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Modification of the Brice Light-Scattering Photometer for Photoelectric Polarimetry by the Rouy Method

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Synopsis

Construction details for modifying the Brice light-scattering photometer for use in photoelectric polarimetry have been given. The measuring technique is based on the Rouy method, which is perhaps the most sensitive of all photoelectric methods of measuring the optical rotation of liquids, especially at small angles. A standard deviation of 0.01° has been observed with the use of an instrument modified in this way.

Introduction

The application of photoelectric measurements to polarimetry generally leads to greater precision and convenience than conventional visual methods. This is especially true when working with solutions of low rotation and solutions of proteins and other colloidal systems which scatter so much light that a visual polarimeter is often useless. Photoelectric polarimetry usually employs a beam of light whose path includes the sample, two polarizing optics, and a photosensitive device to measure the final light intensity. Rotation of one polarizing optic through equal and opposite angles from its position of maximum transmission gives data which are applied to the law of Malus to yield values of optical rotation.

In the Rouy method the plus and minus angle through which one polaroid is rotated is set very close to 90°. The readings of light intensity at the two equal angles are related to the optical rotation of the sample by a polarimeter function which is based on the difference of these two readings.[1]

The original paper by Carroll, Tillem, and Freeman[1] suggests constructing a pair of polaroid adapters for a photoelectric colorimeter and making the necessary measurements with this. An alternative approach is to modify a Brice light-scattering photometer. The latter procedure makes it possible to use a standard 1-dm. polarimeter cell, whereas most commercially available colorimeters and spectrophotometers employ a cell of such dimensions that the portion of the optical path through it is very much shorter (often of the order of 1 cm.) and the observed angles of optical rotation are correspondingly small.

Construction and Operation

The optical system of the Brice light-scattering photometer[2] includes a mercury vapor lamp, monochromat and neutral filters, shutter, two polaroid disks serving as polarizer and analyzer which can be rotated through angles of 90°, and a photomultiplier tube with its attendant power supply and indicator. To modify this instrument so that measurements of optical rotation are possible it is necessary to (*a*) make a cradle that will hold a standard 1-dm. polarimeter cell in the light path, (*b*) extend the limits of rotation of the polaroid in the analyzer position, (*c*) replace the slotted cap on the end of the collimator tube with one having a circular pupil, and (*d*) add one fixed and two adjustable stops to the photomultiplier housing to regulate the travel of the analyzer polaroid.

Construction details are given in Figures 1–4, where all dimensions are in inches. The cradle shown in Figure 1 is designed so that it can replace the table which normally holds the light-scattering cell. The two dimensions in the side elevation marked with asterisks were correct for the

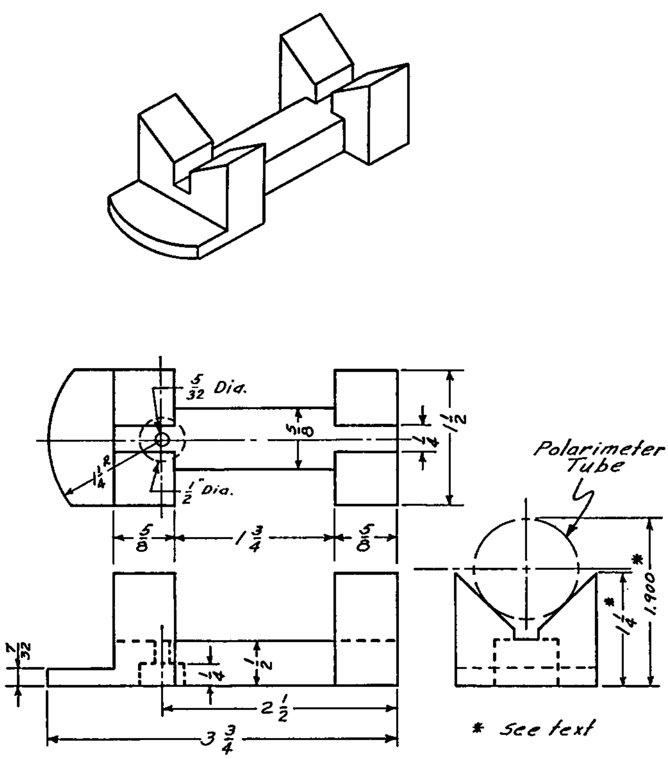

Fig. 1. Support cradle for polarimeter tube.

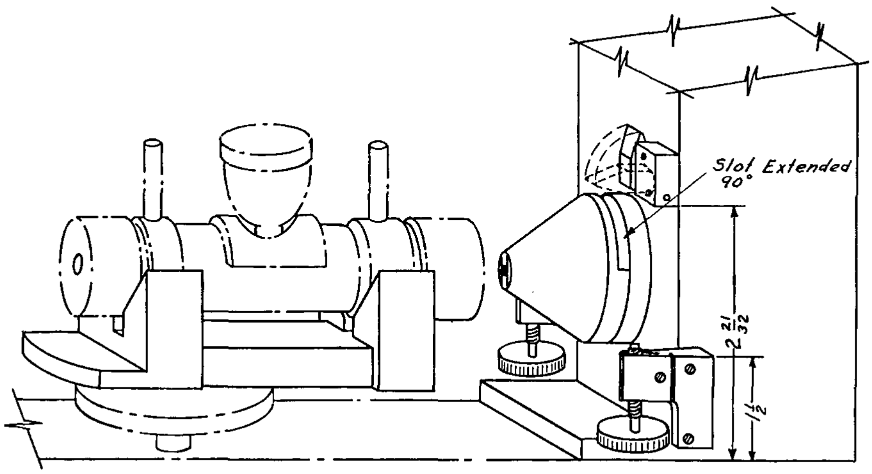

Fig. 2. Modification of photomultiplier housing.

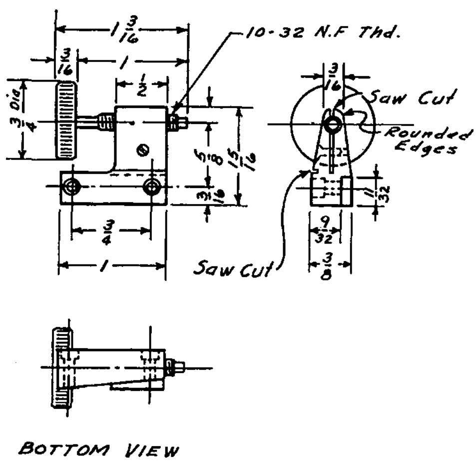

Fig. 3. Adjustable stop.

instrument modified in this laboratory. However, it is possible that in the course of production some models of the Brice light-scattering photometer may have been made with a table mount of a different size. In this case these two dimensions must be changed to values that will locate the center of the polarimeter cell in the optical path.

Construction of the cradle can be avoided if a regular light-scattering cell is used instead of a polarimeter cell, but this will mean a shorter light path through the solution and a corresponding decrease in the angle measured.

The modification of the photomultiplier housing is shown in Figure 2. The slot which guides the motion of the analyzer polaroid is extended to

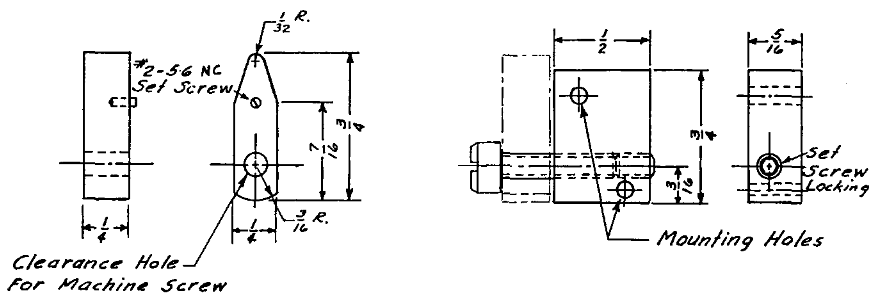

Fig. 4. Fixed stop.

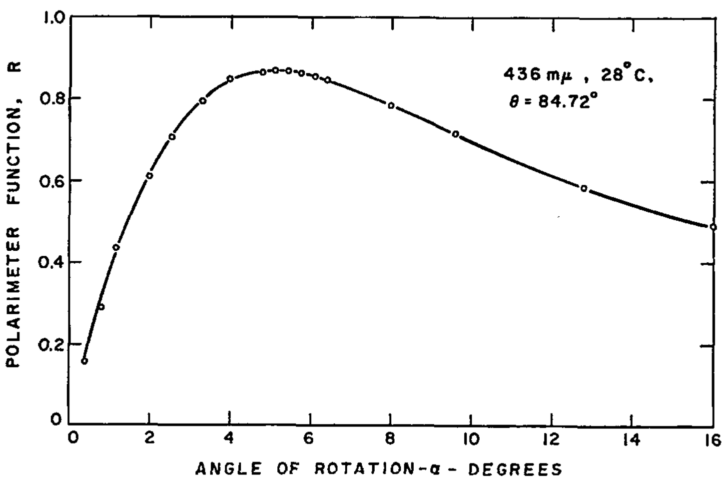

Fig. 5. Plot of polarimeter function vs. angle of rotation for sucrose solutions at 436 mμ, 28°C., and $\theta = 84.72°$.

90° beyond its normal top limit. The adjustable stops detailed in Figure 3 set limits for the rotation of the analyzer polaroid. They are drilled so that they match existing screw holes on the photomultiplier housing. The fixed stop, detailed in Figure 4, is located so that motion of the analyzer polaroid is arrested with its arm in the vertical position when the stop is in the "down" position shown by dotted lines in Figure 2.

The cap on the end of the collimator tube is replaced with one that is identical except that it has a $^1/_4$ in. diameter pupil instead of an exit slit.

To measure optical rotation with the modified light-scattering photometer the photomultiplier is oriented in the 0° position so that all optical components are in line and the working standard (filter) has been removed. The polarizer polaroid mounted on the collimator tube is turned so that its handle is in the vertical position, and the fixed stop on the photomultiplier housing is moved to the "up" position shown in Figure 2. With a polarimeter cell filled with distilled water in position on the cradle the two adjustable stops on the photomultiplier housing are set to give equal deflections on the photomultiplier galvanometer when the analyzer polaroid is rotated to either extreme. For maximum precision the angle through which the analyzer polaroid is turned to either side of its parallel position should be close to and slightly less than the complement of the angle being measured, as is discussed further on. The polarimeter cell is next filled with the solution under investigation and light intensity readings E_1 and E_2 are observed with the analyzer polaroid rotated to each extreme position. A polarimeter function, R, is then calculated from eq. (1):

$$R = (E_2 - E_1)/(E_2 + E_1) \tag{1}$$

and this is related to the angle of optical rotation of the sample via eq. (2)

$$R = 2 \tan \theta \tan \alpha / 1 + \tan^2 \theta \tan^2 \alpha \tag{2}$$

where α is the optical rotation of the sample and θ is the angle of the analyzer polaroid relative to its parallel position as determined by the adjustable stops.

Equation (2) is valid only for monochromatic light, and in actual practice this value of R cannot be achieved because of spectral band-width, the presence of a modicum of unpolarized light, and possibly other factors. For example, according to eq. (2), R is unity when angle α is the complement of angle θ. For a series of sucrose solutions of known optical rotation with the angle θ set for 84.72°, at the 436 mμ line of the mercury arc and at 28°C., the plot of R versus angle of rotation shown in Figure 5 resulted. Here the peak of the curve falls correctly at the angle complementary to θ, but the value of R is 0.870.

Consequently, the instrument must be calibrated. The calibration curve is, of course, valid for only one setting of the adjustable stops, but it makes it unnecessary to know the exact value of θ. From this curve, as well as from trigonometric consideration of eq. (2) it becomes obvious that for a given value of θ one value of R will correspond to two different values of α. The true value of α can be distinguished from the spurious by diluting the sample slightly and noting if the new value of R is larger or smaller.

To restore the photometer to condition for light-scattering measurements the original cell-holding table and collimator tube cap are replaced; the fixed stop is moved to the "down" position shown in dotted lines in Figure 2 and the 2-56 set screw is set so that when the handles of both polaroid mounts are in the extreme vertical position light transmission is a maximum.

Performance

By applying the principles of maxima and minima to the trigonometric relation between R and the angles involved, Carroll *et al.*, and Rouy have demonstrated that the sensitivity of the Rouy method increases as the angle θ is increased to 90°.[1,3] However, since R is a parameter dependent on the intensities E_2 and E_1, in practice these latter values must also be included in any expression for sensitivity. From inspection of eq. (1) it is seen that maximum sensitivity in determining R from the observed data results when the difference E_2-E_1 is a maximum. This occurs either when E_1 vanishes or when E_2 goes to infinity. Under these conditions R is unity and in eq. (2) the angle α is the complement of angle θ. Eliminating the parameter R between the two equations, and plotting E_2 versus α while holding E_1 to a fixed value will give a curve in which E_2 goes to infinity at an asymptote that corresponds to $R = 1$. Thus, sensitivity in determining R increases as the angle of rotation approaches the complement of θ. The sensitivity of determining the value of α also depends on the slope of the plot of R versus α, so that the overall sensitivity is a composite function, which for a given instrument will depend on how closely the recording device can be read, the intensity of random noise present, the scale to which the calibration curve is plotted, and the setting of the stops which limit the travel of the analyzer polaroid. It becomes obvious, however, from the equations and the plot in Figure 5 that θ should be set at an angle less than the complement of the angle of rotation being measured so that the latter will fall on the relatively steep slope of the low value end of the curve. For very small values of α this part of the curve can be made even steeper by increasing θ. In measuring the optical rotation of a sequence of sucrose solutions over a range of 0.16° to 4° at the 436 mμ line of the mercury vapor arc, at 28°C. and with $\theta = 84.72°$, taking five readings at each value of rotation gave a standard deviation of better than 0.01°. The recorder used had a scale of 100 divisions and was read to the nearest quarter of a division. In selecting the above value of θ optimum sensitivity was not sought, but rather a setting of the stops that would allow the instrument to be used over a range of optical rotations that was anticipated in a subsequent research program.

Since the polarimeter function, R, is based on the difference between the light intensities recorded when the analyzer polaroid is rotated to its two extreme positions, errors due to light absorbance, reflections within the cell, etc., tend to cancel. When working with turbid solutions, however, an error due to the depolarizing effect is still present. Experiments seeking a means of correcting this are now in progress at this laboratory.

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Résumé

On donne des détails de construction pour modifier le photomètre à diffusion lumineuse de Brice et ce pour l'utiliser en polarimétrie photoélectrique. La technique de mesure est basée sur la méthode de Rouy qui est peut-être la plus sensible de toutes les méthodes photoélectriques mesurent la rotation optique des liquides spécialement sous faibles angles. Une déviation standard de 0.01° a été observée en utilisant un appareil modifié en ce sens.

Zusammenfassung

Es wurden konstruktive Einzelheiten zum Umbau des Brice-Lichtstreuungsphotometers zur Verwendung für lichtelektrische polarimetrische Messungen angegeben. Das Messverfahren beruht auf der Methode von Rouy, die möglicherweise die empfindlichste photoelektrische Methode zur Messung der optischen Drehung von Flüssigkeiten, besonders bei kleinen Winkeln, ist. Bei einem in der beschriebenen Weise modifizierten Instrument wurde eine Standardabweichung von 0,01° beobachtet.

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