A Study of Line-Width Photographic Photometry for Use in Spectrochemical Analysis.

John A. Perry
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A STUDY OF LINE-WIDTH PHOTOGRAPHIC PHOTOMETRY
FOR USE IN SPECTROCHEMICAL ANALYSIS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemistry

by
John Arthur Perry
B. S., University of Rochester, 1942
M. S., Louisiana State University, 1952
June, 1954
MANUSCRIPT THESES

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ABSTRACT

The field of line-width photometry has been surveyed with respect to pertinent literature and to gaps in knowledge and technique. The nature and varieties of line-width photometry have been clearly and newly defined. Basic data on line-width performance of spectroscopic emulsions have been gathered and reported. Specific emulsions for line-width photometry have been recommended. The independence of line-width photometry from variations in emulsion response due to processing has been explained.

The absolute and relative theoretical and experimental precisions of line-width and densitometric photometry have been evaluated and compared with equations and data derived and obtained in this study. Quantitative spectrochemical analysis is concerned with the estimation of concentration of one or more elements in a sample. Here, densitometry has been shown to be characterized by inability to cover more than a range of two or three in concentration and by relative error which increases exponentially with concentration. In contrast, line-width photometry has been shown in calculations to be capable of exceptionally wide ranges of concentration and to display relative error which decreases with increasing concentration.
An experimental technique for the rapid and precise measurement of line-width has been developed; the technique requires only commercially available equipment. Elimination of photometric full-scale calibration for line-width measurements has been introduced. The time for measuring one line-width has been cut from minutes to less than five seconds; the error of measurement has been reduced at the same time from several microns to one and one-tenth microns. Compared with densitometry, which is the photometric procedure now used in spectrochemical analysis, line-width photometry now offers equal speed, greater simplicity, superior precision, and exceptionally wide concentration range.
INTRODUCTION

Spectrochemical analysis has since 1930 so expanded in application that new such equipment is found in nearly all industrial laboratories. Qualitatively, the method is fast, simple, explicit, and often unique; quantitatively, aside from photoelectric installations, it lacks concentration range and is not precise at high percentages.

Much developmental work has been aimed at increasing the precision of photographic spectrochemical analysis while still retaining its speed. The main sources of error in the present method have been found to be reproducibility of sample excitation and the various aspects of photometry.

Measurement of attenuation of light passing directly through the developed photographic emulsion is known as specular densitometry. This method is now universally used for photometry in photographic spectrochemical analysis; the method demands extreme care and reproducibility in the processing of emulsions. Many papers have been written which point out the serious errors resulting from slight lapses in exact reproducibility in emulsion processing.

The spreading of the photographic image with increasing exposure has been studied at length by astronomers; the phenomenon applied to
spectrochemical analysis has been reported in less than ten papers. Yet the precision of results based on line-width photometry consistently equals or surpasses that of specular densitometry, and the range of concentrations to which line-width photometry can be applied appears to be exceptionally wide. Of equal interest is the apparent independence of the method from plate-to-plate variations in careful emulsion processing.

The study presented here is both general and specific in purpose. Knowledge pertinent to the subject has been gathered and grouped into a coherent review of the various aspects of the problem. An attempt has been made to supply requisite information on those parts of the subject which have been insufficiently treated in the literature. The various line-width methods have been treated in detail and compared with specular densitometry by expressions developed in this paper and evaluated with both new and published experimental data. Radical improvements in the speed and precision of the experimental approaches to the use of line-width methods have been described.

The literature of photography, astronomy, and spectroscopy is vast, and if the line-width technique has not heretofore been given its due attention, at least the basic facts are well known and available. As far as possible, material relevant to line-width photometry has been brought together here in an organized fashion. The conclusions in the literature regarding the nature, history, and mathematical description of the spread of the photographic image have been presented. The intention has been to give separate consideration to each of the variables affecting this spread: the wavelength and
incident angle of the illumination; the silver halide grain size and sise-frequency distribution; the physical and chemical properties of the gelatin of the photographic emulsion; and the phases of emulsion processing.

The methods of studying and measuring image spread and line-width have been reviewed. A technique having good precision and a speed and flexibility matching that of densitometry has been presented for the measurement of line-width. A critical appraisal of a commercial instrument applicable to line-width measurement has been made. The new technique of line-width measurement, used here for the first time in the measurement of small distances, was applied in gathering the experimental data for the appraisal of the instrument.

Line-width photometry not only will supplement densitometric photometry, but for wide application should partially displace this competitive and presently entrenched technique. Densitometry has been surveyed and expressions clearly defining its attainable precision have been developed to make possible an evaluation of pertinent work in the literature and to permit a theoretical comparison of densitometric and line-width photometry.

Expressions relating the operational constants of densitometric and line-width analysis have been developed and evaluated on the basis of data acquired for this purpose. In this particular part of the study, the results have been compared with previously reported work which incorporated both photometric techniques.

Finally, the directions in which line-width photometry can and should advance have been indicated.
The nature of this study has involved presentation of material from the literature as well as original work. For maximum coherence in treatment of the subject, the paper has not been divided into two parts, one new and one old. Instead, the subject has been left intact; for the convenience of the reader, however, the original matter within each section has been indicated by asterisks, as shown below.

*  
[original matter]  
**
HISTORY AND REFERENCE WORKS

Exploratory work in line-width photographic photometry has been reported in only three papers (9, 11, 12), and only five papers (9, 20, 22, 51, 52) have contained applications of the method to spectro-chemical analysis, although several references (1, 31, 49) have contained favorable remarks concerning the line-width approach.

No one of the original investigators (9, 22, 37) gave evidence of having consulted the literature, nor did they seem more than cursorily aware that a great deal of relevant work had been done by astronomers and by researchers in photography. Indeed, the effect has once been rediscovered (11) in an astronomical laboratory.

In 1857, Bond (6) first suggested using the image-spread principle for the measurement of stellar magnitude. The photographic emulsion is a versatile and potentially precise means of photometry, and its properties have been extensively studied by many workers, among whom can be cited Mees (44, 45), Parkhurst (54), Stetson (82), Tugman (87), and especially Ross (61, 62, 63, 64, 65, 66, 67, 68, 69, 70). Many of the results of these investigations were combined in Mees' "The Theory of the Photographic Process" (46), Chap. XXI, "The Physics of the Developed Image;" this work was preceded by Ross' "The Physics of the Developed Photographic Image" (71). Neblette's "Photography, Its Materials and Processes" (48) is another modern
reference work containing less detail that is pertinent to this study. Finally, "Fundamentals of Photographic Theory," (37) by James and Higgins is the most recent book of its type issuing from the laboratories of the Eastman Kodak Company and contains much relevant material, including a good chapter titled, "The Structure of the Developed Photographic Image."
LINE-WIDTH PHOTOMETRY

Definition

The phenomena involved in line-width photometry permits use of the term, "image-spread" photometry. Line-width spectrochemical analysis is not based photometrically on the "physical widths" of lines, that is, the wavelength spread of the wavelengths of light emitted from the sample. This was pointed out by the original investigators (9, 22, 27); it is also clear from descriptions of physical widths in such books as Tolansky, "High Resolution Spectroscopy" (85); White, "Introduction to Atomic Spectra" (93); and Candler, "Modern Interferometry" (8). Physical widths are far too small (ca. 0.005 Å) to account for the image width observed on the photographic emulsion. The presence on spectrograms of spectrographic lines of different widths is explained not only by image-spread but also by insufficient resolution. In series spectra, for example, what are known as "diffuse lines" are groups of two or more unresolved lines, each individual line having the same narrow physical width which has been indicated. Line-width photometry is based on the diffusion of light in the photographic emulsion; the diffusion causes spreading of the image beyond the corresponding geometrical borders of the defining object, the slit of the spectrograph.
James and Higgins (37) have made the valuable distinction between what they refer to as "optical turbidity" and "photographic turbidity." A high proportion of the light falling on a part of an emulsion may be deflected from its original direction by the high optical turbidity of the emulsion; but if this effect does not for one or another reason result in a diffuse image, the emulsion is not said to exhibit high photographic turbidity. The net effect, the photographic turbidity, is the turbidity which is measured. However, photographic turbidity cannot occur unless optical turbidity is present.

The various methods of line-width photometry have been discussed in detail in the section, **Types of Line-Width Analysis**, but for purposes of immediate orientation, the terms "matrix," "constituent," "measured line," and "indicator" or "indicator line" have been defined below.

In this paper, "matrix" and "constituent" have referred, respectively, to the substance making up most of a sample, as, aluminum in an aluminum alloy, and to some element appearing in smaller concentration, as, iron in an aluminum alloy.

The "photometric width" (27) is the width of a line, the "measured line," at a certain density indicated by the density at the center of another line, the "indicator" or "indicator line." These terms have been illustrated in Fig. 1. The terms "matrix width" and "constituent width" have been used here to describe the two variations of the photometric width technique; these terms have been illustrated in Figs. 2 and 3. Matrix width has meant that width
FIGURE 1
PHOTOMETRIC WIDTH

CURVES REPRESENT MICROPHOTOMETER RECORDINGS OF TWO LINES IN A SPECTROGRAM
FIGURE 2

MATRIX WIDTH

MEASURED LINE

INDICATOR LINE

d

c

b

a

MATRIX LINE, ESSENTIALLY CONSTANT IN WIDTH AND DENSITY

CONSTITUENT LINES, SHOWN FOR DIFFERENT CONCENTRATIONS OF CONSTITUENT

INCREASING CONSTITUENT CONCENTRATION

1 2 3 4

CORRESPONDING MATRIX WIDTH

a b c d
FIGURE 3

CONSTITUENT WIDTH

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of a matrix line at a density indicated by the density of a con­
stituent line; constituent width, the width of a constituent line
at a density indicated by a matrix line.

The terms "base line-width" and "spreading factor" have been
illustrated in Fig. 4. In this work, base line-width has meant the
width, at 37.5% transmittance, of the less dense of two lines which
are related by the step-sector used in making the exposure. Spreading
factor, calculated from equation (3), expresses the change in line-
width resulting from a change in exposure.

"Sharpness index" is a term from photography which expresses
density gradient parallel to the emulsion surface at the side of an
image. In this paper, sharpness index has indicated the sharpness
of the sides of spectral line images. Sharpness index has been
illustrated in Fig. 5.

# *

Nature of the Phenomenon

By scratching an emulsion with sandpaper, developing the emulsion
and taking photomicrographs of the scratch pressure-images, Goldberg
(28) showed that the spread of the image in the emulsion is not an
effect caused by transmission of sensitization of the silver grains
before or during development. Although Mees (46) concluded that
infectious development exists, he was simultaneously in context re­
stricting the meaning of the term "infectious development" to the total
development of an only partially exposed "clump." The regular
spreading of an image into neighboring unexposed areas in the precise
and predictable fashion which has been considered in this paper is
FIGURE 4
BASE LINE-WIDTH
SPREADING FACTOR

CURVES ARE REPRESENTATIONS OF MICROPHOTOMETER TRACINGS OF TWO SEGMENTS OF A SPECTRAL LINE IMAGE. THE SPECTRAL LINE PASSED THROUGH A STEP SECTOR HAVING A STEP RATIO \( \frac{E_2}{E_1} \).
SHARPNESS INDEX = $S = \frac{D}{X}$, WHERE $X$ IS GIVEN IN MICRONS.

STRAIGHT LINE SHOWN DRAWN ON MICROPHOTOMETER TRACING REPRESENTATION IS DRAWN TANGENTIAL TO INFLECTION POINT.

$$D = \log \left( \frac{1}{\text{TRANSMITTANCE}} \right)$$
not attributable to the development process. The spread of an image within a photographic emulsion is purely an optical effect, caused by spreading of light within the emulsion; the spread is not to be attributed to interaction of the silver or silver halide grains, or to the action of developing agents.

Equiluminous surfaces have been used to indicate diagrammatically the diffusion of light within the emulsion. Ross (63, 65) drew such surfaces, but Mees (46) criticized both his assumptions and his conclusions. The main conclusions to be drawn from the concept and study of equiluminous surfaces is that they are substantially normal to the emulsion-air interface, at the interface. Photomicrographs presented by Ross (65) and Mees (46) confirmed this, showing no tendency for the image edge to be wedge-shaped in cross section or to taper toward the top or the bottom of the emulsion.

**Mathematical Description**

Many attempts have been made to express the diameter \( w \) of an image as a function of the exposure \( E \) producing the image; Ross (65) and Mees (46) have summarized these. Mees (44) did experimental work on the subject. Although Ross showed that a modification of the Greenwich formula,

\[
\sqrt{w} = s + b \log E, \tag{1}
\]

where \( s \) is the geometrical size of the optical image and \( b \) is the spreading factor, to

\[
\sqrt{w + h} = s + b \log E, \tag{2}
\]
where \( h \) is a constant, would fit experimental data to complete satisfaction, Mees (8) and Wildt (39) found

\[ v = a + b \log E, \]  

proposed earlier by Schelner (76), to hold. Mees (46) has emphasised repeatedly that exposure at a given intensity cannot be expected to produce a photographic effect that varies linearly with time. This non-equivalence of intensity and time in defining exposure is known as reciprocity failure. Many of the results of the astronomers who did not assume reciprocity failure are thus vitiated, though the demonstrated reproducibility is notable.

**Range**

The enormous concentration range of the line-width method is one of its strongest points. Both Ross (65) and Mees (44) found factors of 500 in exposure range to be describable by this approach; Goldberg (28), a range of \( 10^5 \). Eastmond and Williams (20) estimated the analytical concentration range to be at least 1000.

One of the methods of line-width photometry, the matrix width method, has no more range than densitometry, i.e., a two-fold or three-fold concentration range. Taking the width of a reference line at that density indicated by the peak of a constituent line is usable only so long as the constituent line density changes with exposure, i.e., is on or near the linear part of the characteristic D-log E curve (46) of the emulsion.
Because line-width always increases with exposure, both the constituent width method and the method of merely taking differences in line-widths have practically unlimited range, but only the former incorporates the photometric width principle. Only the constituent width method is capable of yielding results of maximum precision, as has been explained in more detail in the section, Types of Line-Width Analysis.

Experimental Study

Previous Methods

The methods used to study image spread have not been numerous. The demonstration by Goldberg (28) that image spread is purely an optical effect has been mentioned. One experimental approach was to lay a sharp edge, such as a knife edge, or a circular hole in a metal plate (28), directly on the emulsion, and then to illuminate the emulsion with a point source. Another was to focus such a well-defined object as a slit or hole on the emulsion (44, 46, 64, 65, 73, 95). In each of the latter two techniques, illumination of the object was not diffuse, an important point; diffuse light spreads twice as much on entering a turbid medium as it does farther down within the medium, where it increasingly resembles focused light because the diffuse light forms an increasingly sharp cone as it proceeds down through the medium (17).

Some emulsions (18) are coated with fluorescent layers so that far ultraviolet light, instead of being absorbed by the gelatin to
to no effect, causes fluorescence in the coating. The light of a line image causes an approach to diffuse light at the emulsion surface, light from the fluorescent layer being given off in all directions rather than just in the direction of the incident beam. The effect tends to produce higher spreading than would radiation from the slit of the spectrograph of equal intensity and wavelength distribution. Experimental results with such emulsion coatings have been described in the following section.

This Study — Normal Procedures

In order to obtain basic data for comparison of behavior of different emulsions and for substitution into expressions derived and used later in this paper, several spectrographic emulsions were exposed and processed under normal spectrographic conditions, subject to the reservation that background was kept from exceeding the threshold of the emulsions. In this way, the variables of background and fog were kept from influencing the results.

Emulsions were exposed in a Jarrell-Ash Wadsworth-mounting grating spectrograph, in which the light is normally incident on the emulsion; and in a Bausch and Lomb large Littrow prism spectrograph, in which the light has approximately a 70° angle of incidence on the emulsion.

All exposures were made with low-current arc excitation of opposing metal electrodes of monel and steel with the grating spectrograph, and copper, brass, and iron with the prism spectrograph. The electrode images were focused on stops, for uniform excitation
and suppression of background. In both spectrographs, the slit width used was 0.01 millimeters. Exposures were made through step sectors, with step ratios of 2.0 with the grating spectrograph, and 1.5 with the prism. All exposures were longer than fifteen seconds, so as to avoid reciprocity failure; exposure level was kept down to desired value by one or more layers of lens paper placed in the light path away from focal points.

All emulsions were processed in the usual fashion. Full-strength developer was used at 68°F. for five minutes. Plates exposed in the prism instrument were developed by hand-rocking in Kodak D-11 developer; in the grating instrument, by machine-rocking in Kodak D-19 developer. All plates were placed after development in acetic acid step baths containing potassium chrome alum, after which they were fixed, washed and dried in still, unheated air.

A Leeds and Northrup Knorr-Albers Recording Microphotometer was used to make tracings from spectrograms. This instrument has been described in some detail under Measurement of Line-Width, later in this paper. Data was acquired principally from the spectrographically useful region around 2800 A. No great or sudden change of emulsion properties with wavelength was noticed in less extended studies on certain emulsions. A general increase in spreading and decrease in sharpness can be expected with longer wavelengths (see the section, Controlled Variables), but not enough to specify or rule out any given wavelength region for line-width photometry.

For each emulsion, density contours of fifteen to thirty lines were recorded, with a pair of contours for the lower and higher
intensity levels of each sectored line. From the contours, the widths in microns of each line at edge percent transmittance definitions of 12.5, 37.5, 62.5, and 87.5 were calculated. From these widths, the spreading factor, \( d \), from equation (3), was calculated for each transmittance level mentioned. Thus, for each line, up to four spreading factors were calculated; these were related to the line-width at 87.5% transmittance of the lighter half of each sectored line, this line-width being called the base line-width. Plots of spreading factor against base line-width represent predictions of behavior on increase of exposure of a line.

No particular selection of given lines was made for these studies; the effort was instead directed toward recording a wide variety of exposure levels of single resolved lines. Resolved lines were desirable so that each line used in a given study should represent a source of uniform brightness; without this condition, the data were quite unrelated. Such lines could be chosen crudely, simply by inspection of the spectrograms. The density contour on the recording was a more sensitive means of detecting and rejecting unresolved lines. Nevertheless, some unresolved lines always eluded both these preliminary screens, and were detected only in plots of sharpness index versus line-width, where they were usually clearly detectable as not of the group of resolved lines. The unresolved lines have much lower sharpness indices; this was the basis for the term "diffuse" in early spectroscopic investigations of series spectra. Unresolved lines detected by their low sharpness indices were not used for studies either of sharpness index or of spreading
factor.

A plot of spreading factor versus line-width often displayed rather scattered points. An example of rather worse than typical scattering of points has been presented in Fig. 6, and an example of negligible scattering in Fig. 7. Scattering of points was apparently a function of the emulsion rather than of the method of measurement. Certain emulsions - SA 1, Lantern Slide, I-L, and 103-0-UV - gave particularly bad scattering, whereas others - SA 2 and IIa-0 - gave very little. No obvious correlation between an emulsion property and scattering of data presented itself.

In general, spreading factors were found to increase with exposure and with transmittance definition of line edge. These characteristics are evident in Figs. 8 through 16, in each of which spreading factor has been plotted against base line-width for each of the four selected definitions of line edge. Numerical data from which these curves were plotted have been presented in Appendix I.

The constancy of spreading factor which indicates actual conformity to the Scheiner formula (equation (3)) (44, 76, 95) is evident in Figs. 12 and 15, for exposures in the prism spectrograph of emulsions SA 1 and Lantern Slide, respectively. However, the SA 1 emulsion exhibited quite different behavior when exposed in the grating spectrograph, as has been shown in Fig. 11. The reason for this difference, apparently only a function of angle of incidence of the light, is not clear, particularly since the line contours from both normal and oblique incidence were quite symmetrical, for all emulsions.
FIGURE 6

SPREADING FACTOR VERSUS BASE LINE-WIDTH

SPECTRUM ANALYSIS No. 1 EMULSION
2800 A. REGION
GRATING SPECTROGRAPH

EDGE TRANSMITTANCE 62.5%
FIGURE 7

SPREADING FACTOR VERSUS BASE LINE-WIDTH

SPECTRUM ANALYSIS No. 2 EMULSION 2800 A. REGION PRISM SPECTROGRAPH

EDGE TRANSMITTANCE 62.5%
FIGURE 8
SPREADING FACTOR VERSUS BASE LINE-WIDTH
IIa-0 EMULSION
2800 A. REGION
GRATING SPECTROGRAPH
FIGURE 9

SPREADING FACTOR VERSUS
BASE LINE-WIDTH

IV-0 EMULSION
2800 A. REGION
GRATING SPECTROGRAPH
FIGURE 10

SPREADING FACTOR VERSUS BASE LINE-WIDTH

III-O EMULSION
2800 A. REGION
GRATING SPECTROGRAPH

EDGE TRANSMITTANCE

37.5

62.5

37.5

12.5

BASE LINE-WIDTH IN MICRONS

SPREADING FACTOR IN MICRONS
FIGURE 11
SPREADING FACTOR VERSUS BASE LINE-WIDTH

SPECTRUM ANALYSIS No. 1 EMULSION
2800 A. REGION
GRATING SPECTROGRAPH

EDGE
TRANSMITTANCE
87.5

62.5
37.5
12.5

SPREADING FACTOR IN MICRONS

BASE LINE-WIDTH IN MICRONS
FIGURE 12

SPREADING FACTOR VERSUS BASE LINE-WIDTH

SPECTRUM ANALYSIS No. 1 EMULSION
2800 A. REGION
PRISM SPECTROGRAPH
FIGURE 13
SPREADING FACTOR VERSUS
BASE LINE-WIDTH
SPECTRUM ANALYSIS No. 2 EMULSION
2800 A. REGION
PRISM SPECTROGRAPH

EDGE TRANSMITTANCE

87.5
62.5
37.5
12.5

SPREADING FACTOR IN MICRONS

BASE LINE-WIDTH IN MICRONS
FIGURE 14

SPREADING FACTOR VERSUS
BASE LINE-WIDTH

I-L EMULSION
2800 A. REGION
PRISM SPECTROGRAPH

EDGE TRANSMITTANCE

87.5
62.5
37.5
12.5

BASE LINE-WIDTH IN MICRONS

SPREADING FACTOR IN MICRONS
FIGURE 15

SPREADING FACTOR VERSUS BASE LINE-WIDTH

LANTERN SLIDE EMULSION
2800 A. REGION
PRISM SPECTROGRAPH

EDGE TRANSMITTANCE
87.5
12.5
37.5
62.5
FIGURE 16

SPREADING FACTOR VERSUS
BASE LINE-WIDTH

103-O-UV EMULSION
2800 A. REGION
PRISM SPECTROGRAPH

EDGE TRANSMITTANCE

SPREADING FACTOR IN MICRONS

BASE LINE-WIDTH IN MICRONS
Most curves of spreading factor versus base line-width have a minimum beyond which the spreading factor has increased with further exposure. The photographic line-images seem to grow rapidly with increase in exposure until a certain width, characteristic of the emulsion, has been attained; the spreading factor becomes lower and lower as this width is approached, but then becomes larger with further exposure. The width for minimum spreading factor is also the width for maximum sharpness index, but does not correspond to the slit width. For the emulsion, SA 2, described in Figs. 13 and 22, the width for minimum spreading factor and maximum sharpness index has been found to be about 280 microns, or over twenty times the slit width. This increase of photographic image dimensions - the dimensions for optimal image definition or contrast - over the dimensions of the optical image has not been a result of an out-of-focus condition in the spectrograph, since other emulsions show much smaller characteristic widths for the same slit width in the same spectrograph.

The fluorescent-surface ultraviolet-sensitized emulsion (103-0-UV) displayed the greater spreading predicted for it in the section, Controlled Variables (Figs. 16 and 25). The shape of the curves for spreading factor for this emulsion was about the same as for the other emulsions, but the base line-width and spreading factor values were so much greater that contracted ordinates were required.

The precision of the matrix width method (equations (46) and (48)) is inversely proportional to $g$, the sharpness index, or change
in density per micron travel across the edge of the line. From the same charts recorded for the study of spreading factor, measurements were made for the change of sharpness index with exposure. This variation for the various emulsions has been given in Figs. 17 through 25.

Although the very high attainable contrast of emulsion IV-0 is accompanied by unusually low spreading factor and narrow lines, a high sharpness index does not necessarily imply low spreading factor. A summary has been given in Table I of the maxima and approximate lower limits of sharpness index and of the optimum values and minima of spreading factor for eighteen Figures, along with the base line-widths at which these values occurred. The difference of SA1 behavior under prism and grating illumination possibly indicates similar behavior by all emulsions, except for those which are ultraviolet-sensitized. In general, prism illumination seems to cause higher spreading factor and lower sharpness index than grating (normally incident) illumination. The main point of the figures of sharpness index versus line-width is that the operator, in using the matrix width method, should choose a large matrix line as the measured line.

* *
FIGURE 17
SHARPNESS INDEX VERSUS LINE-WIDTH
2800 A. REGION
IIa-0 EMULSION
GRATING SPECTROGRAPH
FIGURE 18
SHARPNESS INDEX VERSUS LINE-WIDTH
IV-0 EMULSION
2800 A. REGION
GRATING SPECTROGRAPH
FIGURE 19

SHARPNESS INDEX VERSUS LINE-WIDTH

III-O EMULSION
2800 A. REGION
GRATING SPECTROGRAPH
FIGURE 20

SHARPNESS INDEX VERSUS LINE-WIDTH

SPECTRUM ANALYSIS No. 1 EMULSION
2800 A. REGION
GRATING SPECTROGRAPH
FIGURE 21

SHARPNESS INDEX VERSUS LINE-WIDTH

SPECTRUM ANALYSIS No. 1 EMULSION
2800 A. REGION
PRISM SPECTROGRAPH
FIGURE 22

SHARPNESS INDEX VERSUS LINE-WIDTH

SPECTRUM ANALYSIS No. 2 EMULSION
2800 A. REGION
PRISM SPECTROGRAPH

LINE-WIDTH IN MICRONS

SHARPNESS INDEX x 100
FIGURE 23

SHARPNESS INDEX VERSUS LINE-WIDTH

I-L EMULSION
2800 A. REGION
PRISM SPECTROGRAPH
FIGURE 24
SHARPNESS INDEX VERSUS LINE-WIDTH
LANTERN SLIDE EMULSION
2800 A. REGION
PRISM SPECTROGRAPH
FIGURE 25
SHARPNESS INDEX VERSUS LINE-WIDTH
103-O-UV EMULSION
2800 A. REGION
PRISM SPECTROGRAPH
<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Spectrograph</th>
<th>Spreading Factor**</th>
<th>Sharpness Index***</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Opt. (a)</td>
<td>Min. (a)</td>
</tr>
<tr>
<td>III-0</td>
<td>Grating</td>
<td>8</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(140)</td>
</tr>
<tr>
<td>IV-0</td>
<td>Grating</td>
<td>9</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(90)</td>
</tr>
<tr>
<td>III-0</td>
<td>Grating</td>
<td>10</td>
<td>275</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(110)</td>
</tr>
<tr>
<td>SA 1</td>
<td>Grating</td>
<td>11</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(230)</td>
</tr>
<tr>
<td>SA 1</td>
<td>Prism</td>
<td>12</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(26)</td>
</tr>
<tr>
<td>SA 2</td>
<td>Prism</td>
<td>13</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(380)</td>
</tr>
<tr>
<td>I-L</td>
<td>Prism</td>
<td>14</td>
<td>465</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(260)</td>
</tr>
<tr>
<td>Lantern Slide</td>
<td>Prism</td>
<td>15</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(260)</td>
</tr>
<tr>
<td>103-O-UV</td>
<td>Prism</td>
<td>16</td>
<td>2160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(700)</td>
</tr>
</tbody>
</table>

* Figures for spreading factor have been given in microns.
** Figures for sharpness index have been given in density units X 10^2/micron.
*** Approximate lower limit.

(a) = Corresponding value of base line-width.
(b) = Corresponding value of line-width.
Variables Other Than Mensuration

Controlled Variables

Identical plate-to-plate processing, reproduction of a given gamma, or tracking small shifts in gamma are, to a first approximation, not requirements of line-width photometry which incorporates the photometric width principle (equations (10), (13)).

Calibration for line-width photometry is merely the recording of observed line-width behavior of a set of samples which have been taken as standards for a given analysis.

Nevertheless, certain considerations such as reciprocity failure (46) have remained of general importance for such non-analytic aspects of line-width photometry as study of emulsion behavior and mapping emulsion response versus wavelength. A short review of the more important of the controllable variables has been presented in this section.

As early as 1911, Parkhurst (54) wrote on "Precautions in Photographic Photometry." Recently, Mees (46) has re-emphasized the existence of many and elusive variables in photographic photometry. Two excellent papers by Harrison (29, 30) contained the advice that calibration of an emulsion should be conducted as much as possible under the conditions of use, and if possible concurrent with the study for which the calibration is made. The application of this advice to line-width (or to densitometric) photometry is that in evaluating an emulsion for spectrochemical analysis, a spectrograph should be used for illuminating the emulsion; and in using the
emulsion in spectrochemical analysis, control samples should be
provided for analysis along with unknowns.

Mees (46) has described the history and nature of reciprocity
failure, which states that an emulsion does not respond according to

\[ E = J \cdot t \]  

(4)

where \( E \) is exposure; \( J \), light intensity; and \( t \), time of exposure.
Neither is the Schwarzschild constant \( p \), in

\[ E = J^p t \]  

(5)

actually constant. Finally, the intermittency effect, which states
that

\[ E \text{ (continuous)} = E \text{ (intermittent)} \]  

(6)

is actually a form of reciprocity failure (91). Because of these
phenomena, Harrison (29) cautioned against the use of the rotating
step sector in spectrographic photometry. Subsequent work showed
that a rotating step sector can be used safely if it rotates fast
enough (for a given exposure time); Feldman (25) recommended 600 rpm
or faster with exposure time the same as that used to analyze samples
(30-120 seconds, usually). The speed used is inversely related to
exposure time (18).

With a metallized filter, two related light intensities can be
obtained from a given source at the same time, and exposures can be
nonintermittent, as has been advocated (18). Since the densities of
steps of such filters are specified only to two significant figures
and for a specified wavelength, their relative precision is about four percent at that wavelength, far higher than the theoretical precision of photographic photometry, and four times higher than the (poor) experimental precision currently attained with densitometric photometry.

Although the procedure permits nonintermittent exposures, the use of two lines of an element which presumably have a permanent intensity relationship regardless of excitation has not been given unqualified support (25, 29).

The light source used in studies of emulsions should be convenient in availability and operation; it should be stable and contain some area of uniform emissivity so that some finite part of the slit can be uniformly illuminated. Feldman (25) has recommended a simple iron arc run in a draft-free room. A generator rather than a rectifier should supply the current (about 0.7 amperes) for the arc if a rotating sector is to be used. Another convenient source of light is a controlled iron spark; pains should be taken to insure that the spark and the sector are not in synchronism.

If light intensity differences are obtained by means of a step sector or metallized filter, then the illumination of the sector or filter must be uniform along the length of the slit; Feldman (25) has given clear and detailed directions for this.

Even though little doubt may exist regarding the relationship of exposures being used in calibration or emulsion study, the emulsion being exposed may not be uniform. This possibility has been considered later.
The photographic emulsion does not react uniformly to light of differing wavelengths. This fact has been recognized for many years and has been described at some length by Mees (46) and Neblette (48). The wavelength differences of emulsion reaction are functions of several variables, among which are the silver halide grain size, the emulsion thickness, the gelatin itself, the opacity of the emulsion as altered by additions such as yellow dye, and the turbidity of the emulsion.

Neblette (48) has noted that gelatin strongly absorbs wavelengths below 2500 Å; such absorption would diminish image spread as well as emulsion gamma (gamma is the change in photographic density with change in log of exposure). Ross (62) remarked that the immediate scattering of shorter (blue) wavelengths on entering the emulsion tended to restrict the image to the emulsion surface.

The results of Wildt (95), reprinted by Mees (46), demonstrated very clearly the increase in spreading factor with increase in wavelength, for a given emulsion. Curves were presented by Ross (62) showing the relative changes in spreading factor with wavelengths of visible light; in general, the rate of spreading was shown to increase with wavelength. Ross (63) drew curves which showed the theoretical (increasing) intensity of light at the edge of an image with (increasing) wavelength. Prints of knife edge exposed to varying wavelengths were in this article, showing the decrease of sharpness with longer wavelengths. Tugman (87) considered the dependence of resolving power on wavelength; the greater penetration of longer wavelengths into the emulsion was noted. Sandvik and Silberstein (74)
concluded that these results were in agreement with those of other investigators.

Another factor in the variable response of emulsions to light of different wavelengths is the yellow dye incorporated into some spectroscopic emulsions for the purpose of increasing the opacity of the emulsion to blue and ultraviolet light; the dye is not so effective with yellow or red light. For the shorter wavelengths with which the dye is effective, the dye increases emulsion opacity and thereby decreases image spread, also tending to restrict the image to the surface of the emulsion (43). Ross (65) studied the effect of this dye in restricting image spread under exposure to white light; the dye cut the spread by a factor of about two.

Hess (46) has indicated the wavelength-sensitive effects in light diffusion to be diffraction and Rayleigh scattering, both of which increase with decreasing wavelength. (Rayleigh scattering is proportional to the fourth power of the frequency of the light being scattered when the scattering particles are small relative to the wavelength of light being scattered.) The increase in absorption with shorter wavelengths is therefore directly opposed to these two effects.

The coating of emulsions (18) with fluorescent ultraviolet-sensitizing layers has been mentioned. Not only does the layer emit light in all directions, thus increasing image spread, but the image spread is further increased by the fact that the light emitted by the coating is visible and so more effective in causing spread than the incident ultraviolet light. The values in Table I for the coated emulsion, 103-0-UV, bear out these statements. Because the radiation
emitted from the coating tends to be more effective than the incident radiation, coated plates should show a high spreading factor quite or almost independent of wavelength. Fig. 16 has confirmed the prediction of high spreading factor for coated plates, and the well-known constancy of gamma for various wavelengths is evidence of the independence of response of coated plates from the wavelength of the incident light.

In summary, the overall conclusion with regard to the value of spreading factor as a function of the wavelength of light is that the value is higher with longer wavelengths, especially above 5000 Å. Fluorescent coatings on emulsions tend to render emulsions independent of wavelength, except as the coating itself is dependent on wavelength.

Different emulsions offer different sizes and size-frequency distribution of silver halide crystals; Mees (46) has pointed out how the diffusion of light within the emulsion is affected by grain size. Diffusion is presumed to occur primarily because of the presence in the emulsion of the silver halide crystals, the smaller ones favoring diffraction and Rayleigh scattering, the larger, reflection and refraction.

Emulsion sensitivity is a function of grain size; a more sensitive grain just outside an image may be rendered developable by the diffuse irradiation, and so increase image spread. Silberstein (81) studied the relationship between grain sensitivity and sizes; although the sensitivity per unit area of a silver bromide grain decreases with increase in size, the total sensitivity of a grain increases with size. This variational characteristic helps to
explain the concurrence of high resolution and low sensitivity in the finer grained emulsions.

According to another work by Silberstein (80), the size-frequency distribution for a given emulsion type is characterized by a minimum size only slightly below the size of highest frequency, with larger sizes present according to a Gaussian-like distribution. From these results, one should expect an emulsion labeled fine-grain to contain only few large crystals, as predicted by the tail of the Gaussian curve.

The dependence of resolution on grain size was studied by several of the earlier investigators such as Goldberg (28), Tugman (87), and Ross (63). Generally, high resolution has been associated with fine grain (46), and also, as mentioned before, Sandvik and Silberstein (74) concluded that resolving power is necessarily opposed to image spread. And yet, in mentioning the effect of grain size on image spread, both Coheur (9) and Coleman and Yeagley (11) concluded that image spread increases with decreasing grain size.

Unfortunately, specific data on emulsion grain sizes are considered proprietary (84). The trends of emulsion behavior with granularity can be definitely established, however, from relevant publications (18, 19) of the Eastman Kodak Company and from experimental data collected in the course of this study.

An attempt has been made to assign an arbitrary granularity index \( g \) to several spectroscopic emulsions. In one publication (19) of the Eastman Kodak Company, microdensitometer tracings over plates uniformly exposed and developed to density 0.3 have been given. It
has been assumed only that these tracings were all made with the same microdensitometer sensitivity and rate of scan. The tracings were photographically enlarged, and lines parallel to the tracing and one millimeter apart from each other were inscribed over the enlargement of each tracing. A diagrammatic representation of a tracing enlargement and the inscribed scale has been presented in Fig. 26. A graph was then constructed, with the number of excursions of the trace over the outside lines of the scale plotted on the y-axis against the number of scale lines required to cover the trace, on the x-axis. A family of smooth curves could then be drawn; the curves were roughly parallel, and there was one curve for each emulsion. The parallel nature of the curves indicated the next step to be taken in reducing each microdensitometer trace to a number which would be an index of grain size.

The value of $x$ corresponding to the point $(x, 15)$ was then found for each curve, so that the $x$-values were therefore numbers relating the appearance of the microdensitometer traces. Since trace excursions corresponded originally to partial interruptions of the microphotometer light beam by developed grains, the $x$-values were presumed to be a function of grain area. The three-halves power of $x$ should therefore have indicated a function of grain volume, that is, grain size, at least roughly, and this was taken as the definition of the granularity index $G$. 

A private communication from the Eastman Kodak Company relevant to the concept of the granularity index stated that they felt "it is not possible to obtain size frequency data from granularity traces."
FIGURE 26

FIRST STEP IN
DERIVING THE GRANULARITY INDEX

CURVE IS DIAGRAMMATIC REPRESENTATION OF MICROPHOTOMETER
TRACE OF EMULSION WHICH HAS BEEN PARTIALLY EXPOSED AND
THEN DEVELOPED. SCALE IS INSCRIBED OVER TRACE ENLARGEMENT.
The communication continued:

"It is stated in the reference material that these granularity traces were made with a slit having an effective diameter of 500 times 5 microns. It is clear that with this scanning area of 2500 square microns, a very large number of grains are scanned at any one time; consequently no density fluctuation can result from the interruption of the microdensitometer light beam by a single developed grain as implied in the above underlined statement [from this text, which statement was modified to the present reading as a result of this letter. JP]

"While data derived in this way are referred to in your letter as being indicative of grain size, they are referred to in Table II as a granularity index. It is perfectly proper to describe the numerical value obtained from these traces in the manner described in your letter as a granularity index, but it should not be assumed that it has any unique relation to grain size."

This communication has been taken as expert criticism of the proposed granularity index as an indication of grain size. However, the author has nevertheless presented the granularity index as a potential indication of grain size.

Some of the numerical expressions of emulsion behavior which are available in published literature or which have resulted from the experimental work connected with this study have been presented in Table II. Resolving power is seen to increase with sharpness, as indicated by sharpness index, and to decrease with granularity index and with sensitivity. Both maximum and minimum spreading factors have been listed for each emulsion; maximum spreading shows good correlation with granularity index, but minimum spreading at first decreases with increasing granularity index and then increases again.

An investigator using only narrow lines and rather fine-grain
<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Resolving Power</th>
<th>Sensitivity</th>
<th>Granularity Index</th>
<th>Sharpness Index (maximum)</th>
<th>Spreading Factor Maximum</th>
<th>Spreading Factor Minimum</th>
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</thead>
<tbody>
<tr>
<td>SA 2</td>
<td>55</td>
<td></td>
<td></td>
<td>1.3 P</td>
<td>390 P</td>
<td>75 P</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[3.1 G]</td>
<td>[23 G]</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>55</td>
<td>35.0</td>
<td>17.3</td>
<td>1.5 P</td>
<td>465 P</td>
<td>120 P</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[3.6 G]</td>
<td>[37 G]</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>75</td>
<td>8.9</td>
<td>16.9</td>
<td>5.6 G</td>
<td>300 G</td>
<td>25 G</td>
</tr>
<tr>
<td>III</td>
<td>95</td>
<td>3.0</td>
<td>14.3</td>
<td>6.4 G</td>
<td>275 G</td>
<td>20 G</td>
</tr>
<tr>
<td>IV</td>
<td>120</td>
<td>0.8</td>
<td>7.4</td>
<td>12.5 G</td>
<td>165 G</td>
<td>30 G</td>
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<tr>
<td>V</td>
<td>160</td>
<td>0.08</td>
<td></td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA 1</td>
<td>130</td>
<td></td>
<td></td>
<td>7.0 G</td>
<td>590 G</td>
<td>30 G</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[2.9 P]</td>
<td>[180 P]</td>
<td>[95 P]</td>
</tr>
</tbody>
</table>

P signifies emulsion exposed in prism spectrograph; G, grating.
Brackets indicate calculated values based on SA 1 performance.
Figures for resolving power indicate resolvable lines per millimeter.
Figures for sensitivity are reciprocals of exposure time required to produce given density.
Figures from reference (18) have been quoted for Resolving Power.
Figures from reference (19) have been quoted for Sensitivity.
Radiation from 2800 A region was used in acquiring data in last three columns.
fine-grain emulsions might conclude that spreading increases as
grain size decreases; perhaps this explains the statements of
Cohen (9) regarding grain size versus image spread. For best
precision with either the matrix width or the constituent width
methods, the analyst should use the more intense, broad lines as
the measured lines, since sharpness decreases and spreading increases
with increasing line-width, when the line-width is larger than a
certain (small) value characteristic of the emulsion. This
behavior has been shown in the preceding figures on spreading
factor and sharpness index.

In making measurements on an emulsion for spectrochemical
purposes, the analyst does not desire individual grains or clumps
in the emulsion to be reflected in his measurements. Such reflection
is harder to avoid as the grains become larger. A compromise between
large spreading - from large grains - and precise measurements
is necessary. Kodak emulsions I-L, I-O, II-L, II-O, IIa-O, and
SA 2 are apparently to be recommended for line-width work.
Emulsions III, IV, V, 548, and 649 are listed in order of decreasing
grain size and are not best suited for line-width analysis.

In summary, grain size affects the mechanism of diffusion of
light within the emulsion and also the relative sensitivity of the
emulsion. A fine-grain emulsion tends to restrict the image to the
surface, to require greater exposure, and to inhibit spreading of
the image. Kodak emulsions I-L, I-O, II-L, II-O, IIa-O, and SA 2
have been found particularly suitable for line-width analysis.
* *
Whether the aperture size influences the spreading factor has been considered several times. Goldberg (28) and Ross (61) found aperture to have an effect in determining the spreading factor; Wildt (95) reported the spreading factor to be independent of aperture. Coheur (9) tried different slit widths, values twenty to fifty-five microns, with the object of increasing precision by lowering the profile slope of the line used to indicate constituent concentration by its width; his prediction that a larger slit would decrease the slope and consequently increase photometric precision was supported by his results.

In this study, also, the question of aperture size versus spreading factor has been put to test. Slit widths of 5, 10, 20, 25, 30, 80, 130, 180, and 230 microns were tried. Exposure conditions producing negligible background were used. The conclusion which has been drawn from these tests is that slit width per se has no effect on spreading factor; see Fig. 27.

A spectrograph exhibiting high dispersion is capable of producing relatively wide separation of the lines in a spectrum. If the spectrograph slit is narrow, then the wavelength separation produced by the spectrograph is made useful and the lines are distinct. If the slit is too wide, the lines become like bands and may overlap. But the wavelength distribution of the radiant energy of a spectrum line passing through a slit is not changed by the slit.

The pattern of radiation from the slit is the diffraction pattern of a single slit (78). Dispersion does not change this pattern.

Essentially the same photographic spreading is produced regardless
FIGURE 27

SPREADING FACTOR VERSUS
SLIT WIDTH

SPECTRUM ANALYSIS No. 1 EMULSION
PRISM SPECTROGRAPH
of the width of the slit or of the dispersion of the spectrograph.

The variation found by Coheur (9) was not the result of a wider slit insofar as the slit defines a certain size of aperture. Instead, experiment has shown that the line-to-background intensity ratio decreases rapidly as the slit is opened. Since fog has the effect of increasing the spreading factor, increasing the slit width also has the effect of increasing the spreading factor by increasing the relative amount of fog (background). Only if the background is kept from exceeding the emulsion threshold can the independence of spreading factor from slit width be shown.

Ross (62) and Tugman (87) found variations in image growth with varying exposures, and Ross (65) found a variation with intensity, also. The more expected and highly uniform results of Wildt (95) and Mees (44) exhibited no such deviation from the logarithmic behavior expressed by equation (3).

Figs. 8 through 16 of this work have indicated no contraction of image with increasing exposure, but without exception, spreading factor was found to change. Each figure has shown the spreading factor, $f_e$, as always positive, but also passing through a minimum. The minimum corresponded to low exposures, but its exact value was characteristic of the emulsion. This minimum was not to be explained on the basis of development procedures, since on the one hand, the developers used (D-11 and D-19) were not the type which cause image shrinkage, and on the other hand, the development was not too short.
(5 minutes) or too fast (68°F) to prevent adequate influx of fresh developer into the image or efflux of development products from the image. (The points just mentioned have been discussed later in this section.) The size of the slit-images could be taken as the image width, as far as diffusion processes are concerned; most images were less than 0.1 mm. wide.

The width of the geometrical image was the slit width, 0.01 mm. in all cases. Such small image sizes have not been used in former investigations on image contraction effects. Former investigators were not so concerned with the demarcations of the image by the careful transmittance definition of the edge. As the defining transmittance is lowered, the minimum in value of spreading factor becomes less apparent; most work has taken a rather low transmittance as the edge definition.

Perhaps the image growth can be divided into three parts. Fig. 8, for example, can be referred to in substantiation of the following conclusions. 1) The appearance of the image is characterized by a high relative spread as the image width increases rapidly from zero to some small value. 2) With increasing exposure, the image changes primarily by increasing in density, spreading slowly and uniformly. 3) Further exposure brings more and more of the exposed grains outside the image area to a developable state, and the image grows at an increasing rate. The increase is the more noticeable, the lower the value of the defining transmittance.

The image before development is known as the "latent image."
The "Brush effect," based on the work of Brush (7), was a change in latent image just after exposure; later workers (92) showed that no such change existed. Blair and Hylan (5) reviewed the question and found that several variables were involved, thus accounting for the contradictory results of various investigators. Later, Hylan and Blair (36) proposed that a latent image tends to approach an equilibrium density the value of which depends on the temperature of storage; evidence in support was presented. The times of storage were large in comparison with the ordinary delay in developing after exposure; contemporary writers (25, 46, 48) have not indicated that any measures should be taken for the Brush effect.

Halation is the name given to the result of illumination of an emulsion by reflection from its support. Adequate measures have been available for some time to prevent halation from being a problem (48), although not all plates carry antihalation backing (18), presumably because blue and ultraviolet light do not penetrate the emulsion.

There are several controllable variables and effects with respect to the processing of the emulsion; these have been discussed in the following paragraphs.

The change of gamma with such variables as time of development has been shown (9, 51) to be unimportant with respect to the difference in width of two lines. The explanation of this independence has been taken up later in this study (equations (10), (13)); but let it be emphasized here that only with the use of the photometric width principle are line-width differences independent of gamma. The
variables which affect gamma are released from stringent control in these line-width methods which incorporate the photometric width principle. This may be the very basis for the superior precision reported for line-width photographic photometry, as Cochran speculated (9). Processing of the emulsion is usually far more variable, despite rigid control, than the emulsion itself (84), and densitometric photometry is very sensitive to resultant unappreciated changes in gamma. (24)

The line-width methods do depend on processing in that the developed, visible, measurable photographic image should retain the exact dimensions of the latent image. In the change from latent to developed image, the complex gelatin support must be swelled, immersed in base, subjected to the heat of the development reaction (which can melt the gelatin locally), immersed in acid, then water, and finally dried. Obviously, processing is critical, despite freedom of line-width methods from reproduction of a given gamma.

The effects of processing on the physical dimensions of gelatin have been described in Chapters III and XXI of Mees (46). The gelatin emulsion which must carry and retain the image in its original dimensions is about 0.025 mm thick on the packaged spectroscopic plate (46). Page (42) concluded that the slight concavity of photographic plates is not a function of width or length of the photographic plates but only of the emulsion thickness. The tension transmitted from the gelatin to the plate must then be distributed evenly throughout the gelatin, and so the purely vertical expansion of gelatin on swelling is understandable.
Gelatin can form a bond of great strength with a glass support (46); in the swelling resulting from processing, the expansion is almost all perpendicular to the support (46, 66). Ross (66) found that images could move as much as 0.05 mm. within the five millimeter boundary strip around the edge of an emulsion, as a result of processing.

Several effects may occur at the development stage of processing which can distort the image. The gelatin first expands on immersion in developer; at this time, the silver particles forming the image are produced. Ross (61) considered distortion of images and found different results for different developers, pyrametal and caustic hydroquinone (Kodak D-6)(18) reacting in development in such a way as to tan the gelatin supporting the image. Hydroquinone (Kodak D-11 and D-19)(18), metol-hydroquinone, and chlorohydroquinone did not produce this effect. Photomicrographs of developed images in the swollen gelatin (46) showed the gelatin supporting the images resulting from the distorting developers to be crowded and shrunken with respect to the surrounding gelatin; gelatin supporting the other images was as evenly swollen as its surroundings. On drying, the images in tanned gelatin suffered a decrease in dimensions; this decrease is known as the Ross effect.

Strains present in the gelatin may be released on swelling, causing possible distortion of an image on the site of such a strain. A possible preliminary release of such a strain by prolonged swelling in water may be valuable (12), but confirmation of the need for such a release is lacking (88, 89). Further comment on this point has been
made in the next section, Uncontrolled Variables.

Tugman (87) concluded that the rate of image spread was not a function of development conditions; general agreement on this point is evident (9, 27, 28, 46, 51, 52, 63). Coleman and Keagley (11) traced the spread of a given image with time of development. A brief period exists during which the developed image apparently attains the dimensions of the latent image; after this, no further change occurs (aside from eventual development of fog).

Tugman (87) and Ross (63) pointed out that grains of silver halides which are developable need not be developed long enough for full development, so that the actual developed image, measured across from one given density to another, can have various sizes for various times of development. (Although the developer infuses the gelatin in about ten seconds, the chemical reaction of development is less rapid, a matter of minutes (46).) The same effect, apparently, is achieved by dilution of the developer (46). In each case, a finer grain results because development centers on a given crystal do not spread until fusion results; before this happens, development is stopped and the undeveloped portion of the crystal dissolved away. Fine grain of this type is accompanied by low gamma.

Although fine-grain developers have been presented in the literature (47, 60), the conclusion has been (37, 46) that in general the desired effect of such developers vanishes if development is carried to attainment of equal gamma. Wright (96) described a variety of ways to overcome, optically, graininess in developed
plates.

The Eberhard effect (21) and its complement, the Mackie line (23, 68, 79), are the results of production of greater and lesser densities at the edge and just outside the edge, respectively, of an image. Both are results of the concentration of products of the development reaction, and both effects can be minimized by adequate stirring of the developer and lengthening the time of development. Agitation also prevents other undesired results such as streaking. Harriss (29) commented on prevention of these effects; Mees (46) has given a good discussion of this topic, and the matter has been mentioned in a publication (18) of the Eastman Kodak Company.

Although Ross (69) reported that he had found the most uniform development across a plate to be attained by leaving the plate in a still development bath, this treatment would also be the best way to invoke the Eberhard and Mackie effects, which would lead to incorrect conclusions regarding the size of the latent image. Crabtree (14) recommended a frequent regular passing of a squeegee-type plane just over the horizontal surface of the emulsion. Harriss (29) recommended merely a positive agitation of the developer, though regular rocking may set up standing waves resulting in non-uniform development along the plate and consequent different image sizes from identical exposures. In a publication (18), the Eastman Kodak Company has advised brushing with a soft brush wider than the plate.

The independence of analytical results from inadvertent changes in normal development conditions which is claimed for line-width
methods means only a freedom from some given value of gamma required for successive plates, but not from the necessity for uniform treatment of the whole plate. This has been considered further under Measurement; let reference now be made, however, to an article by Lay and Cornog (42) in which the errors in photographic (densitometric) photometry were considered with great care and with quantitative expression of results. The residual non-uniformity in specular density across the plate, after the most highly recommended techniques were used, was quite appreciable, but at least partially susceptible to study and correction; such correction was apparently necessary for each plate, a procedure not likely to be adopted by an industrial laboratory handling a large volume of work. The Eastman Kodak Company has also urged such treatment of each plate (18).

The work of Lay and Cornog is pertinent to line-width photometry, since even though no measurement of density as such is required in either of the photometric width techniques, the identity between the indicator line density and the density-definition of the edges of the measured line is dependent on a residual uniform density.

Although the gelatin is subject to repeated strain during processing (46), distortion apparently does not come about from immersion in the stop or fixing baths, or from hardening. Reticulation can be avoided if the bases and acids used are not too strong, and if the temperature of the wash water is not above that of the processing solutions (46). (A temperature-induced case of reticulation has been described and discussed later, under Uncontrolled Variables.)

The Ross effect, the shrinking of a developed image presumably
because of the tanning of the supporting gelatin by the products of development of certain developers, has been noted earlier. The measured shrinking depends on the size of the image, the exposure involved, the type of developer and the time of development. Mees (46) has shown some experimental results for these relationships; an image larger than one millimeter diameter is subject to shrinkage of up to ten microns, the shrinkage increasing with image diameter. The effect is similar for images having edges separated by less than 0.1 mm., the centers being drawn together by the same mechanism.

Another reason to avoid use of lines quite close together is the turbidity effect (46); intra-emulsion diffusion of light from each image causes the neighboring borders to overlap.

The Kostinsky effect is analogous to the Eberhard effect, except that here again two nearby images are involved. Depletion of developer between the images causes an apparent separation of the images; the images must have edges nearer than about 0.1 mm. to each other for the Kostinsky effect to be noticeable (46).

These shrinking effects just described should not affect spectral lines to be used in line-width measurements, because first, the object is the spectrograph slit, of normal width less than 0.1 mm., and second, a spectral line greater than 0.1 mm. distant from another can generally be found for use in analysis. Avoidance of lines closer than 0.5 mm. seems indicated.

On the other hand, duplication of sensitivity and contrast of two regions of an emulsion becomes less likely as the regions are further apart (18). Therefore, lines for analysis should be as near
as possible on the plate, up to a minimum separation of 0.5 mm.

As mentioned before, Ross (66) found images in a strip five millimeters wide around the edge to be moved by the swelling and drying of the gelatin; this area should not be used for line-width measurements.

In summary, processing brings about the transformation of the latent into the measurable image. Uniform processing, especially in development, takes care of several sources of error. Lines closer than 0.5 mm., or lying within one centimeter of the edge of the plate should not be used; aside from these restrictions, analytical lines should be as close as possible (where “close” refers to both wavelength separation and physical separation.) Although each part of a given plate should receive identical processing, the line-width methods of photometry ease considerably the requirement of densitometry, that each plate receive identical processing in order to exhibit identical contrast. In line-width photometry, the sources of error in processing are largely subject to proper technique.

Uncontrolled Variables

The residual errors in exposure of the emulsion are those that are characteristic of the emulsion and its support, and those that cannot be eliminated from the sample excitation procedure.

Since the analysis itself constitutes calibration in line-width photometry, sample excitation and calibration errors are identical.

Mees (46) and Feldman (25) have pointed out that light of longer
wavelengths has a greater tendency to penetrate the emulsion. Three effects, all sources of error, could result from penetration of the emulsion by the incident light, and reflection from the support. In the first place, the proportion of light reflected would depend on the reflectivity of the support; only uniform reflectivity over the plate could guarantee the proportion of reflected light to be constant. Such uniformity may be the case; nevertheless, the reflectivity of the support, if used, would be an uncontrolled variable. In the second place, photographic plates are not flat, and so the reflected light could return into the emulsion at (slightly) different angles, directly but erratically affecting the line-width. No increase in line-spread would result from reflected light since the spread is a result of change in exposure, i.e., concentration of a constituent; reflected light would have the effect of increasing the initial width, but not of increasing the spreading factor. Finally, a ten to fifteen percent variation of the thickness of the emulsion probably exists (§4). Both the transmitted and reflected light would on reaching the support have passed through an attenuating layer of variable thickness, and so the line-width would vary in a corresponding erratic fashion.

The three sources of error originating from use of reflected light are very possibly of a lower order of magnitude than the other sources of error. Nevertheless, for highest reproducibility of line-width, the spectrographer should not use wavelengths above 4000 Å unless he wishes to obtain maximum spreading at the risk of additional error.
Difference in distribution of silver halide grains across the plate would cause differences in spreading of the image, and in reproducibility of line-width. But although this question has not been studied, opinion is that "the distribution is extremely uniform," with "any variations...extremely small."¹ Chapters I and II in Mees' work (46) support such an assumption. (Plate-to-plate or batch-to-batch identity of emulsions should not be assumed. Control samples should be run along with unknowns.)

If the image is confined to the emulsion surface, if the grain distribution is extremely uniform, and if slit illumination is uniform, then possible lack of reproducibility could be caused by the supporting gelatin. Mees (46) has pointed out that gelatin is by no means merely a viscous carrier, but also functions as a protective colloid for the silver halides; indeed, chemical adsorption may be present. Such intimate interaction very probably affects the light-diffusing properties of both the gelatin and the silver halide grain; discussion of turbidity should consider inhomogeneity of the gelatin as a possible source of variation in the pattern of light diffusion.

Some emulsions are coated with a fluorescent material for sensitization to the ultraviolet, as has been mentioned. If such plates are used, then any variation in thickness of the fluorescent coating could be a large source of error. Whether such variations occur depends entirely on the process of manufacture; large relative variations in coating thickness are not hard to imagine, since the

¹Private communication from M. F. Swann, representative of the Eastman Kodak Company.
coating is one which remains after evaporation of an organic solvent. Good results have been reported from the use of such plates, however (20).

In summary, in line-width photometry, sources of error in the illumination and irradiation of an emulsion and in its response before processing include possible inhomogeneity in diffusion of light due to interaction of locally inhomogeneous gelatin and silver halide particles, nonuniform transmission and reflection of the penetrating longer wavelengths which may be used, and unequal thicknesses of sensitizing fluorescent films over the emulsions so treated. Line-width photometry enjoys an advantage over densitometry in an identity of calibration and analytical procedures.

Schlesinger (77) and Perrine (58) considered the errors in photographic registration of position. Schlesinger measured the distortion after development of drops of ink spattered on plates before development. A mean distortion error of 0.9 microns was reported. Perrine used photographic images and found distortions in thick emulsions to be larger than those in thin ones, and experienced difficulty in making a visual fix on the boundaries of the image.

Ross (66) established that a five-millimeter-wide strip at the edge of the emulsion is particularly subject to distortion, as has been mentioned; he also stated that thin emulsions are preferable to thick for freedom from distortion. Ross further brought out the very important fact that images have the same dimensions in both the wet and the dry gelatin; the gelatin swells only normal to the plane of the plate. Concomitant to this is the independence of image
dimensions from humidity changes. For images five millimeters or more from the edge, Ross found only local distortions of about 0.5 microns.

Berndt (2, 3, 4) studied with elegant and incisive technique the distortions to be found with both plates and films. By superimposing a sharply-figured mask directly on the developed image from the mask, he was able to measure distortions of one part in 100,000 (i.e., one micron in ten centimeters) with an ordinary filar micrometer. Since both the mask and the plate were of glass, measurements made at different temperatures revealed the strict adherence of the gelatin to the glass, and in consequence the feasibility of using the temperature coefficient of expansion of glass in connection with measurements of position in glass-supported emulsions.

Berndt agreed with Ross that distortions are in general purely local, that the very largest of these measure three to six microns (Ross: four microns); also tested and confirmed was the invariance of image dimensions with changes in humidity. Although dimensions were only locally variant up and down and straight across the plate, the diagonals showed much larger distortions; the conclusion apparently was that images to be measured should not lie near the corners of the plate. Another point emphasized by Berndt concerned forced drying; distortions are three times as large, approximately, on plates dried in a current of air as on those dried in still air. (Ross found less distortion from alcohol-dried plates, as compared with air-dried plates.)

An error of about one micron in image dimensions was reported in one of Ross' experiments; a maximum of 4.4 microns was found with the
use of a thick triple-coated plate (66). In another work (72), Ross found the probable error of a measured distance across an emulsion to be plus or minus two microns if the emulsion was air-dried, 1.2 if alcohol-dried. Stetson and Carpenter (83) agreed that errors caused by the emulsion were local rather than general. They recommended 1) use of plate glass as an emulsion support, 2) soaking the plate for one hour between exposure and development, 3) development in hydroquinone, and 4) drying in still air, corner down.

Ross (17) hardened plates with formalin and found, after the hardening, no change in image dimensions whether the plate was wet or dry. Since the line-width increase which is to be measured is already present in the latent image, the purpose is to develop the image with no change in its dimensions. Mees (46) has written that hardeners can be used in the developing bath, as in tropical countries, to control swelling. Such hardening, if effective, would seem superior to a preliminary relieving of strains in the gelatin as advocated either by Cooksey and Cooksey (12) or by Stetson and Carpenter (83).

* Image distortions a) may conceivably be produced by inhomogeneities in the emulsion causing distortion of the latent image with respect to the shape of the incident optical image, or b) the distortions may occur in processing, the developed image being distorted by its movement through the gelatin or by movement of the gelatin itself in release of strain imposed earlier or in reaction to strains induced by processing.
Schlesinger's spattering of ink drops on the surface of the emulsion (77) provided a means of evaluating distortion of type a) versus type b), since type a), involving only the interaction with light, would not have come into play, except that the whole emulsion was exposed (as opposed to only slit images being exposed, as usual). The masking technique of Ross (66) and Berndt (2) included both types of distortion, and so the magnitude of type a) distortion can be estimated by difference. Since Ross, Berndt, and Schlesinger all reported mean distortion errors of about 0.8 microns, and since their measurements were of the same order of accuracy, the conclusion must be that distortion of type a), that is, distortions of the latent image, was incapable of detection. Presumably the latent image is not distorted, though further proof would be valuable. The "extremely uniform" distribution of the silver halide in the emulsion (84) also leads one to believe in an undistorted latent image.

An instructive case of distortion by release of strain was observed by the writer. A filtering system designed to produce particle-free wash water had been devised; the temperature of the wash water, however, was about 34° C., compared with the 20° C. of the processing solutions. This change in temperature caused reticulation of a Kodak III emulsion, an emulsion which is comparatively thick. (The interior of the emulsion remained briefly at 20° C., while the surfaces - the emulsion was supported on X-thin glass - came abruptly to the higher temperature. Allowing the whole plate to come to room temperature was later found effective in preventing reticulation from the warmer wash water.)
Reticulation was noticed at once as a sort of dimpling of the surface, though to the eye, the line-images in the spectra remained undistorted. With the thought of relieving strain, and perhaps salvaging the plate (52, 74), the writer replaced the plate in the bath, leaving it for about ten minutes. The emulsion greatly increased in thickness, and distortion of the images was then first observed, the gelatin apparently softening and responding to the pressures originally set up by the temperature gradient. The plate was now quite ruined, but washing was continued for interest. Resultant further softening of the emulsion led to outward migration of the image silver, an actual dissolution of the images. Drying did not, of course, reverse these changes.

This study implied that any and all chemical, mechanical and thermal changes in the environment of the gelatin produce strains which in turn tend to produce distortion. The viscosity of the gelatin is usually so high, and the strains so small, that response to the strains is undetectable. Let the strains be greatly increased, or, more important, the gelatin viscosity be lowered, and distortion becomes noticeable.

A source of "distortion" often neglected is the air in which the washed plate must be handled and dried. The moist surface of the emulsion is an ideal dust-sampling device, and a particle of collected dust on a line of interest leads to error in both line-width and densitometric measurements. Very little can be done about this in an air-conditioned industrial laboratory in which dirty air is taken from the outside with little or no filtering and kept from
settling by the strong air currents set up by the air conditioner. The best solution here is to keep the darkroom clean and the air quiet.

Washing the plate with alcohol, as recommended by Ross (66), would reduce the time in which the softened gelatin could respond to strain, and also in which it could collect dust. On the other hand, an alcohol bath is both an inconvenient additional processing bath and another source of dirt.

In summary, the residual distortion resulting from processing has been estimated at about 0.5 to 1.0 microns average, with a maximum of about five microns. The edges of plates inward for about five millimeters must not be used; areas near the corners are also to be avoided. Distortion seems to come about wholly in the processing rather than residing partly in a distortion of the latent image, though more proof of this could be used. Hardening before and during processing may be a means of preserving the latent image dimensions more nearly intact. Intentional softening of the emulsion is not good practice.

**Mesuration**

**Types of Line-Width Analysis**

The various ways to perform line-width analyses, the instrumentation involved, and the problems peculiar to the method have been presented in this section.
Two general methods have been reported for line-width analytical measurements: the line-width difference, and the line-width ratio. The line-width difference method will be considered first.

Gerlach and Rollwagen (27) first proposed that the concentration of a constituent could be traced by the line-width difference method. They suggested that the term "photometric width" be taken as the distance across one line with the density used for starting and stopping the measurement of the width of the line being the specular density of another line (see Fig. 1). The photometric width could be taken from a line of either a matrix or a constituent element, some line of a constituent element or matrix element, respectively, indicating the density to be used in the width measurement.

Using this approach, Coheur (9) did several analyses and some investigational work; a partial report of this work has been made available in English (10). Coleman and Yeagley (11), O'Conner et al (34, 51, 52, 53), and Eastmond and Williams (20) also used the photometric width method.

Hunt and Timma (35) used not only the photometric width, but also width ratios at width-defining densities of 0.2, 0.3, and half-intensity band width. All were found to be indicative of concentration.

Actually, the photometric width is a difference in line-width, one line being measured at zero width (50). The photometric width has been shown to be independent of such usually critical variables as time and temperature of development (9, 27, 51) which directly affect the emulsion gamma. The independence of line-width differences from variations in gamma has been explained by the derivation presented in
Let light of intensity $I_o$ fall on an emulsion and be diffused parallel to the emulsion surface so that at a distance $d$ from the point of entry, the light has intensity $I$ as follows:

$$\log I/I_o = -kd,$$  \hspace{1cm} (7)

where $k$, a constant, is an expression of turbidity. The scattered light of intensity $I$ sensitises grains according to the relationship,

$$D = a + \gamma \log I_t,$$  \hspace{1cm} (8)

where $a$ expresses inertia of the emulsion, $\gamma$ is gamma, expressing contrast, and $D$ is the developed density of the image border, $d$ microns from the geometrical border of the image.

If (7) is substituted into equation (8), we have

$$(D-a/\gamma) = -kd + \log I_o t,$$

or

$$d = (1/k)(\log I_o t - [D-a/\gamma]).$$  \hspace{1cm} (9)

But $d$ is the distance from the edge of the optical image, and so therefore the image width (line-width) $w$ is

$$w = 2d + s,$$

where $s$ is the geometrical line-width (i.e., the slit width), and so, finally,

$$w = (2/k)(\log I_o t + a/\gamma - D/\gamma) + s.$$  \hspace{1cm} (10)
Another line has its own width \( w^* \) corresponding to its own \( I_0^* \), and so for a given \( \phi \) common to both lines, the difference between the widths of the two lines is

\[
\Delta w = w - w^*,
\]

or

\[
\Delta w = \frac{2}{k} \left( \log \frac{I_0}{I_0^*} \right).
\]

Since in the spectrographic analytical gap, the light intensity of a given wavelength is proportional to the concentration of the emitting element, we have from equation (11),

\[
\Delta w = \frac{2}{k} \left( \log \frac{c_\gamma}{c_\gamma^*/c_{st}} \right),
\]

\[
= \frac{2}{k} \left( \log \frac{c_\gamma}{c_{st}} + \log k_3 \right),
\]

or

\[
\Delta w = \frac{2}{k} \left( \log \frac{c_\gamma}{c_{st}} \right) + k_3,
\]

where \( k_3 \) and \( k_4 \) are proportionality constants between the emitted light intensities \( I_0 \) and \( I_0^* \) given off by concentrations \( c_\gamma \) and \( c_{st} \) of the minor constituent \( \gamma \) and the matrix element (the standard) \( st \), respectively. Even though the concentrations \( c_\gamma \) and \( c_{st} \) may be equal, the spectrographer may not choose lines of equal intensity from the spectra of \( \gamma \) and \( st \), and so a basic and constant difference in line-widths, expressed by \( k_3 \), results. Equation (12) shows that the line-width difference is independent of changes in \( \gamma \) and therefore of conditions of development which affect the whole plate equally.
An expression for line-width difference has been derived which takes account of the different response of a spectroscopic emulsion to different wavelengths.

Let $a$, the emulsion threshold, and $b$, the density-definition of line-edge, be the same for each wavelength. The time of exposure, $s$, and the slit width, $s$, have also been considered identical. Then let equation (10) be expressed for one line of width $y$, characterized by $\lambda$ and by $K$ (instead of $2/k$); and similarly for the other line of width $y^*$, characterized by $\lambda^*$ and by $K^*$:

$$w = K(\log I_0 t + a/\lambda - D/\gamma) + s,$$

and

$$w^* = K^*(\log I_0^* t + a/\lambda^* - D/\gamma^*) + s.$$

Then for the line-width difference, we have

$$\Delta w = w - w^*,$$

or

$$\Delta w = \log (I_0 t)/(I_0^* t)^K_{_{a-K^*}} + (a - D)[(K/\gamma) - (K^*/\gamma^*)].$$

Simplify by changing exponents, expanding, factoring, and rearranging.

Let

$$K_1 = K - K^*,$$

or

$$K = K_1 + K^*.$$
Then,

\[ w = K^* \log \frac{I_0}{I_0''} + K^* (a - D) \left[ (\gamma'' - \gamma)/\gamma'' \right] + K_r \left[ \log I_0 + (a - D/\gamma) \right]. \]

But by equation (8), the last term drops out, and as the result of the derivation, we have

\[ w = K^* \log \frac{I_0}{I_0''} + K^* (a - D) \left[ (\gamma'' - \gamma)/\gamma'' \right]. \quad (13) \]

Therefore, in actual line-width differences, the relevant expression contains a rather small term which is a function of the difference in gamma between the two lines and is inversely proportional to the square of gamma. The gamma term probably never attains detectable magnitude.

Nevertheless, equations (10) and (13) are both simplifications of reality. Inspection of Figs. 8 through 25 shows that image growth and image contour are not mathematically simply expressible, and that equations (10) and (13) are just approximations of the width of the photographic image of a spectrograph slit. That is why only the photometric width principle gives line-width results characterized by maximum precision and reproducibility.

The photometric width principle defines a line-width difference for the case wherein one line has zero width. The analytical curve based on such a line-width difference incorporates the profile of only one line. The identical densities of the indicator line and of the edges of the measured line increase and decrease, with experimental
variations, together, so that the same cross section of the measured line is always obtained, and variations in exposure and gamma cancel out very well.

If, on the other hand, the analytical curve involves the width difference of two line-images at some such arbitrary density that both line-images have finite width, then the independence of the analytical curve from inevitable experimental variations in exposure is lost. A line pair in line-width analysis is composed of a rather light line and a rather heavy line. For lines which are so different in base line-width, the spreading factor \( b \), the sharpness index \( S \), and especially the changes of \( b \) and \( S \) with exposure, that is, the slopes of the curves in Figs. 8 through 25, are all marked functions of exposure; line-width differences, both widths being finite, are also functions of exposure. Small variations in exposure are noticeable and cause error unless the photometric width principle is used.

Although each depends on the photometric width principle, the matrix width and constituent width methods differ fundamentally from each other.

The matrix width method involves the changing density of a constituent line, and the constant profile of a matrix line. The accuracy and precision of the matrix width method therefore depends on a high gamma and a low sharpness index. The high gamma implies a large density change per unit concentration change of the constituent. A low sharpness index implies a large width change per unit density change indicated by the density of the constituent line. High gamma
is obtainable by selection of emulsion and developer, and low
sharpness index by selection of a large matrix line. The limited
range of the matrix width method has already been mentioned under
Range.

The constituent width method involves the constant density of
a matrix line, and the changing width of a constituent line. The
accuracy and precision of the constituent width method therefore
depends not at all on the gamma or on the sharpness index, but
instead on the spreading factor which describes the changing width
of the constituent line and on the definition of the edge which is
given by the density of the matrix line. Use of a light matrix line
affords the advantage of the higher spreading factor associated
with a high-transmittance definition of the edge (see Figs. 8 through
16). Since there is no limit to the spreading of a line image, the
constituent width method may be said to have practically unlimited
concentration range.

Under Line-Width Photometry, the similarity of the matrix and
constituent width methods with respect to mathematical representation
of errors has been shown, and the quality factor for each method
has been defined.

Eisenlohr and Alexy (22) suggested that the ratio \( R \) of two line-
widths, both evaluated at a given density, could serve as an index of
concentration. A smooth curve of increasing slope was obtained from
a plot of \( R \) against the logarithm of the concentration of the
element sought.
Let a simplified version of equation (10), for the photographic line-width \( w \), be taken as

\[
v = K \log a_x + K_0,
\]

where \( K_0 \) contains \( \chi \).

The quotient \( R \) of two widths is then

\[
R = \frac{w_x}{w_y},
\]

or

\[
R = \frac{(K \log a_x + K_0)/(K \log a_{st} + K_0)}{1}. \tag{15}
\]

Let the slope of the plot for \( R \) versus \( \log a_x \) be determined:

\[
\frac{dR}{d \log a_x} = \frac{1}{(K \log a_{st} + K_0)},
\]

or

\[
\frac{dR}{d \log a_x} = \frac{1}{(\log a_{st} + K_0^*)}. \tag{16}
\]

The upward trend of the plot has been explained by equation (16). If \( a_x \) is very small, then \( a_{st} \) is almost, for a binary, 100\%, so that the slope is nearly constant; the denominator, which contains \( \log a_{st} \), changes little. As \( a_x \) increases, \( a_{st} \) and \( \log a_{st} \) decrease and the slope increases, approaching as a limit,

\[
(\frac{dR}{d \log a_x})_{\text{lim}} = \frac{1}{(K_0^* + 1)}.
\]

Measurement of Line-Width

The measurement of line-width is subject to stringent requirements which, fortunately, can be met. Not only are the most delicate
and yet flexible techniques of measuring distance needed, but also incorporated in the precise estimation of light intensity.

Usable methods of measuring line-width should exhibit a reproducibility approaching one micron, since this is the precision of a good precision screw; a comparable accuracy would be preferable, though not necessary. A range of up to two millimeters in the distance to be measured is required, since spectrographic lines may attain this width. The usual spectrographic plate is ten inches wide; any line on it should be easily and quickly accessible to the measuring device. In order that the line-width technique be capable of wide application, the measurements should be easily made and comparable in speed to the measurements of densitometry. In summary, then, the method of distance measurement in the estimation of line-width must be easy to use, rapid, and capable of providing reproducibly a specification within one micron of any length up to two millimeters; the length to be specified must be able to occur at any position within a ten inch range. The edges of the line, marking the ends of the measured distance, must also be clearly indicated.

The location of the edges of the line requires photometry. The photometric system must be compact and closely integrated with the length-measuring device. The photometric system must be stable enough to retain a given value (a given pen position) for a particular density, although the fact that the photometric requirements of line-width photometry can be eased considerably from the corresponding requirements of densitometry will be pointed out later in this
section. The response time of the photometric system must be short
eough to allow measurement of a line-width within five seconds;
this implies a full-scale deflection time of one second or less.

In the past, using the eye alone to judge the edge of an image
was standard practice (44, 45, 54, 61, 62, 63, 64, 65, 66, 72, 76, 82,
83, 87), but aside from the obvious inaccuracy of the eye as a photo-
meter, the additional limitations of human fatigue and variability
render this approach inadequate.

Direct measurement of the distance a plate carriage has moved
in carrying a line across a photometer slit has been done (22). A
microscope and filar micrometer might be used for this purpose, the
combination giving a powerful method for the measurement of small
distances with very good accuracy. The image of the object being
measured is projected onto a plane which also contains a graduated
scale and movable cross-hairs. If some point of the object is taken
as reference, then movement of the object parallel to the direction
of movement of the cross-hairs and in a plane perpendicular to the
optic axis of the microscope can be followed by the movement of the
cross-hairs, and measured in terms of the graduated scale. The
operation described in the last sentence is subject to several sources
of error; these sources have been elegantly treated by Whitehead (94).

The graduated scale can be calibrated by using as an object a
specially made slide bearing graduations at known separations. The
magnification of the microscope governs first, the calibration of the
filar micrometer scale and second, the size of the field. For,
although use of high magnification permits the estimation of very
small distances to the limit of resolution of a microscope (about
0.002 microns)(81), the concomitant restriction of the lateral
dimension of the field tends to keep such precision from being
useful for line-width measurements. If the width of an ordinary
line is taken as the diameter of the field of view, then the dis-
tance which can be estimated (with some difficulty) is about one
micron. However, this technique suffers seriously from requiring
the close physical and mental attention of the operator, and
could not be expected to afford consistently accurate results,
particularly with a large volume of routine work.

An interferometer (8, 13, 86) yields a measure of distance in
terms of the wavelength of light used. The technique usually is
such that the observer sees circular fringes which are concentric and
which feed continuously from the center as one mirror of the
interferometer is moved; the fringes are counted, each signifying
a movement of the mirror through a distance equal to half a wave-
length of light, i.e., a quarter of a micron. A movement through
two millimeters would require 8000 fringes to be counted; obviously,
for practical application, fringe counting would have to be automatic.

The extreme sensitivity of the interferometric technique renders
it susceptible to many variables, not the least of which are the room
temperature and humidity; the temperature affects the dimensions of
the instrument itself, to which the instrument is sensitive; and the
temperature and humidity each affect the refractive index of the air,
to which index the length of the light wavelength - and therefore the
indicated distance itself - is inversely proportional. Nevertheless, many of the variables in interferometry refer to the establishment of standard conditions of operation, and so can be bypassed if measurements are made with at least moderate speed and include the measurement of a reference standard. These last two requirements are easily met.

Aside from the variables of operating conditions which affect interferometry, there is the additional necessity for critical optical adjustment. This last difficulty has been alleviated by the development of the corner-cube interferometer by E. R. Peck (56, 57); his design also increasing the range of interferometry, previously restricted for routine practice to uses such as comparison of nearly equal lengths. Recently, Peck and Obets (55) announced the application of automatic reversible fringe counting to the corner-cube interferometer. This advance seems from its descriptions to be the specific answer to most of the problems of line-width measurement, and may be of great importance in the future development of line-width measurements.

In the fringe-counting corner-cube interferometer, two fringe patterns mutually out of phase by 90° are simultaneously viewed by phototubes. The phase relationship of the resulting signals furnishes a criterion for the direction of movement of the indicating mirror. In addition to the fringe count, the rotational position of the spot on an oscilloscope indicates the fraction of the last fringe to be counted, since the viewing phototubes of the interferometer furnish
the axial signals for the oscilloscope beam, causing it to move in a circle as the distance being measured is traversed. The combination of counter and oscilloscope should permit the direct measurement of any desired line-width to within 0.1 microns in five seconds or less. Since optical adjustment need not be exact, the mirror should be capable of reflecting usable light from its position on a photometer plate carriage - as with the Leeds and Northrup, Jarrell-Ash, or Bausch and Lomb instruments - despite the disturbance of carriage movement, especially since the instruments themselves are examples of excellent machine work.

Only one adaptation of this device would be required: a signal to indicate when to start and stop counting. Such a signalling device is very simple if the densitometer is recording, somewhat more complex if not. Both types have been adapted to line-width measurement by the writer, but only the adaptation of the recording type has been described, in later paragraphs of this paper.

The precision screw is the device ranking next to the interferometer in the precise measurement of length. Whitehead (94) has described a number of arrangements for the use of a precision screw and has presented some fine relevant discussion of precision mechanisms; an account of the Hilger Comparator is also given. The Hilger Comparator can be used to measure within one micron any distance up to fifteen centimeters. Since the comparator carriage is driven directly from the nut mounted on the precision screw, this statement of precision requires equal precision of the screw. The
long-term error of the screw must not exceed 0.01%, and the short-
term errors must not cause the nut to be more than one micron from
the value indicated on the graduated drum which rotates with the
screw. The carriage could be linked to the screw in such a way as to
tend to cancel out short-term errors; such a linkage is used on the
Bausch and Lamb Densitometer. In this instrument, two spur gears
bear on opposite sides of the drive screw (which is not a precision
screw). The spur gears are coaxial and rigid with friction drums, so
that the carriage can be moved laterally by hand, causing the spur
gears to turn; the spur gears do not rotate easily because of the
friction drums, therefore rotation of the drive screw causes the
carriage to advance. But if the screw is not even, that is, if the
screw has short-term errors, the two spur gears tend to alleviate the
short-term errors of the screw by splitting the difference of the
short-term error between themselves. The importance of these
mechanisms for the discussion here is two-fold: the presence of
short-term error in precision screws is emphasized; and a criterion
of excellence - one micron error - is furnished by which to judge
mechanical drives.

The Knorr-Albers Recording Microdensitometer has been used (35,
51, 52) for line-width measurements, and its high quality is a result
of excellent design (40). The drive gears permit the operator to
select carriage velocities in either direction of 0.1, 0.2, 0.5, 1.0,
2.0, 5.0, 10.0, 20.0, and 50.0 millimeters per minute. The photome-
ter light source is the side of a tungsten ribbon filament. A line
of light 0.07 mm. wide in the plane of the plate is projected onto
the plate; the attenuation of this light is measured by a phototube. The phototube is part of a d.c. amplifier employing current feedback; a small fraction of the amplifier output is measured and indicated by a Speedomax recorder, capable of full scale deflection in about 0.2 seconds. The following discussion primarily concerns the experimental use of the Leeds and Northrup Knorr-Albers Microdensitometer — hereafter referred to as the L. and N. instrument —, the conversion of the L. and N. instrument to rapid measurement of line-width, and the evaluation of the apparent and the attainable precision of the L. and N. instrument in the measurement of line-widths.

In the literature, all measurements concerning the L. and N. instrument have been via chart recording of lines and subsequent measurements from the charts. The fastest chart speed of the recorder is about two inches per minute, and the slowest carriage speed, 0.1 mm./min. The corresponding maximum magnification of the unaltered instrument has been given (40) as 500. One micron on the plate thus becomes 0.5 mm. on the chart, or about the width of the inked line. The minimum probable error of measurement from the chart is therefore at least two microns, assuming only reading errors. The error is no doubt higher than two microns, since the chart is driven by gears which contain imperfections, causing the chart to advance unevenly. The required time of measurement for minimum error is at least one to two minutes. (During this time, the photometer scale is required to hold absolutely steady; that this condition is probably met has been shown later.) Shorter times of recording increase proportionately the minimum error of measure-
ment from the chart. Since the minimum error of one to two microns should be at least retained if not bettered, and since the time for line-width measurement must include not only recording time but also the time for measurements from the chart, an improvement is obviously necessary if line-width photometry is to compete with densitometry.

*  

An adaptation of the L. and N. instrument to rapid and precise line-width measurement has been made. The adaptation depends on the relationship that, with uniform velocity, time is a measure of distance. Passage of a line across the image of the side of the L. and N. ribbon filament causes the recorder pen to move downscale from 100% transmittance. In the altered L. and N. instrument, as the pen passed a certain transmittance arbitrarily designated as indicating the edge of the line, a device moving with the pen allowed a precision clock to begin measuring time. As the line moved on and away from the filament image, the recorder pen returned upscale toward 100% transmittance, the device moving with the pen stopped the precision clock, and the clock displayed a large number proportional to the width of the line. The measurement of the line-width required less than five seconds and was precise to about one and one-tenth microns.

The adaptation of the instrument thus involved a device geared to the pen and acting as a switch for the precision clock, and the clock itself. The clock consisted of a pulse generator and a counter separated from the generator by the switching device.

The pulse generator designed and built for this purpose was completely electronic, and experience of several months proved it
completely satisfactory. No tubes were replaced.

The design of the pulse generator was based on considerations which included the slightly varying house line frequency, the characteristics of the L. and N. recorder, and the characteristics of spectroscopic emulsions.

The alternating current furnished by power companies is maintained at a frequency of sixty cycles per second with a precision much better than one part in a thousand, if a long enough time is used for finding the average frequency. The short-term frequency can vary from 59.8 to 60.2 cycles per second, especially during periods of light electrical load. Since the frequency variations of the line could have caused the synchronous carriage drive motor to run slower or faster, the pulse generator was designed to produce a pulse frequency which was an integral and fixed multiple of the line frequency. Selection of the particular multiple to be used depended on the characteristics of the L. and N. recorder and of spectroscopic emulsions.

Let it be set down that

$$\frac{dD}{du} = \frac{(dD/dt)(dt/du)}{du/dt} \frac{(d log x/dt)}{(dx/dt)} = \frac{(1/x)(dx/dt)}{(dD/du)}.$$ (17)

The ratio $(dx/dt)$, the time rate of change of transmittance, was set
equal to the response time of the recorder, or approximately one second for full scale response (i.e., one transmittance unit, or 0% to 100% transmittance). The transmittance definition $x$ of the edge was taken as 0.6, or 60% transmittance. The ratio $(dn/dt)$, or sharpness index $S$, the distance rate of change of density, varies from about 0.0025 for a moderately broad line to as much as 0.15 for a very sharp one. Substituting these values into equation (17) gave the value for scanning speed as

$$\frac{dn}{dt} = \frac{(5/3)(1)/(0.0025)}{(5/3)(1)/(0.15)} \text{ microns/second,}$$

or approximately,

$$\frac{dn}{dt} = 40 \text{ mm/min for a broad line, to 1 mm/min for a sharp line.}$$

If the recorder was to keep up with the line moving across the photometer, then the scanning speed should not have exceeded the indicated values. If the line crossed the photometer at such a velocity as to have exceeded the response time of the recorder, then the line would have seemed to the recorder to have infinitely steep sides, and a less dense part of the line having a characteristically gentler slope would have actually furnished the definition of line-width. That is, the effective line edge would have been farther away from the center of the line, at the point where the recorder would have assumed full speed.

This difference in effective definition of edge is crucial in measurements of photometric width, since a given measured density is part of the definition of the photometric width. Fortunately, if
emulsions giving favorable spreading for line-width measurements are used, sharpness indices greater than about 0.04 are not encountered, and therefore a scanning speed of two millimeters per minute with the Speedomax recorder is both conservative and rapid. At two millimeters per minute, lines can be measured in less than five seconds per line.

Once the carriage scanning speed was estimated, the counting rate, or pulse generator frequency, could be specified. If a change of 0.1 micron in a line 0.1 mm wide was to be detected, then at least 1000 counts would have to be used. If the line was scanned in three seconds, the counting speed had to be at least 330 counts per second. Since this exceeds the speed of a mechanical counter, and since the glow transfer counter to be used has a rated maximum speed of 2000 counts per second, the pulse generator was designed for 900 counts per second. This was a comfortable margin over 330 counts per second, and a speed which would not push the counter.

The design of the 900 cps pulse generator was straightforward (87, 88). The 60 cps signal from the house line was amplified to a square wave by a 6AC7 double triode. The square wave was differentiated to give pulses which synchronized a free-running 300 cps multivibrator (87); this multivibrator would pull in to synchronization from 291 cps. Since the proportional variation of the line frequency is between 299 and 301 cps, the synchronization of the 300 cps multivibrator by the 60 cps pulses was perfect. The 300 cps multivibrator output was used to synchronize a second free-running 900 cps multivibrator. The original design called for the second
multivibrator to run at 1500 cps, but synchronization was unsure, and so the lower frequency multiplication factor of three was chosen, with satisfactory performance. The output of the second multivibrator was just fifteen times the line frequency, regardless of changes in the line frequency.

As shown in Fig. 28, the counter input was permanently connected to the output of the pulse generator. The signal lead was also connected to the contact leaf of a dismantled telephone switch; the leaf could make contact with a cam mounted coaxial with the drum around which is wound the cable which drives the recorder pen. Part of the cam surface was recessed, so that the cam broke contact with the telephone leaf after turning through a certain number of degrees. Since the pen cable drive drum turned through only about 300° to drive the pen full scale, the cam did not remake contact until the drum had reversed direction. When contact was made, the leaf was grounded through the cam, and the signal was grounded out.

In action, then, the signal was grounded out when the pen indicated 100% transmittance. As the pen moved downscale, the ground contact was broken and the counter received pulses from the pulse generator. This counting continued until the pen moved upscale again - as the line passed the photometer and moved away - , grounding the signal line and stopping the counter.

Some emphasis has been placed on the fact that the signal generator was designed to produce not a given frequency, but a fixed multiple of the slightly varying line frequency. Since signal generators of very high precision and accuracy are commercially
FIGURE 28

ADAPTATION OF LEEDS AND NORTHRUP MICROPHOTOMETER

TO LINE-WIDTH MEASUREMENT
available, the justification for building a synchronized oscillator depends on the size of the error to be avoided. If one micron is the unit minimum error, and the percent frequency variation of 0.6% is the error to be avoided, then the line to be measured must be at least (1/0.006) or 150 microns (0.15 mm.) wide to justify building instead of buying an oscillator. Probably at least half of the lines to be measured are wider than 0.15 mm., but on the other hand, the frequency variation quoted is an extreme value, the usual daytime error probably not exceeding 0.2%. Therefore, usually no or negligible error will be incurred if a stabilized rather than a synchronized oscillator is used.

Although the crux of using time as an analogue of distance is the assumption of uniform velocity, only a little incisive work provided convincing evidence that the plate carriage velocity was not uniform. A quantitative expression of the error introduced by non-uniform velocity was desired, and also what measures could possibly be taken to reduce such error. In Table III, the measurements taken in the evaluation of error from various sources have been given. A description of the carriage drive mechanism has been given below to help reveal the reasons for the method of measurement.

The carriage is connected to the drive by a steel tape fastened at each side of the instrument to a drum. One drum serves to load the drive system by the support of a weight. The other drum is coaxial with a large gear which meshes with the worm drive. In this way, the whole carriage drive is always loaded against the gear-worm drive contact, and so a given position of the carriage relative to the instrument proper corresponds to a given surface on the worm drive.
TABLE III
EVALUATION OF PRECISION OF LEEDS AND NORTHROP MICROPHOTOMETER

Line Widths in Counts

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
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<tbody>
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<td>3882*</td>
<td>3885*</td>
<td>3878*</td>
<td>3849*</td>
<td>4453*</td>
</tr>
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<td>3836</td>
<td>3853</td>
<td>4038</td>
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</tr>
<tr>
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<td>3887</td>
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<td>3862</td>
<td>3862</td>
<td>3822</td>
<td>4451*</td>
</tr>
</tbody>
</table>

\[
T = \frac{t^2}{n}
\]

* = Full scale and zero checked and/or reset at given point on plate.
/ = Column 6 refers to line different from that of Cols. 1 through 5.
A = Carriage movement by motor only.
B = Carriage reset by hand wheel.
5 = Plate moved laterally on carriage between each measurement; carriage reset by hand wheel.
6 = Plate removed from carriage between each measurement, but replaced at fixed point on carriage so that same contact with worm drive was used for each measurement. Standard deviation indicates reproducibility of about 1.12 microns.

Carriage velocity: 2.0 mm./min. or 0.037 microns/count.
Counting speed: 900 counts/second.
Moreover, an extended rule is fastened to the carriage, with a marker and vernier placed on the instrument proper, so that the position of the carriage can be noted to within 0.05 mm. Since the ribbon filament of the photometer is fixed laterally relative to the instrument proper, the repeated positioning of a spectrum line with respect to a given worm drive surface becomes possible; the line is fixed relative to the filament while the carriage is set at a given mark on the rule.

The carriage can be moved either by means of the motor control or by turning the hand wheel. A clutch separates the worm drive from the motor and the gears of the transmission. Therefore, a given position of the carriage does not correspond to any given position or contact surface of the motor and transmission gears.

These facts permitted the separate evaluation of the error from the imperfections of the motor drive and transmission gears, and from the worm drive. A plate was placed on the plate carriage and aligned vertically so that a portion of a Cu 2824 line in a copper spectrum would be measured. Exactly 1.5 mm. to the right of the copper line, on clear film, the photometer was set for 100% transmittance. The plate and the carriage were not touched again until all the measurements shown in the four columns under A and B, in Table III, had been obtained. Those figures in the columns under A were therefore obtained with all resetting of the carriage done via motor control and with no shifting of gears. In other words, all measurements in the columns under A were made with the same drive contact-surfaces throughout the carriage drive system. The figures under B were obtained with resetting by the hand wheel, thus forcing the clutch to
slip and so obtaining different parts of the drive gears on the 
motor side of the clutch. Comparison of the B figures with the 
A figures allowed an estimation of the error due to the gears on the 
motor side of the clutch.

In the following discussion of errors, these symbols have been 
used:

\[
\begin{align*}
g &= \text{standard deviation due to the gears on the motor side of the clutch;} \\
f &= \text{standard deviation due to the worm gear;} \\
p &= \text{standard deviation due to photometric error;} \\
h &= \text{standard deviation due to unassigned errors;} \\
t &= \text{total standard deviation;} \\
G &= g^2; \\
F &= f^2; \\
P &= p^2; \\
H &= h^2; \\
T &= t^2.
\end{align*}
\]

First, let the photometric error be evaluated. The d. e. 
amplifier and filament power unit were assumed to drift; to offset 
and measure this drift, the figures under columns 1 and 2 were 
acquired with frequent recalibration on clear film. Results showed 
that the recalibration caused more error than the drift; the figure 
which has been calculated for "photometric error" represents the 
error introduced by local variations in the selected area of clear
film used for recalibration, and the reading error in setting up the calibration.

Taking the difference of the squares of the standard deviations of columns 1 and 2, and 3 and 4, as the photometric error, and lumping any photometric drift in with the unassigned errors, we have

\[
\begin{align*}
T_2 &= H + P, \quad (18) \\
T_3 &= H, \quad (19) \\
T_4 &= H + G + P, \quad (20)
\end{align*}
\]

and

\[
T_5 = H + G. \quad (21)
\]

Therefore,

\[
P = T_1 - T_2 = T_5 - T_4, \quad (22)
\]

\[
= 88.5 - 64.0 = 181.6 - 128.7, \\
= 24.5 \pm 52.9,
\]

and so

\[
p = 4.95 \pm 7.27
\]

The photometric error due to reading error and local variations in clear film was about 6.1 counts, or 0.22 microns, for this plate. (The photometric error \( p \) which has been evaluated here should be nearly negligible in spectrochemical measurements of photometric width, since the photometric width principle requires no full scale or zero settings, or actual reading of a density value.)

\[
p = 6.1 \text{ counts} \quad (23)
\]

\[
p = 0.22 \text{ microns}
\]

The error \( g \) has been evaluated from equations (18) and (20), and
(19) and (21).

\[ G = T_3 - T_1 - T_4 - T_2 \]  
\[ = 181.6 - 88.5 - 128.7 - 64.0 \]
\[ = 93.1 \pm 64.7 \]

The error caused by the gears on the motor side of the clutch has therefore been taken as

\[ \delta = \frac{9.6 + 8.0}{2} \]
\[ \delta = 8.8 \text{ counts} \]  
\[ \delta = 0.33 \text{ microns} \]  

(25)

Since different contact area on the worm gear were deliberately used in the measurements shown in column 5, so that

\[ T_5 = H + G + F + F_s \]  
\[ \text{(26)} \]

\( F \) has been evaluated by subtracting equation (20) from equation (26), giving

\[ F = T_5 - T_4, \]
\[ = 17793.3 - 128.7, \]
\[ = 17664.6. \]

The error \( \delta \) due to the imperfections in the worm gear has been found to be

\[ \delta = 132.9 \text{ counts} \]
\[ \delta = 4.9 \text{ microns} \]
The foregoing calculations have shown that the error introduced by the worm gear is about fifteen times the error introduced by the other gears, and about twelve times the indeterminate error. If the error caused by the worm gear is a result of local changes in pitch rather than simply a rough surface, then the worm gear error should be greatly reduced if the same spot is used successively in repeated measurements of a given line-width. This can be done; its accomplishment has been described earlier. The measurements in column 6 were conducted with the idea of simulating a set of operations widely separate in time, as one would get in a series of routine analytical measurements spread over weeks. The plate was physically removed from the plate carriage between each measurement, and the full scale calibration also renewed each time. Care was also taken that the motor-side gears' contacts were changed, the motor being kept running while the plate was removed from the carriage. The standard deviation of the figures in column 6 is the square root of 909.9, or 30.2 counts, corresponding to a standard reproducibility of 1.12 microns.

The technique of reproducing the worm contact is therefore effective in reducing error insofar as error affects reproducibility. Use of a very fine line in the spectrum as a marker, instead of the thick one that was used, would probably have improved the reproducibility still more.

A careful distinction must be drawn between reproducibility and accuracy. The imperfect gears cause the carriage to advance irregularly, so that reproducible measurement of a set of successively thicker lines results in a set of measurements irregularly increasing
in size. An analytical working curve good enough to reflect errors in line-width measurement is therefore not smooth. Eastmond and Williams (20) reported such a curve, ugly to see, but honest.

Initiation of counting before the carriage had a fair chance to get rolling smoothly may have been a possible source of error. (This was found to be a significant source of error in measurements made on an instrument of a different make.) Perhaps an interval should have been allowed before actual measurement, during which all moving parts could have come to full and even speed. (Such was the procedure followed in obtaining the data shown in Table III; five seconds were allowed before each measurement.) This "grace-period" procedure was tested for value. The results have been presented in the first two columns of Table IV. The "grace-period" standard deviation was 5.7 counts, slightly lower than the 6.0 counts standard deviation found for immediate initiation of counting. Since the standard deviation in counts which was taken as the basic minimal error in Table III was 8.0 counts (from \( t_2 \)), the difference between the errors from the "grace-period" and immediate counting procedures was considered insignificant (i.e., 0.01 microns). No time need be wasted waiting for the carriage to move up to the line.

In routine spectrochemical work, measurement of the same line in different spectra requires vertical displacement of the carriage between measurements. Here is another possible source of error; this was also tested. The value, 8.0 counts, from column 2, Table III, has been taken as the standard error for no disturbance of the carriage between measurements. The corresponding standard error, from the
# TABLE IV

**FURTHER EVALUATION OF PRECISION OF LEEDS AND NORTHRUP MICROPHOTOMETER**

<table>
<thead>
<tr>
<th>Immediate Counting</th>
<th>Grace Period</th>
<th>Vertical Adjustment Between Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1560</td>
<td>1575</td>
<td>2023</td>
</tr>
<tr>
<td>1558</td>
<td>1574</td>
<td>2011</td>
</tr>
<tr>
<td>1560</td>
<td>1575</td>
<td>2009</td>
</tr>
<tr>
<td>1551</td>
<td>1570</td>
<td>1992</td>
</tr>
<tr>
<td>1558</td>
<td>1571</td>
<td>2021</td>
</tr>
<tr>
<td>1559</td>
<td>1571</td>
<td>2027</td>
</tr>
<tr>
<td>1560</td>
<td>1565</td>
<td>2010</td>
</tr>
<tr>
<td>1553</td>
<td>1573</td>
<td>2022</td>
</tr>
<tr>
<td>1559</td>
<td>1566</td>
<td>2012</td>
</tr>
<tr>
<td>1558</td>
<td>1558</td>
<td>2007</td>
</tr>
<tr>
<td>1550</td>
<td>1563</td>
<td>2004</td>
</tr>
<tr>
<td>1568</td>
<td>1564</td>
<td>2008</td>
</tr>
<tr>
<td>1561</td>
<td>1556</td>
<td>2003</td>
</tr>
<tr>
<td>1564</td>
<td>1562</td>
<td>2001</td>
</tr>
<tr>
<td>1561</td>
<td>1563</td>
<td>2024</td>
</tr>
<tr>
<td>1564</td>
<td>1566</td>
<td>2020</td>
</tr>
<tr>
<td>1559</td>
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<td>2012</td>
</tr>
<tr>
<td>1568</td>
<td>1561</td>
<td>2031</td>
</tr>
<tr>
<td>1555</td>
<td>1570</td>
<td>2013</td>
</tr>
<tr>
<td>1574</td>
<td>1564</td>
<td>2021</td>
</tr>
</tbody>
</table>

| t, counts | 6.0 | 5.7 | 9.9 |
| t, microns | 0.22 | 0.21 | 0.36 |

* = Standard deviation
Last column refers to line different from that of first two.

Carriage velocity: 2.0 mm/min., or 0.037 microns/count.
Counting speed: 900 counts/second
last column of Table IV, for vertical displacement of the carriage between measurements, was 9.9 counts. The error resulting from vertical motion of the plate rack has been found to be the square root of the difference, \((9.9^2 - 8.0^2)\) counts. This is 5.8 counts, or 0.21 microns.

Several basic sources of error existed which could not have been cancelled merely by improving the quality of the worm drive screw, although such improvement could have eliminated the need for careful duplication of worm screw contact surfaces. These errors were the basic indeterminate error of measurement, 8.0 counts, from column 2, Table III; the photometric error, which might possibly have been eliminated or which could easily have been increased, 6.1 counts, from equation (23); the error due to the gears on the motor side of the clutch, 8.8 counts, by equation (25); and the error due to disturbance of the carriage by vertical motion of the plate rack between measurements, 5.8 counts. The square root of the sum of the squares of these errors is 14.6 counts, or 0.54 microns. If the error of the worm screw had been about equal to these other errors, then the expected standard deviation would have been 18.6 counts, or about 0.7 microns, as opposed to the achievable 1.12 microns which reflected all the mentioned sources of error.

A discussion of "edge" error has been postponed to this point. Edge error has not been mentioned before, and so has been included in the indeterminate error. Important in measurement of photometric width, edge error is a recognizable but variable source of error caused by the imperfect photometry of the indicator line density and
of the edge of the measured line. Let transmittance difference Δ occur between the indicator transmittance \( t_{\text{r}} \) and the transmittance of the edges of the measured line; the density error \( D_{\text{e}} \) which results is approximately

\[
D_{\text{e}} \approx 2.3 \text{ c/tr}.
\]  

(28)

The edge error \( d_{\text{e}} \) in line-width will reflect the photometric error \( D_{\text{e}} \) according to the sharpness of the line being measured. The sharpness is given by the sharpness index \( S \), where \( S = (dD/d\alpha) \).

Therefore,

\[
d_{\text{e}} = D_{\text{e}}/S,
\]

and

\[
d_{\text{e}} = 2.3 \text{ c}/\text{S tr}.
\]  

(29)

In line-width measurement, the usual sharpness index \( S \) is about \( 10^{-2} \), when evaluated, as in this paper, from inflection points which occurred at 60% to 70% transmittance. The usual \( S \) is low, since no zero, no full-scale settings, and no reading errors need be taken into account; \( S \) can be given the tentative value, 0.05. If a light indicator line, of about 70% transmittance is used, the line-width measurement is accompanied by an edge error of

\[
d_{\text{e}} = (2.3)(0.05)/(10^{-2})(70)
\]

\[
= 0.16 \text{ microns, for each edge.}
\]

or

\[
\sqrt{2} d_{\text{e}}^2 = 0.23 \text{ microns total edge error.}
\]
A total edge error of 0.23 microns is not damaging, but an insidious choice of operating conditions could easily make the edge error limiting. If, for instance, $t$ were 0.15 instead of 0.05% transmittance; if the indicator line were too dark, say 20% transmittance; and if the line being measured were very broad with a very gradual slope, so that $E$ were $0.50 \times 10^{-3}$, then the edge error would be

$$d = \frac{(2.3)(0.15)/(0.005)(20)}{\sqrt{2}} = 3.4 \text{ microns for each edge, or}$$

$$\sqrt{2} d = 4.7 \text{ microns total.}$$

The time required to obtain individual line-width measurements with this counter-adaptation of the L. and N. instrument has compared favorably with densitometry. Time of measurement per line has varied from one to five seconds. Densitometric measurement requires at least five seconds per line, even with a very rapid operator.

One adjustment, which is simple and fast, has been required in the measurement of photometric width with the cam-switch device. The indicator transmittance must be made equal to the transmittance at which the cam makes and breaks contact with the telephone leaf; this can be done in either of two ways. If the scale were adjustment is changed, the whole scale shifts, and the transmittance identity can be established. Or if the cam contact-transmittance is greater than the indicator transmittance, then increasing the filament power adjustment expands the scale, until the identity is established; this method
decreases photometric error by the factor \((tr/y)\), where \(tr\) is the transmittance of the indicator, and \(y\) is the transmittance of the cam contact point. On the other hand, the response time of the recorder should not be exceeded, and scale expansion has the effect of demanding a shorter response time, if the same scanning speed is used.

In the application of the reversible fringe-counting corner-cube interferometer to any similar pen-recording densitometer, cam switches could be used, without the necessity of introducing new electronic circuits into the existing ones. Speed of line measurement should be as good with interferometry as with the counting system, and the error possibly one-tenth as great. On the other hand, except for the cams, all the necessary components of the counting adaptation of the L. and N. instrument, which has been described in this study, are commercially available and easily installed in a pen recording photometer. Estimation of the photometric precision to be expected from the system which has been described and from interferometry has been given in detail under Comparison of Photometric Errors. **
DENSITOMETRIC PHOTOMETRY

Densitometric photometry, which has been thoroughly covered in the literature (1, 29, 46, 48, 49), has been surveyed briefly, in preparation for a comparison of line—width photometry with densitometry.

Definition

There are two methods of densitometry, called specular and diffuse. Diffuse densitometry takes account of all the light transmitted through the photographic image, whereas specular densitometry is concerned only with light emergent in the direction of the incident beam. Spectrochemical analysis is concerned only with specular densitometry, which has been hereafter referred to only as densitometry.

Variables in Densitometric Photometry

Many variables affect densitometry (29). Emulsions vary in thickness and sensitivity from spot to spot on a given plate or section of film, and from plate to plate. The thickness variation is less important than it might seem, because most spectrochemical analysis is done with ultraviolet light, and images produced by ultraviolet light are largely confined to the surface of the emulsion.
The response of the photographic emulsion to light can be described over a certain range of exposure as

\[ D = a + \gamma \log E, \]

and the emulsion can be used for spectrochemical analysis by densitometry only when gamma, \( \gamma \), is constant. Since gamma varies with wavelength, development time, development temperature and method of development, and since knowledge and reproducibility of gamma are of the first importance (1, 24, 29, 49) in achieving accurate and precise spectrochemical analysis, any method of either stabilizing gamma or rendering it irrelevant is of prime importance. The failings of densitometric photometry lie in the variable processing rather than in variable response of the emulsion (84); this should be remembered in the reading of the following theoretical comparison of line-width with densitometric photometry. The line-width method is very largely independent of many of the variables in processing, insofar as they affect the reproducibility of gamma from plate to plate.
COMPARISON OF THEORETICAL PHOTOMETRIC ERRORS

Densitometric Photometry

In the following comparison, the error to be expected in spectrochemical analysis (hereafter, analysis) utilizing densitometric photometry has been considered first. For a given analysis with a given line-pair (l, 49), increasing concentration of the "unknown" component decreases logarithmically the ability of unit concentration of the component to produce unit blackening in the photographic emulsion. The blackening produced can in turn be measured less and less well, so that the accuracy of measurement also falls off logarithmically. In this study, an expression relating these effects has been developed; errors due to the reference line have been neglected, and the reference line density has been considered constant.

The density measurement error \( D_e \) for a given constant measurement error \( e \) in transmittance \( x \) of the emulsion is

\[
D_e = \log \left( \frac{1}{x} \right) - \log \left( \frac{1}{x + e} \right);
\]

therefore,

\[
D_e = \log \left( 1 + \left[ \frac{e}{x} \right] \right).
\]  

The change in density \( \Delta D \) (or \( D_e \)) due to a change in concentration \( \delta \) at a given concentration \( e \), with the light falling on an emulsion developed to gamma \( \gamma \), is
\[ D_0 = \gamma \log (1 + \delta e/e) \]
\[ D_e = \gamma \log (1 + [\delta e/e]). \] (31)

To find an expression for \( \delta e \), eliminate \( D_e \) from equations (30) and (31):

\[ \log (1 + [\delta e/e]) = \gamma \log (1 + [\delta e/e]). \]

\[ 1 + (\delta e/e) = 1 + \gamma (\delta e/e) \]

\[ \delta e = (\delta e/e) \] (32)

Equation (32) shows that the smallest absolute error or change in concentration \( \delta e \) which is detectable by densitometric photometry is directly proportional to the transmittance error in measurement and to the concentration of the emitting element, but inversely proportional to the gamma of the emulsion and to the transmittance of the line.

Next, an expression has been developed showing how the absolute error in concentration can be defined as a function of the lowest absolute error obtainable in any analysis using densitometry. Let \( c_1 \) signify the higher concentration, \( c_2 \) the lower (optimal) concentration, and \( \delta c_1, \delta c_2 \) the corresponding absolute errors in concentration. The density increase of the constituent line, resulting from an increase in concentration of the constituent from \( c_2 \) to \( c_1 \), is manifested by a decrease in transmittance \( x \) through the line.
density change produced = density change measured

\[ \gamma \log \left( \frac{c_1}{c_2} \right) = \log \left( \frac{x_2}{x_1} \right) \]

\[ \left( \frac{c_1}{c_2} \right)^{\gamma} = \frac{x_2}{x_1} \quad (33) \]

If equation (32) is expressed both for concentration \( c_1 \) and for concentration \( c_2 \), with \( c_1 > c_2 \), then

\[ \delta c_1 / \delta c_2 = \left[ \left( \frac{c_1}{x_1} \right) \left( \frac{x_1}{c_1} \right) \right] / \left[ \left( \frac{c_2}{x_2} \right) \left( \frac{x_2}{c_2} \right) \right] \]

\[ \delta c_1 / \delta c_2 = \left( \frac{c_1}{c_2} \right) \left( \frac{x_2}{x_1} \right) \quad (34) \]

Let equation (33) be substituted into equation (34):

\[ \delta c_1 / \delta c_2 = \left( \frac{c_1}{c_2} \right)^{1 + \gamma} \]

or

\[ \delta c_1 = \left( \frac{c_1}{c_2} \right)^{1 + \gamma} \delta c_2 \quad (35) \]

Equation (35) shows that, for densitometric photometry, absolute photometric error increases exponentially with concentration, and that gamma, which ranges from one to five, makes up a large part of the exponent.

The minimum error \( \delta c_2 \) in equation (35), for the lower concentration \( c_2 \), is attained at the minimal blackening consistent with plate response, i.e., at about 70% transmittance. The smallest detectable change in transmittance, about 0.1%, defines a minimum for \( \delta c_2 \) at this blackening level (70% transmittance).

Rewrite equation (32) with relevant subscripts.

\[ \delta c_2)_{\text{min}} = \left( \frac{c}{x} \right) \left( \frac{c_2}{\gamma} \right) \quad (36) \]
Substitute equation (36) for \( e_2 \) into equation (35):

\[
(\delta e_1)_{e_2 \min} = \left( \frac{e}{x} \right) \left( \frac{e_2}{e_1} \right) \left( \frac{e_1}{e_2} \right)^{1 + \delta}, \tag{37}
\]

where the line transmittance for \( e_2 \) is fixed and optimal.

Equation (37) is the specification for the maximum absolute photometric precision of a densitometric analysis. The precision indicated is theoretical; dividing by \( e_1 \) and multiplying by 100 gives the theoretical best relative precision as

\[
100 \left( \delta e_1/e_1 \right) = \left( \frac{e}{x} \right) \left( \frac{1}{\gamma} \right) \left( \frac{e_1}{e_2} \right)^{\gamma} (100) \tag{38}
\]

\[
= (0.1/70)(1/2)(1)^{\gamma}(100)
\]

\[
= 0.0775,
\]

at the lowest percentage treated by the analysis, for a gamma of two.

That this relative precision is never attained is well known.

\* \*
A similar treatment for line-width photometry has been carried out. The constituent width method has been discussed first; the matrix width method, second. The similarity of the error functions of the two methods has been noted. Further development of error functions for line-width photometry has then been presented.

The constituent image width \( w \) resulting from the spreading of light in the emulsion has been represented by the Scheiner formula \((44, 76, 95)\),

\[
v = a + b \log E,
\]

where \( a \) is the geometrical size of the image (here, the width of the slit) and \( b \) is the spreading factor, so that the constituent line-width difference \( \delta w \) found for two different exposures to samples of constituent concentrations \( c \) and \( c + \delta c \) is

\[
\delta w = b \log [(c + \delta c)/c],
\]
or

\[
\delta w = b \log [1 + (\delta c/c)].
\]

The smallest concentration difference measurable by the constituent width method is therefore

\[
\delta c = e \left(10^{\delta w/b} - 1\right),
\]

where \( \delta w \) is the smallest reproducibly measurable distance difference on a photographic emulsion.
In the matrix width method, in which the constituent line changes density, the change in density $D_\omega$ due to a change $\Delta c$ in concentration $c$, with the emulsion developed to gamma $X$, is

$$D_\omega = \gamma \log (1 + \frac{\Delta c}{c}). \quad (41)$$

This density change, divided by the sharpness index $S$ (where $S = \frac{dD}{du}$, the density change per micron travel across the edge of the image) of the measured matrix reference line, gives half the width difference $\Delta w$ in the matrix line-width corresponding to concentration change $\Delta c$:

$$\Delta w = \frac{D_\omega}{S}. \quad (42)$$

Combine equations (41) and (42):

$$\Delta w = 2 \frac{D_\omega}{S} \log (1 + \frac{\Delta c}{c}). \quad (43)$$

Therefore,

$$S = e^{\frac{\Delta w}{[2 \gamma/3]}} (10^{-1}). \quad (44)$$

If the width difference $\Delta w$ is taken as the smallest measurable distance on an emulsion, equation (44) gives the smallest concentration change $\Delta c$ measurable by the matrix width method.

The similarity in form of equations (40) and (44) is obvious. To have a general expression, let a quality factor $q$ be defined for application to both the constituent width and matrix width methods, as follows: for the constituent width method, let
\[ q_a = \frac{d}{w/2} \]  \hspace{1cm} (45)

and for the matrix width method, let

\[ q_n = \frac{d}{\sqrt{2 \delta s}}. \] \hspace{1cm} (46)

The general expression is then

\[ \delta e = c (10^q - 1). \]  \hspace{1cm} (47)

If the approximation

\[ 10^q - 1 = 2.3 \pi \]

for small \( \pi \) is applied to equation (47), then equation (48) is the result:

\[ \delta e = 2.3\delta s. \] \hspace{1cm} (48)

The absolute error \( \delta e_1 \) is related to some other absolute error \( \delta e_2 \) in the same analysis, and the relation comes directly either from equation (47) or equation (48), as

\[ \delta e_1 = (s_1/s_2) \delta e_2, \] \hspace{1cm} (49)

or as

\[ (\delta e_1/s_1) = (\delta e_2/s_2). \] \hspace{1cm} (50)

To facilitate comparison, the final expressions for relative and absolute photometric error for the line-width and densitometric methods have been reviewed on the next page.
Absolute Errors as functions of concentrations and operating constants:

Line-Width:
\[ S_0 = 2.3 Q e \]  \hspace{1cm} (48)

(where \( Q_e = \frac{Qw}{z} \) \( \text{m} \)) \hspace{1cm} (45)

\[ Q_e = \frac{Qw}{[2 \beta /S]} \] \hspace{1cm} (46)

Densitometry:
\[ S_0 = (e/x)(1/y) e. \] \hspace{1cm} (32)

Absolute Errors as functions of concentration ratios and other errors:

Line-Width:
\[ S_{e_1} = \left( \frac{e_1}{e_2} \right) S_{e_2} \] \hspace{1cm} (49)

Densitometry:
\[ S_{e_1} = \left( \frac{e_1}{e_2} \right)^{1 + y} S_{e_2} \] \hspace{1cm} (35)

\[ \left( S_{e_1} \right) S_{e_2} \min = \left( \frac{e}{x} \right)(1/y) \left( \frac{e_1}{e_2} \right)^{1 + y} S_{e_2} \] \hspace{1cm} (37)

Relative Errors:

Line-Width:
\[ S_{e_1}/e_1 = S_{e_2}/e_2 \text{ is constant} \] \hspace{1cm} (50)

Densitometry:
\[ \left( S_{e_1}/e_1 \right) S_{e_2} \min = \left( \frac{e}{x} \right)(1/y) \left( \frac{e_1}{e_2} \right)^{y} \] \hspace{1cm} (38)

Relative error, with line-width photometry, is constant; with densitometry, relative error increases exponentially with the concentration.
Comparison of Photometric Errors

Theoretical Comparison

In the following treatment, by means of the expressions developed in the preceding sections, line-width and densitometric photometry, as applied under optimum conditions for spectrochemical analysis, have been compared. For a shorter terminology, let densitometric analysis designate, hereafter, a spectrochemical analysis utilizing densitometric photometry; and similarly, line-width analysis.

Equation (43) has been taken as representative of line-width analysis, and equation (37) has been taken as representative of optimum densitometric analysis. If they are equated, the relationships of the functional constants can be clarified:

\[ 2.3 Q e_1 = (c/x)(1/y)(e_1/e_2)^1 + \beta e_2. \]

Let this be rearranged to give

\[ c_1/c_2 = \sqrt{2.3 \beta(x/e) Q}. \quad (51) \]

Equation (51) expresses that ratio of concentrations at which the error of a densitometric analyses, optimal for \( c_2 \), is equal to that of a line-width analysis.

In equation (51), let the ratio \( c_1/c_2 \) be made equal to unity, so that the line-width and densitometric analyses are also set equal in precision and sensitivity. If the line-width constants are separated from the densitometric, we have
where \( Q^* = 1/Q \), and where \( x \) is constrained to be the maximum transmittance available within the region of linear behavior of the emulsion.

The condition for equal analytical precision therefore rests on the value of \( Q^* \), the inverse of the line-width quality factor (\( Q^* \) has the property of increasing with better precision); \( g \), the minimum photometric error in estimation of transmittance, taken as 0.17, i.e., \( \sqrt{3 \times 0.1} \), in view of the errors in setting zero and full scale as well as in reading; and \( \gamma \), the emulsion response, usually taken as two. If equality of precision is attainable at any concentration, then, since the densitometric error increases the more rapidly, the line-width method is superior at all other concentrations. As mentioned before, such seems to have been the case reported by Eastmond and Williams (20).

The results of assigning some values to the constants involved in \( Q^* \) of equation (52), have been presented in Table V; the condition that line-width analysis must fulfill, to better densitometric analysis, is that

\[
Q^*/2.3 = \gamma(x/s) \tag{52}
\]

As can be seen from the figures presented elsewhere in this study, the values in Table V for \( b \), \( S \), and \( \gamma \) are typical, except for \( b = 2000 \), for coated emulsions (Fig. 16). Measurement of distance to within 0.1 microns has not yet been demonstrated in line-width
TABLE V
LINE-WIDTH PHOTOMETRY VERSUS OPTIMAL DENSITOMETRY

\[ Q^2/2.3 = \gamma(x/e) \]

Let \([\gamma(x/e)] = 824.\]

Then \([Q^2/2.3]\) must be greater than 824.

<table>
<thead>
<tr>
<th>(v)</th>
<th>(Q^2/2.3)</th>
<th>(Q^2/2.3)</th>
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</thead>
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<tr>
<td>(b = )</td>
<td>(s = )</td>
<td>(s = )</td>
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<td>1.0</td>
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</tr>
</tbody>
</table>

\[ Q^2_e = \frac{b}{\Delta v} \]

\[ Q^2_m = \frac{[2 \gamma s]/\Delta v} \]
measurements, but the value is not out of reach of interferometry.

If line-width could be measured to within 0.1 microns, then practically any emulsion would be suitable for a constituent width method which would be superior to the densitometric method not only in concentration range but also in precision.

The matrix width method is no more favorable than the densitometric method in the matter of concentration range, and the values in Table V have shown it to be also less sensitive than the constituent width method.

For the present limit of about one micron in distance measurement, only the fluorescent-surface emulsion comes close to matching the analytical precision of the densitometric method, and working with these coated emulsions is troublesome and unsuited to routine application. The emulsions also exhibit an uneven fog which has the effect of sloppy and uneven processing in densitometry, or of distortion in line-width photometry.

Up to this point, the comparison of the densitometric and line-width methods has been aimed at defining conditions under which the two would be theoretically equal in precision. Substitution of actual data from this study into equation (48) has yielded a precision which is interesting and more nearly attainable than the similar precision found earlier for densitometry.

With the adapted Leeds and Northrup microphotometer, a line-width has been measured to within 1.12 microns in less than five seconds. From Fig. 14, for a I-L emulsion at 2800 A, a spreading factor of 450 has been taken. For the precision \( \sigma \) given by equation (48),
\[ \delta e = 2.3 q_0, \]  
(48)

with \[ q_0 = \frac{\omega}{h}, \]  
(45)

or \[ = 1.12/450; \]

then \[ \delta e = [2.3 (1.12/450)] e, \]

\[ \delta e = 0.0064 e. \]

In this case, the relative photometric error, \( \delta e / e \), has been found to be 0.64%. This can be compared with the 1% generally taken (33) as the best relative precision achievable with densitometry.

The precision of densitometry is theoretically better than that of line-width photometry, but so many disturbing variables affect densitometry that its theoretical precision is quite impossible to realize. Line-width photometry presents an easier case.

**Hasler (32) called for a reappraisal of spectrochemical analysis based on the improved photometric precision (0.1%) of the direct-reading Quantometer (33) as compared to that of the photographic emulsion (1%). (Others attribute this error of 1% largely to variable processing rather than to the emulsion (18, 19, 84).) Some analyses on stainless steels were quoted, with as low as 0.3% relative error for Cr and Ni, to show the precision of analysis by the Quantometer. As a result of this work, Hasler indicated the importance of reducing photometric error.

The Quantometer differs from the ordinary spectrograph essentially only in the system of photometry. The unusually good
results were achieved not only by improved photometry, but also by homogeneous and well analyzed standards, and by excellent excitation conditions (32) which were found only after quite a search.

Actual Comparison

Theoretical errors have been compared with actual errors, in the following section, with the help of an unusually precise and thoroughly studied analysis by Vincent and Sawyer (90). They repeatedly analyzed a set of steel bars drawn from a thicker steel bar of composition certified by the Bureau of Standards, and treated the results (for percentage Cr) statistically. Truth was taken as 0.977% Cr, and a total uncertainty (or error) of 0.98% of content was found for the analysis. This uncertainty was broken down into the various contributing factors (although that these did not add up to give the total uncertainty should be remembered). The plate grain contributed 0.56% of content to the relative uncertainty and the microphotometer, 0.38% of content; these were the errors pertinent to this study.

The absolute photometry-based error from plate grain was 0.0055%, and from the microphotometer, 0.0035% (i.e., 0.977 x 0.0036).

Theoretically, the following error would have been expected, by equation (32):

$$
\delta e = \left(\frac{e}{x}\right)^{1/2} \cdot e^{1/2}
$$

$$
= \left(\frac{0.027}{21}\right)^{1/2} (0.977)
$$

$$
= 0.00066%.
$$
Let the assumption be made that the analytic scheme could have been used for lower percentages of Cr, and that 0.977% Cr was at about the middle of the range, then the error for the bottom of the range can be calculated. With this assumption, \( \frac{e_1}{e_2} = 1.5 \); from equation (35),

\[
\Delta e_1 = (e_1/e_2)^{1/2} \Delta e_2, \quad (35)
\]

\[
\Delta e_2 = (0.0055%) / (1.5)^3
\]

\[= 0.0016\% \text{ from plate grain;}
\]

\[
\Delta e_2 = (0.0035%) / (1.5)^3
\]

\[= 0.0010\% \text{ from the microphotometer.}
\]

These figures represent the actual minimum photometric error possible for this analysis. Calculated directly from equation (32), for \( e = 0.67\% \) (i.e., the bottom of the concentration range of the analysis), the error would be

\[
\Delta e = (0.027/70)(0.67/2)
\]

\[= 0.00013\%.
\]

In each case, the theoretical error has been lower than the actual error by a factor of about ten. If the measurement error for the internal standard line had been included in the calculation of the theoretical error, the error \( e \) would have been roughly \( \sqrt{2} \) times as large, and \( \Delta e \) correspondingly larger. The factor of discrepancy between theory and practice would then have been about five. Even in
this tightly controlled and idealized analysis (89), the actual photometric error exceeded the predicted photometric error by a factor of about five. # #
COMPARISON OF REPORTED ANALYTICAL RESULTS

Those line-width analyses which have been duplicated by densitometric analyses have shown superior or at least equal precision.

Hunt and Timma (35) reported a comparative study. Their conclusion was that line-width analysis offers about the same precision as densitometric (see the last paragraph of the SUMMARY of this paper); the experimental data shows unusually high errors, and so no comparison of the two methods is really available from their paper, because the error of photometry must have been small relative to the other errors.

Coheur (9), the first investigator to perform both types of analysis on the same sample, reported 1.31% relative error for line-width analysis versus 3.10% for densitometric; Coheur concluded that the better precision was a result of freedom from those processing factors affecting gamma.

Eastmond and Williams (20) were forced to use a line of very short wavelength, 2137 A, in an analysis for zinc. An emulsion, sensitized by a fluorescent coating, was used to improve sensitivity, but the observed low gamma caused the spectrographers to try line-width photometry. The results of the densitometric and line-width analyses were compared. By chance of circumstance, the analysis apparently
conformed to the conditions developed earlier in this paper in equations (31) and (33). The precision of both methods was equal for the lowest percentage analysed, and the line-width method was better for all others.

No attempt was made in this study to present an analysis illustrative of the applicability of line-width photometry to spectrochemical analysis; indeed, this was avoided. A plot of line-width values versus corresponding values of constituent concentrations could only have misled the reader who would tend to judge the line-width technique by the analytical results shown in the plot.

If the analysis had been characterised by low precision, the reader would have been wrongly biased against line-width photometry. If the analysis had been precise enough to reveal the effects and errors of photometry, the analytical working-curve would have been a reflection of the imperfections in the worm drive of the microphotometer. The resulting odd appearance of the working curve, which has been commented on under "Measurement of Line-Width," would again have given the reader an erroneous impression of the usefulness of line-width photometry.

A statistical treatment of analytical results of an illustrative analysis, in the manner of Vincent and Sawyer (90), was considered outside the scope of this study. The practically unlimited concentration range (21) of the line-width method would not have been illustrated in such a statistical treatment, and yet the wide concentration range of line-width photometry is of prime importance.
SUMMARY

A review of the literature relevant to the history, nature, and variables of line-width photometry has been presented. Line-width photometry has been reported not only to be free of several experimental difficulties in spectrochemical analysis, but also to have yielded results which were more precise than those from its competitor, densitometric analysis. The basis of these reports has been examined in detail from several points of view.

The basic constants in line-width photometry are spreading factor, sharpness index, and emulsion response. The last is known. The first two have been measured for most of the spectroscopic emulsions, in this study. The coarser-grained emulsions (I, II, SA 2) have been found to be the more favorable for line-width photometry.

Independence of line-width photometry from variations of response of the photographic emulsion has been explained and qualified by derivations.

Equations permitting the evaluation of absolute and relative precision of densitometric photometry and of the two important types of line-width photometry have been developed. Densitometry has been shown to be theoretically more precise than line-width methods, at least with presently available techniques of measurement of line-
width; but the literature of spectrochemical analysis has shown that the conditions necessary for attainment of the theoretical precision of densitometry are practically impossible to fulfill.

Line-width photometry has not only a more favorable experimental position than densitometry for yielding results of improved precision, but the advantage is further enhanced by the exceptionally wide concentration range of one of the two methods of the line-width technique.

By this study, the experimental use of line-width photometry has been brought to the point where routine application is possible. That line-width measurement should actually be simpler and faster than densitometry has been pointed out. The experimental technique devised and used in this study has permitted the measurement of a line-width in five seconds or less, with a standard deviation of one and one-tenth microns. Measurements for quantitative spectrochemical analysis have been shown to require no calibration of the photometric scale, as is necessary with densitometry.

A survey of the possible methods of rapid and precise measurement of line-width has indicated that the recent development of the reversible fringe-counting corner-cube interferometer may be valuable in the future expansion of line-width methods.

The main sources of error in the more precise spectrochemical analyses are the lack of absolute standards, the lack of reproducibility in emission of light from the sample, and photometry; sample inhomogeneity and variations in preparation of the sample for excitation are two other common sources of error. Error in photometric
procedures is therefore only one of a number of errors in spectrochemical analysis.

One value of thorough discussion of photometric error, as in this study, has been to show that spectrochemical analysis can exhibit a relative precision of 0.1% to 0.5%, without being limited by the theoretical errors of photographic photometry. Apparently, the practical limitations to the attainment of the theoretical precision of photographic photometry have been shown in theory in this study and in statements in the literature to be much less restrictive in the case of line-width photometry than in the case of densitometric photometry.

The theoretical considerations in this study have indicated that in those spectrochemical analyses having relative errors greater than about 3%, either line-width or densitometric photometry can be used with equal overall precision of analytical results. Since the constituent width method of line-width photometry permits much greater concentration ranges to be utilized, line-width photometry appears to have definite advantages over densitometric photometry.
A SELECTED BIBLIOGRAPHY


(12) Cooksey, D. and Cooksey, C. D.—Unreliability of Photographic Emulsions on Glass for Recording Distances and a Method of Minimizing This Defect. 
Phys. Rev. 36, 80-84 (1930).

(13) Cooper, H. J.—"Scientific Instruments."

(14) Crabtree, J.—Uniformity in Photographic Development. 

(15) Craft Laboratory Staff.—"Electronic Circuits and Tubes."

(16) Dewall, J. H.—"A New Measuring Micrometer."
Adam Hilger.


(18) Eastman Kodak Company.—"Materials for Spectrum Analysis."
Eastman Kodak Company. (1950).

(19) Eastman Kodak Company.—"Kodak Photographic Plates for Scientific and Technical Use."
Eastman Kodak Company. (1953).

(20) Eastmond, K. E., and Williams, B. E.—Wide Range Analysis for Zinc Using Spectrographic Line-Widths. 


(25) Feldman, C.—"Photographic Photometry."

Natureiss. 25, 570 (1927).

Phot. J. 52, 300-318 (1912).


(30) Harrison, G. R.— Current Advances in Photographic Photometry.

(31) Harvey, C. E.— "Spectrochemical Procedures."

(32) Hasler, M. F.— The Direct Reading Analysis of Low Alloy, Tool and Stainless Steels with the Quantometer.


(37) James, T. H. and Higgins, G. C.— "Fundamentals of Photographic Theory."
Wiley and Sons. (1948).

(39) Jones, L. A. and Sandvik, O.—Photographic Characteristics of Sound Recording Film.

(40) Karr, H. V. and Albers, V. M.—New Recording Microphotometer.

(41) Kruyt, R. H.—"Colloid Science."


(44) Mees, C. E. K.—On the Ratio Between the Diameter of the Photographic Image of a Point and the Exposure Which Produced It.
Astrophys. J. 33, 81-84 (1911).


(49) Nachtrieb, H. H.—"Principles and Practice of Spectrochemical Analysis."


(67) Ross, F.E.—Mansurational Characteristics of Photographic Films.

(68) Ross, F.E.—An Abnormal Phenomenon on Photographic Plates.

(69) Ross, F.E.—Photographic Photometry.

(70) Ross, F.E.—Limiting Magnitudes.

(71) Ross, F.E.—"The Physics of the Developed Photographic Image."

(72) Ross, F.E.—Special Publication.
U. S. Coast and Geodetic Survey No. 27.


(76) Scheiner—"Photography of the Stars."
Leipsig. (1897).

(77) Schlesinger, F.—On the Distortion of Photographic Films.
Pub. Alleghany Obs. 1, No. 1.

(78) Sears, F. W.—"Optics."
Addison-Wesley Press. (1949).


(80) Silberstein, L.—On Size-Frequency Distribution in Photographic Emulsions.


Swann, M. F.—Private Communication (1953).


(95) Wildt, R.—Investigations of the Photographic Halo from Diffusion of Light.

(96) Wright, F. E.—Optical Methods for Reducing the Effects of Photographic Plate Graininess.
APPENDIX I

EXPERIMENTAL METHODS AND DATA

In this appendix, a convenient reference has been provided to expedite any future reproduction of the experimental work described in the thesis and to present in tables the data on which Figs. 3 through 11 were based.

Experimental Methods

The experimental work in this study was conducted with two objectives in mind: 1) to gather data on spreading factor and sharpness index as exhibited by the common spectroscopic emulsions, and 2) to devise and implement a much faster, more precise, and more convenient method of measuring line-width than was available at the start of the study.

Spreading Factor and Sharpness Index

Data on spreading factor and sharpness index have been lacking in the literature. Such data are necessary for the evaluation of suitability of emulsions for line-width work; for the evaluation of constants in theoretical expressions, developed in this study, which describe photometric precision; and for the description of emulsion response to different exposure levels.

All data presented refer to emulsion response to light from the wavelength range 2750–2900 Å. In this range of wavelengths, many of
the most used lines of spectrography occur. Few lines of wavelengths below 2700 Å are used much or frequently for quantitative analysis. Since longer wavelengths produce higher spreading factors and lower sharpness indices in emulsions, both of which are favorable for the precision of line-width photometry, the data from the 2800 Å region are conservative with respect to the general practice of spectrochemical analysis by line-width photometry.

The methods used in exposure and processing have been presented under This Study, pages 13 through 15. In Tables VI through VIII have been presented the numerical data described by the curves in Figs. 3 through 11.

Measurement of Line-Width

The problem of devising a much quicker, more precise, and more convenient method of measuring line-width involved recognition of the necessary characteristics of the desired measuring device as well as the actual instrumentation.

Presentation of the desired characteristics of an instrument for measuring line-width, and the available methods of measuring small distances, has been made under Measurement of Line-Width, on pages 77 through 84.

The adaptation of the Leeds and Northrup Recording Microphotometer has been described in the same section, on pages 85 through 93. Evaluation of the precision of this instrument as a means of measuring line-width has been described on pages 93 through 100. The experimental use of the adaptation has been presented on pages 96, 100, and 102.
**TABLE VI**

NUMERICAL DATA ON SPREADING FACTOR

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TABLE VII
NUMERICAL DATA ON SPREADING FACTOR
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<tr>
<th>Figure</th>
<th>Emulsion</th>
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<th>Base Line Width in Microns</th>
<th>Spreading Factor in Microns</th>
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THE APPLICATION OF LINE-WIDTH PHOTOMETRY TO QUANTITATIVE SPECTROCHEMICAL ANALYSIS

The object of the presentation of this appendix has been to provide the reader with a detailed guide to the application of line-width photometry in spectrochemical analysis.

Sample Preparation: Sample Excitation

Since spectrochemical analysis with line-width photometry differs from that with densitometric photometry only in the means of measuring emitted light, there is no difference between the two methods either in sample preparation or in sample excitation.

Selection of the Emulsion

Coearser rather than finer grained emulsions should be used. Such emulsions are I, II, and SA 2 (see p. 49).

Selection of Analytical Wavelengths

No wavelength region usually used for spectrochemical analysis is unsuitable for line-width photometry. Other considerations equal, the longer wavelengths cause emulsions to exhibit somewhat higher spreading factors and lower sharpness indices, both of which conditions are generally favorable for better precision in line-width photometric measurements.
Densitometric Photometry

The object in densitometric photometry is to pick a pair of lines (one matrix line, one constituent line) which are as nearly as possible identical in intensity and in wavelength. This procedure tends to alleviate the inevitable fluctuations in gamma which occur in practice, and to lessen the dependence of analytical results on accurate and consistent calibration of the emulsion.

Line-Width Photometry

The definition of photometric width (Fig. 1) has shown that the two lines of the analytical pair are not identical in intensity. Equations (10) and (13) have shown that the inevitable fluctuations of gamma which occur because of changes in the emulsion or because of variations in processing are of no importance in line-width photometry. Selection of a line pair, the members of which differ quite a bit in wavelength, is less likely to give trouble in line-width photometry than in densitometric photometry.

The general exposure level of the complete spectrum should be kept so low that the spectrum background does not exceed the threshold of the emulsion. Small variations in exposure level are easily tolerated in line-width photometry, since the photometric width principle tends to cancel out such variations in exposure.

Line-Width Photometry; The Matrix Width Method

The concept of matrix width has been illustrated in Fig. 2. The constituent line is the lighter of the two lines of the analytical line pair. Both the constituent line and the matrix line
should be members of an homologous pair, as is usual good practice in spectrography (31, 49).

Equations (46) and (48) have shown that the matrix line should be as large as possible. The figures on sharpness index have shown that the larger lines tend to display lower sharpness indices, and the equations cited have stated that a low sharpness index is favorable to precision of results in the matrix width method.

The matrix width method is as limited in concentration range as the densitometric method, and therefore should be used only for quantitative analysis of traces. In other words, the constituent line should be one of the most sensitive lines of the constituent. When any line of the constituent is fairly heavy, so that it is characterized by a large spreading factor, the constituent width method should be used in preference to the matrix width method.

**Line-Width Photometry; The Constituent Width Method**

The concept of constituent width has been illustrated in Fig. 3. The matrix line is the lighter of the two lines of the analytical line pair, which should be homologous.

Certain of the considerations of densitometric photometry, as given in equation (32), apply to the selection of the matrix line. Measurement of matrix width requires measurement of the density of the matrix line, although no record of this measurement is made, nor is the calibration of the photometer in terms of 0% and 100% transmittance necessary. Equation (32) has shown that the most accurate measurement of optical density can be made on the lightest line.
Since the line must reflect changes in exposure conditions, the matrix line must be dense enough to lie on the linear part of the Huerter-Driffield curve. To summarize, the matrix line selected for use in the constituent width method should have a transmittance of about 70%.

Since a maximum but no minimum exposure is specified in line-width photometry, exposure conditions may be adjusted when the analysis is set up to reduce the matrix line in density to the desired transmittance value of 70%.

The constituent line selected for use in the constituent width method should be the heaviest (the most intense) line available. The figures on spreading factor have shown the heavier lines to exhibit larger spreading factors, and equations (45) and (46) have shown that large spreading factors are favorable to precision of analytical results in the constituent width method.

A practically unlimited range of concentrations is coverable with the constituent width method, and so the constituent width method is preferable to the matrix width method except for the quantitative analysis of traces of constituents.

**Processing the Emulsion**

Normal care should be taken in processing the emulsion, since distortion is to be avoided. Dirt-free processing baths and drying air are necessary. Forced drying should not be used. Developers which do not produce distortion should be used (Kodak D-11, D-19).
Measurement of Line-Widths

Reference to Figs. 1, 2, and 3 convinces the reader that the photometric width principle, which is used in both the constituent width and matrix width methods, does not require any establishment of photometric scale. That is, there is no need to set the photometer for 0% transmittance and for 100% transmittance before line-width measurements can be made. This is one way that line-width measurements afford both simpler and more precise measurements to the spectrographer, since the trouble and errors of setting the photometric scale are eliminated.

In the measurement of photometric width, the analyst merely uses the density of the indicator line (Fig. 1) to indicate the density definition of the edge of the line to be measured. The photometric scale itself is not involved at all.

An actual technique of measuring line-widths has been described on pages 102 and 103. Fig. 22 has presented one scheme for adaptation of a recording microphotometer to the measurement of line-width. Other schemes are of course feasible.

Calibration of the Emulsion

Emulsion calibration and analytical working curves are identical in line-width analysis. The analyst merely records and plots line-widths versus the logarithms of the corresponding constituent concentrations in the standards used to set up the analysis; the plot is the calibration of the emulsion and also the analytical working curve.
Use of Calibration Curve

Once having plotted the results of the analyses of standard samples, the analyst can find the concentrations of constituents of subsequent samples by noting the concentrations corresponding to measured line-widths.

Since the absolute constancy of the calibration curve implies the absolute reproducibility of emulsions on different plates, good practice dictates the running of standards along with unknowns. Corrections indicated by the standards are then applied to the values of constituent concentrations found for the samples. Such a practice of running standards is common to all spectrography and is not peculiar to line-width analysis.

Interpretation of Analytical Results

If any means other than interferometry have been used to obtain photometric widths, the errors of the carriage advance mechanism will have been included in the total error. If the total error is very small, the working curve may reflect the errors of the mechanism and have a jagged appearance. Such a jagged curve should not be smoothed.
VITA

John Arthur Perry was born in Ridgefield, Connecticut, on November 11, 1921. He attended Edward Drummond Libbey High School in Toledo, Ohio, and was graduated as valedictorian in May, 1939.

He was awarded a Prize Scholarship at the University of Rochester and graduated from that institution with a Bachelor of Science degree in December, 1942.

From 1943 to 1950, he was employed in industry, working in the general field of spectroscopy.

In September, 1950, he entered Louisiana State University with an appointment as graduate assistant. He was elected to Phi Lambda Upsilon and Sigma Xi in the academic year 1951-1952. In June, 1952, he received the degree of Master of Science in Chemistry from Louisiana State University.

In the academic year 1952-1953, and up to the present, he has held the research fellowship sponsored by the Stanolind Oil and Gas Corporation. In 1953, he was elected to Sigma Pi Sigma. He is now a candidate for the degree of Doctor of Philosophy.
EXAMINATION AND THESIS REPORT

Candidate: John A. Perry

Major Field: Chemistry


Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Olen R. Hance
James E. Traunham
Helen B. Williams
John F. Chretian
Robert V. Nauman

Date of Examination: Jan. 22, 1954