POLARIMETRIC SENSIBILITY AND ACCURACY.

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This article is a theoretical investigation of polarimetric instruments and methods. Particular attention is given to the construction and use of the fundamental polarimetric equations, to the limits of accuracy with different forms of analyzer, and to the errors due to lack of homogeneity in the sources of light employed.

The fundamental equation of polarimetry is an expression for the light transmitted by a pair of nicols in terms of the angle between the nicols, the amount of light entering the first nicol and the rotation produced by a body inserted between the nicols. This equation is

$$I = I_0 \sin^2 (\theta - \rho) \qquad \text{or}$$
$$I(\lambda) = E(\lambda) \sin^2[\theta - \rho(\lambda)] \tag{1}$$

expressing as functions of the wave length (λ), quantities which depend upon the quality of the light used. The angle θ between analyzer and polarizer is measured from a crossed position of the nicols. I is the intensity of the light transmitted of the wave length, for which E is the intensity of the source used and ρ is the rotation under investigation.

The setting of the analyzing nicol (or nicols) is an absolutely independent variable, while I, I_0, and ρ are complicated functions of wave length, or more properly, of wave period. Equation (1) holds for any particular wave period, and hence for all wave periods. The total light transmitted by a pair of nicols in any relative position is given by the integral of (1) with respect to wave period. The analyzing nicol is set at such an angle as to make the value of this integral a minumum in case the analyzer consists of a single nicol. With a half shade analyzer the setting is such as to make the value of this integral equal to the value of a similar integral in which θ has been altered by a small constant angle.

The rotation function $\rho(\lambda)$ has been developed in the form

$$\rho = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k}{\lambda^2}$$

by Drude[1] and found to express the rotary dispersion of quartz over a wide range of wave lengths. The author[2] has developed this function in the form

$$\rho = \frac{k(\lambda^2 - \lambda_1^2)}{\lambda^2(\lambda^2 - \lambda_1^2 + a_1)},$$

which was found to represent the rotation of sugar and other solutions in the visible and ultraviolet regions with great accuracy. The function $I_0(\lambda)$ corresponds with the emission function $E(\lambda)$ for the source used. None of these functions have yet been constructed, but they appear to be modifications of the exponential function of the form

$$E = cf(\lambda)\,e^{\phi(\lambda)}$$

The general unlimited expression for the total amount of light transmitted by a pair of nicols is then the integral of (1) with respect to the wave length, or

$$T = \int I(\lambda)d\lambda = \int E(\lambda)\sin^2[\theta - \rho(\lambda)]\,d\lambda. \qquad (2)$$

Consider now the applications of equation (2) to the measurement of rotation with (1) a simple analyzing nicol, (2) a half shade analyzer.

1. ANALYZER CONSISTING OF SINGLE NICOL.

In this case the analyzing nicol is set at such an angle as to make the transmission T in equation (2) a minimum. This condition gives

$$\frac{dT}{d\theta} = \frac{d}{d\theta}\int E\sin^2(\theta - \rho)d\lambda = o;$$

[1] P. Drude: Lehrbuch der Optik, Leipzig, 1900, p. 381.

[2] P. G. Nutting: Physical Review, 18, p. 24, July, 1903.

hence

$$\int 2E \sin (\theta - \rho) \cos (\theta - \rho) d\lambda = o$$

$$\int E \sin 2(\theta - \rho) d\lambda = o, \tag{3}$$

from which

$$\tan 2\theta = \frac{\int E \sin 2\rho d\lambda}{\int E \cos 2\rho d\lambda} \equiv \theta(E, \rho) \text{ say.}$$

This value of θ gives the setting of the analyzer for which the intensity of the transmitted light is a minimum for any sort of heterogenous source whose emission function is $E(\lambda)$. This reading θ is the true rotation for the substance under investigation for some intermediate wave length. This wave length is found by eliminating θ between the equations

$$\frac{dT}{d\theta} = o \text{ and } \frac{dI}{d\lambda} = o.$$

Hence it is evident that if $\theta = \theta(E_1\rho)$ is a solution of the first of these, then the wave length λ_θ sought is given by $\lambda_\theta = \theta(E, \lambda)$ or

$$\tan 2\lambda_\theta = \frac{\int E \sin 2\lambda d\lambda}{\int E \cos 2\lambda d\lambda}. \tag{4}$$

With any heterogeneous source then, a single setting of the analyzer may be made for minimum transmitted light. From this setting may be calculated one or more wave lengths for which this setting (increased or diminished by some integral multiple of π) is the actual rotation of the substance under investigation.

The minimum amount of light transmitted after the analyzer is set is given by (2) after the values of θ from equation (3) and λ from (4) have been substituted. This minimum value will evidently vary from a very small to quite a large quantity as the source is less and less monochromatic. It is of importance in the discussion of errors in measurement later on.

In the following special cases the general equations above admit of complete solution and development in practical working formulas. They are taken up in turn.

(*a*) *Monochromatic Source.*—If the light used is so homogeneous that ρ may be regarded as a constant, (3) integrates into $E_0 \sin 2(\theta-\rho_0)=o$, where E_0 is the total light transmitted by parallel nicols. In this case $\theta=\rho_0$ is a solution; the reading of the instrument gives the actual rotation directly, whatever the value of E_0. Increasing the intensity of the source of light merely increases the accuracy of the setting. But spectrum lines always broaden with increase of intensity. Eventually the increased accuracy due to increased luminosity must be offset by a decrease in accuracy due to heterogeneity of the light used. For $\theta=\rho=$a constant, (2) gives $T=o$, so that the minimum setting is complete extinction.

(*b*) *Two Monochromatic Sources.*—Let λ_1 and λ_2 be the wave lengths of the double source used (say the sodium lines), and let E_1, E_2, and ρ_1, ρ_2 be the corresponding intensities and rotations. Then (3) gives as the condition for a minimum of transmitted light

$$E_1 \sin 2(\theta-\rho_1)+E_2 \sin 2(\theta-\rho_2)=o \qquad (5)$$

Now θ must lie between ρ_1 and ρ_2 in value and hence $\theta-\rho$ can not exceed $\rho_1-\rho_2$. Except in the measurement of rotations amounting to hundreds of degrees then, we are warranted in using the angle for the sine of the angle, hence (5) gives the working formual

$$\theta=\frac{E_1\rho_1+E_2\rho_2}{E_1+E_2}\equiv\frac{\rho_1+K\rho_2}{1+K}$$

where $K\equiv E_2 : E_1$, the ratio of the intensities of the two component sources. From this it appears that the intermediate wave length for which the reading of the analyzer is the actual rotation is given by

$$\lambda_\theta=\frac{\lambda_1+K\lambda_2}{1+K}$$

neglecting the curvature of the rotation curve $\rho(\lambda)$ between λ_1 and λ_2.

(*c*) *Any Symmetrical Source.*—When the components of a double monochromatic source are equal in intensity, $E_1 = E_2$. The setting of the analyzer gives $\theta = \frac{1}{2}(\rho_1 + \rho_2)$, the correct reading for the rotation corresponding to the mean wave length $\lambda = \frac{1}{2}(\lambda_1 + \lambda_2)$. Since any symmetrical source may be considered as composed of pairs of monochromatic elements of equal intensity, it is evident that the analyzer will give directly the true rotation corresponding to the mean wave length until the source becomes so broad that the curvature of the rotary dispersion curve is no longer negligible within the range of wave lengths represented by the spectral width of the source.

(*d*) *Any Aggregate of Monochromatic Sources.*—For an indefinite number of monochromatic sources, equation (1) becomes

$$I = E_1 \sin^2 (\theta - \rho_1) + I_2 \sin^2 (\theta - \rho_2) + \ldots\ldots$$

while the condition for a minimuin (3) becomes

$$E_1 \sin^2 (\theta - \rho_1) + E_2 \sin^2 (\theta - \rho_2) + \ldots\ldots = 0$$

hence the working formula is

$$\theta = \frac{E_1\rho_1 + E_2\rho_2 + E_3\rho_3 + \ldots\ldots}{E_1 + E_2 + E_3 + \ldots\ldots} \tag{6}$$

determining the setting of the analyzer for which it gives the true rotation for the wave length $\lambda_\theta = \dfrac{E_1\lambda_1 + E_2\lambda_2 + E_3\lambda_3 + \ldots\ldots}{E_1 + E_2 + E_3 + \ldots\ldots}$.

2. HALF SHADE ANALYZER.

Suppose the analyzer to consist of two nicols, making a small angle $a = 2\delta$ with each other. Let these two analyzing nicols make angles of θ_1 and θ_2 with the polarizer in its normal position. Then $\theta_2 - \theta_1 = a$, the analyzing angle. Hence by equation (1), the light transmitted by the two halves of the analyzer is, putting the reading of the instrument $\theta = \frac{1}{2}(\theta_1 + \theta_2) = \theta_1 + \delta = \theta_2 - \delta$,

$$I_1 = I_0 \sin^2 (\theta_1 - \rho) = I_0 \sin^2 (\theta - \delta - \rho)$$

and

$$I_2 = I_0 \sin^2 (\theta_2 - \rho) = I_0 \sin^2 (\theta + \delta - \rho).$$

For a setting of the analyzer the two halves are equally illuminated, $T_1 = T_2$, or

$$\int E \sin^2 (\theta - \delta - \rho) d\lambda = \int E \sin^2 (\theta + \delta - \rho) d\lambda \qquad (7)$$

which reduces (without approximation) to

$$\int E \sin^2 (\theta - \rho) d\lambda = 0,$$

an equation independent of the analyzing angle a and identically the same as equation (3) for a simple analyzer. Hence a half shade analyzer will give the same reading as a simple analyzer whatever the heterogeneity of the source. This reading

$$\theta = \frac{E_1\rho_1 + E_2\rho_2 + E_3\rho_3 + \ldots\ldots}{E_1 + E_2 + E_3 + \ldots\ldots}$$

gives the rotation corresponding to the wave length

$$\lambda_\theta = \frac{E_1\lambda_1 + E_2\lambda_2 + E_3\lambda_3 + \ldots\ldots}{E_1 + E_2 + E_3 + \ldots\ldots}$$

The minimum intensity of transmitted light is by (7)

$$\int E(\lambda) \sin^2 \delta d\lambda$$

which is never zero even for monochromatic light sources, and is larger the less homogeneous the source and the larger the analyzing angle 2δ used.

3. CONDITIONS FOR MAXIMUM SENSIBILITY AND ACCURACY.

Since an increase in the intensity of a nearly monochromatic source of light is usually accompanied by a decrease in its homogeneity while accurate polarimetric measurements demand a maximum of both intensity and homogeneity, the best compromise between the two can only be determined after a careful consideration of the conditions governing sensibility and accuracy. These conditions involve the photometric sensibility and threshold value of human vision as well as the form of analyzer used and the form of the $E(\lambda)$ and $\rho(\lambda)$ curves.

With a simple analyzer consisting of a single nicol, any setting of the analyzer such that the total light transmitted is imperceptible is a reading of the instrument. Hence θ differs from ρ by not more than the amount that gives the integral in equation (2) a value equal to the least light perceptible of the color used. Hence in practice, instead of actual extinction we have

$$\int E \sin^2(\theta-\rho)\, d\lambda < T_0$$

where T_0 is the least light perceptible of the color used. If the source is nearly monochromatic and of total intensity E, then

$$E \sin^2 \epsilon < T_0$$

where $\epsilon=\theta-\rho$ is the maximum error in a setting of the analyzer. Hence $\epsilon<(T_0:E)^{\frac{1}{2}}$. To halve the maximum error in a single setting then, it is necessary to increase the intensity of the source four times. Increasing the intensity of the source is not an effective means of increasing sensibility.

The threshold value T_0 varies enormously with different colors. It is about 0.0005 meter-candle [3] in the blue-green, twice as great for the green of the mercury lamp, perhaps twenty times as great for sodium yellow and more than a thousand times as great for the hydrogen red. The reciprocal of T_0 may be regarded as a measure of the sensibility of the eye to light of a given color, and has been made the subject of investigation by Ebert,[4] Langley,[5] König,[6] and Pflüger.[7] I have taken the results of Ebert on two persons, König on two persons, Langley on four persons, and of Pflüger on eleven persons, representing over forty series of observations in all. This

[3] This value 0.0005 meter-candle was supplied me by Dr. E. P. Hyde, of the photometry division of the Bureau of Standards, and is the result of much personal observation.

[4] H. Ebert, Wied. Ann. **33**, 136; 1888.

[5] S. P. Langley, Phil. Mag. **27**, 1; 1889.

[6] A. König, Beiträge Psy. Phys., Hamburg, 1891.

[7] A. Pflüger, Ann. Ph., **9**, 200; 1902.

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data is so discordant that no mean curve of any value can be drawn, but the curve

$$V=e^{-a(\lambda-\lambda_m)^2}$$

with $a=5$ and $\lambda_m=5.1$ was found to be as good a mean as any that could be drawn, and it was adopted as representing the sensitiveness of a sort of mean standard eye. Calculated values are given below with values referred to the maximum at $\lambda=510\ \mu\mu$ as unity.

$\lambda=$		500	490	480	470	460	450	440	430	420 $\mu\mu$
	510	520	530	540	550	560	570	580	590	600 $\mu\mu$
$V=$	1.00	0.95	0.82	0.64	0.50	0.29	0.16	0.086	0.041	0.017

The sensibility of a polarimeter having a simple analyzer will then vary by the square roots of these amounts with the wave length of light used, and will be fifty to one hundred times less in the red and violet than in the green, even with sources of the same intensity.

Since T_0 and E are expressible in the same units, a rough limit to the angle ϵ may be determined. For $E=100$ meter-candles, a source appears of painful brightness to the eye. Giving to T_0 the mean value of 0.001 meter-candle, $\epsilon^2=10^{-3}$: $10^2=10^{-5}$ radian^2, $\epsilon=.003$ radian or about 0.17 degree.

As the source departs from homogeneity two additional sources of error appear; the limits of integration are so wide that ρ (λ) can no longer be considered constant between them and the minimum transmission is not extinction. A setting on a minimum of intensity is much less accurate than a setting on extinction and decreases in accuracy as the value of the minimum increases. For an approximately homogeneous source the total energy transmitted is

$$E \sin^2 (\theta-\rho)$$

where E is the integrated intensity of the source. Hence if $\delta\rho$ is the variation in the rotation ρ between the extreme wave lengths represented in the source $E\,(\lambda)$, and T_0 is the threshold value of the luminosity as above,

$$\delta\rho < (T_0\colon\ E)^{\frac{1}{2}}$$

If then a green line 0.1 $\mu\mu$ broad and having an intensity of 100 meter-candles is used, a rotary dispersion equal to that of 15 cm of quartz will give an error less than the possible error in setting the analyzer (0.17 degree). 0.1 $\mu\mu$ is about the width of the sodium lines as ordinarily produced in an oxy-hydrogen flame.

When discrete sources (such as the two D lines) are used, the minimum intensity of the light transmitted is $I=E\,(\delta\rho)^2$. In case sodium light is used in measuring the rotation of a plate 1 cm thick, $\delta\rho=0.43$ degree $=7.5\times10^{-3}$ radians, $(\delta\rho)^2=.000056$, so that the minimum light transmitted is about .000056 of the whole.

Half-Shade Apparatus.—When a double analyzer is used, the accuracy of a setting depends primarily on the sensibility of the eye in judging of the equality of the illumination of adjacent fields. The eye is able to detect differences of about one-tenth of one per cent in intensity under the most favorable conditions. Aside from personal variations due to the observer and the amount of eye fatigue, etc., this sensibility varies to a slight extent with the color of the light used and with the absolute intensity of illumination of the halves of the analyzer field. The sensibility appears to be a maximum for a field intensity equal to that of diffuse daylight, or, say, 20 meter-candles, and falls off rather slowly for greater and for less intensity. It is a maximum for green or white light and falls off slightly toward the red and violet. But with intensities varying from 1 to 100 meter-candles and colors ranging from deep red to violet, the variation in visual sensibility is small in comparison with variations due to the individual observer and the amount of his fatigue.

Let σ be the fraction of the whole by which the illumination of two adjacent fields must differ in order that the difference may be just perceptible; 0.1 per cent to 5 per cent or more according to conditions. Then calling these two intensities T_1 and T_2

$$T_1=(1+\sigma)T_2$$

But by equation (7)

$$T_1=\int E\sin^2(\theta-\rho+\delta)d\lambda$$

and

$$T_2=\int E\sin^2(\theta-\rho-\delta)d\lambda$$

Let ϵ be the error in a setting of the analyzer, that is, the amount by which the setting of the analyzer θ differs from the rotation ρ to be measured, or $\epsilon = \theta - \rho$. Hence for a narrow source

$$(\epsilon + \delta)^2 = (1 + \sigma)\,(\epsilon - \delta)^2$$

from which the error

$$\epsilon = \tfrac{1}{4}\sigma\delta,$$

or one-fourth the product of the analyzing angle and the photometric sensibility. In other words, the sensibility of the analyzer is inversely proportional to the analyzing angle over a wide range of intensity and color of the light used.

It is of interest to know what analyzing angle is best for maximum sensibility. When this condition is fulfilled, the derivative with respect to the analyzing angle, of the difference in the illumination of the two halves of the analyzer is zero, since $I_1 < (1 + \sigma)\, I_2$ and hence $I_1 - I_2 < \sigma I$, where σ is the photometric sensibility of the eye (about 0.1 per cent). Hence to determine the best analyzing angle

$$\frac{d}{d\delta}(I_1 - I_2) = \frac{d(\sigma I)}{d\delta} = \frac{d(\sigma I)}{d\,I}\,\frac{d\,I}{d\delta} = I\frac{d\sigma}{dI} + \sigma = 0 \tag{8}$$

or since $I = E\delta^2$, we have from (8) to determine the best analyzing angle ($a = 2\delta$)

$$\frac{\sigma}{E\delta^2} + \frac{d\sigma}{d\,I} = 0.$$

As to dimensions, it is to be noted that E and I are measured in the same units, say meter-candles, σ and δ are pure numbers. This condition shows that if the photometric sensibility σ were independent of the full illumination ($d\sigma : d\,I = 0$), the smaller the analyzing angle the greater would be the sensibility. But with an illumination below 1 meter-candle, we know that σ increases rapidly as I decreases. That is with fainter field illumination, the least difference that can be detected in the intensity of two adjacent fields becomes a larger percentage of the whole. The best analyzing angle to be used can not be fixed without more exact photometric data on the values of $d\sigma : d\,I$. As a rough estimate consider $d\sigma : d\,I = -1$, a probable value when I is about 0.1 meter-candle and σ about two per cent. Then with a source $E = 500$ meter-candles, $\delta = (0.02 : 500)^{\frac{1}{2}} = 0.002$ radian $= 6$ minutes of arc. Hence a good value for 2δ, the analyzing angle, would be 0.2 degree.

Errors due to the spectral width of the source are the same when a half-shade analyzer is used as with a simple analyzer, the equation determining these errors being the same. The chief error in the use of a source of considerable spectral width is due to the change in the rotation to be measured within that width.

Comparing the sensibility ϵ_2 of the half shade with that of the simple polarimeter ϵ_1 we have

$$\epsilon_1 = \left(\frac{T_1}{E}\right)^{\frac{1}{2}} \text{ and } \epsilon_2 = \frac{1}{4}\sigma\delta = \frac{\sigma}{4}\left(\frac{T_2}{E}\right)^{\frac{1}{2}}$$

hence

$$\frac{\epsilon_2}{\epsilon_1} = \frac{\sigma}{4}\left(\frac{T_2}{T_1}\right)^{\frac{1}{2}}$$

where T_1 is the threshold value or the least perceptible illumination and T_2 is the mean full illumination in the half-shade analyzer. As a numerical illustration, take one per cent for the photometric sensibility of the eye ($\sigma = 0.01$), eighty minutes for the analyzing angle ($\sigma = 40' = 0.01$ radian). Then

$$\frac{\epsilon_2}{\epsilon_1} = \frac{0.01\sqrt{0.01}}{4\;\sqrt{0.001}} = 0.025$$

or the half-shade analyzer is forty times as sensitive as the simple analyzer.

The sensibility of either analyzer increases with the square root of the intensity of the source. As the errors due to a lack of homogeneity of the light used are negligible until the spectral width of the source is of the order of 0.5 $\mu\mu$, the most intense sources at our command may be employed. *Unsymmetrical* sources, and particularly double unsymmetrical sources like the pair of D lines, are to be particularly avoided as leading to graver errors than the use of symmetrical sources of much greater spectral width. Having determined upon a suitable intense source and knowing the relation between visual photometric sensibility and intensity of illumination, the best value of analyzing angle to give maximum polarimetric sensibility may be determined. The sensibility might then be still further increased by a method of photographic interpolation.