Designation: E 116 – 97

Standard Practice for
Photographic Photometry in Spectrochemical Analysis[1]

This standard is issued under the fixed designation E 116; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the calibration of photographic emulsions and their use in measuring spectral line intensity ratios. Several methods of external illumination are outlined. Instructions are given for using regression in a computer program for defining the emulsion calibration from preliminary curves prepared by using the two-step and two-line methods and the line-group procedure. Correction for spectral background is discussed in some detail, and instructions are given for preparing analytical curves.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis[2]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[2]

E 172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis[2]

E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves[2]

E 356 Practices for Describing and Specifying the Spectrograph[3]

E 409 Practice for Description and Performance of the Microphotometer[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *density functions*, *n*—the blackness of a spectral-line image is usually measured as transmittance, *t*; percent transmittance, T; or optical density, D. *Transmittance* is the ratio of the microphotometer reading at the darkest portion of the line image to that obtained on an unexposed portion of the plate or film (the "clear-plate" reading). In practice, this ratio is often expressed as a percentage. For example, $t = 0.38$ is equivalent to $T = 38$. *Optical density* is defined as $D = 2 - \log T$. The optical density corresponding to $T = 38$ is $D = 2 - \log(38) = 2 - 1.580 = 0.420$. For determining emulsion calibrations in this practice these measurements of density are transformed to the Seidel density, Δ, (Note 1) defined as $\log[(1/t) - 1]$ or $\log[(100/T) - 1]$ or $\log(10^{-D} - 1)$. Conventionally, these Seidel densities have been expressed as log to the base 10. Use in computer, or electronic calculators, makes it more convenient to revise these definitions on the basis of natural logs.

Note 1—This function was first suggested by Baker (Ref 1).[4] It was brought to the attention of spectrochemists in a talk by W. Seidel in 1939. Properties of the original function and several modifications were explored by Kaiser (Ref 2).

The essential linearity of the Seidel preliminary curve within the 5 to 95 % T range is an empirical observation based on the experience of many spectrographers (Refs 3-6). This linearity may not apply to all emulsions under all conditions, however (Refs 7 and 8).

4. Significance and Use

4.1 In order to derive intensity ratios from spectral line pair readings, an emulsion characteristic curve relating microphotometer readings (either percent transmission or density) and relative intensity is necessary. The intensity ratios obtained from the emulsion calibration curve are used to prepare analytical curves relating intensity ratio and concentration in all spectrographic methods, that is, those methods using emulsions.

4.2 *Emulsion Calibration Curve*—In spectrographic analysis, an emulsion calibration curve represents the degree of blackening of the developed photographic emulsion as a function of the intensity of the spectral line to which it has been exposed. The shape and location of the curve can be affected by various factors:

4.2.1 *Emulsion Properties*—Type, preparation conditions of individual batch, and storage history;

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[4] The boldface numerals in parentheses refer to the list of references at the end of this practice.

4.2.2 *Exposure Conditions*—Wavelength and intensity of radiation, spectrum range of radiation, exposure time, and intermittency;

4.2.3 *Instrumental Factors in Spectrograph and Microphotometer*—Slit width, scattered light, resolving power, and under some conditions, aperture and location of plate (see Practices E 356E 356); and

4.2.4 *Development*—Type and age of developer, time and temperature of development, and degree of agitation.

4.3 In order to obtain accurate intensity ratios, all these factors should be the same for both calibration exposures and analytical exposures. Some changes in operating conditions are occasionally permissible (for example, a calibration curve made with a continuous dc arc may be valid for a 120 pulse-per-second spark exposure), but any proposed change in the above factors should be checked for its effect on the validity of previously prepared calibration curves. If a change in operating conditions is contemplated, the best approach is to prepare a new calibration curve under the new conditions.

5. Reference to this Practice in Standards

5.1 The inclusion of the following paragraph, or suitable equivalent, in any ASTM spectrographic method (preferably in the section on calibration) shall constitute due notification that this recommended practice shall be followed:

Emulsion Calibration—Calibrate the emulsion in accordance with Practice E 116.

6. The Photographic Emulsion

6.1 *Selection of Emulsion Type*—Select the emulsion in accordance with the resolving power, contrast, speed, and spectral sensitivity needed. As a rule, fine-grained emulsions have higher resolving power and higher contrast than coarse-grained emulsions, but lower speed. Photographic emulsions are sensitive only in the ultraviolet and visible, blue to blue-green, spectral regions ($\lambda \leq 4500$ Å), unless they have been specially sensitized for other regions. If the ultraviolet spectrum is to be photographed, especially in the second or higher order of a grating spectrograph, use an unsensitized emulsion. (This reduces interference from scattered visible light and from overlapping spectral orders.) If the visible or infrared region is to be photographed, select an emulsion that is sensitized as specifically as possible for the region under consideration.

6.2 *Selection of Wavelength Filter*— If a prism spectrograph is used, or if the first-order ultraviolet region of a grating spectrum is to be photographed, do not use a filter. If the 2000 to 2300-Å region of a grating spectrum is photographed in the second order, eliminate the overlapping 4000 to 4600-Å radiation with a filter that absorbs this radiation but transmits the desired radiation. If the 2300 to 4000-Å region is photographed in the second order, do not use a filter unless the photographic emulsion is sensitive to visible light of wavelengths greater than 4600 Å. If the visible or infrared range is photographed, use a glass filter to eliminate second and higher orders of ultraviolet radiation. A wavelength filter may be placed at any point on the optical bench, but a nonstigmatic position is preferable.

6.3 *Purchase and Storage of Emulsions*— Purchase a quantity sufficient to last for several months. If possible, arrange for rapid delivery of sealed packages in a frozen condition, especially if the emulsion is highly sensitive or is intended for the visible or infrared region. Store the sealed packages in a frozen condition, especially if the emulsion is highly sensitive or is intended for the visible or infrared region. Store the sealed packages at approximately −18°C (0°F) if facilities are available; if not, store at approximately 8°C (46°F). Bring the package to room temperature before opening. Do not refreeze after opening, but if kept unsealed in a refrigerator, use a desiccant.

6.4 *Rechecking of Calibration Curves*— Contrast (γ) may vary among plates within a batch, and may change slowly in storage, even at −18°C (0°F) (**9**). Calibration curves should, therefore, be rechecked as often as is found necessary with a given emulsion.

7. Required Spectrographic Conditions

7.1 The following spectrographic conditions must be fulfilled in order to obtain valid results:

7.1.1 *Alignment*—It is assumed that the centers of all lenses lie on the optical axis of the spectrograph, that the axes of cylindrical lenses are properly oriented, and that the optical bench is parallel to the optical axis of the spectrograph. As a lens is moved away from the slit, the center of the lens must remain on the optical axis. If it does not, perform the alignment procedure recommended by the manufacturer of the spectrograph.

7.1.2 *Vertical Uniformity of Illumination*—Before the calibration filter or stepped sector is put in place, each line in the spectrogram must be uniform in optical density over the entire height to be used. Refer to Practice E 356E 356.

7.1.3 *Absence of Stray Light*—Insofar as conditions permit, light inside the spectrograph should fall only on the optical elements (for example, lenses, mirrors, prisms, gratings), and not on their supports or on other internal parts of the spectrograph.

7.1.4 *Minimization of Continuum*—Light from incandescent solids, for example, electrode tips, produces a spectral background and should not be allowed to fall on optical elements inside the spectrograph. There are other possible sources of background in an arc (such as, molecular bands and unquantized electronic transitions), but these should be negligible in the ultraviolet region under the recommended conditions.

7.1.5 *Wavelength Setting for Spectrographs in Which the Range of Wavelengths Falling on the Plate Can Be Varied*— The shape and location of a calibration curve can be affected by line shape. In some spectrographs of this type, the apparent shape of a particular spectral line varies with its distance from the center of the plate. (This is particularly true for an Ebert spectrograph.) Thus, a calibration curve made on such an instrument with the 3100-Å region at the center of the plate may not be valid if the wavelength setting is changed to bring the 3100-Å region near the edge of the plate. If such a spectrograph is used, emulsions should be calibrated with the same wavelength setting as will be used for analytical exposures.

7.2 *Light Source*:

7.2.1 *General Considerations*—The light source used for emulsion calibration should have ample spectral lines in all wavelength ranges of interest. It should be operated for approximately the same period of time and in the same way that the specimens will be exposed, that is, as a continuous dc arc, or as an intermittent arc or spark. For some emulsions at certain wavelengths, the calibration curve obtained with continuous illumination may differ from that obtained with intermittent illumination. If tests show such a difference exists under the user's conditions, exposures for analytical purposes should be referred only to a calibration curve derived using a similar light source. Typical light sources are described in 7.2.2 and 7.2.3. See Practice E 172 E 172.

7.2.2 *Continuous DC Arc*—Construct an all-iron globule arc (10) as shown in Fig. 1. The pellet should weigh 50 to 100 mg. Operate the arc at as low an amperage as possible; arcs of 0.7 A have been found to be quite stable in a draft-free room with a 230-V dc power supply and a suitable ballast resistance. The lower electrode is the anode. Make the arc gap as wide as possible. Shield the arc from cross-drafts.

7.2.3 *Intermittent Radiation Sources*— If an intermittent radiation source is used for calibration, it should resemble the analytical exposure as closely as possible with regard to the pulse duration, intensity, and frequency of individual pulses.

7.3 *External Illumination System*:

7.3.1 *Intermediate Image System*:

7.3.1.1 *Description of System*—The most desirable way of satisfying the requirements of 7.1.3 and 7.1.4 is through the use of an intermediate image, that is, an image of the light source located between the light source and the slit (see Fig. 2). To accommodate such an image, the optical bench should be at least 100 cm long. If such a bench is available, proceed with the instructions in 7.3.1.2-7.3.1.4. If not, use the direct projection system in 7.3.2.

7.3.1.2 *Isolation of Intermediate Image*— Position the excitation stand well back on the optical bench. Using a fused silica spherical lens (focal length approximately 77 cm), project a slightly enlarged (1.5 to 2×) image of the discharge on a diaphragm held by a bench rider. Center the image on the optical axis. Make a rectangular opening in the diaphragm, with its center at the optical axis. Make the height of the
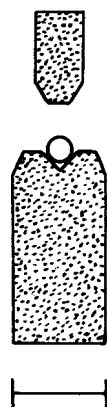
opening sufficient to isolate the center third of the image of the light source; exclude the images of the tips of the electrodes if incandescent. Make the opening wide enough to accommodate the normal lateral motion of the discharge.

7.3.1.3 *Elimination of Scattered Light, Direct Method*— Place a vertical-axis cylindrical-fused silica lens between the diaphragm (see 7.3.1.2) and the slit. With this lens, project an image of the discharge onto the slit. (This image will be narrow and well defined in the horizontal direction, but blurred in the vertical direction.) Open the slit wide, or remove it if possible, and look at the first optical element (lens, mirror, or grating) which the light strikes after entering the spectrograph. If light is falling above or below this element, or both, mask the cylindrical lens at the top or bottom, or both, with opaque strips to remedy this condition (Fig. 2, "Side View"). If light falls on either side of the first optical element, mask the same lens with vertical strips at the sides (Fig. 2, "Top View").

7.3.1.4 *Elimination of Scattered Light, Indirect Method*—If the front surface of the first optical element cannot be viewed, measure or estimate the useful height of the first optical element (h_c), the distance (l_c) from this element to the slit, the distance (l_o) from the slit to the vertical-axis cylindrical lens and the distance (l_i) from this lens to the intermediate image. To find the height of this lens, which should be left open (h_o), use the equation: $h_o = (h_o l_i)/(l_c + l_o + l_i)$. To find the width of this lens, which should be left open (w_o), measure or estimate the useful width of the first optical element (w_c) and use the equation $w_o = l_o w_c/l_c$. If possible, use the direct observation procedure (7.3.1.3) rather than this estimation procedure.

7.3.2 *Direct Projection System*:

7.3.2.1 *Description of System*—If the optical bench is too short to permit the use of an intermediate image, an image of the discharge may be projected directly onto the plane of the first optical element by means of a lens located at the stigmatic position. As used here, "stigmatic position" refers to the position on the optical bench of a certain vertical plane perpendicular to the optical axis. If the spectrograph is stigmatic in at least the vertical direction, horizontal straightedges placed in this plane will sharply delimit the height of the spectrum. The stigmatic position is usually specified by the manufacturer. It is the plane of the entrance slit in all prism spectrographs, and also in the Wadsworth and Ebert (Jarrell-Ash Co.), and Dual (Bausch and Lomb Co. or Baird Corp.) grating spectrographs. It is at a fixed point in front of the slit in the Abney grating mounting (early Applied Research Laboratories 1.5-m instruments), at a point which depends on the wavelength in the Eagle grating mounting (Baird Corp.), and is usually inaccessible in the Paschen-Runge mounting (Applied Research Laboratories 2-m instrument). Since part of this image will fall on the supporting structure of this element, some light will be scattered within the spectrograph. Suitably placed baffles and flat black paint can reduce the amount of such scattered light that reaches the spectrographic emulsion.

7.3.2.2 *Cylindrical Lens Variant*—Place a fused silica cylindrical lens (axis horizontal) as close as possible to the stigmatic position (see Fig. 3).

7.3.2.3 *Spherical Lens Variant*—If a cylindrical lens is not available, place a spherical lens near the stigmatic position,

FIG. 1 Iron Globule Arc
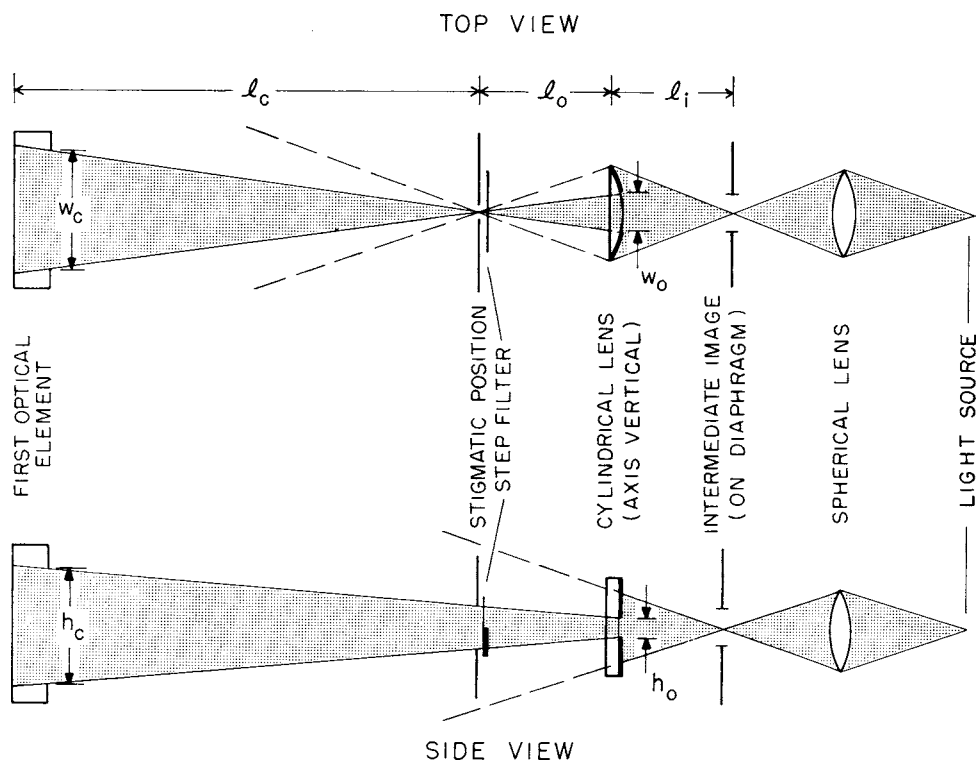
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NOTE 1—The stigmatic position is at the slit in many spectrographs.
FIG. 2 Illumination of the Spectrograph by the Intermediate Image Method Using a Spherical Lens and a Cylindrical Lens
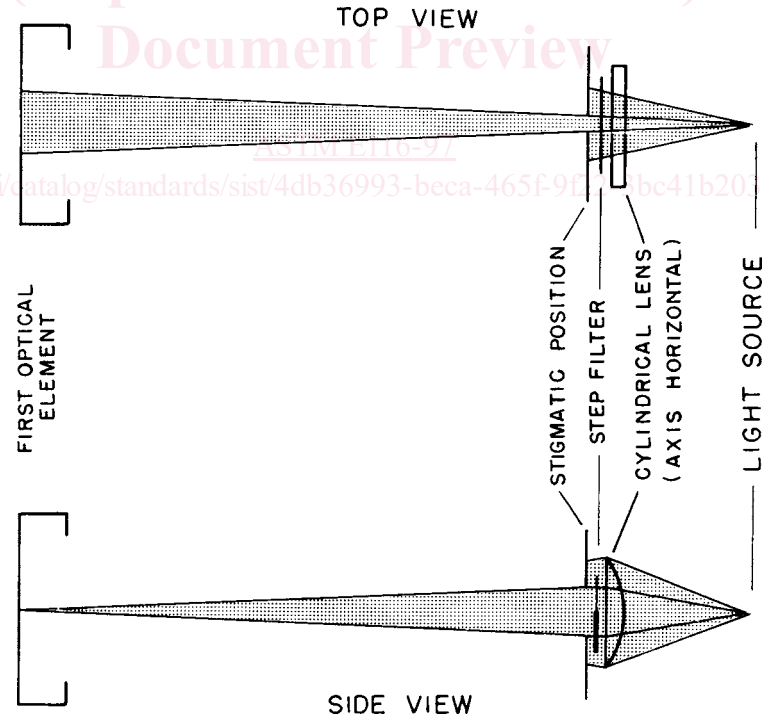
NOTE 1—The stigmatic position is at the slit in many spectrographs.
FIG. 3 Illumination of the Spectrograph by the Direct Projection Method, Using a Horizontal-Axis Cylindrical Lens

projecting an image of the discharge on the first optical element. In this case, an ordinary image of the discharge will

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be formed. Adjust the electrode gap or partially mask the first optical element so that only the center third of the gap image falls on the optical element.

7.3.2.4 *External Auxiliary Image System*— An auxiliary image is desirable outside the spectrograph to help control the position of the image inside the spectrograph, especially if the Direct Projection System is used. Project an image of the discharge on any convenient target (front of spectrograph, wall, or the like) using an auxiliary glass spherical lens (focal length 50 to 100 mm). Position this auxiliary lens with its center on the optical axis. To locate the target, open or remove the slit and place a sharply pointed rod in one electrode clamp. With a light bulb behind the rod, project the image of the rod on the first optical element inside the spectrograph. Position the rod so that the image of its tip is at the center of this optical element. Then position the light bulb so as to project an image of the rod through the auxiliary image system. Place the target so that the origin of its coordinate system is at the tip of the image. Measure the degree of magnification of the image by comparing the width of the image of the rod with the diameter of the rod itself. Make horizontal calibration marks on the target corresponding to actual vertical intervals of 1 mm or less at the location of the arc image. This imaging system is preferable to the internal optics of some modern optical stands. Such stands continue to show perfect alignment, for example, even if the floor shifts and the image leaves the optical axis.

7.3.2.5 *Checking Vertical Uniformity of Illumination*— Photograph the spectrum of the iron arc, with the spectral lines 5 to 6 mm high. Examine the lines on the spectrogram by eye, or by means of a comparator-microphotometer. If all lines appear to vary in density in the same direction, top to bottom, check the vertical placement of the arc and lenses and make sure that the optical bench is parallel to the optical axis of the spectrograph. If some of the spectral lines show good vertical uniformity while others do not, use a narrower portion from the center of the image of the arc when making subsequent exposures. If the spectrum appears vertically uniform, reduce the scanning slit height of the microphotometer to its minimum. Scan a spectral line at several places along its length, avoiding the extreme top and bottom. Note the wavelength of the line for possible subsequent identification. Repeat this procedure with several lines at several wavelengths. If the vertical nonuniformity of most of the lines exceeds 2 % in terms of intensity as read on a previous calibration curve, adjust as indicated previously. If the vertical uniformity is satisfactory for all but a few lines, proceed with the calibration but do not use the unsatisfactory lines.

7.3.3 *Step Filter*:

7.3.3.1 *Choice of Filter*—Obtain a two-step fused silica neutral density filter: the coating should be uniform; the border between the coated and uncoated steps should be as sharp as possible. Check the transmittance versus wavelength curve furnished with the filter to make sure that the transmittance ratio of the coated and uncoated steps is at least 1.5 at all wavelengths. (Higher ratios may be needed for calibrating emulsions of low contrast.) Record the value of the ratio at 100-Å intervals. If no transmittance curve is available, measure these values with an ultraviolet spectrophotometer. The filter

should be free of dust, fingerprints, and scratches. If blemished, move the filter sidewise until an unblemished area is in front of the slit. If a blemish exists on a filter that is being used at some other position on the optical bench, clean the filter according to the manufacturer's directions. If this cannot be done without damaging the coating, replace the filter.

7.3.3.2 *Placement of Filter*—If the stigmatic position (7.3.2.1) of the spectrograph is accessible, place the filter at this position (see Fig. 2 and Fig. 3). Position the boundary between the steps at the level of the optical axis. (When the stigmatic position is not accessible, the manufacturer usually makes it possible to mount one or more step filters directly in front of the photographic emulsion, and also provides calibrated filters.)

7.3.3.3 *Step Sector*—If stroboscopic effects and other difficulties are avoided (see 8.2.2), a step sector can be used at the stigmatic position in place of a step filter. Use only two steps of the sector. Use of more than two steps is not recommended because vertical uniformity is difficult to achieve for stepped sector spectra of heights from 20 to 30 mm, even if all the precautions in Section 7 are taken.

8. Methods for Emulsion Calibration

8.1 Methods are described for using adjacent spectra with a fixed-intensity ratio, employing a specified pair of lines in several spectra (the ratio of the line pair is known and is constant). Use of a set of several lines in one spectrum for which relative intensities are known is not recommended since this approach does not take advantage of the averaging of data that a preliminary curve offers and requires a more involved way to define a final emulsion calibration. The choice of method depends on the equipment available (two-step filter or stepped sector or none). Although through the reapproval of this practice in 1991, details were given for graphical plotting, this revised practice only considers use of a computer for defining the preliminary curve and for translating this into an emulsion calibration.

8.2 *The Two-Step or Two-Line Method*:

8.2.1 In one method, numerous line pairs are generated by filtering the spectrum through a two-step neutral density filter, using sufficient height on each step to permit easy measurement. Optical density readings are taken for the upper and lower halves of several lines simple linear regression fit between "weak" and "strong" Seidel readings by entering a list of the "stronger" lines as the independent X components and entering a list of the "weaker" lines as the dependent Y components. The relationship established in the regression is as follows:

8.2.2 In another method, a two-step rotating sector can often be substituted for the two-step filter. The exposure ratio is accurately known for the two steps of a rotating sector, and is the same for all wavelengths. However, this device operates by varying the time of exposure (rather than the intensity) from step to step, thus leading to a time-scale calibration curve. An ordinary (continuous) time-scale calibration curve cannot be used to measure relative intensities unless the applicable reciprocity failure coefficient is known. If a rotating sector is used, and its rate of rotation is great enough, the intermittent time-scale calibration curve thus produced will often coincide

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with the desired intensity-scale curve. This equivalence is an empirical observation and must be proven to apply to the emulsion and wavelength in question before the rotating step sector can be used for calibration. This could be done by comparing the rotating sector calibration curve with a curve obtained by an intensity-scale method such as the two-step filter method.

8.2.3 In another method, two lines in the same exposure of an iron spectrum, such as 3084 Å and 3092 Å (ratio 1.42), can be used provided their ratio is known and is constant. Several exposures varying from very light to very dark are made, and readings from these two lines in all the spectra are used to prepare the preliminary curve. Table 1 shows groups of iron lines recommended for calibration purposes by Dieke [11] and by Crosswhite [12]. These provide workable pairs for a practical emulsion calibration. Precaution should be used, however, by calculating intensity ratios for other line pairs in the same general wavelength region to confirm that they show consistent intensities. Some adjustment of the schedule of

intensities may be necessary to show the least amount of error to the reported intensities, as was done by Anderson & Lincoln [6].

8.2.3.1 Select a pair of iron lines in the wavelength region of interest. The lines should have the following characteristics: one line should be approximately 1.3 to 2.5 times as intense as the other; the intensity ratio of the two lines should be as insensitive as possible to changes in the amperage of the arc and to air currents; and the ratio should be reproducible from exposure to exposure. Great care must be taken to stabilize the arc if it is desired to have the slope of the calibration curve reproducible to within 5 %. When using the two-line method, it is preferable to replace the iron arc with a light source less subject to short-term fluctuations. A capillary gas discharge tube serves quite well for calibration, provided sufficient intensity can be obtained, or use a spark.

8.2.3.2 Any illumination system may be used, provided the aforementioned precautions are observed for minimizing scattered light within the spectrograph and preventing continuous

TABLE 1 Groups of Iron Lines for Emulsion Calibration

Wavelength, Å	Log Intensity	Possible Interferences	Wavelength, Å	Log Intensity	Possible Interferences
2500 Å Group (FeII: 2/3 KVA, 0.32 MHz Spark)[A]			3600 Å Group (FeI: 2.2 A, DC Arc)[B]		
2451.21	1.47	Ni 2450.986	3572.00	2.147	...
2461.28	2.49	...	3594.64	2.093	...
2461.86	2.58	...	3599.62	1.477	...
2463.28	2.14	FeI 2462.644 (in d-c arc)	3612.07	1.822	...
2464.01	2.32	...	3623.19	2.051	...
2464.90	2.21	FeII 2465.200	3625.15	1.749	...
2465.91	2.26	...			
2470.41	2.28	FeII 2470.658	3800 Å Group (FeI: 2.2 A, DC Arc)[B]		
2497.30	1.31	...	3756.94	1.754	...
2503.32	2.35	V 2503.020; FeII 2503.556	3774.83	1.663	...
2506.09	2.38	...	3776.46	1.685	...
2514.91	1.69	...	3805.34	2.449	...
			3807.54	2.096	...
2800 Å Group (FeII: 2/3 KVA, 0.32 MHz Spark)[A]			3836.33	1.929	...
2753.29	3.17	V 2753.404			
			4000 Å Group (FeI: 2.2 A, DC Arc)[B]		
2779.30	2.82	...			
2783.70	2.92	...	3971.33	1.882	...
2793.89	2.13	...	3977.74	2.127	...
2799.29	1.99	V 2799.451	3981.77	1.706	...
2813.61	1.63	...	3983.96	1.893	...
2827.43	1.64	...	4009.72	2.004	...
2831.56	2.69	...	4021.87	2.046	...
			4024.74	1.573	...
3200 Å Group (FeI: 2.2 A, DC Arc)[B]					
3151.35	1.909	...	4200 Å Group (FeI: 2.2 A, DC Arc)[B]		
3156.27	1.604	...	4175.64	2.018	...
3157.04	1.997	...	4176.57	1.668	...
3157.89	1.863	...	4184.90	1.920	...
3175.45	2.089	...	4208.62	1.331	...
3178.02	1.968	...	4210.35	2.134	...
3182.98	1.581	...	4213.65	1.464	...
3199.52	2.283	...			
3205.40	2.318	...			
3217.38	2.176	...			
3400 Å Group (FeI: 2.2 A, DC Arc)[B]					
3369.55	1.978	...			
3370.79	2.203	...			
3394.59	1.722	...			
3402.26	1.811	...			
3415.53	1.543	...			
3425.02	1.732	...			

[A] Dieke, G. H., "A Study of Standard Methods for Spectrographic Analysis," *Progress Report W-90*, War Metallurgy Committee for the National Academy of Sciences, National Research Council, March 20, 1944.

[B] Crosswhite, H. M., "Photoelectric Intensity Measurements in the Iron Arc," *Spectrochimica Acta*, Vol 4, 1951, p. 122.