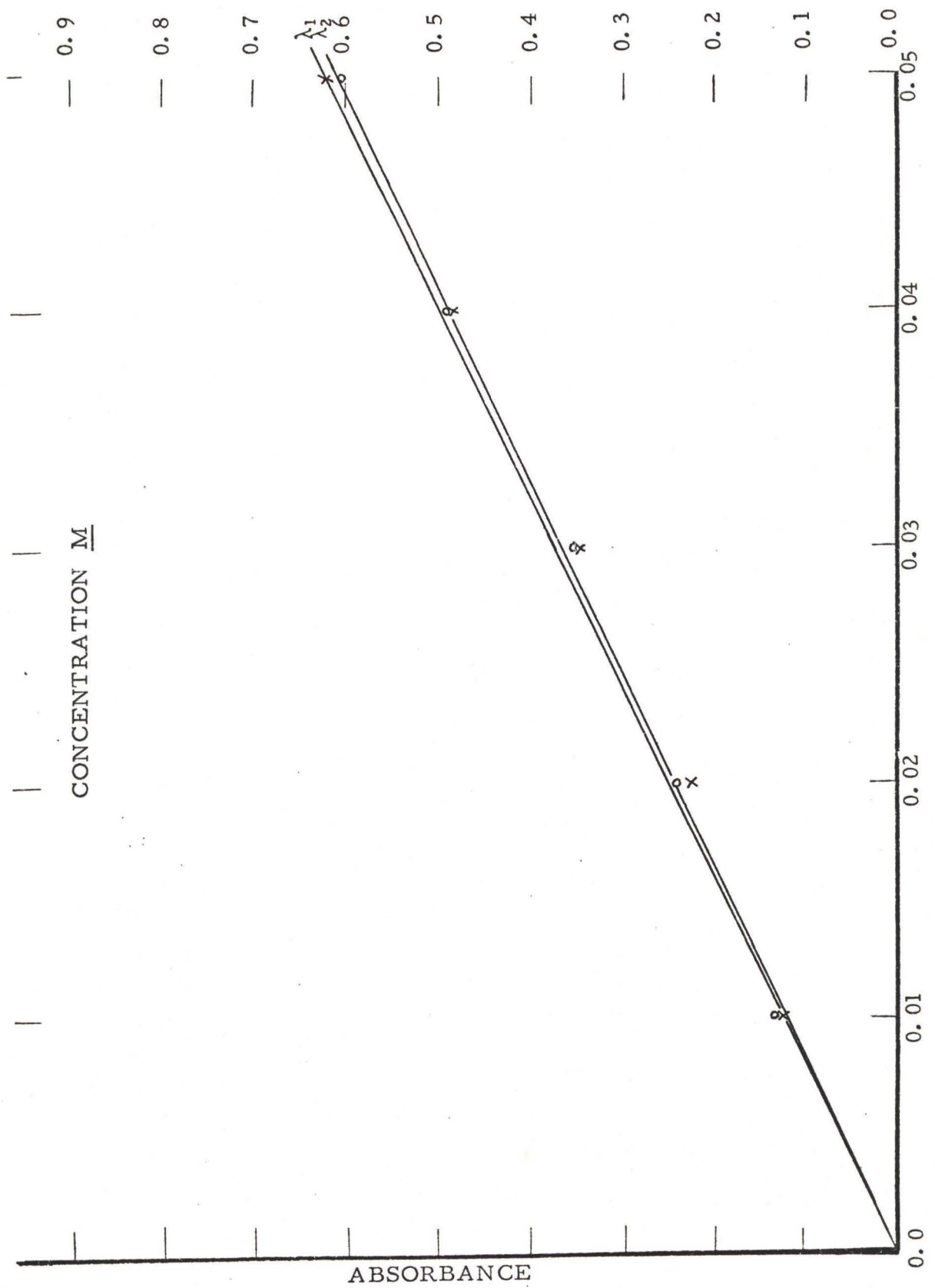


Figure 18

Beer-Lambert Law Plots at $410(\lambda_1)$ and $580(\lambda_2)$ nm Obtained with Welch Chem Anal Spectrophotometer.

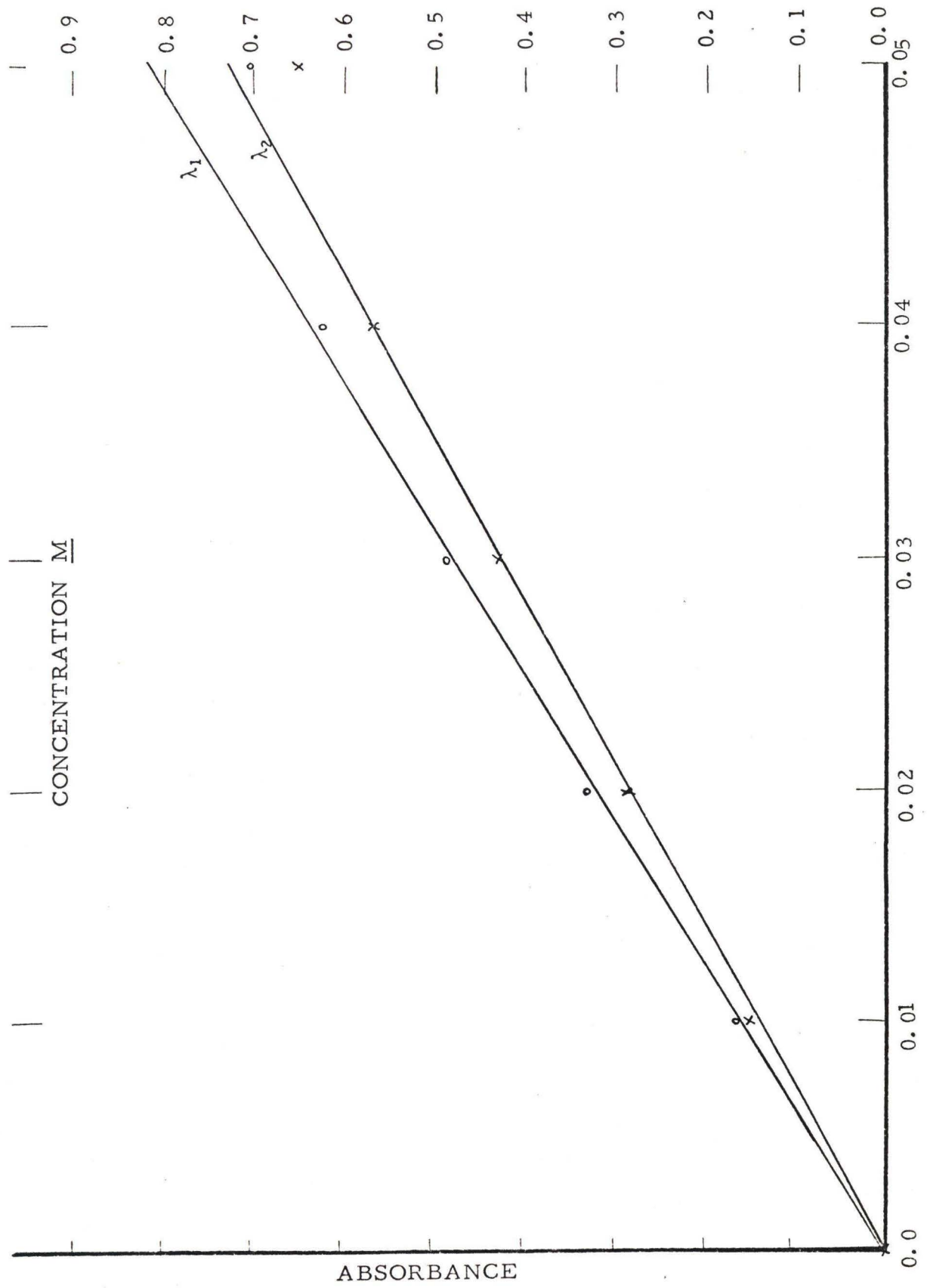


Figure 19

Beer-Lambert Law Plots at $410(\lambda_1)$ and $580(\lambda_2)$ nm Obtained with Perkin-Elmer 202 Spectrophotometer.

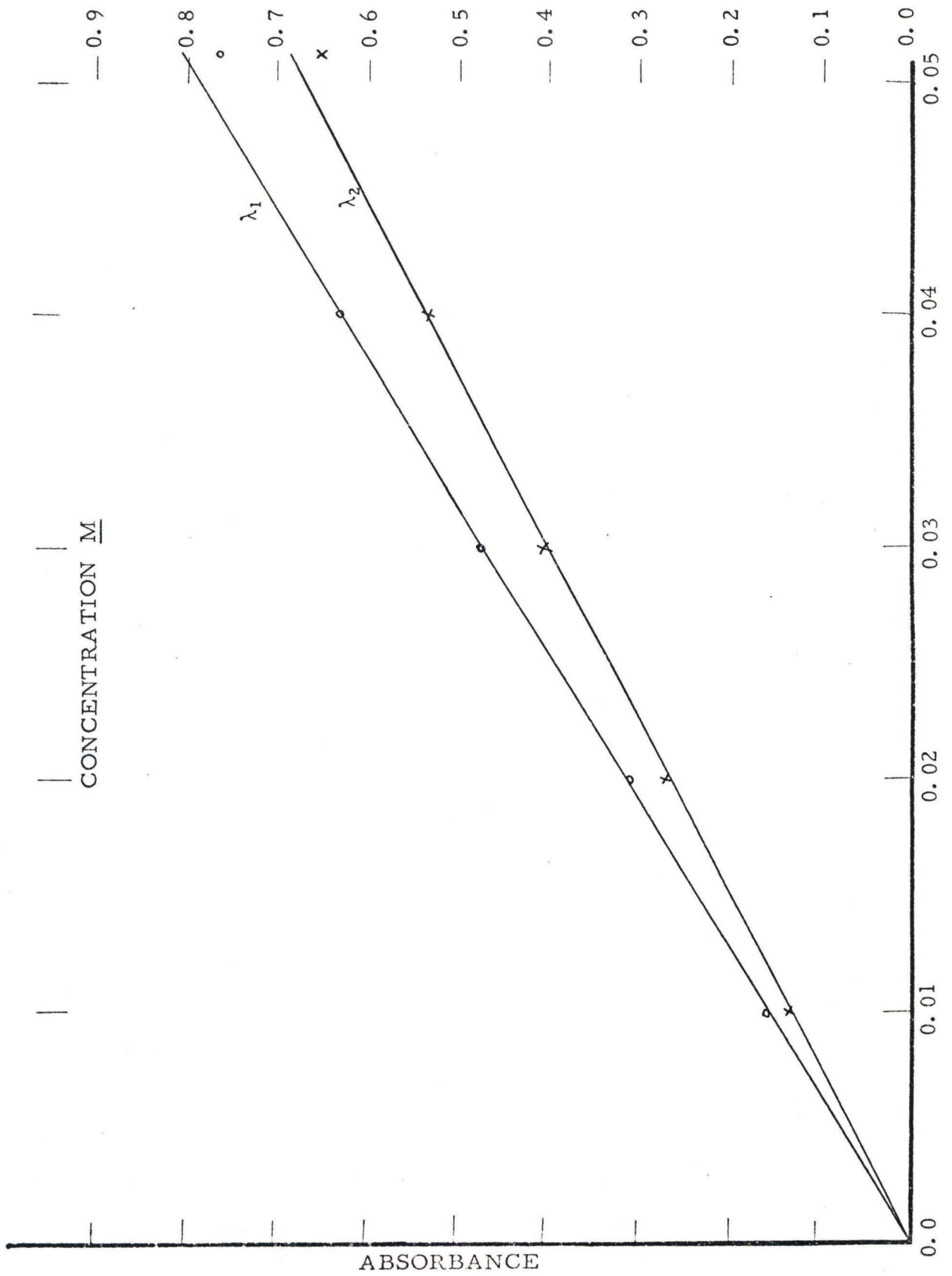


Table 4

Molar Absorptivity Coefficients for $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Solutions at 410 and 580 nm Using the Self-Designed Spectrophotometer.

$$\epsilon_{410} = A/bc$$

$$\epsilon = 0.131 / (1) 0.01 = 13.1$$

$$\epsilon = 0.237 / (1) 0.02 = 11.8$$

$$\epsilon = 0.347 / (1) 0.03 = 11.6$$

$$\epsilon = 0.481 / (1) 0.04 = 12.0$$

$$\epsilon = 0.602 / (1) 0.05 = 12.0$$

$$\epsilon = 12.1 \pm 0.6$$

$$\epsilon_{580} = A/bc$$

$$\epsilon = 0.119 / (1) 0.01 = 11.9$$

$$\epsilon = 0.222 / (1) 0.02 = 11.1$$

$$\epsilon = 0.347 / (1) 0.03 = 11.6$$

$$\epsilon = 0.481 / (1) 0.04 = 12.0$$

$$\epsilon = 0.620 / (1) 0.05 = 12.4$$

$$\epsilon = 11.8 \pm 0.5$$

Table 5

Molar Absorptivity Coefficients for $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Solutions at 405 and 580 nm Using the Welch Chem Anal Spectrophotometer.

$$\epsilon_{405} = A/bc$$

$$\epsilon_{580} = A/bc$$

$$\epsilon = 0.164 / (1) 0.01 = 16.4$$

$$\epsilon = 0.149 / (1) 0.01 = 14.9$$

$$\epsilon = 0.328 / (1) 0.02 = 16.4$$

$$\epsilon = 0.280 / (1) 0.02 = 14.0$$

$$\epsilon = 0.480 / (1) 0.03 = 16.0$$

$$\epsilon = 0.426 / (1) 0.03 = 14.2$$

$$\epsilon = 0.619 / (1) 0.04 = 15.5$$

$$\epsilon = 0.561 / (1) 0.04 = 14.0$$

$$\epsilon = 0.703 / (1) 0.05 = 14.1$$

$$\epsilon = 0.648 / (1) 0.05 = 13.0$$

$$\epsilon = 15.7 \pm 1.0$$

$$\epsilon = 14.0 \pm 0.7$$

Table 6

Molar Absorptivity Coefficients for $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Solutions at 405 and 580 nm Using the Perkin-Elmer Model 202 Spectrophotometer.

$$\epsilon_{405} = A/bc$$

$$\epsilon = 0.160 / (1) 0.01 = 16.0$$

$$\epsilon = 0.310 / (1) 0.02 = 15.5$$

$$\epsilon = 0.470 / (1) 0.03 = 15.7$$

$$\epsilon = 0.630 / (1) 0.04 = 15.8$$

$$\epsilon = 0.760 / (1) 0.05 = 15.2$$

$$\epsilon = 15.6 \pm 0.3$$

$$\epsilon_{580} = A/bc$$

$$\epsilon = 0.130 / (1) 0.01 = 13.0$$

$$\epsilon = 0.270 / (1) 0.02 = 13.5$$

$$\epsilon = 0.400 / (1) 0.03 = 13.3$$

$$\epsilon = 0.530 / (1) 0.04 = 13.2$$

$$\epsilon = 0.650 / (1) 0.05 = 13.0$$

$$\epsilon = 13.2 \pm 0.2$$

commercial instruments.

Beer-Lambert law plots are shown in Figures 17, 18, and 19 at wavelengths 410 and 580 nm for the $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions. The self-designed instrument shows excellent linear plots of absorbance versus concentration. Molar absorptivity values calculated from the Beer-Lambert law are listed in Tables 4, 5, and 6. The value of ϵ taken at 410 nm for the self-designed instrument is in less satisfactory agreement, due to low sensitivity in that region.

2. Simultaneous Analysis of a Two-Component Mixture

The simultaneous analysis of a two-component mixture often is performed by spectrophotometry. Analysis can be successfully executed with the constructed instrument as with any other visible range assembly. The purpose of this experiment is to demonstrate that the absorbance values of the single components are additive and equal to the absorbance of the mixture. The Cr(III)-Co(II) mixture is chosen as an example (9), because there is no interaction between these ions and absorption takes place at different wavelengths. The Cr(III) ion absorbs at 580 nm, and the Co(II) ion at 510 nm. Absorption spectra are presented in Figures 20, 21, and 22 for solutions containing Cr(III), Co(II), and a Cr(III)-Co(II) mixture. These spectra demonstrate that the absorption is additive for each instrument, and that simultaneous analysis of Cr(III)-Co(II) is possible. The additive spectrum of the self-designed spectrophotometer compares favorably with the commercial instruments.

Figure 20

Simultaneous Analysis of a Two Component Cr(III)-Co(II) Mixture
Obtained with Self-Designed Spectrophotometer.

- a = Base Line (distilled H_2O)
- b = 0.0752M Co(II)
- c = 0.0200M Cr(III)
- d = Calculated additive absorbance
of the two components
- e = Actual spectrum of Cr(III)-Co(II) mixture
(0.0752M in Co(II) + 0.02M in Cr(III)).

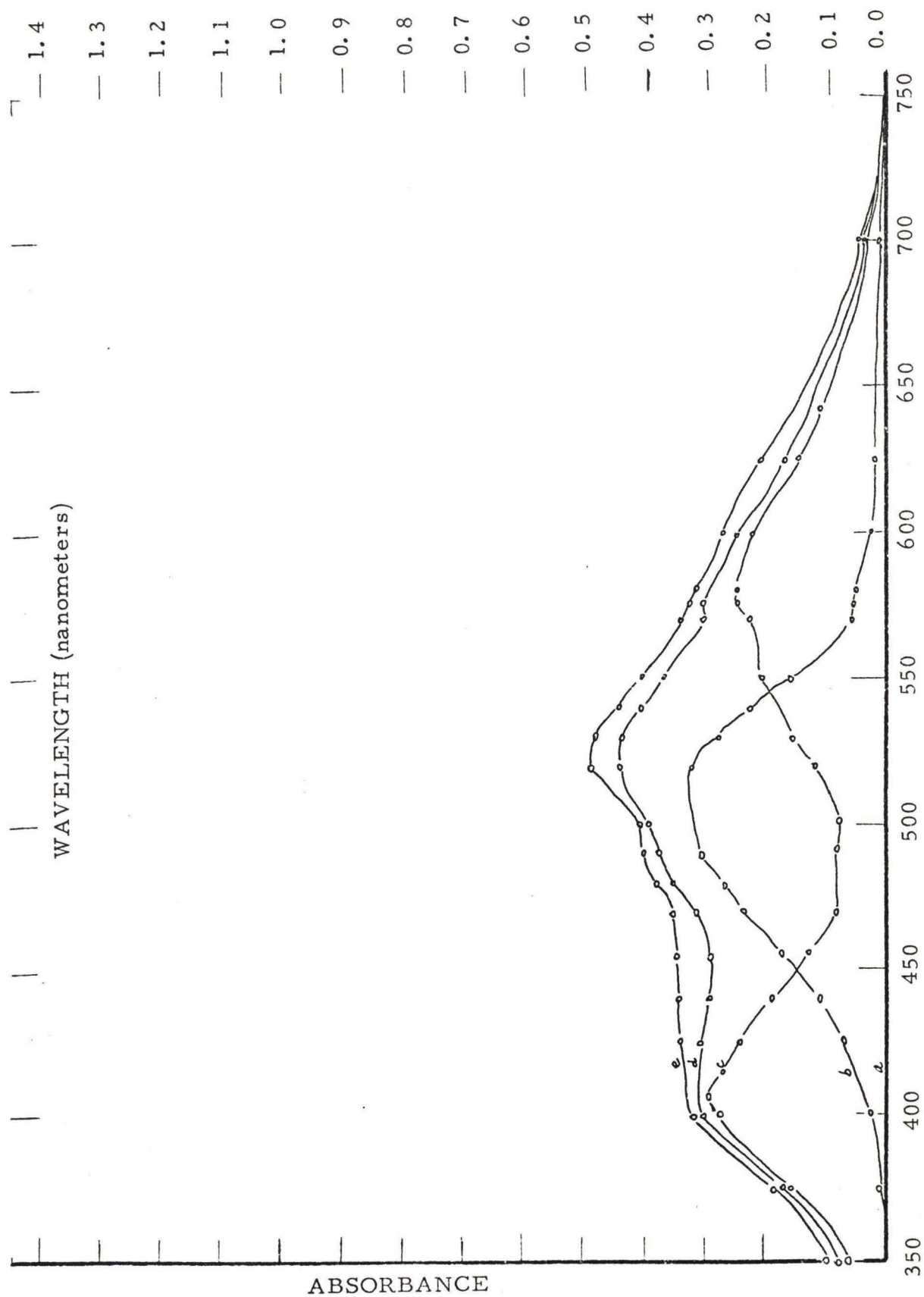


Figure 21

Simultaneous Analysis of a Two Component Cr(III)-Co(II) Mixture
Obtained with Welch Chem Anal Spectrophotometer.

- a = Base Line (distilled H₂O)
- b = 0.0752M Co(II)
- c = 0.0200M Cr(III)
- d = Calculated additive absorbance of the two
components
- e = Actual spectrum of Cr(III)-Co(II) mixture
(0.0752M in Co(II) + 0.02M in Cr(III)).

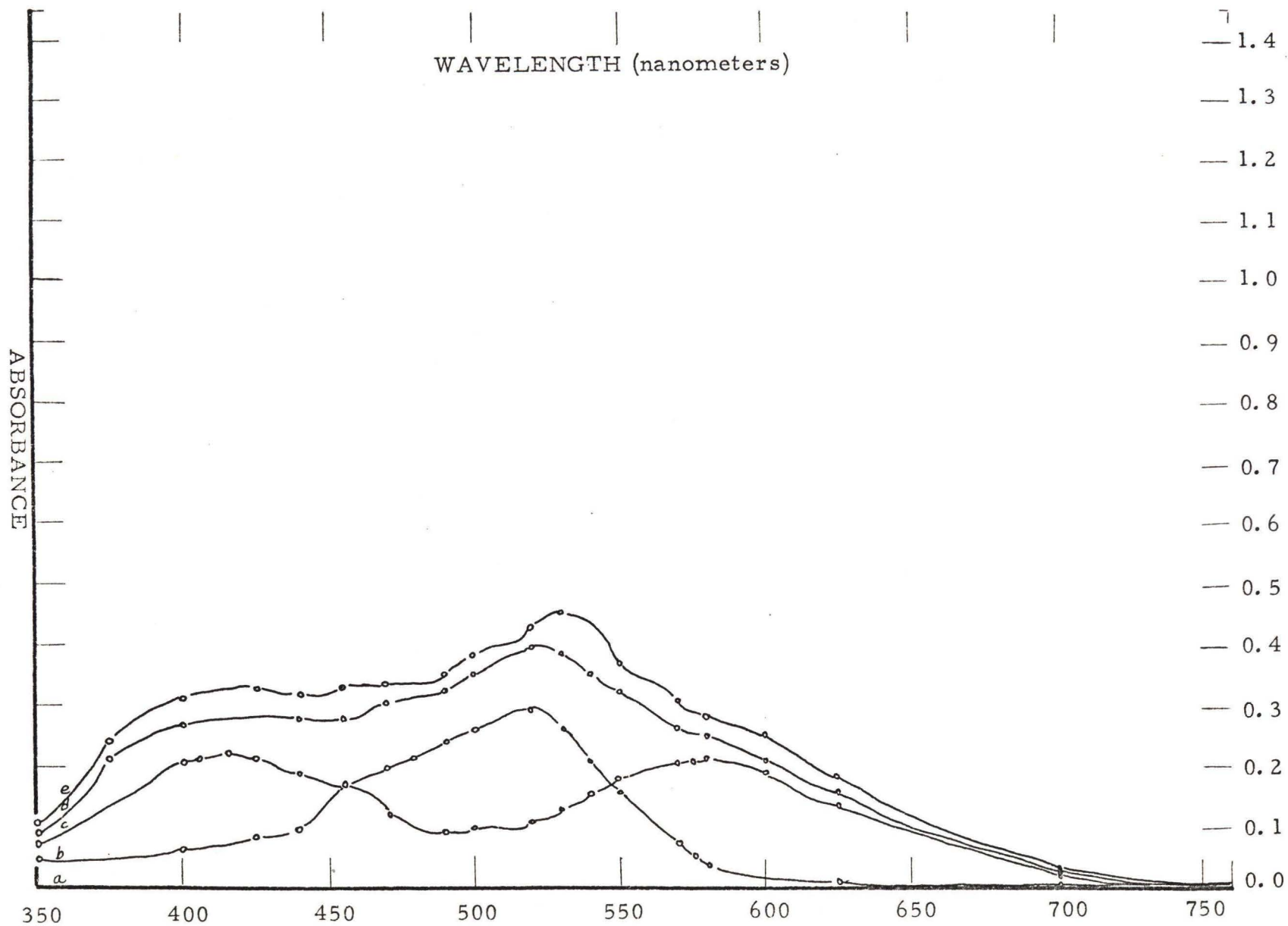


Figure 22

Simultaneous Analysis of a Two Component Cr(III)-Co(II) Mixture
Obtained with Perkin-Elmer Model 202 Spectrophotometer.

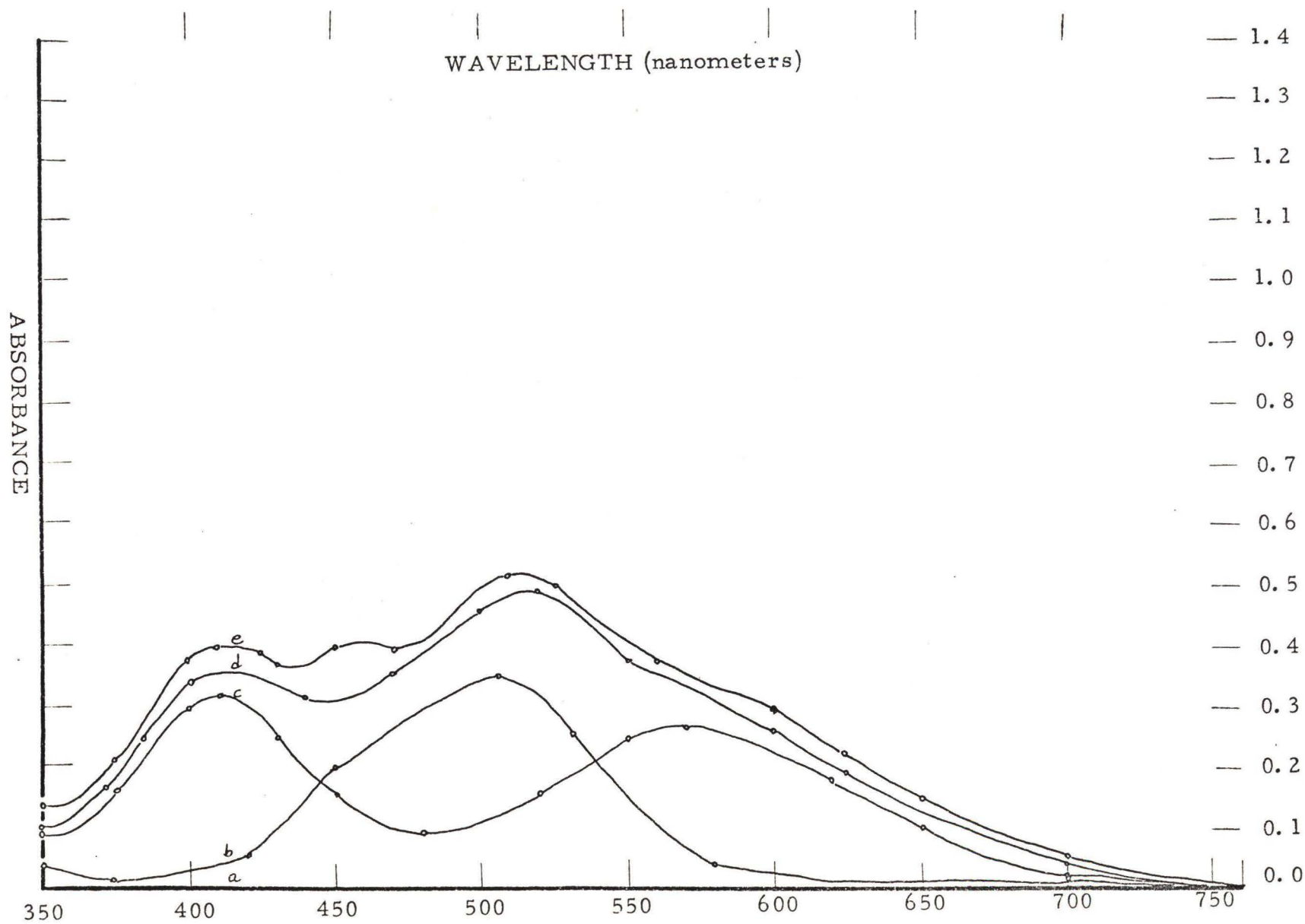
a = Base Line (distilled H₂O)

b = 0.0752M Co(II)

c = 0.0200M Cr(III)

d = Calculated additive absorbance of the two
components.

e = Actual spectrum of Cr(III)-Co(II) mixture
(0.0752M in Co(II) + 0.02M in Cr(III)).



3. The $pK_{\text{protolysis}}$ of an Indicator

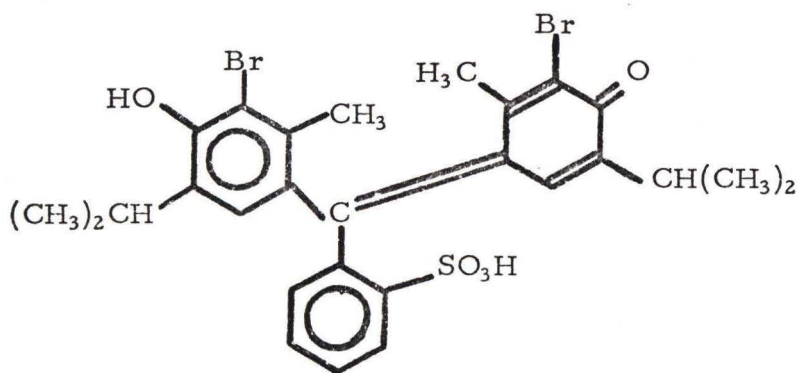
Determination of the pK_{prot} of an indicator is a challenging experiment for a visible range spectrophotometer. This experiment demonstrates the stability of the instrument over the entire visible region. If absorbance is plotted as a function of pH for a constant concentration of indicator, an isobestic point is observed for the absorbing species HIn and In^- . An isobestic point is characteristic of an equilibrium existing between two species. For acid-base indicators the chemical equilibrium is:



with an equilibrium constant mathematically represented as:

$$K_{\text{prot}} = [\text{H}^+][\text{In}^-] / [\text{HIn}] \quad (23)$$

The indicator chosen for this experiment is Brom Thymol Blue:



$$\text{gfw} = 624.39 \text{ and } pK_{\text{prot}} = 7.3$$

The experimental procedures were adapted from those described in the Reilley and Sawyer laboratory manual (10). A stock solution containing 0.1 g per liter of the indicator was prepared in 20% ethanol. A one ml aliquot of stock solution was diluted to 50 ml in a volumetric flask with buffer, giving a total indicator concentration of $3.20 \times 10^{-5} \text{ M}$. Buffer solutions ranging from pH 6 to 10 were prepared for this purpose from Na_2HPO_4 and KH_2PO_4 . The pH values were measured with a pH meter. A 0.01M HCl solution was used for the pH 2 buffer.

Figure 23 and 24 represent the spectra of Brom Thymol Blue at various pH values obtained with the self-designed and Perkin-Elmer instruments. Agreement between spectra taken with the two instruments is favorable. The base form of the indicator exhibits a strong absorption maximum at 620 nm, and the acid form a less intense maximum at 446 nm. A clearly defined isobestic point is observed at 502 nm for each instrument.

A qualitative procedure for determining pK_{prot} is to plot absorbance versus pH. At the inflection point of the curve $\text{pH} = \text{pK}_{\text{prot}}$. Figure 25 shows the inflection point when absorbance at 620 nm is plotted against pH for the self-designed and Perkin-Elmer instruments. Figure 26 shows similar plots at 446 nm. The inflection points fall within a range of 7.2 to 7.4 pH units. These results are in excellent agreement with the known literature value of $\text{pK}_{\text{prot}} = 7.3$ (11).

A quantitative procedure for the determination of pK_{prot} is to plot $\log[\text{In}^-]/[\text{HIn}]$ versus pH. Equation 23 can be expressed in log-

Figure 23

Absorption Spectrum of Brom Thymol Blue at pH 2, 6; 6.5, 7, 7.5, 8, and 10 Obtained with Self-Designed Spectrophotometer.

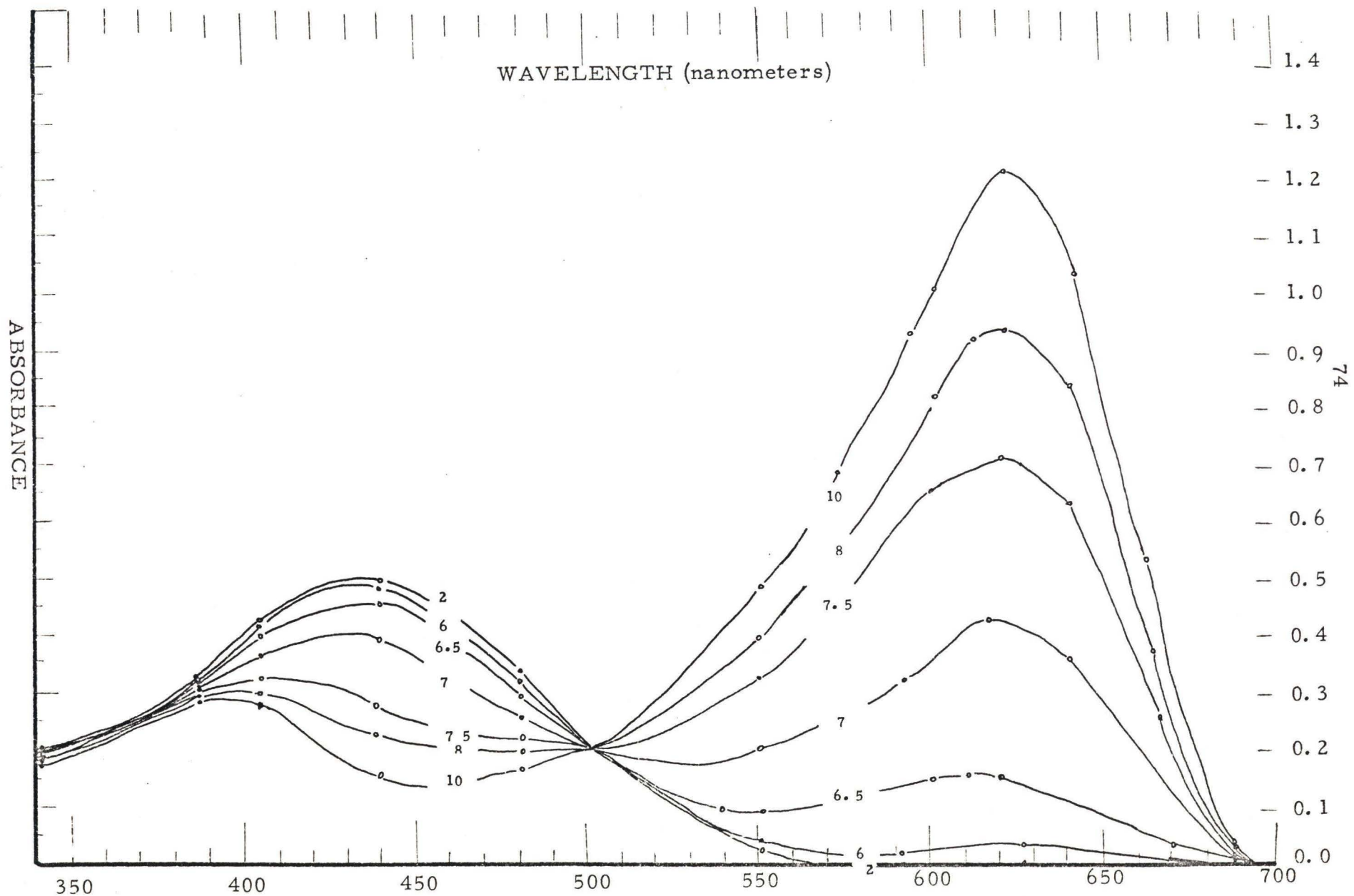


Figure 24

Absorption Spectrum of Brom Thymol Blue at pH 2, 6, 6.5, 7, 7.5, 8, and 10 obtained with Perkin-Elmer Model 202 Spectrophotometer.

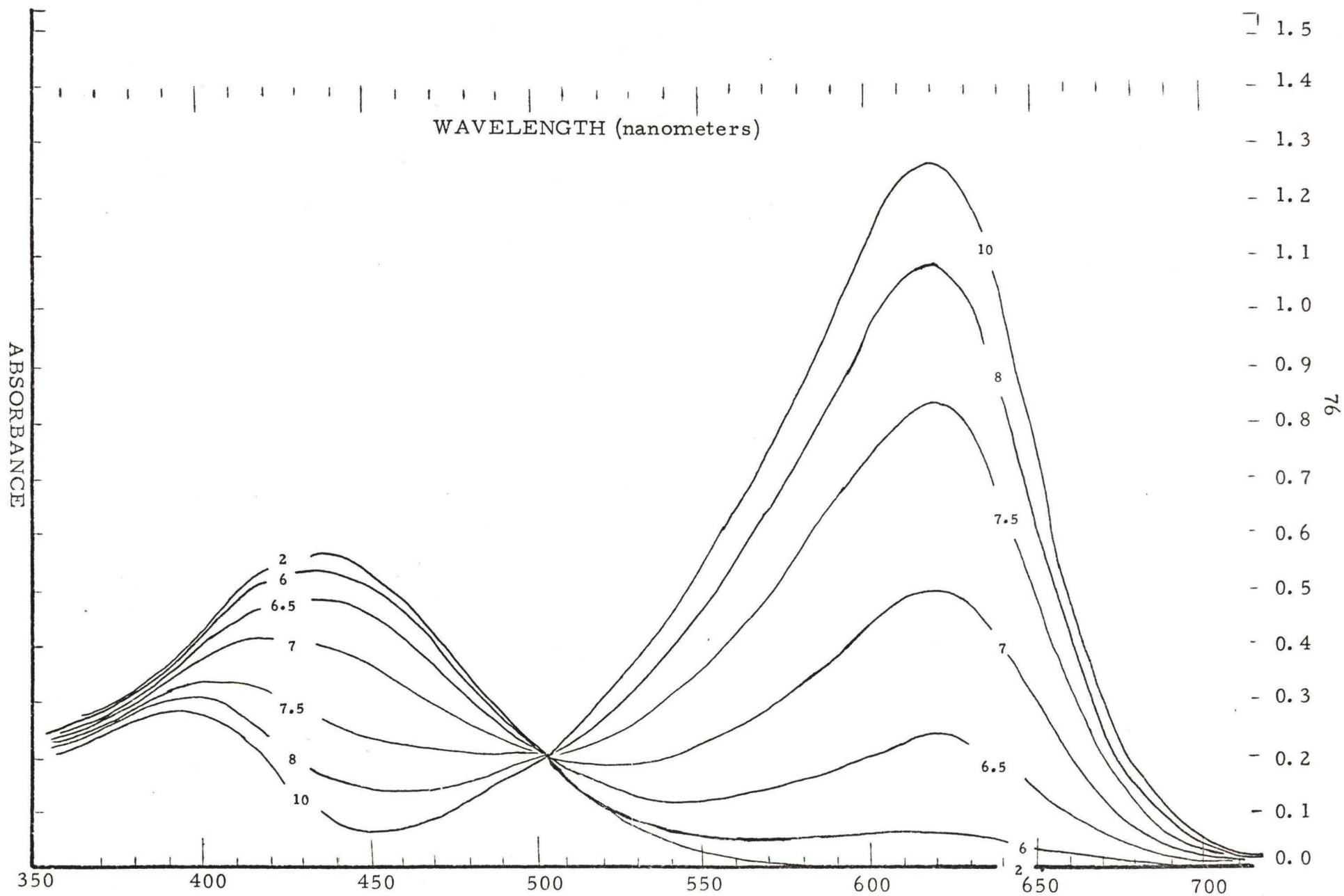


Figure 25

Plots of Absorbance at 620 nm Against pH for Brom Thymol Blue Using
Self-Designed and Perkin-Elmer Model 202 Spectrophotometers.

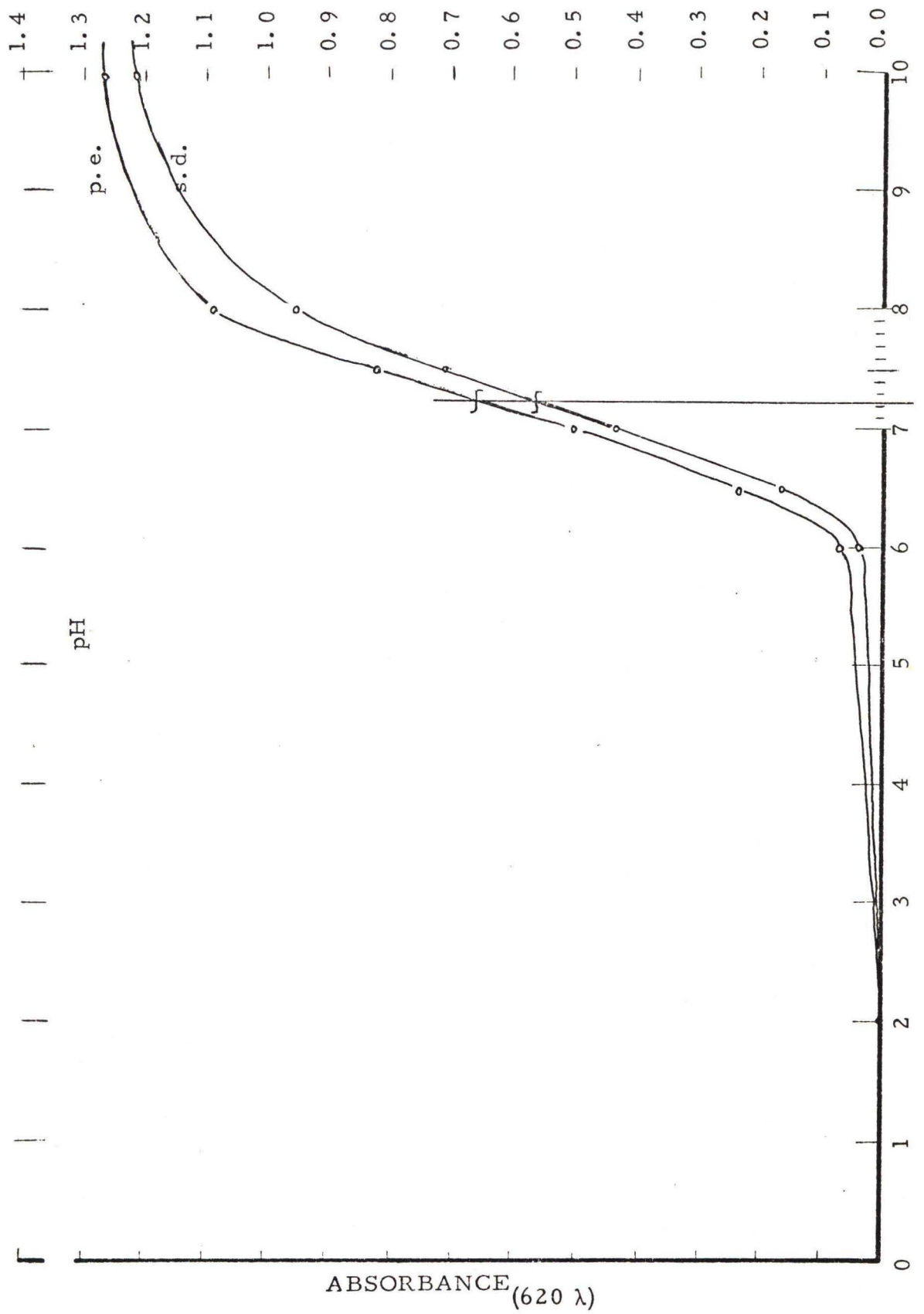
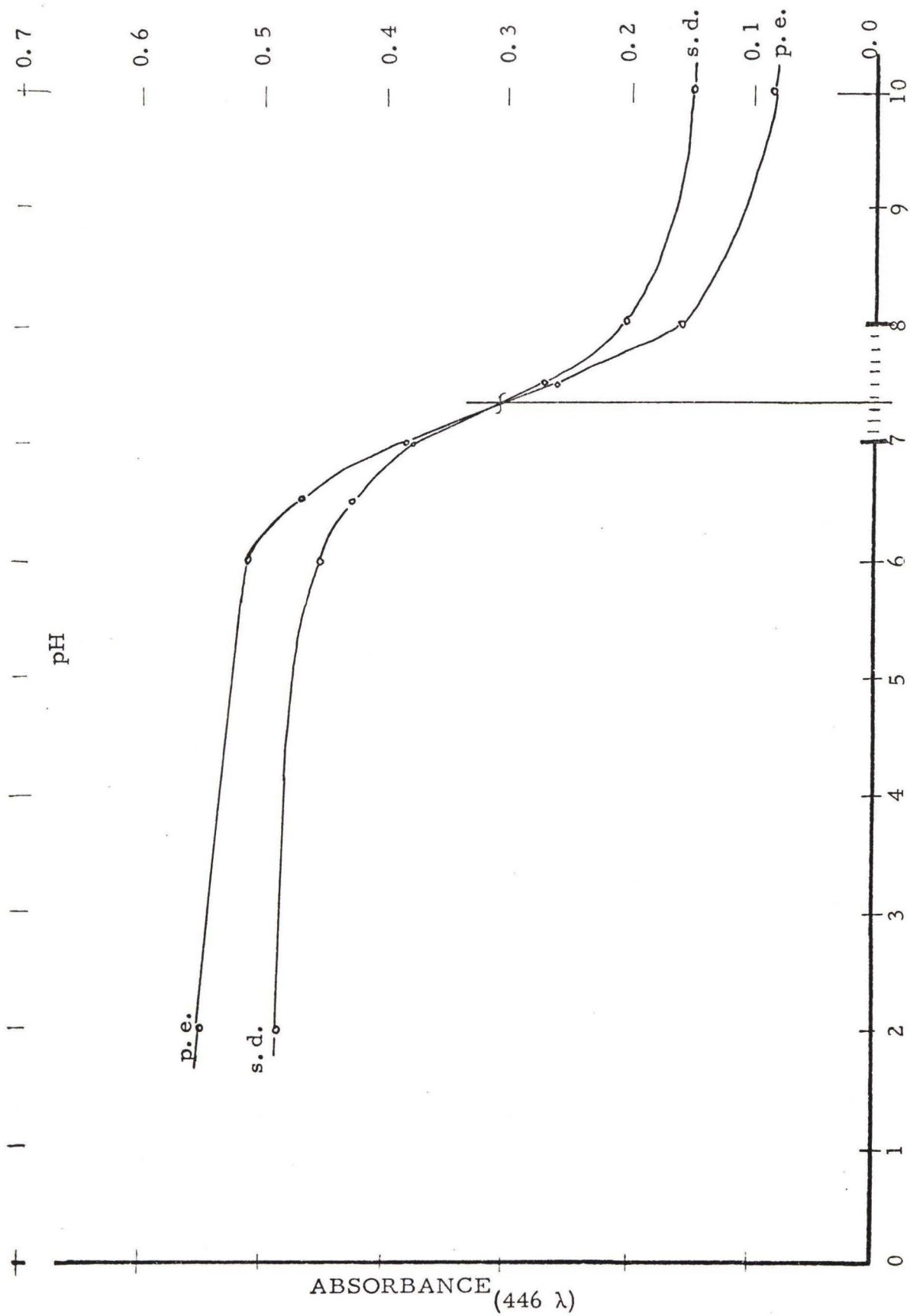


Figure 26

Plots of Absorbance at 446 nm Against pH for Brom Thumol Blue Using
Self-Designed and Perkin-Elmer Model 202 Spectrophotometers.



arithmetic form as:

$$\log K_{\text{prot}} = \log H^+ + \log[\text{In}^-]/[\text{HIn}] \quad (24)$$

so that when \log of $[\text{In}^-]/[\text{HIn}] = 0$, $\text{pK}_{\text{prot}} = \text{pH}$. Only the base form of the indicator absorbs at 620 nm. Since there is no significant increase in absorbance beyond pH 10, it is assumed under these conditions that $[\text{HIn}] = 0$, and $[\text{In}^-] = C_{\text{HIn}} = 3.20 \times 10^{-5}$. Absorbance values at 620 nm for Brom Thymol Blue as a function of pH are listed below:

<u>pH</u>	<u>Absorbance at 620 nm</u> <u>Self-Designed Model</u>	<u>Absorbance at 620 nm</u> <u>Perkin-Elmer Model 202</u>
10	1.23	1.27
8	0.94	1.09
7.5	0.71	0.83
7	0.43	0.50
6.5	0.16	0.24
6	0.045	0.06
ϵ for In^- at 620 nm:	38,400	39,000

The molar absorptivity of In^- is calculated from the data at pH 10 by applying the Beer-Lambert relationship, $\epsilon = A/bc$. Once the molar absorptivity of In^- is established, $[\text{In}^-]$ can be calculated for each pH value by dividing A by ϵb , ($b = 1$ cm). The concentration of HIn is obtained by subtracting the results obtained in the previous step from the initial concentration. The results are as follows:

<u>pH</u>	<u>[In⁻] (s. d.)</u>	<u>[HIn] (s. d.)</u>	<u>[In⁻] (p. e.)</u>	<u>[HIn] (p. e.)</u>
8	$2.45 \times 10^{-5} \underline{\text{M}}$	$0.76 \times 10^{-5} \underline{\text{M}}$	$2.75 \times 10^{-5} \underline{\text{M}}$	$0.45 \times 10^{-5} \underline{\text{M}}$
7.5	$1.35 \times 10^{-5} \underline{\text{M}}$	$1.35 \times 10^{-5} \underline{\text{M}}$	$2.09 \times 10^{-5} \underline{\text{M}}$	$1.11 \times 10^{-5} \underline{\text{M}}$
7	$1.12 \times 10^{-5} \underline{\text{M}}$	$2.08 \times 10^{-5} \underline{\text{M}}$	$1.26 \times 10^{-5} \underline{\text{M}}$	$1.94 \times 10^{-5} \underline{\text{M}}$
6.5	$0.42 \times 10^{-5} \underline{\text{M}}$	$2.79 \times 10^{-5} \underline{\text{M}}$	$0.61 \times 10^{-5} \underline{\text{M}}$	$3.05 \times 10^{-5} \underline{\text{M}}$
6	$0.12 \times 10^{-5} \underline{\text{M}}$	$3.09 \times 10^{-5} \underline{\text{M}}$	$0.12 \times 10^{-5} \underline{\text{M}}$	$3.05 \times 10^{-5} \underline{\text{M}}$

The results at 620 nm are plotted in Figure 27. The values of pK_{prot} obtained are 7.33(s. d.) and 7.21(p. e.).

At 446 nm the acid form of the indicator is the predominant absorbing species, but there is also a small amount of absorption by In^- . Absorbance values as a function of pH are listed below:

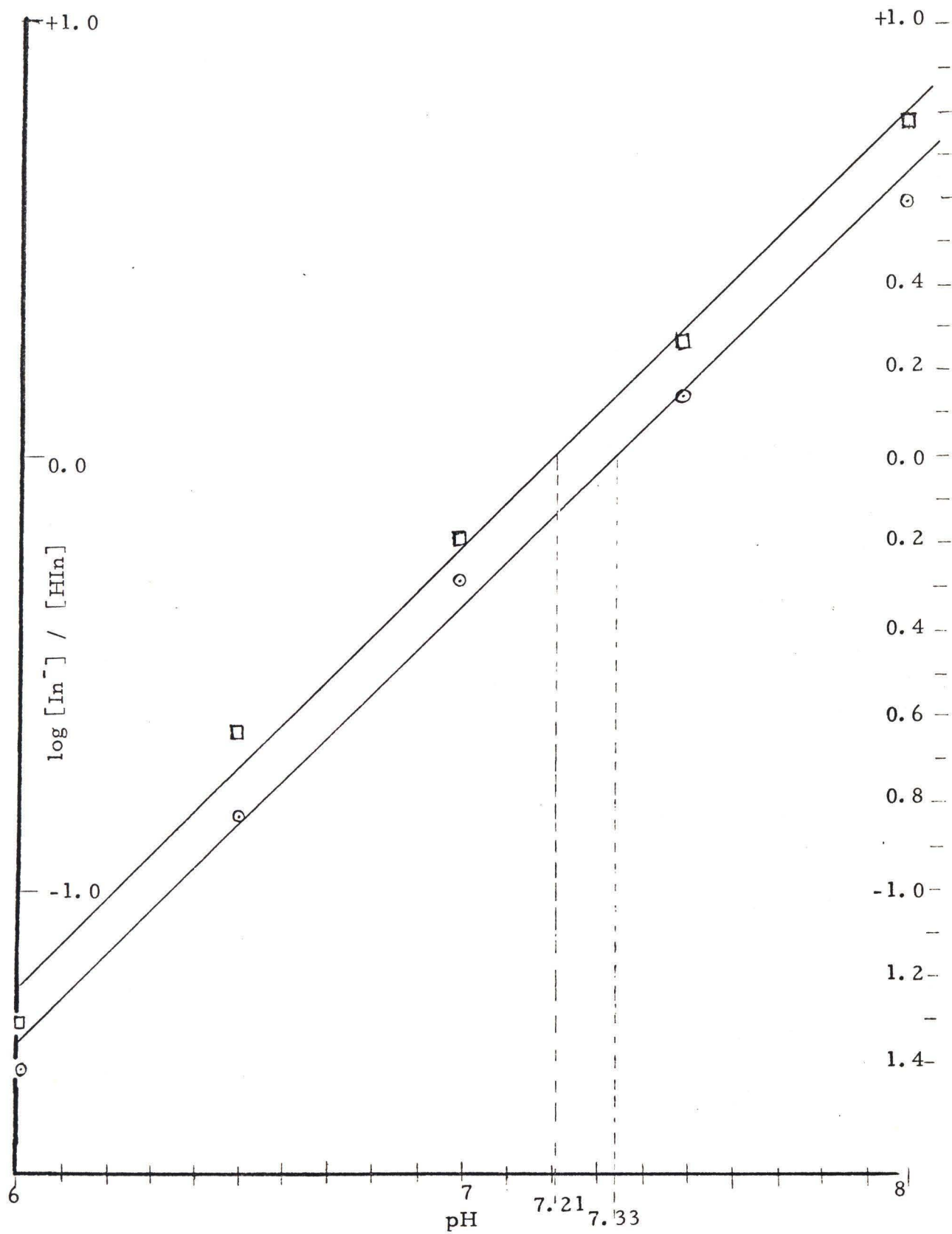
<u>pH</u>	<u>Absorbance at 446 nm Self-Designed Model</u>	<u>Absorbance at 446 nm Perkin-Elmer Model 202</u>
2	0.53	0.57
6	0.47	0.525
6.5	0.45	0.47
7	0.38	0.38
7.5	0.25	0.25
8	0.20	0.165
10	0.09	0.09
ϵ for HIn at 446 nm	18,100	16,600
ϵ for In^- at 446 nm	2,800	2,800

Figure 27

Plot of $\log [\text{In}^-] / [\text{HIn}]$ versus pH at 620 nm for Brom Thymol Blue

⊙ = Self-Designed Spectrophotometer

□ = Perkin-Elmer Model 202 Spectrophotometer



Molar absorptivities of HIn and In^- are calculated at pH 2 and 10, respectively, where only a single form of the indicator exists in solution.

The concentrations of HIn and In^- at each pH value are calculated by solving the following simultaneous equations.

$$A = \epsilon_{\text{HIn}} \cdot b[\text{HIn}] + \epsilon_{\text{In}^-} \cdot b[\text{In}^-] \quad (25)$$

and

$$C_{\text{HIn}} = [\text{HIn}] + [\text{In}^-] = 3.20 \times 10^{-5} \text{ M} \quad (26)$$

Results are as follows:

pH	$[\text{In}^-]$ (s. d.)	$[\text{HIn}]$ (s. d.)	$[\text{In}^-]$ (p. e.)	$[\text{HIn}]$ (p. e.)
2	$0.01 \times 10^{-5} \text{ M}$	$3.19 \times 10^{-5} \text{ M}$	$0.06 \times 10^{-5} \text{ M}$	$3.14 \times 10^{-5} \text{ M}$
6	$0.44 \times 10^{-5} \text{ M}$	$2.76 \times 10^{-5} \text{ M}$	$0.35 \times 10^{-5} \text{ M}$	$2.85 \times 10^{-5} \text{ M}$
6.5	$0.58 \times 10^{-5} \text{ M}$	$2.61 \times 10^{-5} \text{ M}$	$0.71 \times 10^{-5} \text{ M}$	$2.49 \times 10^{-5} \text{ M}$
7	$1.10 \times 10^{-5} \text{ M}$	$2.10 \times 10^{-5} \text{ M}$	$1.30 \times 10^{-5} \text{ M}$	$1.90 \times 10^{-5} \text{ M}$
7.5	$2.04 \times 10^{-5} \text{ M}$	$1.16 \times 10^{-5} \text{ M}$	$2.15 \times 10^{-5} \text{ M}$	$1.05 \times 10^{-5} \text{ M}$
8	$2.40 \times 10^{-5} \text{ M}$	$0.80 \times 10^{-5} \text{ M}$	$2.71 \times 10^{-5} \text{ M}$	$0.49 \times 10^{-5} \text{ M}$
10	$3.19 \times 10^{-5} \text{ M}$	$0.29 \times 10^{-7} \text{ M}$	$3.20 \times 10^{-5} \text{ M}$	$0.39 \times 10^{-7} \text{ M}$

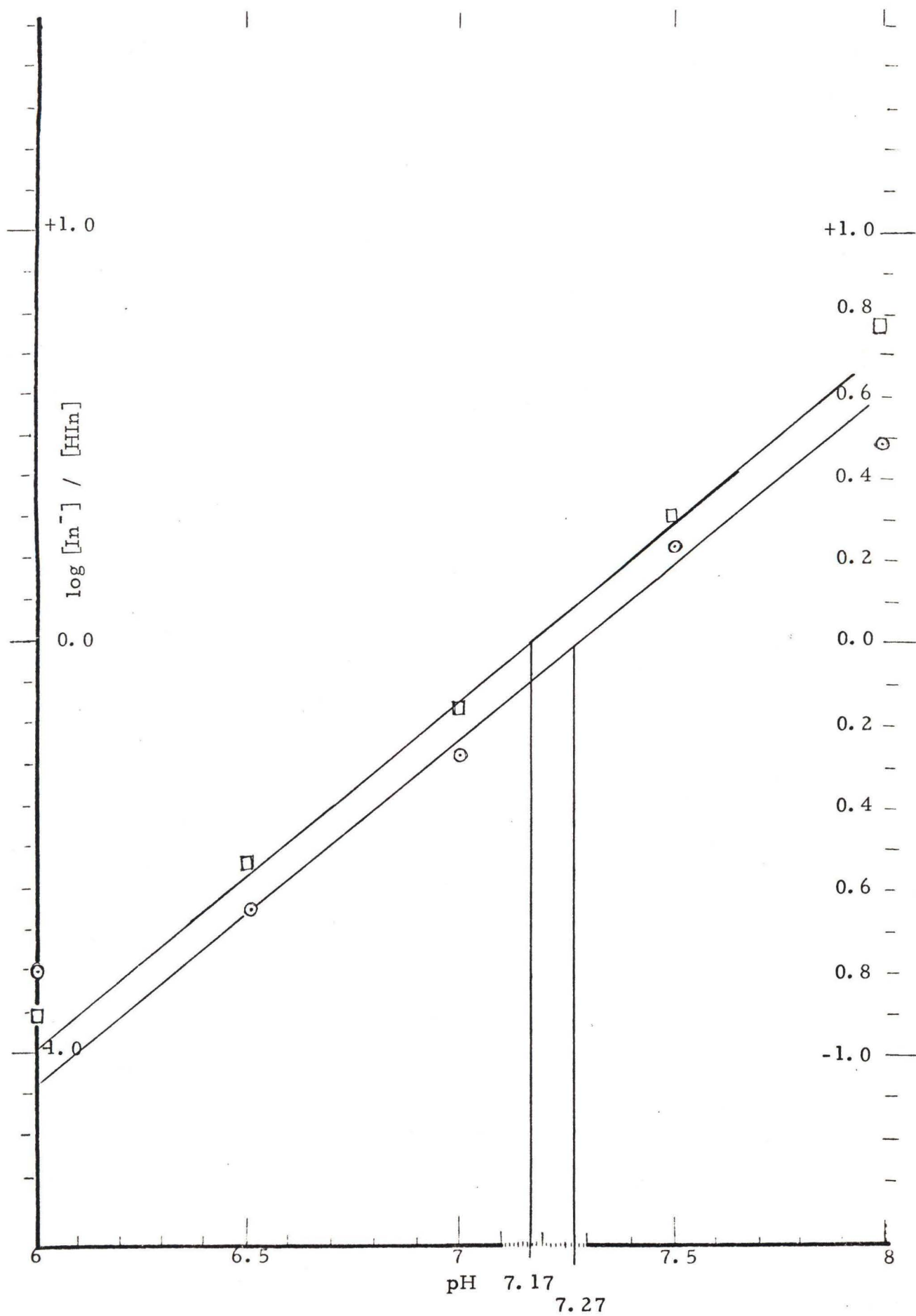
The results are plotted in Figure 28. The values of pK_{prot} obtained are 7.27(s. d.) and 7.17(p. e.).

Figure 28

Plot of $\log [\text{In}^-] / [\text{HIn}]$ versus pH at 446 nm for Brom Thynol Blue

⊙ = Self-Designed Spectrophotometer

□ = Perkin-Elmer Model 202 Spectrophotometer



B. Conductimetry

1. The Equivalence Point of an Acid-Base Titration

In this experiment HCl is titrated with NaOH using the self-designed conductance bridge to monitor the titration. Sodium hydroxide solutions were standardized with potassium acid phthalate, and the HCl solutions were standardized against NaOH. In each experiment a 50 ml aliquot of HCl, weaker by a factor of ten than the NaOH solution, was diluted to 150 ml with distilled water and the resistance was measured. Sodium hydroxide titrant was added in 0.5 ml increments, and the resistance measured after each addition until the end-point has been passed by the same volume needed to reach equivalence. The titration was repeated at different molarities, maintaining a factor of 10 difference between the acid and base (12). Typical titration data are shown in Tables 7 and 8 and Figures 29 and 30 for the titration of 0.0986M and 0.0102M HCl samples. Conductivity measurements were taken on the self-designed and the YSI Model 31 conductance bridges. The later instrument is calibrated to read from 0.2 to 2,500,000 ohms with a rated accuracy of 1%. All readings were taken with the same conductance cell.

Essentially identical results are obtained for the two instruments, and the resulting titration curves are superimposable. Any difference in measurement may be due to small differences in mixing time between readings and not to the bridges themselves. The equivalence point errors in titration of the 0.0986M and 0.0102M HCl samples are ± 0.07 ml and ± 0.02 ml, respectively. These values correspond to analytical errors

Table 7

Conductimetric Titration Data for 0.0986 M HCl Sample

Volume of Base Added, ml	Self-Designed Bridge		YSI Model 31 Bridge	
	R, ohms	$L \times 10^2$, mho	R, ohms	$L \times 10^2$, mho
0.0	54.6	1.83	54.4	1.84
1.0	84.1	1.19	84.1	1.19
2.0	104	0.96	102	0.98
3.0	142	0.70	140	0.71
3.5	164	0.61	162	0.62
4.05	199	0.50	200	0.50
4.5	246	0.41	248	0.40
5.0	229.5	0.44	229	0.44
5.5	190	0.53	190	0.53
6.0	171	0.58	170	0.59
6.5	147	0.68	148	0.68
7.0	127	0.79	128	0.78
8.0	111	0.90	110	0.91
9.0	95	1.05	94	1.06
10.0	87	1.15	86	1.16

Calculated number of milliliters needed to reach equivalence
point is:

$$X \text{ ml (1.0494M)} = 50 \text{ ml (0.0986M)}$$

$$X \text{ ml} = 4.9300/1.0494 = \underline{4.70 \text{ ml}}$$

Table 8Conductimetric Titration Data for 0.0102M HCl Sample

Volume of Base Added, ml	Self-Designed Bridge		YSI Model 31 Bridge	
	R, ohms	$L \times 10^3$, mho	R, ohms	$L \times 10^3$, mho
0.0	537	1.862	537	1.862
1.0	660	1.515	660	1.515
2.0	840	1.190	841	1.189
3.0	1100	0.909	1100	0.909
3.5	1300	0.769	1300	0.769
4.0	1720	0.581	1722	0.581
4.5	2100	0.476	2100	0.476
5.5	1540	0.649	1541	0.649
6.0	1340	0.746	1340	0.746
6.5	1200	0.833	1200	0.833
7.0	1080	0.926	1080	0.926
7.5	985	1.015	986	1.014
8.0	901	1.109	901	1.109
9.0	782	1.279	783	1.277
10.0	686	1.458	686	1.458

Calculated number of milliliters needed to reach equivalence point
is:

$$X \text{ ml } (0.1155\text{M}) = 50 \text{ ml } (0.0102\text{M})$$

$$X \text{ ml} = 0.5100/0.1155 = 4.42 \text{ ml}$$

Figure 29

Graph of Conductimetric Acid-Base Titration

Sample: 50 ml of 0.0986M HCl

Titrant: 1.0494M NaOH

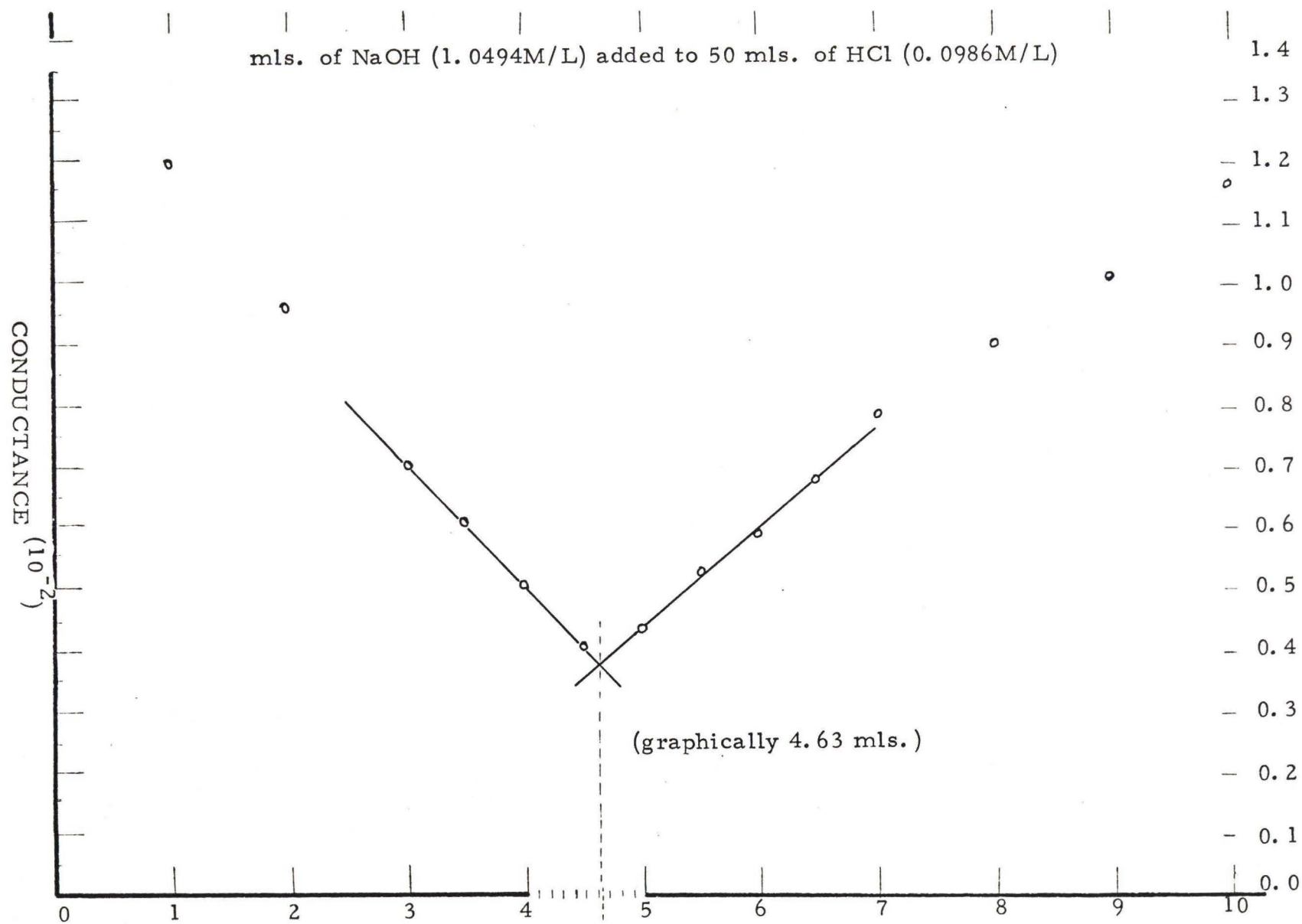
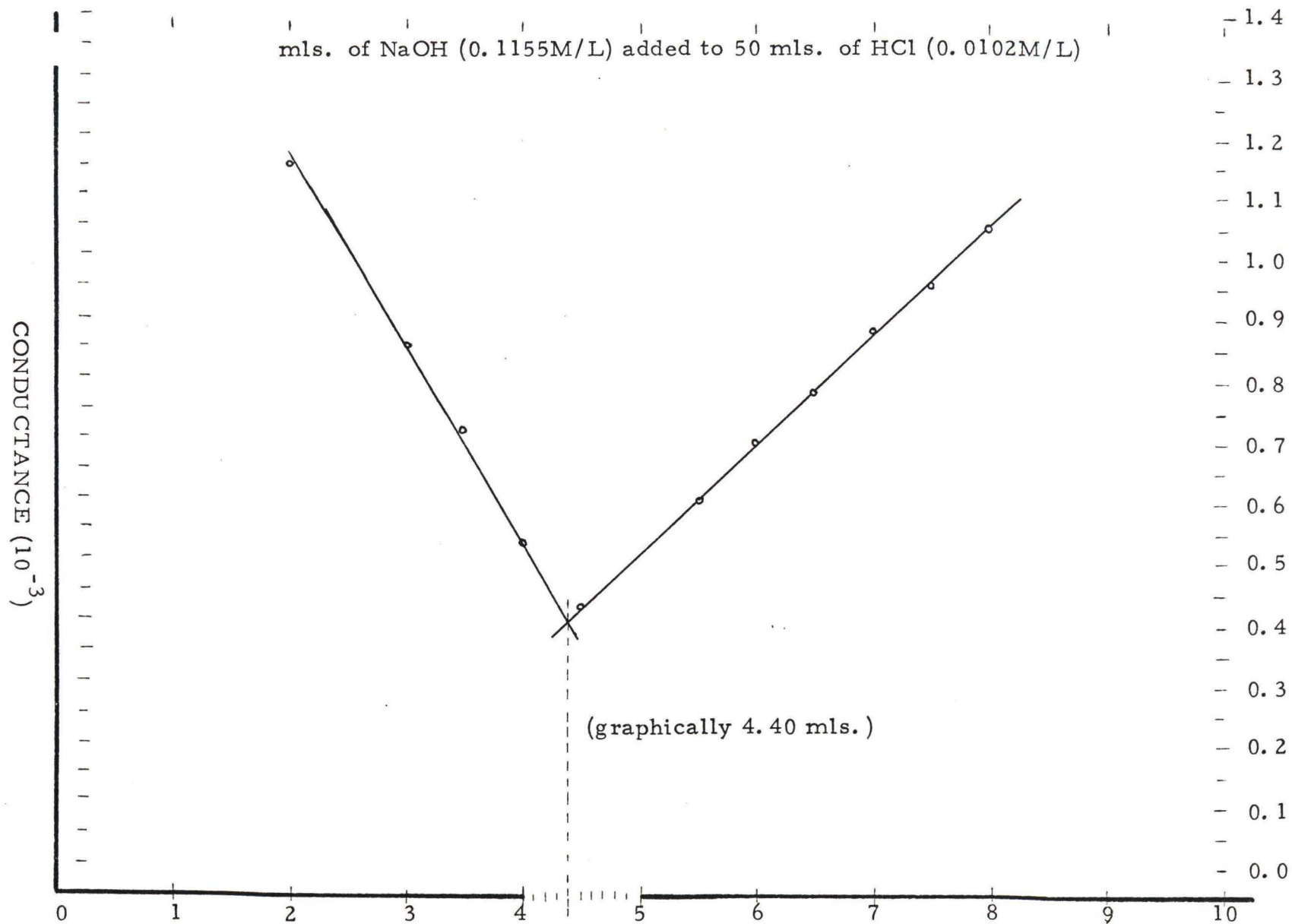


Figure 30

Graph of Conductimetric Acid-Base Titration

Sample: 50 ml of 0.0102M HCl

Titrant: 0.1155M NaOH



of $\pm 1.5\%$ and $\pm 0.5\%$ indicating the accuracy of the self-designed bridge.

2. Determination of the Number of Dissociable Ions in Metal Complexes

In this experiment the number of dissociable ions in two metal complexes are determined by conductance measurements. The metal complexes carbonatotetraamminecobalt(III)nitrate, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$, and chloropentaamminecobalt(III)chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were prepared and analyzed by the procedures outlined in Angelici (13). By measuring the conductivity of equally concentrated solutions of these complexes, it is possible to tell if a formula unit contains 2, 3, 4, or more dissociable ions. Molar conductances, Λ_M , may be used to determine the number of ions present in a given salt by comparison to measurements on substances of known ionic composition. General ranges of Λ_M for 2, 3, 4, and 5 ion conductors at 25°C are tabulated as follows (14):

<u>Number of Ions</u>	<u>Λ_M</u>
2	118 - 131
3	235 - 273
4	408 - 435
5	~ 560

The experiments were carried out with the Self-Designed (s. d.) and YSI Model 31 (y. s. i.) conductance bridges at 22°C . It was first necessary to determine the cell constant as accurately as possible at this temperature. Values given earlier in this writing for the specific

conductance of a 0.02M KCl solution were $L_{18^{\circ}\text{C}} = 0.002394$ and $L_{25^{\circ}\text{C}} = 0.002768 \text{ mho cm}^{-1}$. The extrapolated value for 0.02M KCl at 22°C was $0.002608 \text{ mho cm}^{-1}$. The measured resistances for the cell containing 0.02M KCl on the two instruments were

$$R_{(\text{s. d.})} = 381 \underline{\Omega}$$

and

$$R_{(\text{y. s. i.})} = 380 \underline{\Omega}$$

Using the formula $k = R(L)$ the following cell constants were obtained:

$$k_{(\text{s. d.})} = 0.002608 (381) = 0.9936 \text{ mho cm}^{-1}$$

and

$$k_{(\text{y. s. i.})} = 0.002608 (380) = 0.9910 \text{ mho cm}^{-1}$$

Next, the resistances were measured for 0.001M aqueous solutions of the two octahedral Co(III) complexes. The values for the carbonate complex were:

$$R_{(\text{s. d.})} = 8205 \underline{\Omega}$$

and

$$R_{(\text{y. s. i.})} = 8200 \underline{\Omega}$$

The values for the chloride complex were:

$$R_{(s.d.)} = 3790 \underline{\Omega}$$

and

$$R_{(y.s.i.)} = 3788 \underline{\Omega}$$

The specific conductances for both complexes are calculated from the relationship:

$$L = k/R$$

For the carbonate complex, the data are:

$$L_{(s.d.)} = 0.9936/8205 \underline{\Omega} = 1.211 \times 10^{-4} \text{ mho cm}^{-1}$$

and

$$L_{(y.s.i.)} = 0.9910/8200 \underline{\Omega} = 1.208 \times 10^{-4} \text{ mho cm}^{-1}$$

For the chloride complex, the data are:

$$L_{(s.d.)} = 0.9936/3790 \underline{\Omega} = 2.621 \times 10^{-4} \text{ mho cm}^{-1}$$

and

$$L_{(y.s.i.)} = 0.9910/3788 \underline{\Omega} = 2.616 \times 10^{-4} \text{ mho cm}^{-1}$$

At this point the molar conductances, $\Lambda_{\underline{M}}$, are calculated from equation 17 with \underline{c} expressed in moles/liter. The data for the carbonate complex are:

$$\underline{\Lambda}_M(\text{s. d.}) = 10^3(1.211)10^{-4} \text{ mho cm}^{-1}/10^{-3} = 121.1$$

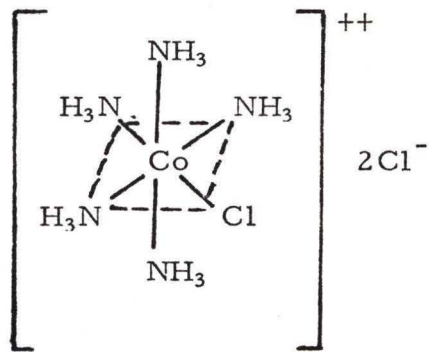
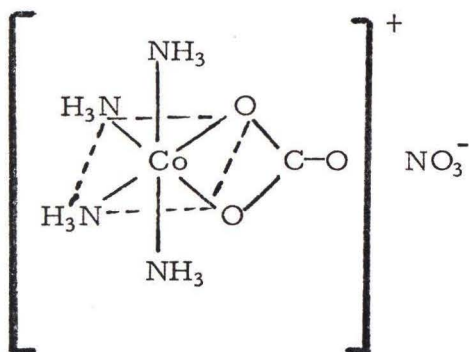
$$\underline{\Lambda}_M(\text{y. s. i.}) = 10^3(1.208)10^{-4} \text{ mho cm}^{-1}/10^{-3} = 120.9$$

and for the chloride complex are:

$$\underline{\Lambda}_M(\text{s. d.}) = 10^3(2.621)10^{-4} \text{ mho cm}^{-1}/10^{-3} = 262.1$$

$$\underline{\Lambda}_M(\text{y. s. i.}) = 10^3(2.616)10^{-4} \text{ mho cm}^{-1}/10^{-3} = 261.6$$

All values found are in keeping with the literature values, which indicate that two ions are formed on dissociation of carbonate complex and three ions on dissociation of the chloride complex. These results are in agreement with the structural formulae:



C. Polarimetry

The experimental data discussed in this section were taken on the self-designed and Steeg and Reuter Type SR-6 polarimeters. These instruments were used to measure optical rotation in two experiments on the specific rotation and inversion of sucrose and specific and molecular rotation of the optical isomers of tris(ethylenediamine)cobalt(III), Co(en)_3^{3+} .

1. Specific Rotation and Inversion of Sucrose

A polarimeter cell was filled with distilled water and both instruments were adjusted to give a zero reading on the verniers. A 10% sucrose solution in water was prepared according to the directions of Willard, Merritt and Dean (15). The observed rotations were:

$$\begin{aligned}\alpha_{\text{obs. (s.d.)}} &= +7^\circ \\ \alpha_{\text{obs. (SR-6)}} &= +6.8^\circ\end{aligned}$$

The specific rotation were then calculated from equation 18 to be:

$$(\text{s.d.})[\alpha]_D^{22.5} = +7^\circ (100)/(1) 10 = +70^\circ$$

$$(\text{SR-6})[\alpha]_D^{22.5} = +6.8^\circ (100)/(1) 10 = +68^\circ$$

The sucrose solution was denatured with hydrochloric acid by transferring 50 ml of the stock solution into a 100 ml flask and adding 25 ml of water and 5 ml of concentrated HCl. The flask was maintained at 69°C for 15 minutes in a water bath. The contents were cooled to

22°C, the thermometer rinsed with distilled H₂O, and the flask filled to the 100 ml mark. The solution was mixed thoroughly and measurements were taken immediately. Since the sucrose was diluted by this procedure, the measured rotation must be multiplied by two in order to obtain the correct values of observed rotation:

$$\alpha_{\text{obs. (s.d.)}} = -1.5^{\circ} (2) = -3^{\circ}$$

$$\alpha_{\text{obs. (SR-6)}} = -1.8^{\circ} (2) = -3.6^{\circ}$$

The specific rotation for each assembly becomes:

$$(\text{s.d.}) [\alpha]_{\text{D}}^{22.5} = -3^{\circ} (100)/(1) 10 = -30^{\circ}$$

$$(\text{SR-6}) [\alpha]_{\text{D}}^{22.5} = -3.6^{\circ} (100)/(1) 10 = -36^{\circ}$$

In this experiment sucrose is denatured in the presence of acid to fructose and glucose. Since fructose is more levorotatory than glucose is dextro-rotatory the resulting rotation is to the left. The observed changes in optical activity is referred to as the inversion of sucrose. The literature reports the following values for specific rotations of the sugars (16):

$$\text{Sucrose } [\alpha]_{\text{D}}^{20} = +66.5^{\circ}$$

$$\text{D-Glucose } [\alpha]_{\text{D}}^{20} = +52.5^{\circ}$$

$$\text{D-Fructose } [\alpha]_{\text{D}}^{20} = -92^{\circ}$$

It is obvious that if D-fructose and D-glucose are produced in equal

amounts upon complete denaturization of sucrose, the specific rotation of the mixture would be $-92^{\circ} + 52.5^{\circ}$, or -39.5° . The experimental values obtained on the two instruments give satisfactory results in this regard.

2. Specific and Molecular Rotation of Co(en)_3^{3+}

In this experiment the octahedral enantiomers of Co(en)_3^{3+} were prepared and purified as their iodide salts according to procedures described by Angelici (17). One gram of each isomer was dissolved in 20 ml of water, and the polarimeter cell was filled with this solution. For the dextrorotatory isomer, $(+)\text{Co(en)}_3\text{I}_3 \cdot \text{H}_2\text{O}$ the following data were obtained on the two instruments:

$$\alpha_{\text{obs. (s. d.)}} = 4.2^{\circ}$$

$$\alpha_{\text{obs. (SR-6)}} = 4.3^{\circ}$$

Therefore, the specific rotations are:

$$(\text{s. d.})[\alpha]_{\text{D}}^{22.5} = 4.2(100)/(1)5 = 84^{\circ}$$

$$(\text{SR-6})[\alpha]_{\text{D}}^{22.5} = 4.3(100)/(1)5 = 86^{\circ}$$

The data obtained on the two instruments for the levorotatory isomer, $(-)\text{Co(en)}_3\text{I}_3 \cdot \text{H}_2\text{O}$, were as follows:

$$\alpha_{\text{obs. (s. d.)}} = -4.4^{\circ}$$

$$\alpha_{\text{obs. (SR-6)}} = -4.4^{\circ}$$

consequently,

$$(\text{s. d.})[\alpha]_{\text{D}}^{22.5} = -4.4(100)/(1)5 = -88^{\circ}$$

$$(\text{SR-6})[\alpha]_{\text{D}}^{22.5} = -4.4(100)/(1)5 = -88^{\circ}$$

The formula for calculating molecular rotation is given in Equation 19 as:

$$M_{\text{D}} = (\text{gfw})[\alpha]_{\text{D}}/100$$

where gfw is the gram-formula weight of $\text{Co(en)}_3\text{I}_3 \cdot \text{H}_2\text{O}$. The calculated molecular rotations are:

$$(\text{s. d.}) M_{\text{D}} = 637.96(84^{\circ})/100 \quad \underline{535.89^{\circ}}$$

$$(\text{SR-6}) M_{\text{D}} = 637.96(86^{\circ})/100 \quad \underline{548.64^{\circ}}$$

$$(\text{s. d.}) M_{\text{D}} = 637.96(-88^{\circ})/100 \quad \underline{-561.40^{\circ}}$$

$$(\text{SR-6}) M_{\text{D}} = 637.96(-88^{\circ})/100 \quad \underline{-561.40^{\circ}}$$

The literature reports (18) that the observed, specific, and molecular rotations for the two enantiomers are $\pm 4.5^{\circ}$, $\pm 89^{\circ}$, and $\pm 567.78^{\circ}$, respectively.

V. DISCUSSION

The object of this thesis was to construct instruments that functioned well at a reasonably low cost. In the experimental section the success of the instruments was demonstrated through a comparison of their performance with that of commercial models. The experiments performed were ones that could be used for instructional purposes and executed in a simple manner by students.

The self-designed spectrophotometer functions well, is portable, and is relatively inexpensive. The instrument reproduces spectra well at long wave lengths; however, its performance is less satisfactory in the short wavelength (violet) region. This was caused by a combination of low source intensity and photocell sensitivity, thus suggesting a possible area for improvement. The results of the experiments indicate that the spectrophotometer faithfully reproduces spectra, demonstrates the Beer-Lambert law, and performs satisfactorily in simultaneous analysis of a two-component mixture and in measuring the pK_{prot} of an indicator. The constructed instrument is therefore reliable for purposes of laboratory instruction and teaching principles of spectrophotometry.

When compared to commercial models, the conductance bridge is accurate as well as inexpensive. It is somewhat limited in measurements of extremely low conductances, but this deficiency could be corrected by minor changes or additions to the circuitry. The present design is more accurate than commercial models in measurements of highly conducting solutions. The bridge has satisfactory analytical accuracy for

acid-base conductimetric titrations and is effective in determining the number of dissociable ions in a metal complex. On this basis it is concluded that the bridge can be very useful for instructional purposes.

The polarimeter provided adequate measurements in experiments on the specific rotation and inversion of sucrose and the specific and molecular rotation of optical isomers of Co(en)_3^{3+} . Improvements are desirable in the accuracy of the vernier and quality of the polarizing lenses. Nevertheless the self-designed polarimeter is effective in demonstrating the principles of optical activity.

Using these ideas that have been suggested instrumental analysis can easily be introduced into the chemistry curriculum. Many instruments are as simple as the ones discussed, but limited time was available for the completion of this work. With a basic understanding of the concepts of design and construction presented in this thesis, the reader should become confident in approaching his own problems in the laboratory and classroom.

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