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The Design, Construction, and Application of a Multibeam Fiber Optics Photometric Titrator

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THE DESIGN, CONSTRUCTION, AND APPLICATION OF A MULTIBEAM FIBER OPTICS PHOTOMETRIC TITRATOR

by

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INTRODUCTION

Photometric Titrations

Historical

The determination of titration end points by means of photometric measurements dates back to 1918. Tingle (1), using a pocket spectroscope, isolated desired colors to detect end points visually. Müller and Partridge (2) in 1928, described an instrument capable of performing automatic photometric titrations. Although the potential of photoelectric colorimeters and spectrophotometers for automatic titrations had been demonstrated, relatively little use was made of this technique for many years. Many investigators (3, 4) seemed to prefer manual instruments which required point by point plotting of data. Later, Malmstadt and Gohrbrandt (5) modified a Cary recording spectrophotometer for automatic photometric titrations. Other workers (6, 7, 8) felt it more advantageous to modify lower cost instruments such as a Beckman Model B or DU spectrophotometer for automatic titrations.

Malmstadt and Roberts (9), using a modified DU, introduced the first substantial improvements in automatic photometric titrations since Müller and Partridge (2). Malmstadt's instrumentation allowed the operator to obtain first, second, and third derivatives of the titration plot during the course of the titration. The second or third derivative pulse could be selected to fire a thyratron which in turn actuated a solenoid, terminating the titration automatically.

Although automatic termination of the titration was not new, this was the first time a derivative technique had been employed.

Lingane (10, 11) utilized an interruption circuit to terminate the titration when the output voltage of the detector reached a preset value relative to a internal reference. The Beckman Automatic Titrator (12) employed an "anticipation circuit" which interrupted the normal continuous flow of current during coulometric generation of titrant, and slowly approached the equivalence point by allowing pretimed increments of current to pass. Originally this circuit was used in conjunction with potentiometric end point determinations; however no modification for photometric detection is required (13).

Principles

The fundamental law of light absorption governing photometric titrations is the Bouguer-Lambert-Beer Law (14, 15, 16). Its general form is given by equation 1,

$$A_\lambda = -\log T_\lambda = \sum_{i=1}^{i=n} a_i b c_i \qquad (1)$$

where A_λ signifies the absorbance at wavelength λ; T_λ is the corresponding transmittance; a_i is the absorptivity of an absorbing species "i" at wavelength λ; b is the length of the light path through the absorbing medium; c is the concentration of the light absorbing constituent "i", and n represents the total number of distinctive moieties absorbing at wavelength λ.

Certain limitations in the application of the law arise from a number of assumptions made in its derivation (17). Of principal

concern in photometric titrations are the restrictions of monochromatic radiation and that each absorbing species be an independent moiety, free from any interaction with any of its neighboring species, a condition ideally realized at infinite dilution.

The Bouguer-Lambert-Beer's Law relationship predicts that the absorbance is proportional to the concentration of the absorbing ions in dilute solutions. From this it may be deduced that in a titration where a single species absorbs, whether it be the titrant, the analyte, or a reaction product, a plot of absorbance versus volume of titrant added will consist of two straight lines intersecting at the equivalence point. In practice, however, considerable curvature in the vicinity of the equivalence point is observed due to the existing states of chemical equilibria. This curvature is of little concern in photometric titrations since the equivalence point volume is readily ascertained by graphically extrapolating the initial and final linear segments of the titration plot to their point of intersection. Theoretical titration curves may be calculated from Beer's Law and the reaction stoichiometry if the appropriate equilibrium constants are known. The shapes of photometric titration curves are dependent upon the concentrations and the combined spectral characteristics of the titrant, analyte, and products of the reaction at the wavelength used. Figure 1 illustrates a number of typical plots one might encounter (18, 19).

Advantages and Applications

Photometric titrations have a number of distinct advantages over conventional titrations. First, they serve as an unbiased means of

detecting color intensity changes and perhaps equally important, they are capable of observing a relatively narrow band width of light thus minimizing difficulties from color masking by other absorbing species. Consequently a greater degree of precision may be obtained than is often possible by visual techniques. Thirdly the photometric titrator has a much lower threshold of detection over a greater wavelength range than has the eye. The photometric titrator also permits visual observation as well as graphical recording of the entire course of a titration. Subsequently, a graphical determination of the equivalence point may be made rather than an observation of an end point.

Areas of particular applicability for the photometric titration method are often found with reactions which are incomplete at the equivalence point. Examples of incomplete reactions are: precipitation of moderately soluble substances, neutralization of very weak acids and bases, oxidation-reduction reactions involving couples with potentials not greatly differing in magnitude, and reactions which are slow to come to equilibrium in the vicinity of the equivalence point. Since the equivalence point in a photometric titration is determined only from the initial and final segments of the titration plot, little or no consideration is given to the behavior of the system in the vicinity of the equivalence point.

Photometric titration of precipitation reactions to maximum turbidity offers certain significant advantages over absolute turbidimetric measurements (20, 21). The multitude of experimental factors which contribute to the lack of reproducibility in the light scattering characteristics of suspensions are relatively unimportant in the titra-

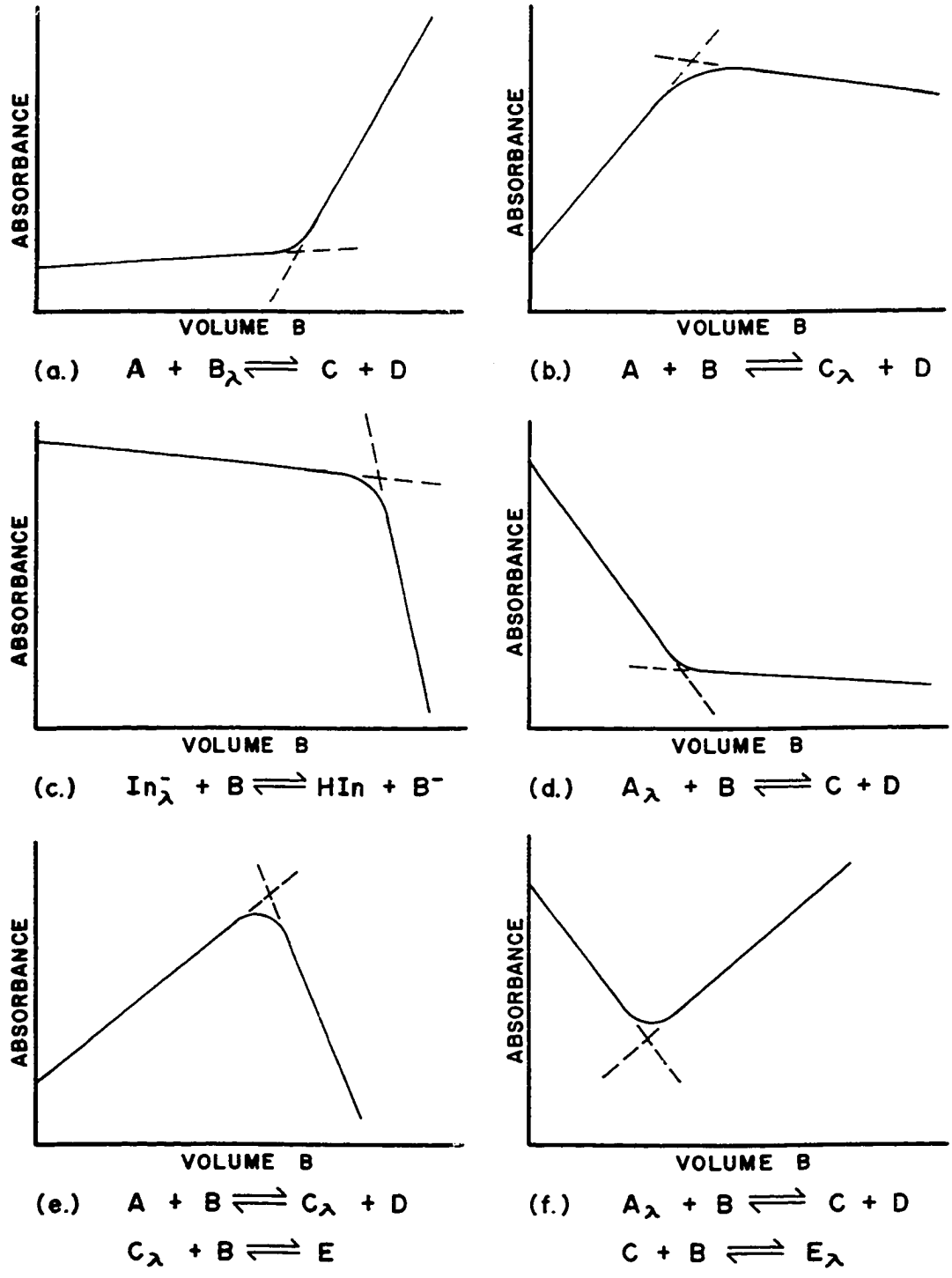


FIGURE 1

Typical Photometric Titration Plots.
Denotes an Absorbing Species at the Selected Wavelength.

tion method. If a relatively stable colloid with a constant degree of dispersion is obtained the relative changes in transmittance during the course of an individual titration is the only factor of concern. Absolute turbidimetric measurements, however, require highly reproducible experimental parameters from sample to sample and under a variety of conditions.

Relative to other instrumental techniques of equivalence point detection, photometric titrations may often be performed at low concentrations where potentiometric inflection points are barely perceptible. In solutions of high ionic strength, where conductometric methods of equivalence point detection are often inadequate, the photometric titration experiences little or no difficulty. It is also advantageous to use the photometric detection system in conjunction with titration systems utilizing coulometrically generated titrant. The photometric system is free from the electrical interactions frequently encountered when equivalence point detection methods such as potentiometry, amperometry, and conductivity are used. Due to the vast number of chemical systems which are adaptable to color changes at the equivalence point, photometric titrations have a wide range of applicability.

Photometric Titrators

General design

The instrumentation required for photometric titrations is often simpler than for colorimetric determinations since we are interested only in a change in relative absorbance. Consequently photometric titrators do not require features such as: linear amplifiers, high

resolution monochromators, reproducible slit widths, and matched cells, to name a few.

Photometric titrators consist of six basic elements: a light source, a means of wavelength selection, a cell containing the solution to be titrated, a mixing apparatus, a detector, and some type of readout device. Some of the early photometric titrators employed tungsten or mercury vapor lamps, filters, beakers, motor driven stirrers, barrier layer cells, and galvanometer readout circuits (22, 23). In addition to the six basic design features, most modern photometric titrators have built into them some method of terminating the titration at or near the equivalence point or some preset point, if desired. The method of delivering titrant during the titration may be accomplished by any one of the following: a constant head buret with a solenoid valve, a constant drive buret, or the constant current coulometric generation of the titrant. Currently the latter two methods appear to be the most popular. Detectors which have been used consist of photovoltaic cells, photoconductive cells, photojunction diodes, photodiodes (vacuum and gas-filled), and photomultipliers. The first two detectors have the advantage of requiring simple circuitry, but occasionally lack the desired sensitivity and also exhibit fatigue and hysteresis effects (24, 25). Photodiodes and photomultipliers have become very popular in spectrophotometers and consequently have been widely adopted as detectors in photometric titrators requiring high sensitivity. To date, most readout systems in photometric titrators produce data proportional to the transmittance of the solution rather than absorbance. While this is adequate for most purposes, occasionally it is desirable

to have a linear concentration relationship such as that given by absorbance readout systems.

Limitations

From their inception photometric titrators have been limited in the type of titrations that could be performed as a result of their basic design. The range of temperatures at which titrations could be performed has often been limited by the type of cell and light path. Low temperature titrations frequently fog the cells or optics due to condensation unless the light path is purged with a dry gas (26). High temperature titrations generally have not been attempted because of the problem of modifying the instrument for heating the solution without affecting the detector or optics. In some instances, the kinematic considerations of cell location from titration to titration can give rise to serious problems affecting sensitivity and reproducibility (27). All photometric titrators designed thus far, with the exception of the instrument of Nichols and Kindt (4), have been single beam instruments and therefore have no means of compensating for source variations during the course of the titration.

Fiber optics photometric titrators

Currently only one fiber optics photometric titrator is known (28). Unfortunately, this titrator has produced no new innovations in photometric titrimetry other than the use of fiber optics. Also the limitation to single beam applications has been necessitated because of its design. This titrator does, however, have the advantage of being able to accommodate high and low temperature reactions without difficulty.

MULTIBEAM FIBER OPTICS PHOTOMETRIC TITRATOR

General Design and Layout

Optical and electrical design

A multibeam fiber optics photometric titrator differs optically from previous photometric titrators in that more than one "optical channel" may be used to follow phenomena rising from one or more origins. As a consequence of its capabilities a multibeam instrument can be extremely versatile in its application to a wide variety of titrations and measurements which until now have not been considered within the realm of photometric titrators. The prototype of this instrument must, of necessity, be limited in electro-optical configurations since total versatility is not likely to be realized in any single instrument because of the seemingly infinite number of possible combinations. The general principles involved in the double beam design can be extended to a larger number of beams, subject to certain spatial and economic limitations. However, only the more fundamental configurations of dual and single beam operation will be considered in the forthcoming paragraphs.

A multibeam photometric titrator may have numerous optical components. Figure 2 is just one of many possible arrangements. The particular optical configuration employed in any given measurement will be determined by the nature of the phenomenon being measured. Various optical configurations may be obtained through the use of a series of shutters, not shown in Figure 2, which are closed for elements

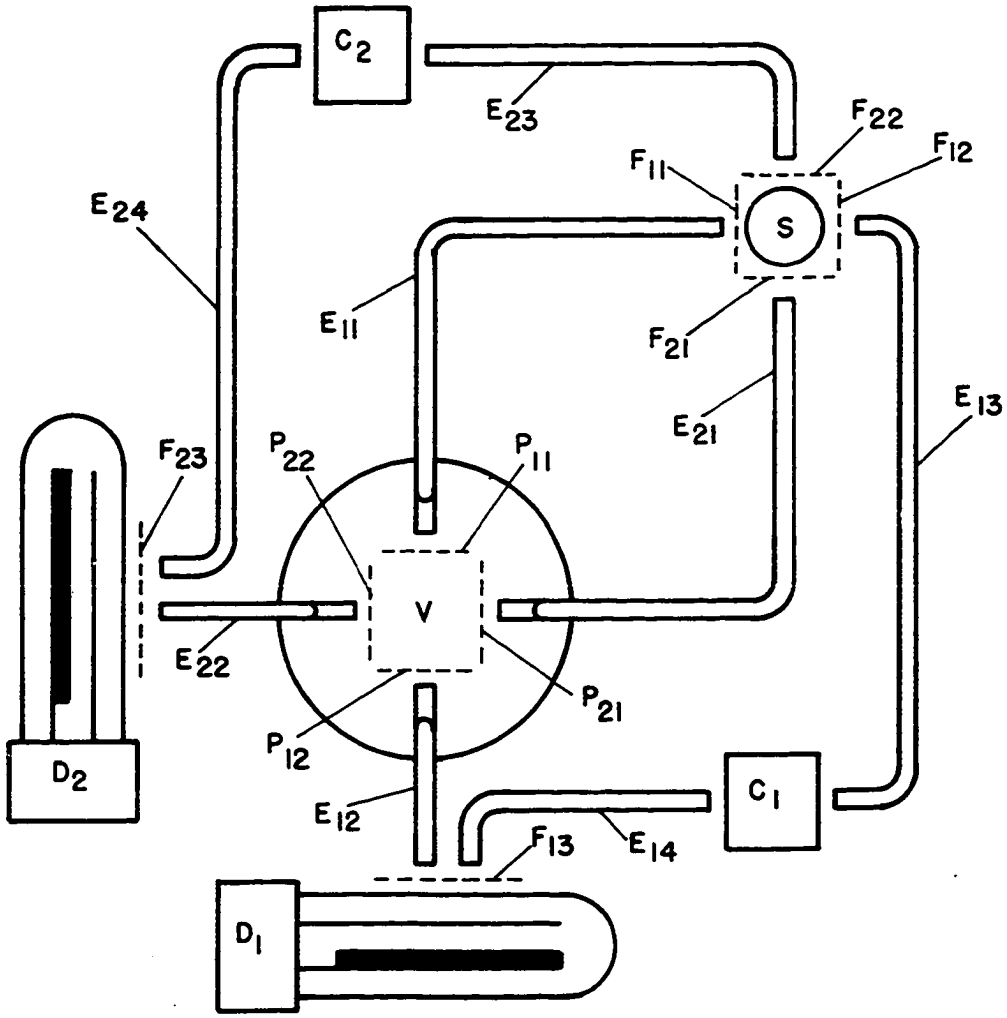
not being utilized and opened for those elements which produce the desired light pathways within the instrument.

An even greater degree of versatility may be achieved if the multi-beam photometer has various options of signal combination and computation for display on the readout device. These options may be obtained by various electrical-electronic configurations some of which are shown in Figure 3. In all configurations, solid state operational amplifiers may be used, taking advantage of their stability, low noise output, and impedence input characteristics when and where these characteristics are required. In addition, the small size of the power supply associated with solid state circuitry is ideal for this application. The following discussion will be a brief description of each element shown in Figure 3. It should be noted that constant, k, found in several of the equations, may be selected by the adjustment of various circuit parameters.

Figure 3a illustrates an inverting amplifier circuit. Since the summing point, S, is a "virtual ground", the effective input resistance of this circuit is approximately R_i. As this circuit cannot function properly with large values of R_i, its application must be limited to moderate and low impedence circuitry.

Figure 3b illustrates a simplified divider or ratio circuit. This circuit is inverting, and k is a weighing factor which is dependent upon amplifier characteristics. It should be noted, however, that the operational amplifier shown actually represents several amplifiers and associated components which are required to perform this function.

Figure 3c illustrates a logarithmic amplifier. A transistor is employed in the feedback network in order to generate the function.



C - CELLS
D - DETECTORS
E - LIGHT GUIDES
F - FILTERS
P - POLARIZERS
S - SOURCE
V - TITRATION VESSEL

FIGURE 2

Optical System of a Dual Beam Photometric Titrator

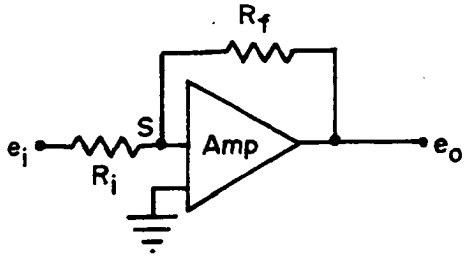
Drift is a serious problem in logarithmic circuitry since the transistors which generate the function are severely temperature sensitive. Temperature correction circuits in conjunction with these transistors are therefore necessary in order to utilize this circuit effectively.

Figure 3d illustrates a simple differentiator. This circuit is inherently noisy and unstable and consequently lower quality operational amplifiers may be used in this circuit since noise and drift are not as critical as in other applications.

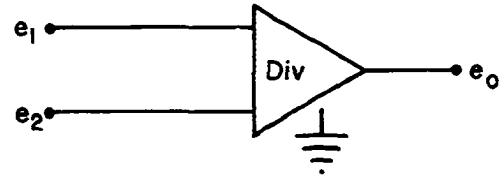
Figure 3e illustrates an adding module. In principal, this is the same circuit as shown in Figure 3a and is subject to the same limitations.

Figure 3f illustrates a non-inverting amplifier which is used as a buffer between high and low impedence components. The most useful property of this configuration is the high input impedence which approaches the common mode resistance of the operational amplifier, usually from 10 to 500 megohms. Another advantage of this configuration is the reduced effect of noise and drift compared with many inverting amplifiers.

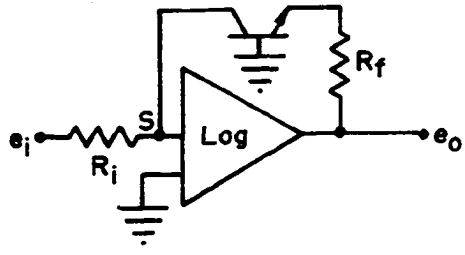
Many variations on the circuits illustrated above are available in handbooks on operational amplifier circuitry (29, 30, 31, 32). Associated solid state circuitry at the amplifier outputs for controlling titrant delivery, print-out devices, clocks, etc., has not been mentioned but may be easily incorporated into the system. Direct concentration readout circuitry may be assembled from solid state devices similar to those described above, however, this particular aspect was not considered to be within the realm of this investigation. This would undoubtedly be desirable for situations requiring a large number of repetitive titrations.



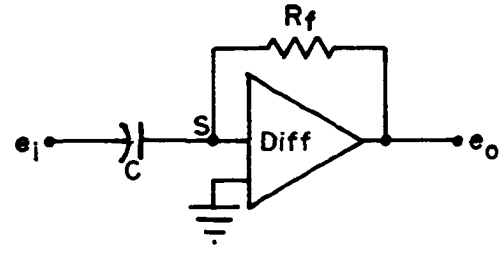
(a.) $e_o = -\frac{R_f}{R_i} e_i$



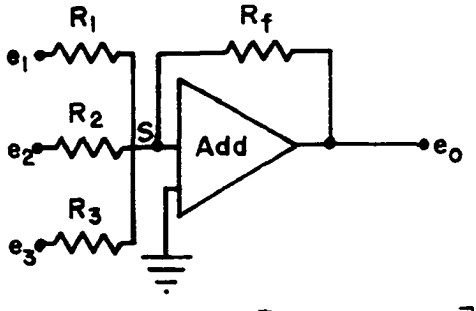
(b.) $e_o = -k \frac{e_1}{e_2}$



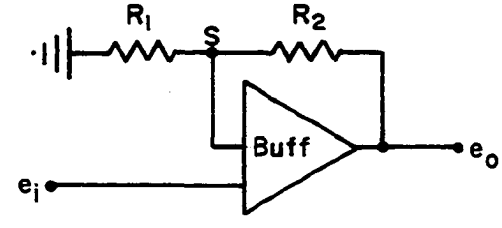
(c.) $e_o = -k_1 \log e_i + k_2$



(d.) $e_o = -R_f C \frac{de_i}{dt}$



(e.) $e_o = -R_f \left[\frac{e_1}{R_1} + \frac{e_2}{R_2} + \frac{e_3}{R_3}\right]$



(f.) $e_o = \left[\frac{R_1 + R_2}{R_1}\right] e_i$

FIGURE 3

Functional Electronic Modules

Functional assemblage:

Colorimetric determinations can be performed utilizing the many combinations of optical and electrical modes illustrated in Figures 2, 3, and 4. Single beam operation may be obtained optically, as shown in Figure 2, by using either internal channel S, F_{12}, E_{13}, C_1, E_{14}, and D_1 or external channel S, F_{11}, E_{11}, V, E_{12}, and D_1. In order to display the resulting signal as transmittance, the signal path would utilize the following components shown in Figure 4: Buffer, E_{ref}, and Divider. If the transmittance-time derivative, dT/dt, is desired components Buffer, E_{ref}, Divider, Differentiator, and Recorder are utilized. However, if absorbance is desired, Buffer, E_{ref}, Divider, and Log are employed. If the operator desires an absorbance-time derivative, dA/dt, output, Buffer, E_{ref}, Divider, Log, Differentiator, and Recorder are used. Both external and internal channels can be utilized in a static mode, e.g. without titrant delivery, as might be desired in kinetic determinations. The external channel, however, will usually be utilized in a titration mode. Double beam colorimetric operation may be performed totally externally by means of optical elements S, F_{11}, E_{11}, V, E_{12}, and D_1; and S, F_{21}, E_{21}, V, E_{22}, and D_2. Half internal-half external operation may be obtained by utilizing S, F_{11}, E_{11}, V, E_{12}, and D_1; and S, F_{22}, E_{23}, C_2, E_{24}, and D_2. Totally internal operation may be accomplished with elements S, F_{22}, E_{23}, C_2, E_{24}, and D_2; and S, F_{12}, E_{13}, C_1, E_{14}, and D_1. Electrically these signals may be combined in a number of ways as previously indicated, except using D_2 in lieu of E_{ref}.

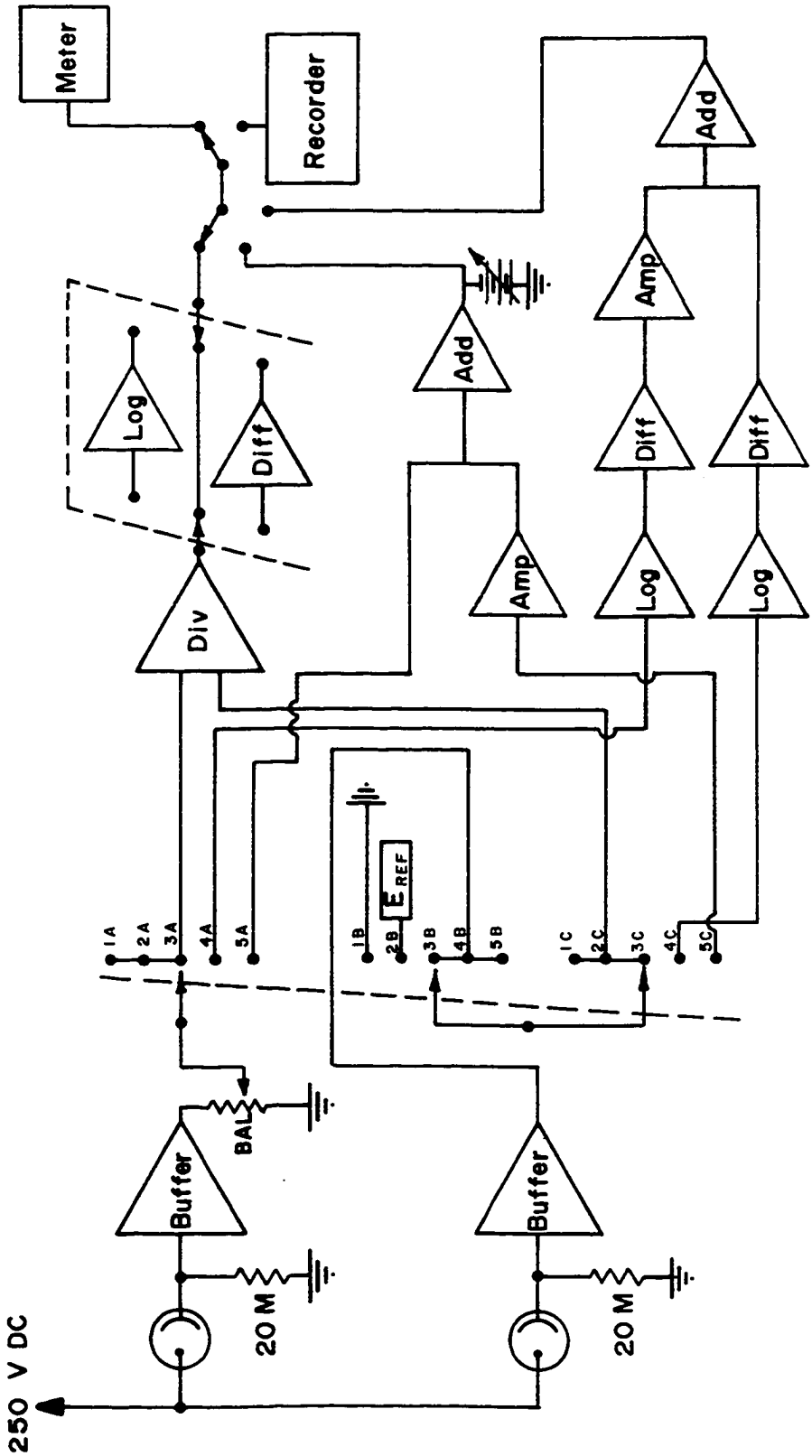


FIGURE 4

A Simplified Circuit Schematic of a
Dual Beam Photometric Titrator

By selecting two different, but appropriate, filters for the two beams, a procedure referred to as differential colorimetry, not to be confused with "relative absorbance spectrophotometry", (33) may be performed. Differential colorimetry may be defined as the simultaneous determination of the reactant at one wavelength and the formation of a product at a different wavelength during the course of a reaction. When applied to titrations having poor inflections at the equivalence point, this procedure greatly improves the level of detectibility and precision of the titration (34). In practice, this technique could be accomplished by taking the first derivative of each signal, using an inverting amplifier on one, adding the two signals, and displaying the sum.

Light scattering methods utilize electrical circuitry similar to that discussed for colorimetric measurements. The function dI/dt, where I is the light intensity, analogous to dT/dt and -d(log I)/dt analogous to dA/dt may be performed in the same manner as their analogs. The measurements may be taken during the course of the titration in V as shown in Figure 2 or as a static measurement in either V or C. Turbidimetric measurements, single or double beam, utilize the same optical pathways as colorimetric measurements. Nephelometric measurements, however, utilize a detector light path at right angles to that of the source, e.g. S, F_{11}, E_{11}, V, E_{22}, and D_2. An internal reference beam may also be utilized in this measurement to obtain additional stability if desired, e.g. S, F_{12}, E_{13}, C_1, E_{14}, and D_1.

The electrical systems for fluorescence measurements, single or double beam, are identical to the corresponding nephelometric systems. The optical system for fluorescence measurements is comprised of elements

S, F_{12}, E_{11}, V, E_{22}, F_{23}, and D_2 for single beam operation and S, F_{11}, E_{13}, C_1, E_{14}, and D_1 if an internal reference channel is desired. Fluorescence measurements utilizing a polarized source and/or polarized detector channel have been utilized by some workers for the determination of optically active fluorescent species (35, 36). The addition of polarizers P_{11} and/or P_{22} to the above optical system is the only modification necessary since the electrical system remains unchanged.

The determination of phosphorescence requires the same optical and electrical configuration as fluorescence. If, however, phosphorescence decay times are to be measured, the source must be modulated either electrically or mechanically. Again, all signals may be displayed as I or log I, dI/dt, or -d(log I)/dt. Titration or static modes of operation are applicable.

A chemiluminescent optical system might utilize a partial optical channel, e.g. V, E_{12}, F_{13}, and D_1; or C_1, E_{14}, F_{13}, and D_1. The electrical system for chemiluminescence would be identical to the single beam colorimetric system, except that I rather than T is being determined.

Polarimetric methods are similar in optical configuration to the single beam colorimetric system except for the addition of polarizers to the entrance and exit light guides. The polarizers may be rotated to produce minimum or maximum light intensity at the initiation of the titration. During the titration, a change in optical activity of the titrated species is observed by a corresponding increase or decrease in light intensity as observed by the detector (37, 38). A modification of the above procedure would be to have a servo-driven polarizer on one of the light guides and a fixed polarizer on the other light guide.

Through a null-balance system, the servo would drive the polarizer to maintain maximum or minimum light intensity through the system. In this procedure the position of the polarizer, determined by a potentiometer slaved to the servo, could be followed as a function of the volume of titrant added.

A polarimetric determination, analogous to the differential colorimetric method previously discussed, permits the simultaneous observation of the change in optical activity of a titrated species at two different wavelengths. Optical and electrical configurations are similar to the differential procedure with the exception of the addition of polarizers on all light guides in the titration vessel, V.

Since most optically active moieties are found in, or are themselves light absorbing media subject to change during a titration, it is often desirable to subtract the portion of the signal attributed to the absorbing species from the total signal. Thus the net signal change during the titration would represent only the change in optical activity of the species under study. Utilizing a reference channel with no polarizers, at the start of the titration, the intensity of light striking the reference detector may be represented by equation 2,

$$I = I_O - I_A \qquad (2)$$

where I_O is the intensity of light entering the solution and I_A is the intensity of light absorbed by the media during the titration. If at the beginning of the titration the polarizers are crossed, then the light intensity at the sample detector may be represented by

$$I = I_O + I_R - I_A - I_{AP} \qquad (3)$$

where I_R is the increased light intensity produced by the change in optical activity of the titrated species and I_{AP} is the intensity loss due to absorption by the polarizers. I_{AP} is a constant for a given wavelength and a given set of polarizers and may be experimentally determined prior to any polarization measurements. By subtracting equation 2 from equation 3 and evaluating I_{AP}, only the signal due to the change in optical activity is obtained. This mathematical operation can be obtained by using the circuits shown in Figures 3a and 3e.

To observe these changes would require a system for detecting optical activity, e.g. S, F_{21}, E_{21}, P_{21}, V, P_{22}, E_{22}, D_2 and a system for observing changes in transmittance at the wavelength in question, such as S, F_{11}, E_{11}, V, E_{12}, and D_1. Both signals pass from the detectors and through their respective buffers. Then the signal arising from the non-polarized channel is passed through an inverting amplifier and combined with the signal from the polarized channel at the input of an "addition" module. A voltage equivalent to I_{AP} is then "bucked off" the output of the "addition" module. The signal is finally displayed as I_R, dI_R/dt, or $-d(\log I_R)/dt$ vs. volume of titrant.

CONSTRUCTION

Components

Source

The most commonly used source in the visible region of the electromagnetic spectrum is the tungsten filament lamp with a glass envelope which produces a relatively high output from the near ultraviolet to the near infrared region. The glass envelope limits the spectral output below 350 nm to a level which is too small to be useful in photometric work. A tungsten filament lamp closely approximates black body behavior and the spectral distribution of its output, for all practical purposes, is governed by Planck's Law. The photocurrent generated by such a lamp is exponentially proportional to the voltage applied to the lamp,

$$I = KV^{x} \qquad (4)$$

where K is a proportionality constant and the exponent, x, has a value between 3 and 4 for tungsten lamps (39).

In single beam operation, photometric instruments generally have some means of minimizing source fluctuations such as a voltage regulation transformer or a regulated power supply. When using tungsten lamps requiring high currents, such as a No. 1133 bulb, a combination of an isolation transformer and a step down transformer was utilized. For lamps requiring currents under two amperes, a voltage regulated D.C. power supply was employed.

Figure 5 shows the schematic diagram of the voltage regulated D.C. power supply constructed for use with the photometric titrator. Basically, this power supply is a low voltage-medium amperage full wave rectifier formed by diodes D_5 and D_6 and "brute filtered" by capacitor C_4. The output of this rectifier at the base of transistor Q_2 is compared with the voltage at the base of transistor Q_1 from the wiper of the potentiometer. When the voltage at the base of Q_2 is less than the voltage at the base of Q_1, the current through Q_2 is increased which is reflected in a simultaneous increase in the current through Q_3. Transistor Q_3 acts as a current amplifying stage feeding a second current amplification stage, transistor Q_4. By varying the impedence or the amplification factor of the power transistors Q_3 and Q_4 from the magnitude of the current drain at Q_2, the voltage output at Q_4 will be made to equal the voltage at the base of Q_1. The maximum voltage output at Q_4 is limited to the output voltage of the full wave rectifier minus the IR drop through the power transistors. The RC network made up of R_5C_6 together with capacitor C_7 are used to prevent spurious oscillations produced by voltage transients. The RC network made up of R_2C_5 is used to prevent the demand for voltage at the output from rising instantaneously when the on-off switch is closed. The power supply was designed and tested to deliver 0 to 9 volts D.C. at 2 amperes maximum with less than 1% ripple. Regulation of the output voltage was found to be $\pm$ 0.10% for line voltage fluctuations of $\pm$ 30% and $\pm$ 0.01% for line voltage fluctuations of $\pm$ 5% at maximum rated voltage-current output.

When ultraviolet-transmitting fiber optics become available for photometric titrators, sources other than tungsten filament lamps

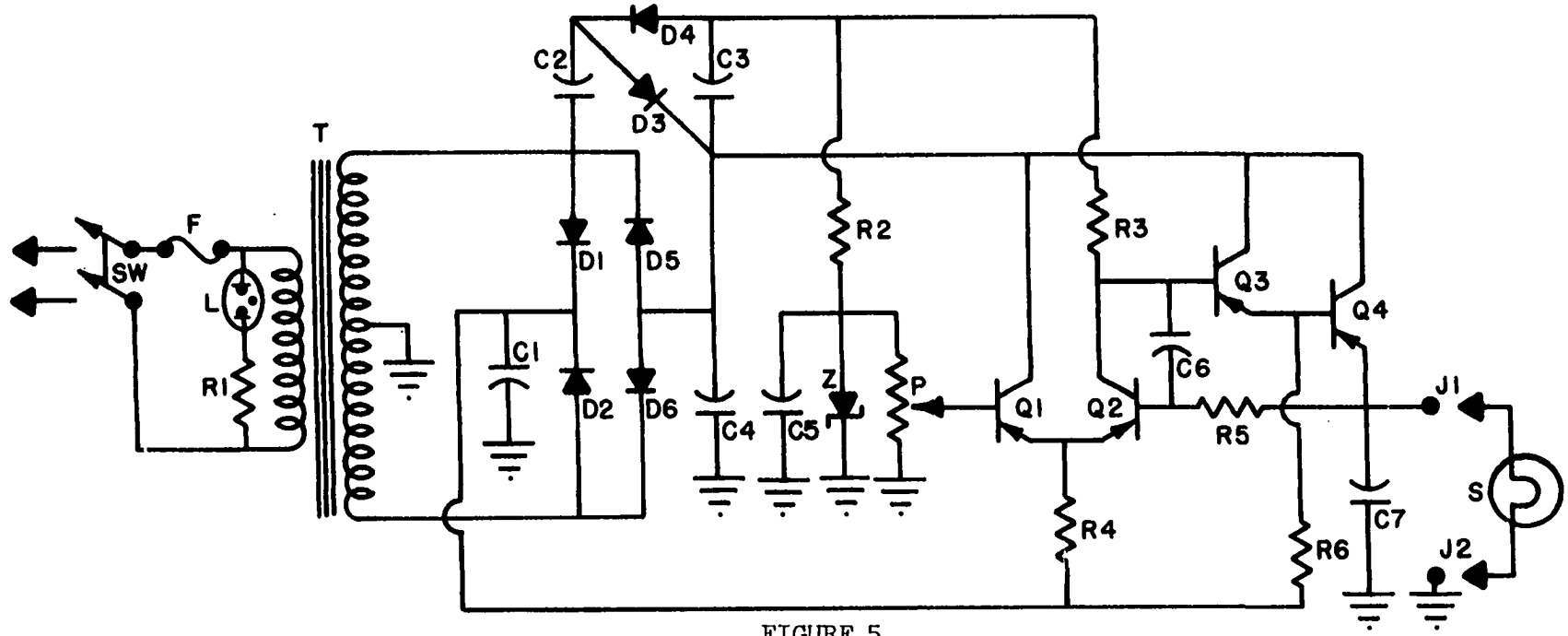


FIGURE 5

Voltage Regulated Power Supply

C_1, C_2, C_3, C_7 - 500 mfd, 50 V electrolytic
C_4 - 8000 mfd, 15 V electrolytic
C_5 - 100 mfd, 25 V electrolytic
C_6 - .004 mfd, 200 V silvered mica
D_1, D_2, D_3, D_4 - Silicon rectifiers, 500 ma, 600 PIV
D_5, D_6 - Silicon rectifiers - 15 A, 100 PIV
F - 5 - A Fuse and holder
J_1, J_2 - Banana jacks
L - Neon lamp, NE - 51
P- 20 K Linear taper potentiometer
Q_1, Q_2 - Transistors, 2N4061
Q_3 - Transistor, 2N2456 A
Q_4 - Transistor, 2N1100
Resistors: 1/2 watt, 10% unless otherwise indicated
R_1 - 120,000 ohms
R_2 - 4,300 ohms
R_3 - 6,800 ohms
R_4 - 2,200 ohms
R_5 - 4,700 ohms
R_6 - 10,000 ohms
S - Source
Sw - Switch, SPDT, 5A, 125 VAC
T - Transformer, primary-125,5A VAC, Secondary-18 VAC CT., 6A
Z - Zener diode, 10 V

will have to be considered. Sources such as mercury arc, high pressure xenon, hydrogen, and deuterium lamps produce spectra suitable for work in the ultraviolet region. The critical factors which must be considered in the implementation of these sources have been reviewed by Lewin (40). Unfortunately, the use of the sources described above greatly increases the complexity of the associated power supply circuitry. In addition to the high amperage and high voltage regulation circuitry, firing circuits for the lamps must also be incorporated. All optical components must be made of ultraviolet transparent materials which are often expensive and difficult to work with. As a result of the large quantities of heat evolved during their operation, high pressure lamps frequently require auxiliary cooling and associated safety interlocking circuitry.

Fiber optics

It has long been known that a smooth transparent cylinder, such as a glass rod, is capable of transmitting light be means of multiple internal reflections along its walls. This phenomenon also occurs when the rod is reduced to a small diameter, as in a fiber. Light, however, is not efficiently conducted unless total internal reflection within the fibers occurs. In principle, the conditions for internal reflection exist at any smooth interface between two transparent media where the refractive index of the outer medium is less than that of the inner medium, for example, between glass and air. Thus, a smooth glass fiber in air should conduct light relatively efficiently. In practice, however, one finds that the presence of minute defects and

contamination at the interface interferes with the reflection phenomenon by absorbing and/or scattering a fraction of the incident light. This is not generally significant in most optical components since only a limited number of internal reflections occur. However, these losses become serious in fiber optics since each ray may undergo hundreds or thousands of reflections in its passage through the fiber. Thus, one usually finds freshly drawn glass fibers rapidly lose their initial transmission efficiency because of surface contamination (41).

When many fibers are formed into a bundle another problem exists called "optical cross talk". This is the leakage of light from one fiber to the next which is due to the penetration of the electromagnetic field into a rarer medium during total internal reflection. The extent of this penetration is only of the order of the wavelength of the light being transmitted. However, when another fiber is brought to within this distance, some of the light from the original fiber leaks across the interface and the total reflection is said to be "frustrated".

Attempts to prevent this leakage by coating the fibers with a highly reflecting material such as silver have been made (42) but a small amount of absorption of light by the metal with every reflection destroyed the transmission efficiency of the fibers. Only through the use of a transparent dielectric coating has it been possible to minimize leakage and also maintain a high transmission efficiency. This may be accomplished by applying a transparent cladding of low refractive index over a fiber core having a higher refractive index. This permits highly efficient transmission of light through tightly packed bundles of clad fibers with each fiber conducting light independently.

Although optical fibers are basically wave guides for electromagnetic radiation at optical frequencies, many of their properties can be expressed in terms of geometric optics. As in the case of simple lens optics the "numerical aperture" is a measure of the light gathering power and is one of the principal properties of a fiber or bundle of fibers. Figure 6 shows two types of cylindrical fibers (a) uncoated and (b) coated. The critical angle I_c represents the largest angle at which the ray can be totally reflected from the interface and thus determines the maximum angle α at which a meridonal ray can be accepted for transmission along the fiber. Rotation of the angle α about the axial ray will sweep out the acceptance cone. The same considerations apply to the light emerging from the other end of the fiber thus defining the exit cone.

The "numerical aperture", N.A., of a fiber optics element is based on Snell's Law and may be calculated from the following relationship:

$$\text{N.A.} = \sin \alpha = \sqrt{n_1^2 - n_2^2} \qquad (5)$$

where $n_2 = 1.000$ for the uncoated fiber surrounded by air or a vacuum,

$$\text{N.A.} = n_3 \sin \alpha = \sqrt{n_1^2 - n_2^2} \qquad (6)$$

or for a coated fiber when the acceptance or exit cone is in a medium of refractive index, n_3 (43, 44). From the numerical aperture one may calculate the "f/Number" of a fiber optics element using the following relationship:

$$\text{f/Number} = 1/(2\ \text{N.A.}) \qquad (7)$$

Strictly speaking, "numerical aperture" applies only to entering rays and therefore it is more appropriate to call this the "nominal numerical aperture." Skew rays incident at angles greater than α are rapidly attenuated by the fibers. In practice, however, the limiting angle, α, is not as sharply defined as it might seem. Diffraction and surface irregularities on the fiber walls tend to diffuse the "acceptance angle." The "acceptance angle" is also dependent on the wavelength of the incident radiation since refractive index is wavelength dependent.

The range of "nominal numerical apertures" available in fiber optics is limited only by the materials from which the fibers can be made. For glass coated-glass core fibers, one has a fairly wide range of refractive indices from which to choose. Unfortunately, not all pairs of glasses can be arbitrarily selected, since other factors must be considered such as; chemical and thermal compatability, stability, light attenuation and cost. In selecting the type of glass to be used a compromise often must be made between numerical aperture and transmittance. In general, the higher the refractive index of the core glass, the higher the "numerical aperture" but the lower the transmittance in the blue end of the spectrum. Figure 7 illustrates nominal transmission characteristics for a core glass commonly used in fiber optics.

For wavelengths beyond 2.5 microns, where most optical glasses attenuate strongly, it is necessary to consider other possible fiber materials. Some work has been done on germanate materials and calcium aluminate glasses to extend the infrared transmission out to about 5 microns, at least in short fiber lengths. Transmission still further

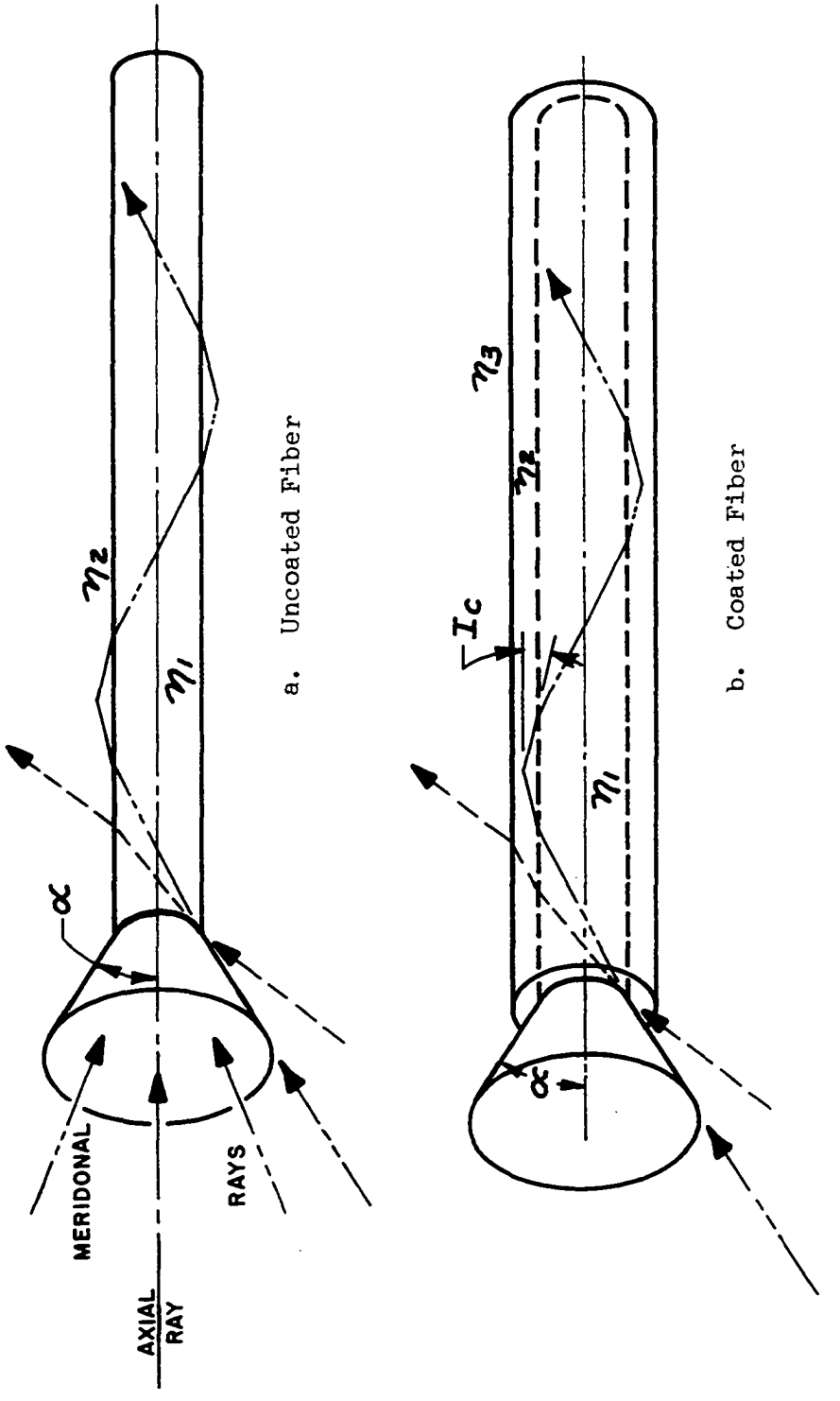


FIGURE 6

Limiting Meridonal Ray in a Fiber

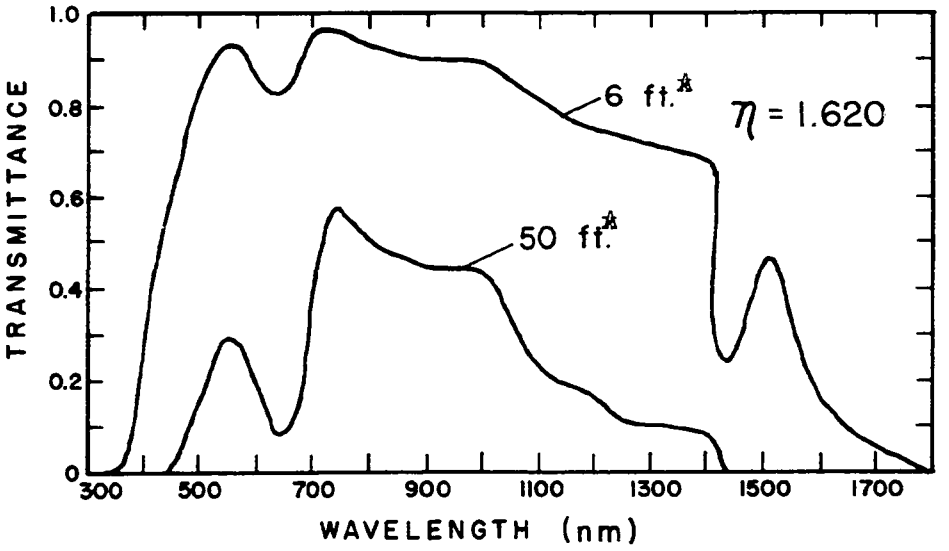


FIGURE 7

Transmittance Curves for Glass Fibers (43)

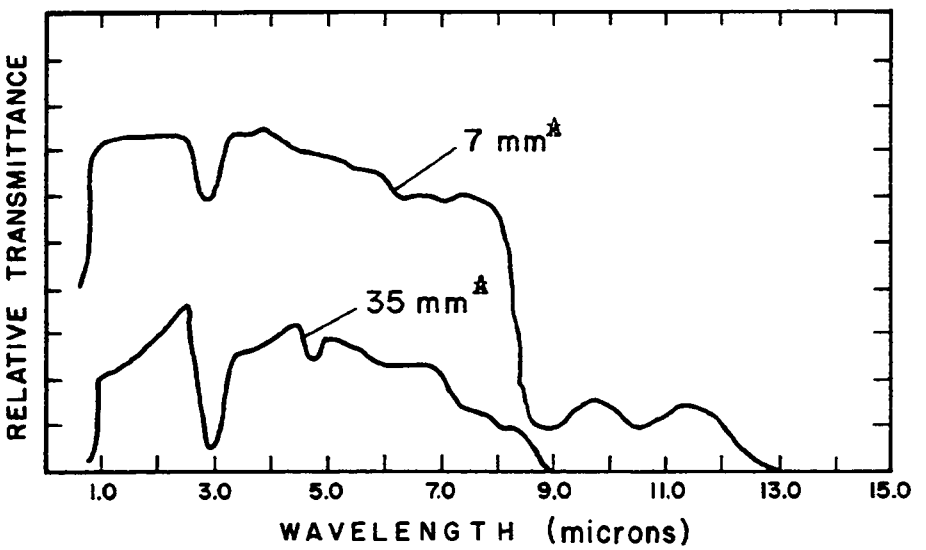


FIGURE 8

Relative Transmittance Curves for Coated
Arsenic Trisulfide Fibers (43)

* Length of the Fiber Optic Bundle

into the infrared has been achieved by using arsenic trisulfide glass. Fibers having As_2S_3 glass core (n=2.47) and a modified arsenic sulfide coating (n=2.416) transmit out to 7 microns as shown in Figure 8.

For wavelengths below 350 nm, where glass again attenuates severely, ultraviolet-transparent materials such as lithium fluoride, calcium fluoride, cesium chloride, quartz, etc. are necessary as a core and/or cladding materials. Due to chemical and physical difficulties associated with most of these materials, quartz appears to be the most feasible core material at this time. Although quartz fiber optics have been made, they are not yet commercially available. Hypothetically, quartz fiber optics could be made by dipping a quartz fiber or rod into a molten calcium fluoride bath. This would produce a thin layer of calcium fluoride on the surface of the fiber. The calcium fluoride in turn would have to be protected from chemical attack by a plastic or resinous film. At 300 nm, the "numerical aperture", the angle of the limiting ray and the "f/number," as calculated from literature data (45), would be 0.32, 18°, and 1.5 respectively.

Filters

Filters do not produce monochromatic light but may produce bands sufficiently narrow to be used in low resolution applications. Deviation from Beer's Law is observed at lower concentrations than is found with most dispersive monochrometers, however, this need not be a serious problem if recognized and accommodated (46). Thus, filters are acceptable for photometric use when working at low concentration ranges. Even though Beer's Law is not obeyed, nonlinearity with a given filter system is reproducible.

Two types of filters were utilized during the testing phase of the photometric titrator: (1) commercially available interference filters, sharp cut off and narrow band pass filters, as well as (2) broad band pass and sharp cut off filters constructed from plastic sheet. In the second case, several selected sheets with appropriate spectral characteristics were superimposed to form a filter with the desired spectral characteristics. Because of the instability of the filter materials, heat from the source must be minimized by either physically locating the filter away from the source or using an infrared filter.

As an alternative to conventional filters, optical wedges or circularly wedged optical coatings may be used to give a system of much better wavelength resolution. Although simple with regard to the mechanical placement in the optical system, this method of wavelength selection is quite expensive in relation to the advantages gained over the inexpensive conventional filter system. The use of optical wedges, however, would permit wavelength scanning if desired. Because of the additional expense, these optical wedges were not considered justifiable at this time.

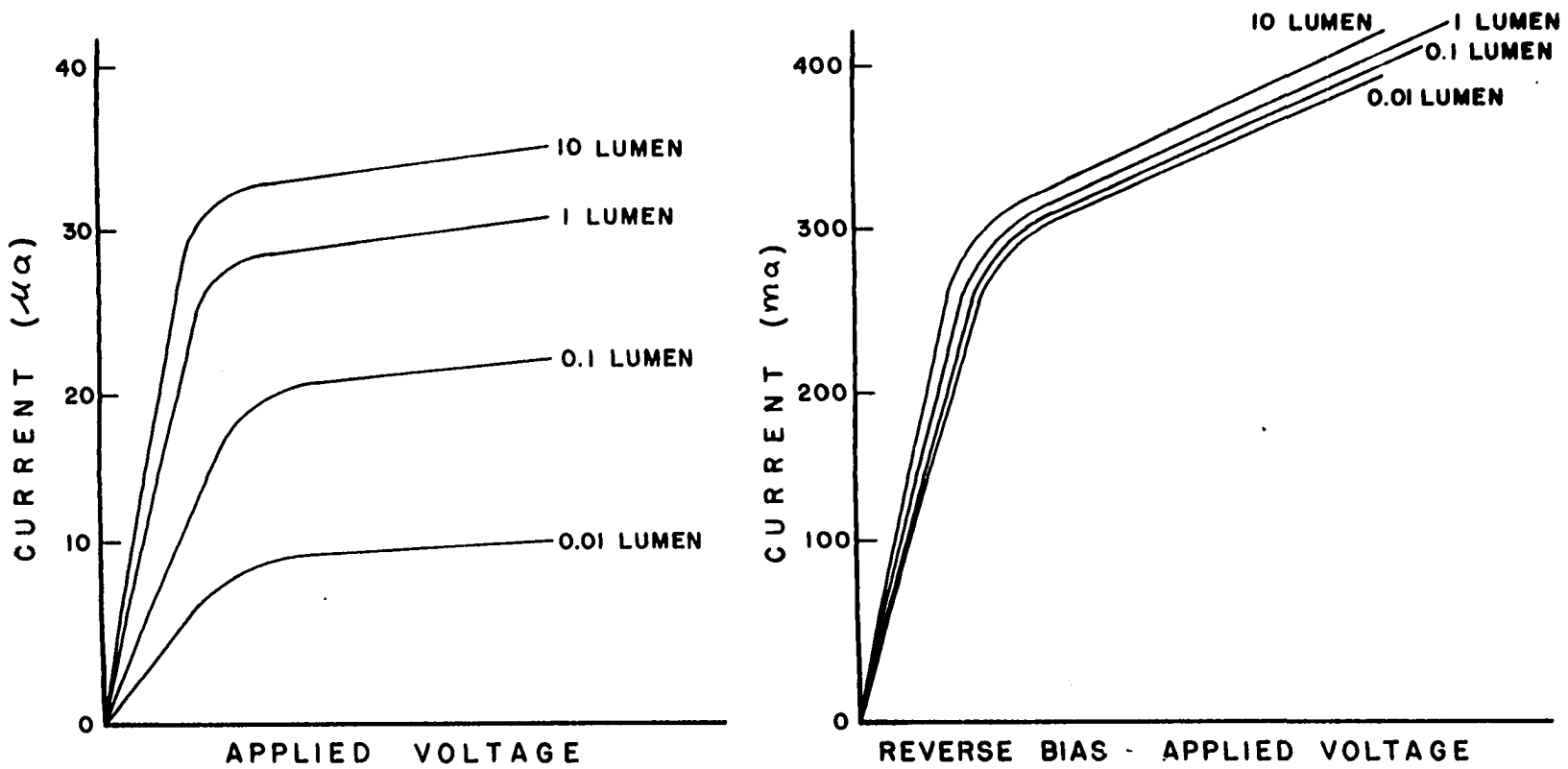
Detector

The selection of the detector for the photometric titrator required careful consideration. Desirable features include: a wide spectral range, sensitivity to small changes in light intensity over a wide range of intensities, simple associated electronic circuitry, low cost, low noise level, linear response, and a small coefficient of temperature variance. With these requirements in mind, several detectors were tested,

and the advantages and disadvantages of each were weighed in light of our particular application.

It was found during the course of selecting a detector that the term "sensitivity" used to describe most detectors is misleading as a criterion for selection. "Sensitivity" is usually determined by the current generated as a function of a given light intensity and is presented in the form of microamperes or amperes per lumen. However, these data do not reflect the change in current with the change in light intensity at different intensity levels. Figures 9a and 9b illustrate the current-voltage curves for a vacuum phototube and a photovoltaic cell at various light intensities. As can be seen from the figures, although the current output of the photovoltaic cell is large relative to that of the vacuum phototube, the relative change in current with respect to changes in light intensities is much greater with the phototube. The phototube having characteristics as shown is therefore the better discriminator between differing levels of light. From this, it can be seen that characteristic curves and not "sensitivities" or outputs are better guidelines for the evaluation of detectors. In addition, since the small currents generated by high impedence detectors such as phototubes are measured across very high resistances, relatively large voltages are actually measured. Low impedence detectors such as photovoltaic cells are current generators and thus require that small currents and not voltages be measured. Table 1 lists the outputs of some typical detectors.

Silicon photovoltaic cells were tested first because of their low cost and the simplicity of their associated circuitry. Since photo-



(a) Vacuum Phototube (b) Photovoltaic Cell

FIGURE 9

Current-Voltage Characteristics of Typical Detectors (24)

Table 1

Characteristics of Some Commercially Available Detectors (47)

Type	Manufacturer's number	Peak wavelength (nm)	Output
Vacuum phototube	RCA 926	420±10(S-3)	6.5 μa/lumen
Vacuum phototube	RCA 929	400±50(S-4)	45 μa/lumen
Vacuum phototube	RCA 934	400±50(S-4)	30 μa/lumen
Vacuum phototube	RCA 935	340±50(S-5)	35 μa/lumen
Vacuum phototube	RCA 1P42	480±50(S-9)	30 μa/lumen
CdS photoconductive	RCA 7163	580±50(S-15)	0.082 amp/lumen
CdS photoconductive	RCA 6957	580±50(S-15)	0.85 amp/lumen
Germanium photodiode	Nucleonic TP-50	1500	30 μa/lumen
Se photovoltaic	Weston Photronic	555	450 μa/lumen
Cu_2O photovoltaic	Westinghouse	565	150 μa/lumen
Si photovoltaic	Hoffmann	750-850	Low
Photomultiplier	DuMont 6292	440±50(S-11)	2,000,000*
Photomultiplier	RCA 931-A	400±50(S-4)	1,000,000*
Photomultiplier	RCA 7200	330±50(S-19)	1,000,000*
Photomultiplier	RCA 7746	440±50(S-11)	17,000,000*
Photomultiplier	RCA 7046	420±50(S-11)	20,000,000*

* current amplification

(S-) denotes Electronic Industries Association spectral code.

voltaic cells generate an electromotive force when light is incident on them, they need no external voltage source. As a result of having a relatively low output impedence, these cells can be connected to nearly any readout device with an input of one thousand ohms or less. Unfortunately the output of photovoltaic cells is seriously affected by temperature. In addition, photovoltaic cells tend to have relatively poor sensitivity at low light levels. As a result of this lack of sensitivity and the magnitude of their temperature coefficients, the use of photovoltaic cells was considered impractical for our purposes.

Photoconductive cells were considered next. These detectors, fabricated from several different materials, are basically light sensitive resistors. In total darkness, the cell resistance may be as large as several megohms, and decrease in a non-linear manner to as low as 10-50 ohms when irradiated with light. Photoconductive cells generally exhibit high sensitivities as can be seen in Table 1. These cells are even more adversely affected by temperature changes than are photovoltaic cells. The photoconductive cell, in general, requires a relatively well-regulated external power supply to produce a flow of current through an appropriate load resistor. Changing the applied voltage changes the response time of the cell as well as increasing its "dark current." In addition, aging and hysteresis are factors known to affect the response characteristics of this detector. In view of these problems photoconductive cells were not tested in the photititrator.

Photomultipliers were considered as possible detectors because of their very high sensitivity, wide spectral range, and long term stability. Unfortunately, the added expense of the photomultipliers and associated

electronic components was not felt to be warranted for our particular application. However, specific applications of the phototitrator could indeed justify the additional expense of photomultiplier detector systems.

Junction photodetectors such as phototransistors and photodiodes were briefly considered because of the simplicity of their associated electronic circuitry. A number of unsuccessful attempts were made to acquire certain types of these detectors from both suppliers and manufacturers. Production of these particular models had unfortunately been discontinued.

A vacuum photodiode was finally chosen because of its relatively high sensitivity, wide spectral response, stability and relatively simple associated circuitry. The vacuum phototube consists of a semi-cylindrical sheet metal cathode coated with a light sensitive material and a centered wire comprising the anode, both encased within a transparent envelope. The composition of the light sensitive material determines the spectral characteristics of the phototube. Listings of cathode coatings and their respective spectral range are readily available in the literature (24, 48). The anode is maintained at a positive potential by a regulated high voltage power supply. Electrons are emitted from the cathode surface as light is incident on it and are accelerated by the potential difference to the anode where they are collected and returned via an external circuit. The number of electrons flowing in this circuit at any instant is proportional to the intensity of the illumination. Only a fraction of the emitted electrons are collected by the anode when the applied potential is small for a given light intensity. As the applied potential is increased, a state exists

where essentially all emitted electrons are collected by the anode. If the applied potential is further increased, complete saturation occurs where no significant current increase for any light intensity can be observed.

Vacuum photodiodes are high impedence current sources with resistances as high as 250 megohms in the dark and 2 megohms at high light levels. Consequently the associated electrical readout circuitry must also have high impedence inputs. Figure 10 illustrates the associated electrical circuitry used with the vacuum photodiode.

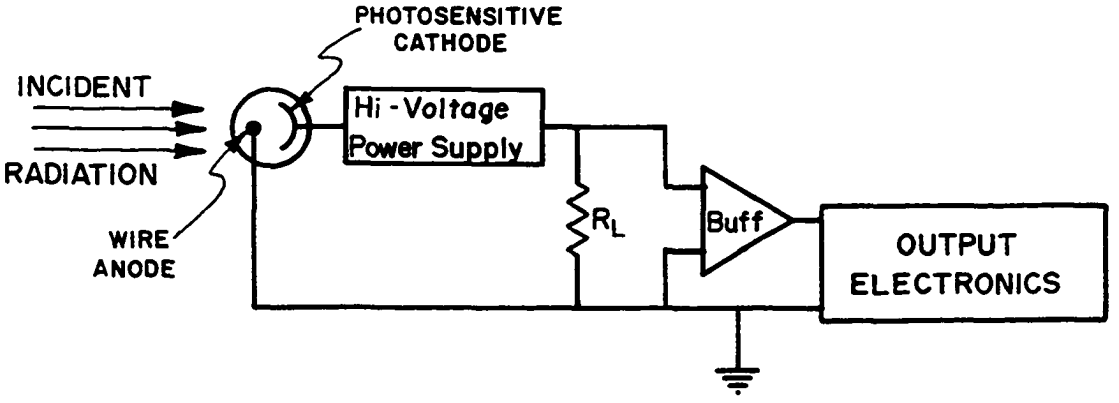


FIGURE 10

Schematic Diagram of a Photometer Circuit

In the initial construction of the photometric titrator an RCA 935 vacuum photodiode was chosen for the previously discussed advantages, and also because of its availability and its projected use in the detection of ultraviolet radiation. However, if just the visible spectral region were to be utilized an RCA 934 vacuum photodiode would have been a better choice because of its reduced size and high sensitivity in the visible region of the spectrum.

Actual Instrumental Configuration

The components utilized in the actual construction of the photometric titrator are described in the following paragraphs and illustrated as modules in Figure 11. As mentioned before, the components utilized in the photometric titrator were chosen from readily available equipment, so the assemblage represents a compromise rather than the optimum condition for each of the various systems.

The titration vessel, consisting of a truncated 600 ml. beaker, was raised and lowered by means of a laboratory jack. Transparent and opaque titration vessels were both used successfully in spectrophotometric and turbidimetric titrations. Nephelometric and fluorometric titrations, however, required opaque titration vessels to minimize "room light" effects.

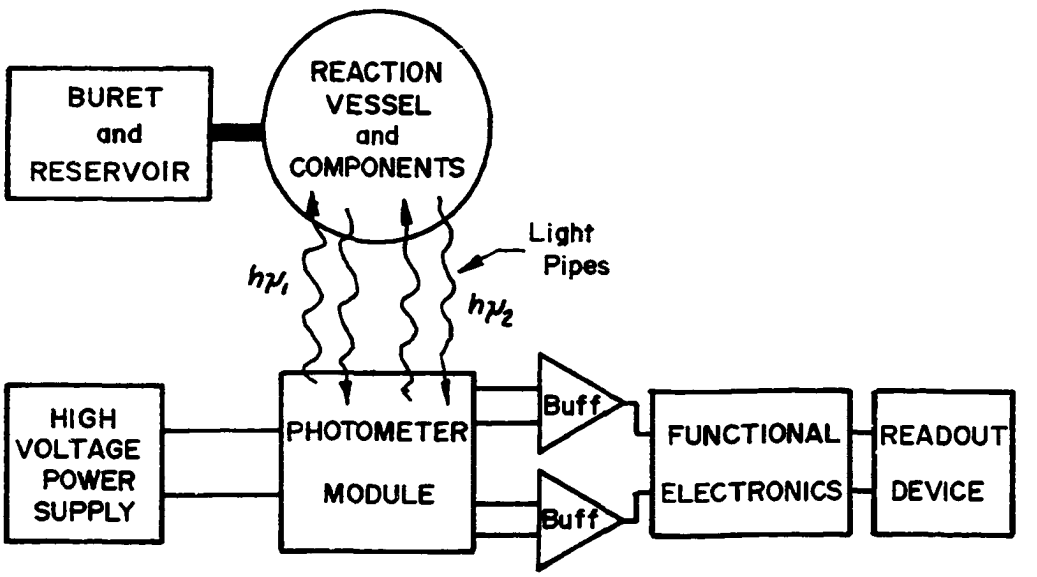


FIGURE 11

Block Diagram of the Photometric
Titrator and Associated Components

Stirring was accomplished by the use of a variable speed magnetic stirrer-hot plate combination. Stirring bars of 3/4 and 1 inch in length were used at speeds just below that necessary to pull a vortex down into the optical path. This stirring system, although recognized to have limitations in the ability to efficiently mix the reacting species, was readily available and easily adaptable to the titration assembly. Stirring bars of a dark color were selected for use with nephelometric and fluorometric systems in attempt to minimize stray light reflecting off the bars.

A Sargent Constant Drive Buret, S-11120-50, Model C, was used to deliver titrants at a rate of 5.00 ml per minute. The delivery rate of this type of buret could not be varied as the equivalence point was approached. This problem together with the previously mentioned stirring problem, compounded the possible sources of errors in some systems. The delivery tip from the buret extending into the titration vessel was drawn from a piece of 1 mm. capillary tubing and bent in the direction of the rotation of the magnetic stirrer. This minimized "bleed-out" of the titrant prior to the initiation of the titration and produced rapid mixing of the titrant and reacting species.

The high voltage power supply used was a Heathkit Universal Power Supply, Model EUW-15. The regulated voltage mode was employed with 250 volts DC. impressed across the phototube. The power supply was specified to have an output variation of less than 1% from no load to full load at 300 volts. Output variation was less than $\pm$ 1 volt for a $\pm$ 10 volt variation in the AC line input. The B+ ripple was less than 10 millivolts rms with an output impedance of less than 10 ohms.

It was found through the use of the voltage regulated circuit that the variation of the current output of the phototube was considerably reduced in comparison with the power supply in the voltage divider mode.

The photometer module is shown in Figure 12. The phototubes, RCA 935, were mounted in the same plane at right angles to one another in order to facilitate the physical arrangement of the light guides. Light guides were comprised of American Optical Image Conduit, IC-100-12. These guides were in the form of 1/8" diameter rigid rods, each comprised of 70,000 individually clad fibers. The transmission of these fibers is severely attenuated below 400 nm but extends beyond 800 nm. The guides terminating in the titration vessel were bent 90° to the vertical such that a cell with a path length of 1 cm was formed by the entering and exiting light guides.

The relation of the two external optical channels was not symmetrical as shown in Figures 2 and 12. Instead, one channel was shifted off center bringing a detection guide, E_{12}, close to the illumination guide, E_{21}, in order to more easily facilitate fluorometric and nephelometric titrations. Internal optical channels shown in Figures 2 and 12, and represented by elements E_{23}, C_2, and E_{24}; and E_{13}, C_1, and E_{14} were not assembled as an integral part of titrator. Instead, this configuration was sucessfully tested as a separate unit.

Filters were placed in the optical paths as shown in Figure 2. Optical paths representing external double beam operation were constructed and tested briefly but did not show any significant improvement over single beam operation. Therefore, in all future discussion, single beam operation will be implied.

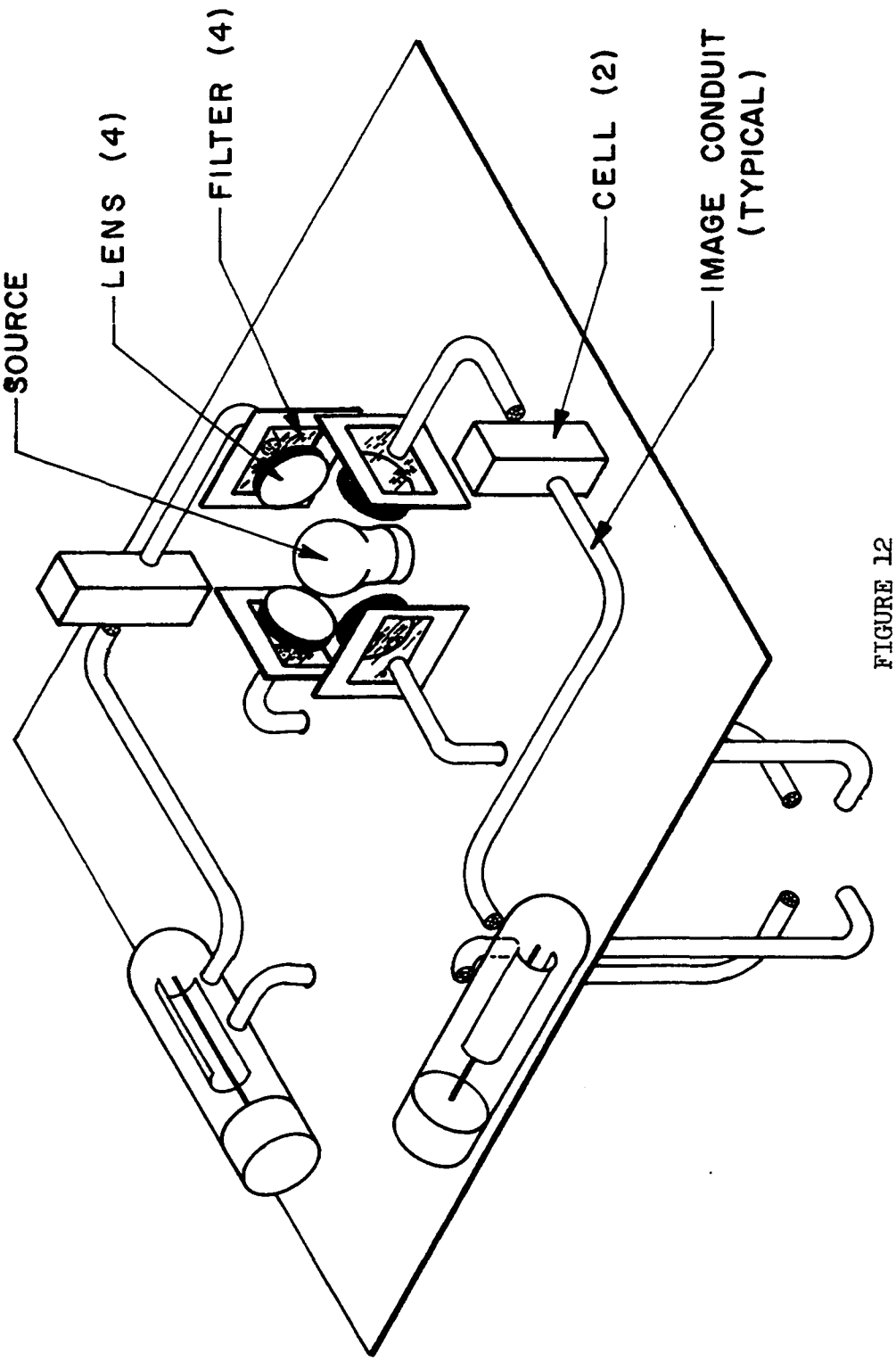


FIGURE 12

Fiber Optics Photometer

The sources used were numbers 1133, 93, and 82 lamps operated at 13, 17, and 9 volts respectively. The number 82 bulb, as a result of its small current demand was powered by the voltage regulated power supply previously discussed. Bulb numbers 93 and 1133 were powered by a combination of a voltage stabilization transformer, a Variac, and a 120 to 17 volt stepdown transformer.

The buffer stages consisted of an Analog Devices Inc. Model 119K operational amplifier and a Burr Brown Model 3129/15 FET Input operational amplifier. The Analog Devices amplifier had a rated output of ± 10 volts at 20 ma., a common mode impedance of 10^9 ohms, and an input voltage offset of ± 5 μv/°C. The Curr Crown amplifier had a rated output of ± 10 volts at 20 ma., a common mode impedance of 10^{11} ohms, and an input voltage offset of ± 3 μv/°C. Both operational amplifiers were wired in the non-inverting mode such that R_1 = 50 K and R_2 = 10K as shown in Figure 3.

Not all functional modes displayed in Figure 4 were tested because of an unexpected failure of one of the buffer stages. A Burr Brown Logarithmic Amplifier Module, Model 1665/16, capable of generating the function

$$E_O = -10 \log_{10}(E_1/E_2)$$

was purchased and was being installed at the time that the buffer malfunctioned. Differentiation circuits were assembled and proven to work in several titration systems but were not utilized to collect data. Other functional electronic systems shown were not tested but are commercially available in component form or as complete modules.

The readout devices consisted of a Beckman Electroscan 30 and a Honeywell Electronik 194 recorder. Both recorders were operated at a chart speed of three inches per minute and at voltage ranges from five millivolts to three volts full scale. At all times a vacuum tube volt meter with an input impedance of 10^{11} ohms was connected in parallel to the recorder to more easily select the appropriate voltage scale at which to operate the recorder.

APPLICATION

Discussion of Experimental Results

Having constructed the photometric titrator, the precision, accuracy, and general utility of this instrument were tested using established analytical procedures. In this section, a brief description of the individual titration systems used in these tests will be presented along with all data obtained. While some of the systems used did not behave as well as one might expect from reading the literature, they did, nevertheless, show reproducible behavior during repetitive titrations. It was not within the scope of this work, however, to explain the apparent anomalies of the systems.

Each system studied was titrated a number of times to obtain a statistical evaluation of the precision of the system. The precision was evaluated by the magnitude of the variance, σ^2, standard deviation, σ, and the coefficient of variation, C.V., based on the mean value of the data. Outlying results were evaluated on the basis of the "Q Test" (49) at a 90% confidence level.

Listed in the tables given for each titration system are the corrected volume of titrant actually delivered and the calculated volume of titrant, as determined from standardized data. The volume of titrant delivered was computed by measuring the distance on the chart to the equivalence point and accounting for the volume of titrant delivered for each division the chart moves. The corrected mean volume, mentioned later in the discussion, is the mean volume of titrant

delivered during a set of repetitive titrations which has had the blank correction subtracted from it.

Two observations should be noted with respect to the volume of titrant delivered and the calculated volume. First, the volume of the titrant delivered does not reflect blank corrections. A series of blanks were run, where applicable, for each system so that an average value could be obtained and subsequently subtracted from the volume of delivered titrant. Secondly, comparison of the mean volume of titrant delivered and calculated volume of titrant do not always compare favorably. In the cases where good agreement was obtained, it was noted that these titrations had been carried out using solutions either made up directly from primary standards or standardized against standard solutions. Standard solutions which had been diluted exhibited the poorest agreement between calculated and actual titration volumes which would tend to suggest that the calculated volumes reflect dilution errors.

This dilution procedure and the physical manipulation of the solutions may very well be the greatest contributing source of error giving rise to the discrepancies between actual and calculated volumes for the more dilute solutions. The uncertainty in the volumetric glassware undoubtedly tended to produce significant errors at concentrations of 0.01 N. These dilutions, however, were necessary since many of the solutions when prepared at concentrations of 0.01 N could not be standardized with adequate precision due to poor visual end points. Volumetric glassware was calibrated, however, these corrections were not included in calculations since their significance did not appear

to be the limiting source of error in any of the systems studied. Also contributing to the discrepancy between mean and calculated volumes is the disparity between the end point, as determined by visual observation, and the equivalence point, obtained by the instrumental method. The high rate of delivery of the constant drive buret coupled with inefficient stirring mentioned earlier led to the production of large blanks relative to those obtained in manual titrations utilizing the same system. These combined problems produced a lag time leading to a titration blank of several tenths of a milliliter. In systems where a blank correction is possible, this source of error can be minimized. However, when systems are titrated for which blank corrections are not possible, large positive errors appear.

Systematic errors encompassing such factors as pipeting, starting synchronization, volume delivery, stirring efficiency, errors associated in the graphical location of the equivalence point, and dead band of the recorder are present in all titrations performed. Under ideal conditions, the combined errors encountered in the titration of a specific system approach a minimum limit asymtotically.

Samples intended for repetitive titration were prepared alternately as a previously prepared sample was being titrated automatically. Samples required an average preparation time of five minutes. The average time required for titration of this sample was approximately five minutes, which includes rinsing the light guides before and after the titration.

Hydrochloric acid vs. ammonia

The titration of ammonia with hydrochloric acid was performed to

illustrate the use of the photometric titrator with common titrimetric procedures such as the Kjeldahl determination. An indicator was selected to further demonstrate the ability of the photometric titrator to locate an equivalence point even though the color change of the indicator is poorly defined visually. Inadvertently, however, phenol red, pK_a 7.8 was chosen as an indicator instead of the more appropriate methyl red, pK_a 5.6. Corrections for this error were calculated, thus relating the equivalence point obtained to that obtainable utilizing the visual standardization indicator.

The titration of a 10.00 ml. sample of 0.1102 N ammonia, standardized against hydrochloric acid using bromocresol purple as the indicator was made in a total volume of 160 ml. using six drops of phenol red indicator. Bromocresol purple, pK_a 6.0, was chosen as the indicator for the visual determination of the end point because of its sharp color change from purple to yellow and also its pH transition range. Preparation and standardization of solutions used for this and subsequent titrations may be found in Appendix 2. A composite narrow band pass filter, 813 + 878, listed in Appendix 1, having a λ_{max} of 560 nm was selected by comparison of the spectra of both the acid and base forms of phenol red. Table 2 lists data obtained from ten determinations of 0.09749 N hydrochloric acid titrated against 0.1102 N ammonia. An average volume of 11.23 ml. of acid was delivered compared to 11.30 ml. calculated, producing a determinate error of - 0.07 ml. The variance, standard deviation and coefficient of variation produced by these titrations are 0.00284, 0.0533, and 0.47% respectively.

Table 3 lists the data obtained from ten determinations of 0.009749 N hydrochloric acid vs. 0.01102 N ammonia. These solutions were diluted in

Table 2

Spectrophotometric Titration of 0.09749 N HCl vs. 10.00 ml. of 0.1102 N NH_3 - phenol red indicator.*

Sample No.	Corr. Vol. HCl (ml.)	Deviation (ml).
1	11.18	-0.12
2	11.33	+0.03
3	11.25	-0.05
4	11.25	-0.05
5	11.16	-0.14
6	11.21	-0.09
7	11.30	0.00
8	11.23	-0.07
9	11.23	-0.07
10	11.16	-0.14
Avg.	11.23	-0.07
Calc'd.	11.30	----
Blank	0.17	----
Corr. Avg.**	----	-0.06

$\sigma^2 = 0.00284$ $\sigma = 0.0533$ C.V. = 0.47%

* Using narrow band pass filter combination 813 and 878, λ_{max} 563 nm.

** Correction applied due to discrepancy between phenol red and bromocresol purple equivalence points.

Table 3

Spectrophotometric Titration of 0.009749 N HCl vs. 10.00 ml. of 0.01102 N NH_3 - phenol red indicator.*

Sample No.	Corr. Vol. HCl (ml.)	Deviation (ml.)
1	10.80	-0.48
2	10.80	-0.48
3	10.78	-0.50
4	10.85	-0.43
5	10.72	-0.56
6	10.75	-0.59
7	10.72	-0.56
8	10.78	-0.50
9	10.78	-0.50
10	10.90	-0.38
Avg.	10.78	-0.50
Calc'd.	11.28	----
Blank	0.20	----
Corr. Avg.**	----	-0.15

σ^2 = 0.00282 σ =0.0531 C.V. = 0.48%

* Using narrow band pass filter combination 813 and 878, λ_{max} 563 nm.

** Correction applied due to discrepancy between phenol red and bromocresol purple equivalence points.

a ratio of ten to one from the standardized solutions used in Table 2. The initial concentration of the ammonia in the titration vessel was 0.0007 N. An average volume of 10.78 ml. was delivered compared to 11.28 ml. calculated, producing an average deviation of -0.50 ml. This quite readily reflects errors previously discussed. Values for variance, standard deviation, and coefficient of variation obtained were 0.00282, 0.0531, and 0.48% respectively. In comparing the coefficients of variation between titrations in Tables 2 and 3, it can be seen that the location of the equivalence point by means of the photometric titrator was accomplished with equal precision at both concentrations. This would also tend to indicate that the discrepancy between actual and calculated volumes observed during repetitive titrations of the system arises from the handling of the solution or from within the system itself.

Ethylenediaminetetraacetic acid vs. iron(III)

Sweetser and Bricker (50) demonstrated the manual spectrophotometric titration of iron(III) with ethylenediaminetetraacetic acid, EDTA, using salicylic acid as an indicator. The authors reported that gradual fading of the Fe(III)-salicylate complex color makes the equivalence point difficult to locate even at concentrations of 0.1 N. Spectrophotometrically, however, the equivalence point was easily located by extrapolation of the initial and final slopes of the titration curve.

The titration of standard Fe(III) with standardized EDTA was carried out on the basis of Sweetser and Bricker's work. A 10.00 ml. aliquot of 0.01012 N Fe(III) solution was placed in the titration vessel with

30 ml. of pH 2 buffer, 6 drops of indicator, and 130 ml. of doubly distilled water. The data generated from ten successive titrations are listed in Table 4. The average volume of EDTA delivered was 10.36 ml. as compared with a calculated volume of 9.62 ml., a deviation of 0.74 ml. This deviation arises in part because a blank could not be determined for the system. In addition, this system suffers from a kinetically slow reaction near the equivalence point which produces further error. A coefficient of variation of 0.41% was obtained, reflecting good reproducibility of the equivalence points.

Further examination of the literature (51) made reference to a warm solution being a requirement for the observation of a correct equivalence point. Table 5 lists the data obtained at 50° to 70°C with solution volumes and concentrations identical to those in Table 4. An average volume of 9.90 ml. obtained from the titrations was found to compare with a calculated volume of 9.62 ml., giving a deviation of 0.28 ml. This large deviation is partially due to the inability to perform a blank correction on this system, as previously discussed. Heating the solution produced better agreement with the calculated value, however, the coefficient of variation decreased slightly to 0.39%. Attempts to further improve the agreement between experimental and calculated volumes were made by heating the solution in the titration vessel above 70°C but without success. The standard solutions used were restandardized against other standard solutions and found to be correct within the limits of experimental accuracy.

Perchloric acid vs. 4-aminopyridine

The non-aqueous titration of amines with perchloric acid has been

Table 4

Spectrophotometric Titration of 0.01052 N EDTA vs. 10.00 ml. of 0.01012 N Fe(III) - salicylic acid indicator*

Ambient Room Temperature

Sample No.	Corr. Vol. EDTA (ml.)	Deviation (ml.)
1	10.35	0.73
2	10.42	0.80
3	10.45	0.83
4	10.35	0.73
5	10.33	0.71
6	10.32	0.70
7	10.32	0.70
8	10.32	0.70
9	10.35	0.73
10	10.35	0.73
Avg.	10.36	0.74
Calc'd.	9.62	----

$\sigma^2 = 0.00178$ $\sigma = 0.0422$ C.V. = 0.41%

* Using filter combination 807 and 877.

Table 5

Spectrophotometric Titration of 0.01052 N EDTA vs. 10.00 ml. of 0.01012 N Fe(III) - salicylic acid indicator.[A]

Temperature 50 - 70 °C.

Sample No.	Corr. Vol. EDTA (ml.)	Deviation
1	9.95	0.33
2	9.83	0.21
3	9.90	0.28
4	9.95	0.33
5	9.97	0.35
6	9.85	0.23
7	9.85	0.23
8	9.92	0.30
Avg.	9.90	0.28
Calc'd.	9.62	----
$\sigma^2 = 0.00152$	$\sigma = 0.0389$	C.V. = 0.39%

[A] Using filter combination 807 and 877.

discussed in great detail by Fritz (52). A standard solution of 4-aminopyridine and a standardized solution of perchloric acid were prepared and titrated in glacial acetic acid using a 2% solution of methyl violet as the indicator.

A 10.00 ml. aliquot of 0.09208 N 4-aminopyridine solution was transferred to the titration vessel with 6 drops of indicator and 10 ml. of acetic anhydride and was diluted with 150 ml. of glacial acetic acid. This solution was then titrated with 0.1172 N perchloric acid. Table 6 lists the data obtained from repetitive titrations of this system. The mean corrected volume of acid delivered was 7.82 ml. as compared with a calculated volume of 7.85, thus producing a deviation of -0.03 ml. A coefficient of variation of 0.42% was observed.

Permanganate vs. oxalate

The titration of oxalate with permanganate was selected to test the photometric titrator at elevated temperatures. The method of McBride (53) was modified by poising the system with manganous ion, purging the system with nitrogen prior to heating the solution, and keeping a blanket of nitrogen above the solution during the titration. It was felt that these procedures would minimize air oxidation of oxalate ion during the titration (54) as well as eliminate the initial buildup of unreacted permanganate at the start of the titration.

A standard solution of oxalate was prepared from primary standard material while the standardized solution of permanganate was prepared by the method of Fowler and Bright (54). A 10.00 ml. aliquot of 0.09984 N oxalate solution was transferred to the titration vessel with 5 ml. of

Table 6

Spectrophotometric Titration of 0.1172 N $HClO_4$ vs.
10.00 ml. of 0.09208 N 4-Aminopyridine - methyl violet indicator[A]

Sample No.	Corr. Vol. $HClO_4$ (ml.)	Deviation (ml.)
1	7.83	-0.02
2	7.88	0.03
3	7.80	-0.05
4	7.85	0.00
5	7.78	-0.07
6	7.78	-0.07
7	7.83	-0.02
8	7.86	0.01
9	7.80	-0.05
Avg.	7.82	-0.03
Calc'd.	7.85	----
Blank	0.22	----

$\sigma^2 = 0.00114$ $\sigma = 0.0338$ C.V. = 0.42%

[A] Using filter combination 813 and 878.

0.1 N manganous ion, 30 ml. of 6 N sulfuric acid, and 140 ml. of doubly distilled water. The solution was purged with nitrogen and heated to 60°C. The bubbler was then withdrawn from the solution and allowed to maintain an atmosphere of nitrogen over the solution. The solution was then titrated with 0.09221 N permanganate solution. Table 7 presents the data obtained from successive titrations of this system. The mean corrected volume delivered was 10.78 ml. as compared to a calculated volume of 10.83 ml., producing a deviation of -0.05 ml. This disparity may well be due to the difference between the equivalence point and the end point. The coefficient of variation for this system was found to be 0.67%.

Hydrochloric acid vs. ammonia

Acid-base titrations rarely use indicators which are based upon fluorescence changes to detect end points. The use of a photometric titrator, however, makes it possible to observe changes in the fluorescence of an appropriate indicator. Since this photometric titrator utilized fiber optics made of glass, the fluorescence changes observed must be excited by visible radiation. When quartz fiber optics become available, the number of fluorescence indicators which may be used will be greatly increased. Dichlorofluorescein, having a pK_a of 5, was selected for use with the ammonia-hydrochloric acid system.

Standardized solutions of hydrochloric acid and ammonia were prepared as described in Appendix II. A 10.00 ml. aliquot of 0.07696 N ammonia was transferred to the titration vessel with 150 ml. of doubly distilled water and 4 drops of 0.2% dichlorofluorescein. This solution

Table 7

Spectrophotometric Titration of 0.09221 N MnO_4^- vs. 10.00 ml. of 0.09984 N $C_2O_4^{--}$.*

Sample No.	Corr. Vol. MnO_4^- (ml.)	Deviation (ml.)
1	10.85	0.02
2	10.67	-0.16
3	10.90	0.07
4	10.82	-0.01
5	10.75	-0.08
6	10.85	0.02
7	10.70	-0.13
8	10.75	-0.08
9	10.70	-0.13
10	10.82	-0.01
Avg.	10.78	-0.05
Calc'd.	10.83	----
Blank	0.15	----

$\sigma^2 = 0.00541$ $\sigma = 0.0735$ C.V. = 0.67%

*Using filter combination 806 and 877.

was then titrated with 0.09749 N hydrochloric acid. The data obtained by repetitive titrations with this system are listed in Table 8. The mean corrected volume of acid delivered was 7.78 ml. as compared to a calculated volume of 7.88 ml. The coefficient of variation obtained was found to be 1.15%, thus reflecting similar problems as described in the following fluorometric titration system.

Ethylenediaminetetraacetic acid vs. calcium(II)

The fluorometric titration of Ca(II) with EDTA using calcein as an indicator has been described by Diehl (55). Standardized Ca(II) and EDTA solutions were prepared as outlined in Appendix II. Primary and secondary filters were selected based on the data presented by Diehl.

A 10.00 ml. aliquot of 0.00992 N Ca(II) solution was transferred into the titration vessel with 150 ml. of doubly distilled water, a few milligrams of ascorbic acid, 50 ml. of 20% triethanolamine, 2 ml. of 1% potassium cyanide, 5 ml. of 5 M potassium hydroxide, and about 5 mg. of calcein indicator. This solution was then titrated with 0.01043 N EDTA. The data obtained from successive titrations of these solutions are presented in Table 9. The mean corrected volume of EDTA delivered was found to be 9.99 ml. as compared to 9.51 ml. calculated volume thus producing a deviation of 0.48 ml. A coefficient of variation of 2.08% was observed. The large deviation was anticipated since a blank correction could not be made correcting for indicator and stirring lag.

The existence of this large coefficient of variation may be explained by reason that the titration circuitry used for this prototype was, at best, a compromise. The amplification of the buffer stage was selected so that large signals from the phototubes, as found in spectro-

Table 8

Fluorometric Titration of 0.09749 N HCl vs. 10.00 ml. of 0.07696 N NH_3 - dichlorofluorescein indicator.*

Sample No.	Corr. Vol. HCl (ml.)	Deviation (ml).
1	7.68	-0.20
2	7.85	-0.03
3	7.88	0.00
4	7.70	-0.18
5	7.78	-0.10
6	7.96	0.08
7	7.68	-0.20
8	7.78	-0.10
9	7.80	-0.08
10	7.68	-0.20
Avg.	7.78	-0.10
Calc'd.	7.88	----
Blank	0.02	----

$\sigma^2 = 0.00841$ $\sigma = 0.0917$ C.V. = 1.15%

* Using filters No. 47B and No. 2A for primary and secondary beams respectively.

Table 9

Fluorometric Titration of 0.01043 N EDTA vs. 10.00 ml. of 0.00992 N Ca(II) - calcein indicator.[A]

Sample No.	Vol. EDTA (ml.)	Deviation (ml.)
1	9.82	0.31
2	9.92	0.41
3	9.80	0.29
4	10.30	0.79
5	10.20	0.69
6	10.28	0.77
7	10.17	0.66
8	9.68	0.17
9	10.25	0.74
10	10.08	0.57
11	10.08	0.57
12	10.00	0.49
13	9.78	0.27
14	10.13	0.62
15	9.67	0.16
16	9.82	0.31
17	9.82	0.31
Avg.	9.99	0.48
Calc'd.	9.51	----
$\sigma^2 = 0.0430$	$\sigma = 0.208$	C.V. = 2.08%

[A]Using filters No. 47B and No. 2A for primary and secondary beams respectively.

photometric and turbidimetric titrations, did not saturate the amplifier. Unfortunately, this limits the sensitivity of the system for detecting very small signals as are found in fluorometric and nephelometric titrations. The inability to detect small signals, recorder dead band, and capacitive inductance each by themselves or in combination tend to produce poor reproducibility about the equivalence point with systems exhibiting poorly defined inflection points. Other factors which undoubtedly play some role in contributing to poor reproducibility in these titrations are inefficient stirring and light scattering.

Cyanide vs. silver(I)

The turbidimetric titration of cyanide with silver ion, commonly referred to as the Liebig titration, is carried out with some difficulty since locally precipitated silver cyanide is slow to redissolve as the solution is stirred. Systematic errors inherent in this system limit the minimum error to about 0.02% (56). Denige's modification of Liebig's method eliminates many of the problems present in the original method (56). Nevertheless, the titration of solutions more dilute than 0.01 M still present difficulty in observing the equivalence point by visual methods.

Repetitive titrations of cyanide vs. silver(I) were carried out utilizing a modification of the Liebig method. The silver cyanide precipitate produces a decrease in light intensity observed at the detector during the first stages of the titration. At the equivalence point maximum turbidity should be observed. In fact, however, the slowly dissolving silver cyanide causes the equivalence point to be shifted slightly so that more cyanide will be required than is predicted

stoichiometrically. As the equivalence point is passed and more cyanide is added, the turbidity of the solution decreases because of the formation of the soluble silver cyanide complex and dilution of the system. A second equivalence point occurs when the last remanents of silver cyanide precipitate dissolve producing a plateau on the intensity vs. volume plot. Unfortunately, the second equivalence point is not as reproducible as the first. Values representing the first and second equivalence points are listed in Tables 10 and 11.

A 10.00 ml. aliquot of 0.009579 N silver(I) solution was transferred into the titration vessel with 150 ml. of doubly distilled water. This solution was then titrated with standardized 0.009445 N cyanide solution. Table 10 lists the first equivalence point data obtained from these repetitive titrations. The mean volume delivered with 10.81 ml. compared with 9.82 ml. calculated. This discrepancy may have arisen from several sources: the equivalence point shift as was described above, dilution errors, cyanate or chloride impurities, and the inability to apply a blank correction to the data. The coefficient of variation of 1.03% reflects inhomogeneities in the solution due to stirring as well as the problems associated with the precipitation process itself.

The mean volume delivered, shown in Table 11, was 20.22 ml. as compared with 19.64 ml. calculated. Many of the same factors as described above contribute to this discrepancy. This time, however, the inability to make a blank correction on the data is probably of greater significance. A coefficient of variation of 0.70% was obtained reflecting the increased volume utilized to obtain the second equivalence point.

Table 10

Turbidimetric Titration of 0.009758 N CN^- vs. 10.00 ml. of 0.009579 N Ag^+. First equivalence point*

Sample No.	Vol. CN^- (ml.)	Deviation (ml.)
1	11.00	1.18
2	10.78	0.96
3	10.72	0.90
4	10.88	1.06
5	10.73	0.91
6	10.68	0.86
7	11.00	1.18
8	10.87	1.05
9	10.75	0.93
10	10.72	0.90
Avg.	10.81	0.99
Calc'd.	9.82	----

$\sigma^2 = 0.0125$ $\sigma = 0.112$ C.V. = 1.03%

* Using filter No. 42.

Table 11

Turbidimetric Titration of 0.009758 N CN^- vs. 10.00 ml. of 0.009579 N Ag^+. Second equivalence point[A]

Sample No.	Vol. CN^- (ml.)	Deviation (ml.)
1	20.08	0.44
2	20.13	0.48
3	20.12	0.47
4	20.33	0.69
5	20.10	0.45
6	20.32	0.68
7	20.50	0.86
8	20.15	0.50
Avg.	20.22	0.58
Calc'd.	19.64	----

$\sigma^2 = 0.020$ $\sigma = 0.140$ C.V. = 0.70%

[A] Using filter No. 42.

It might be noted that during the preliminary testing of the photometric titrator, using the Liebig method, levels of chloride of from 1 to 10 ppm were found and determined simultaneously with cyanide. This was accomplished without any modification to the titration. One needs only observe the second break after the titration of the cyanide ion.

Silver(I) vs. chloride

The titration of silver ion against chloride has been accomplished by several accepted analytical procedures, each having its own characteristic problems (57). Since the mechanism of the silver chloride precipitation is more straight-forward than that of the cyanide titration, it was felt that this system warranted study with the photometric titrator.

A 10.00 ml. aliquot of 0.01046 N chloride solution was transferred into the titration vessel with 150 ml. of doubly distilled water and 10 ml. of 1% gelatin solution. This solution was then titrated with 0.009579 N silver(I) solution. The data obtained from repetitive titrations of this system are presented in Table 12. The mean volume of silver(I) delivered was 11.28 ml. as compared to a calculated volume of 10.92 ml. The primary cause of this deviation is again considered to be the inability to apply a blank correction to the data generated. The coefficient of variation for these titrations was 0.43% indicating good reproducibility.

Table 13 lists data obtained from repetitive nephelometric titrations utilizing the same solutions and titration procedure as described for the turbidimetric system. No filters were used for the nephelometric

Table 12

Turbidimetric Titration of 0.009579 N Ag^+ vs. 10.00 ml. of 0.01046 N Cl^- *

Sample No.	Vol. Ag^+ (ml.)	Deviation (ml.)
1	11.28	0.36
2	11.18	0.26
3	11.33	0.41
4	11.32	0.40
5	11.32	0.40
6	11.25	0.33
7	11.22	0.30
8	11.32	0.40
9	11.28	0.36
Avg.	11.28	0.36
Calc'd.	10.92	----

$\sigma^2 = 0.00242$ $\sigma = 0.0492$ C.V. = 0.43%

* Using filter No. 42.

Table 13

Nephelometric Titration of 0.009579 N Ag^{+} vs. 10.00 ml. of 0.01046 N Cl^{-}.

Sample No.	Vol. Ag^{+} (ml.)	Deviation (ml.)
1	11.55	0.63
2	11.85	0.93
3	11.53	0.61
4	11.73	0.81
5	11.33	0.41
6	11.77	0.85
7	11.55	0.63
8	11.41	0.49
9	11.35	0.43
10	11.78	0.86
11	11.50	0.58
12	11.68	0.76
13	11.25	0.33
14	11.68	0.76
15	11.33	0.41
16	11.12	0.20
Avg.	11.53	0.60
Calc'd.	10.92	----

$\sigma^2 = 0.0433$ $\sigma = 0.206$ C.V. = 1.79%

titrations. A mean volume of 11.53 ml. was obtained as compared to 10.92 ml. calculated. A coefficient of variation of 1.79% was obtained.

Polarimetric titrations

Polarimetric titrations were performed by reacting d-tartaric acid with sodium hydroxide. Solutions containing 10 grams of tartaric acid per 100 ml. were prepared together with a 5 M sodium hydroxide solution. A filter combination, 807 + 877, having a λ_{max} at 518 nm was selected. The polarizers were crossed at the start of the titration so as to give minimum initial light intensity. Significant inflections corresponding to the theoretical equivalence point were obtained. Data from these titrations are of questionable value for demonstrating polarimetric titrations on the titrator since it was not known to what extent changes in optical activity contributed to the observed light intensity changes since a color change also occurred during the titration. Consequently, these data are not presented at this time. It is anticipated that further work will be carried out on this system in order to demonstrate more clearly this important application of the titrator.

Iron(II) tris 1,10-phenanthroline complex ion.

The operation of the internal colorimeter circuit previously described was tested making use of multiple dilutions of an accurately prepared stock solution of the iron(II) tris 1,10-phenanthroline complex. A standard 1.00 cm pyrex cell was employed together with a 518 nm filter combination, 807 + 877. A 10 megohm load resistor was used in the photo-

tube circuit in place of the usual 20 megohm resistor to minimize noise. Data obtained in this manner from the colorimeter circuit are shown in Table 14. Figure 13 illustrates the linearity of this system for about a hundred-fold range in concentration. Figure 14 presents an enlarged view of the linearity region confirming linearity over nearly two decades.

Table 14

Colorimetric Determination of Iron(II)
tris 1,10-Phenanthroline Complex Ion

$[Fe(o\text{-}phen)_3^{+2}] \times 10^6$	Voltage Output (volts)
500	0.0075
250	0.0440
100	0.2590
50	0.4265
25	0.6030
10	0.7560
5	0.7870
2.5	0.8220
Blank	0.8350
Dark Current	0.0001

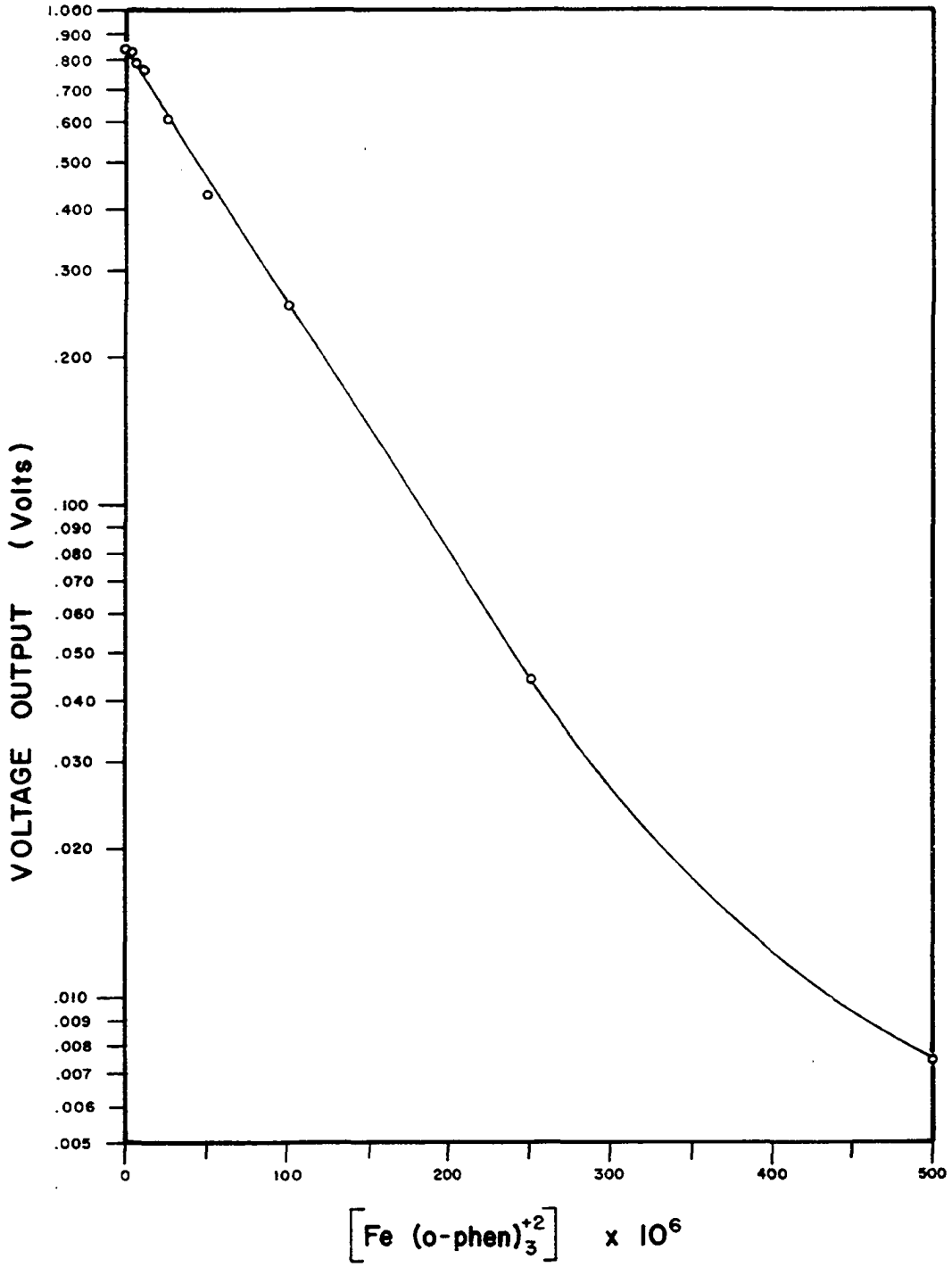


FIGURE 13

Colorimetric Determination of Iron(II) tris 1,10-Phenanthroline Complex Ion

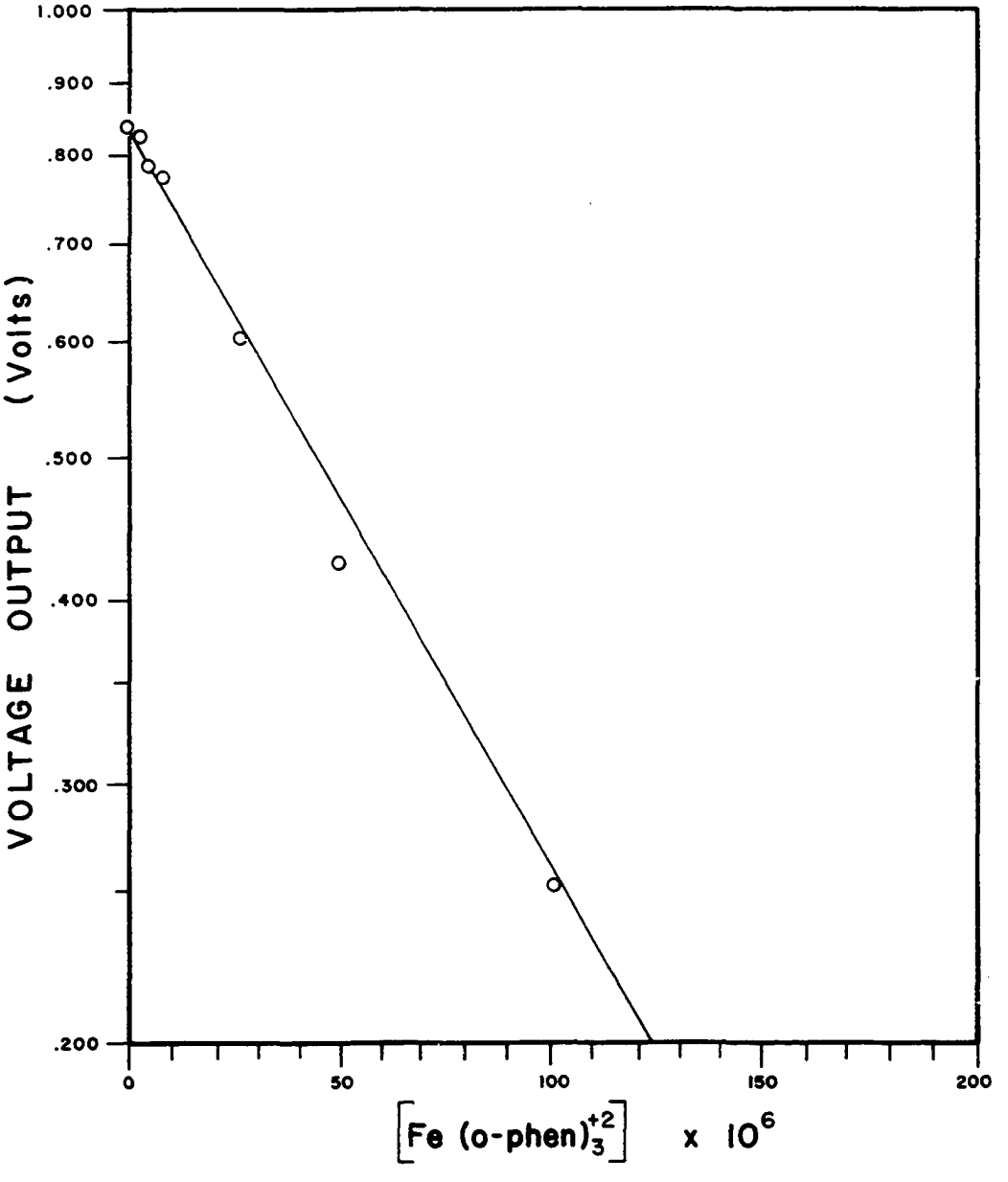


FIGURE 14

Colorimetric Determination of Iron(II) tris 1,10-Phenanthroline Complex Ion - Expansion of the Linear Region

CONCLUSIONS AND RECOMMENDATIONS

The fiber optics photometric titrator has been shown to perform several types of titrations with acceptable reproducibility, ease, and accuracy. Although many modifications of the titrator were made during the construction and testing periods to increase the accuracy and precision, further improvements on the mechanical and electrical systems can still be made. It should be realized, however, that depending on the system titrated, the limiting error may be in the chemical system and not in the photometric titrator, as was found in the iron(III) vs. EDTA titration. Also, it must be kept in mind that in the design of analytical instrumentation one reaches a plateau where a relatively small improvement in performance may not justify a large added expense.

The stirring of the solution could be improved by means of a variable speed shaft driven impeller type stirrer. Stirrer size and fluke pitch could then be chosen to produce the stirring efficiency desired. The delivery tip of the buret should be directed at the impeller, thus producing rapid mixing of the titrant without the problem of an undesirable vortex in the optical path. In nephelometric and fluorometric work, this type of stirrer should minimize problems of light scatter from wandering magnetic stirring bars.

The incorporation of a variable delivery rate buret should be an improvement when used with systems that are kinetically slow in the vicinity of the equivalence point. When such systems are encountered, the operator may choose a slow delivery rate and an appropriate chart speed or he may choose a faster delivery rate until the equivalence

point is approached where he then would be able to slow both the delivery rate and the chart speed to determine more accurately the equivalence point.

A variable load resistor or a variable amplifier following the buffer stage could resolve a number of the problems associated with nephelometric and fluorometric systems having small voltage inflections at the equivalence points. However, associated with higher load resistances is the requirement of better shielding for all the high impedence circuitry. In future models, only those load resistors having the lowest noise characteristics should be selected. Correction should be made for stray capacitance in future models, thus the dead band of the recorder and overshoot of the equivalence point are reduced to a minimum.

Polarimetric titrations would be improved by utilizing a 10 cm. pathlength instead of a 1.0 cm. cell path. Also, a higher quality of polarizing material should allow the instrument to discern smaller changes in optical activity, however, one must realize that this type of system is inherently limited to relatively large changes in optical activity, and correspondingly high concentrations.

An improvement in the absolute error could be obtained by reducing the volume of the titration vessel to about 50 ml. This would require only the rebending of the image conduit.

Automatic termination of the equivalence point and subsequent digital readout would undoubtedly improve the reproducibility of the titration. Also, it is possible that a more precise constant drive buret might justify the use of additional significant figures, thus increasing the accuracy of the measurement. While the accuracy and precision of the

system may be improved by modification of a component or sub-system, some other portion of the system will become the limiting source of error. Therefore, it is postulated that the minimum coefficient of variation with an ideal chemical system would be about 0.1% in light of current technological capabilities. However, for most routine analytical work a 0.5% coefficient of variation is generally considered adequate and this has been achieved.

APPENDIX I

Filter Characteristics

Filter No.	Spectral Characteristics (nm)	T max	Notes
800[a]			0.89 T from 350 to 800 nm
806	SC[b] (502)	N.A.[f]	
807	SC (510)	N.A.	
809	SC (525)	N.A.	Small slope to break
813	SC (548)	N.A.	At wavelengths below 400 nm T is > 0.10
815	SC (564)	N.A.	
817	SC (568)	N.A.	
818	NP[c] (370)	0.60	
	SC (598)	N.A.	
819	NP (375)	0.45	
	SC (610)	N.A.	
821	SC (622)	N.A.	
823	SC (634)	N.A.	
	LC[d] (795)	N.A.	
830	LC (428)	N.A.	
	SC (584)	N.A.	

a. 800 series indicates plastic sheet filters
b. SC indicates short wavelength cut off
c. NP indicates narrow band pass
d. LC indicates long wavelength cut off
e. BP indicates broad band pass
f. T_{max} not applicable to cut off filters

Filter No.	Spectral Characteristics (nm)	T max	Notes
832	BP[e] (390)	0.74	
	LC (605)		
837	BP (395)	0.81	
	LC (445)	N.A.	
	SC (607)	N.A.	
838	BP (400)	0.75	
	LC (445)	N.A.	
	SC (625)	N.A.	
839	LC (455)	N.A.	
	SC (627)	N.A.	
841	SC (646)	N.A.	
843	SC (653)	N.A.	
846	SC (663)	N.A.	
850	SC (676)	N.A.	
856	LC (513)	N.A.	
857	SC (685)	N.A.	
858	BP (485)	0.69	
859	LC (511)	N.A.	
	BP (750)	0.81	
861	SC (684)	N.A.	
	LC (789)	N.A.	
866	NP (425)	0.58	
	NP (765)	0.69	
871	NP (520)	0.60	
874	NP (523)	0.40	

Filter No.	Spectral Characteristics (nm)	T max	Notes
877	NP (500)	0.63	Unsymmetrical-skewed toward blue
878	BP (535)	0.71	
858+807	NP (515)	0.33	
856+806	NP (517)	0.38	
877+871	NP (510)	0.39	
877+806	NP (515)	0.41	
	NP (780)	0.30	
877+807	NP (518)	0.35	
	NP (780)	0.29	
877+858	NP (492)	0.46	
813+878	NP (563)	0.51	
866+817	BP (760)	0.50	
No. 2[g]	LC (382)	N.A.	
No. 4	LC (390)	N.A.	
	BP (725)	0.48	Unsymmetrical-skewed toward blue
No. 8	BP (400)	0.73	Very broad peak
No. 20	SC (369)	N.A.	
No. 23	SC (596)	N.A.	
No. 27	BP (745)	0.66	Unsymmetrical skewed to long wavelengths
No. 42	BP (410)	0.46	
No. 52	BP (520)	0.14	
No. 69	BP (735)	0.83	Unsymmetrical skewed to long wavelengths

g. Numbered filters are Corning filters.

Filter No.	Spectral Characteristics (nm)	T_{max}	Notes
Wratten No. 8	SC (493)	N.A.	
Wratten No. 58	NP (525)	0.56	
	BP (775)	0.52	Unsymmetrical skewed to long wavelengths
Primary B-2	BP (420)	0.48	
B-1[h]	NP (690)	0.55	Very narrow peak
B-3[h]	NP (514)	0.70	Very narrow peak
NP436-No. 473	NP (433)	0.48	
	NP (780)	0.41	
NP460-No. 48	BP (460)	0.34	
	NP (780)	0.46	
NP495-65A[i]	NP (496)	0.46	
	NP (770)	0.70	
NP405-No. 405	NP (403)	0.19	
	BP (753)	0.57	
SC465-No. 4	SC (476)	N.A.	
SC455-No. 3	SC (468)	N.A.	
SC595-No. 25	SC (599)	N.A.	
SC560-No. 22	SC (567)	N.A.	
SC570-23A	SC (582)	N.A.	
SC535-No. 16	SC (540)	N.A.	
SC520-No.2 - 15	SC (518)	N.A.	
SC510-No. 2A - 12	SC (520)	N.A.	
SC485-No. 8	BP (525)	0.49	

h. Baird interference filters
i. Turner fluorometer filters

APPENDIX II

Reagents*

Standard ammonia solution (0.1 N).- 7.6 ml. of 30% ammonia solution, Sp. Gr. 0.90 was diluted to approximately 1 liter with water. This solution was standardized against standard hydrochloric acid using 0.04% bromocresol purple indicator.

Standard ammonia solution (0.01 N).- This solution was prepared by a 10 fold dilution of the standardized 0.1 N ammonia solution and corrected for glassware calibration.

Bromocresol purple indicator (0.04% W/V).- 0.1 g in 18.5 ml. of .01 N NaOH plus 231.5 ml. water.

Buffer, pH 2 - 1 N Hydrochloric acid solution was added to 250 ml. of 1 N sodium acetate solution until the mixture read a pH of 2.0 on a pH meter.

Standard calcium solution (0.01 N).- 1 gram of primary standard calcium carbonate was dissolved in a minimum amount of 1:1 hydrochloric acid and diluted to 1 liter (55).

Calcium indicator (solid).- 200 mg of indicator was finely ground into 10 grams of potassium chloride with a glass mortar and pestle.

Standard chloride solution (0.01 N).- 0.75 grams of dried primary standard potassium chloride was dissolved in a small quantity of water and diluted to 1 liter.

* All chemicals except indicators and gelatin were Reagent Grade. All water used was either doubly distilled or pass through a mixed bed ion exchange column.

Standard copper solution (0.1 N).- 6.4 grams of clean, dry copper metal wire, 99.9%, was dissolved in a minimum amount of concentrated nitric acid. This solution was diluted to about 500 ml. adjusted with sodium hydroxide solution to a pH of 4, and then diluted to 1 liter.

Standard cyanide solution (0.01 N).- 0.65 gram of potassium cyanide was dissolved in a small amount of water and diluted to 1 liter. This solution was then standardized against standard silver solution using Deniges modification of the Liebig method (58).

Dichlorofluorescein indicator (2% W/V).- 0.2 gram of indicator was dissolved in 100 ml. of 70% ethanol.

Standard EDTA solution (0.1 N).- 3.8 grams of the disodium salt of ethylenediaminetetraacetic acid was dissolved in a small amount of water and diluted to 1 liter. This solution was then standardized against a standard copper solution (59).

Gelatin solution (1% W/V).- 1 gram of gelatin was dissolved in 100 ml. of water.

Standard hydrochloric acid (0.1 N).- 8.5 ml. of Sp. Gr. 1.19, 36%, hydrochloric acid was diluted to 1 liter water. This solution was then standardized against primary standard (TRIS or THAM) tris-hydroxymethylaminomethane (60).

Standard hydrochloric acid (0.01 N).- This solution was prepared by making a 10 fold dilution of the standardized 0.1 N hydrochloric acid solution.

Standard iron(III) solution (0.01 N).- 0.56 grams of primary standard iron wire was dissolved in a minimum amount of 1:1 nitric acid and diluted to 1 liter with water. The pH was adjusted to 2-3 with dilute nitric acid or sodium hydroxide as required.

Methyl violet indicator (0.2% W/V).- 0.2 grams of indicator was dissolved in 100 ml. of chlorobenzene.

Standard oxalate solution (0.1 N).- 6.7 grams of dried primary standard sodium oxalate was dissolved in water containing a 5 ml. of concentrated sulfuric acid and diluted to 1 liter with water.

Standard perchloric acid (0.1 N).- 8.5 ml. of 70% perchloric acid was mixed with 200 ml. of glacial acetic acid and 20 ml. of acetic anhydride. This solution was then allowed to stand overnight. It was subsequently standardized against dried primary standard potassium acid phthalate (52).

Standard permanganate solution (0.1 N).- 3.2 grams of potassium permanganate was dissolved in 1 liter of water. This solution was heated to near boiling for several hours and allowed to stand overnight. Subsequently the solution filtered through a Gooch crucible with an asbestos mat to remove any products of oxidation. This solution was then standardized against primary standard sodium oxalate by the method of Fowler and Bright (61).

Phenol red indicator (0.02%).- 0.05 grams of indicator was dissolved in 28.2 ml. of 0.01 N sodium hydroxide and then diluted to 250 ml. with water.

Standard 4-aminopyridine solution (0.1 N).- 9.4 grams of primary standard 4-aminopyridine was dissolved in a small amount of glacial acetic acid and diluted to 1 liter with the same.

Salicylic acid indicator (6% W/V).- 6 grams of salicylic acid was dissolved in 100 ml. of pure acetone.

Standard silver solution (0.1 N).- 17 grams of silver nitrate were dissolved in water, diluted to 1 liter and stored in an amber bottle. This solution was then standardized against primary standard potassium chloride using Fajans method (62).

Standard silver solution (0.01 N).- This solution was prepared by making a 10 fold dilution of the standardized 0.1 N silver solution.

Sodium hydroxide (5M).- 200 grams sodium hydroxide was dissolved in 1 liter of water.

Triethanolamine (20% V/V).- 20 ml. of triethanolamine was diluted to 100 ml. with water.

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