January 1955

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C. 20234

Letter Circular LC-1017

Re-issued January 1967

STANDARDS FOR CHECKING THE CALIBRATION OF SPECTROPHOTOMETERS (200 to 1000 nm)

Contents

1. Introduction.

In continuation of a type of activity carried on for many years at the National Bureau of Standards, there is described in this letter circular the various types of standards that are available for issuance by the Bureau for the purpose of checking or maintaining the over-all reliability of spectrophotometers in the ultraviolet, visible and near-infrared regions of the spectrum. Certain other information of similar purpose is also included.

Experience has shown that spectrophotometers can easily get out of adjustment. Although repeated trials may give the same values over and over again, indicating high sensitivity and precision, and the instrument may otherwise appear to be functioning perfectly, gross errors in wavelength may nevertheless be rendering the values obtained highly unreliable. Other causes of error may likewise be present and unsuspected, particularly with the photoelectric spectrophotometers now comprising so large a percentage of the total in use. The use of the various standards described herein has been found of considerable assistance in detecting and eliminating errors that would otherwise be present, or in confirming that the instrument is in fact giving reliable results.

Reference is made in this letter circular to the NBS test fee schedules currently in effect. Those relating to spectrophotometry are designated as 202.105, Spectrophotometric Standards, and 202.106, Spectrophotometric Measurements. These schedules are obtainable from the National Bureau of Standards.

2. Checking the Wavelength Scale.

Most of the present-day spectrophotometers have a direct-reading wavelength scale; that is, the scale, instead of being divided in uniform linear or circular measure, is divided and engraved directly in nanometers (formerly called millimicrons). This greatly facilitates setting the instrument at any desired wavelength. The accuracy of many of these direct-reading wavelength scales is remarkably good, when put in the best average adjustment, considering the difficulties of quantity production of such scales. When so adjusted, it is not uncommon to find them in error by not more than 1 nm throughout the ultraviolet and visible spectrum. However, if one wishes the uncertainties in his wavelength settings to be of the order of 0.1 nm, a careful check of these direct-reading scales is necessary.

Certain sources and wavelengths that have proved especially suitable for the calibration of various types of spectrophotometers are listed in tables 1a and 1b which are similar in scope and purpose to table 1 of Circular 484 (1)*.

---

*Numbers in parentheses refer to the References, Section 5.

All values of tables 1a and 1b are consistent with those published in the M.I.T. wavelength tables (2). Which of these sources to use, and which wavelengths of the several sources are the most suitable, will depend on the type of instrument. Furthermore, the procedure will vary importantly depending on whether the instrument is a non-recording or a recording spectrophotometer.

Table 1a. Wavelengths of Sources Suitable for Calibration of Spectrophotometers.

Wavelength (nm)	Note	Wavelength (nm)	Note	Wavelength (nm)	Note	Wavelength (nm)	Note
Mercury Arc in Quartz (Same wavelengths in glass above 300 nm)							
205.29		253.48	3*	296.73	*	398.40	
222.47		253.65		302.15		400.63	
223.41		257.63		302.35	6*	404.66	*
225.88		260.32		302.56		407.78	*
230.21		265.20		302.75		435.83	*
232.32		265.37	4*	312.57	*	491.60	
235.25		265.51		313.15	7*	546.07	*
237.83	*	269.95		313.18		576.96	9*
239.94	1*	275.28	*	334.15	*	579.07	
239.97		275.97		349.28		623.44	
244.69		280.35	5*	365.01		671.62	
246.41		280.45		365.48	8*	690.72	
248.20		284.78		366.29		1014.0	*
248.27	2*	289.36	*	366.33		1128.7	
248.38		292.54		390.64			
Helium Discharge Tube in Glass							
318.77		396.47		447.15	*	667.81	*
361.36		402.62		471.31	*	706.52	*
363.42		412.08		492.19		728.13	
370.50		414.38		501.57	*	1083.0	*
381.96		438.79		504.77			
388.86	*	443.75		587.56	*		

* These lines have been found most useful on the Beckman DU spectrophotometer.

1. A value of 239.95 is recommended for the unresolved pair.
2. A value of 248.3 is recommended when the 3 lines are unresolved.
3. The intensity of 253.48 is negligible compared to that of 253.65. The latter value should be used when the lines are unresolved.
4. The 265.20 line is somewhat stronger than the others and a value of 265.3 is recommended when the three lines are unresolved.
5. These two lines are of approximately the same intensity and a value of 280.40 is recommended for the unresolved pair.
6. The two shorter lines are considerably stronger than the other two. It is probable that a value of 302.25 should be used for the unresolved lines.
7. A value of 313.16 is recommended for the unresolved pair.
8. With the arc used on the Beckman DU spectrophotometer the ratio of intensities for 365.01 : 365.48 : 366.33 is 100 : 48 : 36, approximately. The intensity of the 366.29 line appears negligible relative to that of 366.33.
9. These two lines are of approximately the same intensity and a value of 578.0 is recommended for the unresolved pair.

Table 1b. Wavelengths of Sources Suitable for Calibration of Spectrophotometers

Neon Discharge Tube		Aluminum Spark in Air	Hydrogen Arc
Wavelength (nm)	Relative Intensity	Wavelength (nm)	Wavelength (nm)
585.25	5	216.88	434,05
588.19	4	217.40	486.13
594.48	8	220.46	656.28
597.55	2	221.00	
603.00	2	226.35	
607.43	8	226.91	Sodium Arc
609.62	13	236.71	Wavelength
614.31	25	237.21	(nm)
616.36	6	237.31	589.00
621.73	4	237.34	589.59
626.65	11	237.84	
630.48	4	256.80	
633.44	20	257.51	Cesium Arc
638.30	23	257.54	Wavelength
640.22	100	263.16	(nm)
650.65	39	265.25	852.11
653.29	8	266.04	894.35
659.90	12	281.62	
667.83	23	308.22	
671.70	14	309.27	
692.95	23	358.69	
702.41	2	394.40	
703.24	45	396.15	
705.91	--		
717.39	5		
724.52	17		
743.89	4		
748.89	--		
753.89	--		
754.40	--		

2.1 Non-Recording Spectrophotometers.

The best procedure for checking the wavelength scale of a non-recording spectrophotometer is by direct use of a source of radiant energy having spectral lines of suitable intensity and adequately spaced throughout the spectral range of interest. Various sources are available and can be recommended for such purpose. How many sources, or how many wavelengths, to use in such a calibration depends, of course, on the desires of the individual investigator.

In this connection it should be noted that the number of significant figures of importance in spectrophotometry (including "absorption spectroscopy") is of a different order of magnitude than that used in emission spectroscopy or in standard wavelength tables. In the visible spectrum with the usual type of spectrophotometer it seems impossible to maintain the wavelength calibration with uncertainties less than about 0.1 nm. While the uncertainty may be less in the ultraviolet with a prism instrument, there seems no purpose served in giving standard wavelengths to better than 0.01 nm for spectrophotometric calibration.

Two suitable sources for wavelength calibration are the mercury lamp and the helium lamp. A mercury lamp in a quartz envelope is by far the best single source for wavelength calibration from 205 to 1014 nm. A mercury lamp in a glass envelope provides the same spectral lines except that below about 300 nm they are not transmitted by the glass envelope.

The helium lines are especially well placed for wavelength calibration in the visible spectrum, and the strong lines at 388 and 1083 nm are also often very useful. Many other sources, flame or arc, are available for visual wavelength calibration (2, 3) but most of these are too unstable for accurate calibration with a photoelectric detector.

These same sources and many others are also useful for the wavelength calibration of spectrographs used in photographic spectrophotometry. Between 200 and 400 nm the series of doublets obtained from the aluminum spark in air is very useful because they are so readily recognized.

Not all of the lines for any of the sources are given in tables 1a and 1b but only those that are considered especially suitable for the purpose. Furthermore, not even all of those listed for any one source may be suitable for any one particular instrument. The mercury arc in quartz is an example. All of the lines listed (and still others) can be used for wavelength calibration of a photographic spectrophotometer over the range of sensitivity of the plate used. The lines from 404.7 to 690.7 nm can be used for visual calibration of a spectrophotometer. But not all of the lines are suitable for calibration of a photoelectric instrument, and those that prove adequate will depend on the sensitivity and slit widths characteristic of any particular instrument. One must be very careful that other lines are not included, in addition to the one on which the settings are supposedly being made, of sufficient intensity to affect the wavelength setting.

Special attention should perhaps be called to the use of a cesium arc at 852.1 and 894.3 nm (4). From tables 1a and 1b it is apparent that there are few suitable lines between 706.5 and 1014.0 nm, particularly from steady sources necessary or desirable in the calibration of photoelectric spectrophotometers. The neon discharge tube gives many lines between 750 and 1000 nm (2) but these have not been found satisfactory in the calibration of photoelectric spectrophotometers. In the orange and red the neon lines are useful for visual calibration and many of these can be used to calibrate photoelectric spectrophotometers (5) if the sensitivity is such that very narrow slits can be used. The relative intensities (6) given in table 1b will help in case of overlapping.

The best technique to use in wavelength calibration of non-recording spectrophotometers, given a suitable source, will vary from instrument to instrument and method to method. A few general principles can be given here, however.

In photographic spectrophotometry it usually is sufficient to photograph a known spectrum at the top and bottom of the plate, unless the source used for the absorption spectra itself carries such known reference lines. A few of these reference lines will then serve to correlate that particular plate with whatever complete calibration curve has previously been established by more extensive measurements with the various sources.

On visual and photoelectric non-recording spectrophotometers, it usually is necessary, for highest precision, to have a basic reference line to which all of the other wavelengths are compared by direct check. At the Bureau the Hg yellow lines have proved most suitable for the König-Martens visual spectrophotometer (7). At the slit widths used the overlapping of the two lines gives a central brighter "line" taken as 578.0 nm with a luminous background against which the slit jaws are readily seen. A luminous background, or slight illumination of the ocular slit, always facilitates calibration when an eyepiece is used. Visual calibration without an eyepiece is usually less precise unless very narrow slits are used.

Two techniques have been used at the Bureau in the calibration of non-recording photoelectric spectrophotometers. On the Gibson spectrophotometer (8) the slits are always 0.1 mm wide or greater and the most reliable calibration is obtained by plotting galvanometer deflections at closely adjacent wavelengths. The most probably value for the wavelength reading is given by the intersection of the two straight lines resulting from a plot of the data for any given line, the correction being given by the difference between this value and the true wavelength. This is illustrated in reference (1).

On the Beckman DU spectrophotometer the same method has been used (9), but at the Bureau it has seemed preferable and is much more rapid, to calibrate with a narrow slit and record the wavelength dial reading for the maximum left deflection of the galvanometer needle as the wavelength dial is slowly turned. The most suitable reference line on two of the Bureau's instruments has proved to be the Hg green line at 546.07 nm (5).

2.2 Recording Spectrophotometers.

The initial wavelength calibration of a recording spectrophotometer, such as the manufacturer must carry out in connection with cutting his cams or preparing his reading scale, is not here considered, but only the check of such a calibration by the user of the instrument.

Such a user can, of course, follow the procedure prescribed above for checking the wavelength calibration of non-recording spectrophotometers. However, there are two important reasons for following a different procedure for recording spectrophotometers. For such instruments it is desirable to have a calibration that is made with the instrument operating. It is further desirable in most kinds of work to have this calibration appear on the graph sheet so that difficulties connected with positioning of the sheet, expansion or contraction of the paper with humidity or temperature, or instrumental variations can be eliminated.

Wavelength calibrations of this kind can be made if a material is available having a number of strong and narrow absorption or transmission bands suitably spaced over the spectral range of interest. Two materials have been used or suggested for this purpose: (a) Glasses containing rare-earth oxides, such as didymium glasses and holmium oxide glasses, have been used for many years at the National Bureau of Standards (10, 11), (b) quartz-Polaroid combinations have been proposed (12) and may prove useful for such work.

The use of a didymium glass or a holmium oxide glass in this manner would not in general be accurate unless it is calibrated at nearly the same slit widths as are to be used. Most of the absorption bands that are usable for the purpose are multiple bands and the wavelengths of maximum absorption often depend on the slit widths. This has been illustrated in previous publications (1, 10).

While the use of a didymium glass or a holmium oxide glass for checking the wavelength calibrations of a recording spectrophotometer is highly recommended, there are two other uses of these glasses which are not recommended. First, these glasses are not well suited for checking the photometric scale of any spectrophotometer, recording or non-recording. Transmittances at the peaks of the absorption bands are too dependent on slit widths, and transmittances on the steep parts of the curve are too dependent on slight wavelength errors, both as illustrated in Fig. 1 of reference (10) and in Fig. 8 of reference (1). Second, the use of these glasses to check the wavelength calibration of a non-recording spectro-

photometer is considered much inferior from the standpoints of time, convenience and reliability to the direct use of line sources as described in Sec. 2.1. The National Bureau of Standards has consistently refused to accept didymium glasses or holmium oxide glasses for calibration for either of these two purposes.

2.2.1. General Electric Recording Spectrophotometer.

The NBS didymium glass standards were carefully calibrated by point-by-point measurements on the König-Martens visual and Gibson photoelectric spectrophotometers with slit widths approximating the 10- and 20- nanometer slits used on the NBS General Electric spectrophotometer. Some of these values have been published (13).

The most suitable didymium glass for the purpose, considering type of curve and availability, is a Corning 5120 glass of 3.0 mm thickness. While it is not known how much the wavelengths of maximum absorption of this 5120 glass might vary from melt to melt, glasses from at least three melts have been measured, and there has never been any certain variation among the samples tested. For much work it is probably safe to use the values given in table 2.

Table 2. Wavelengths of maximum absorption for Corning 5120 glasses of 3.0 mm thickness as obtained at the National Bureau of Standards for the slit widths indicated.

Wavelength of Maximum Absorption (nm)	Approximate Spectrum Interval Transmitted by Slits (nm)
441.0	10
475.5	10
528.7	10
585.0	10
684.8	10
743.5	10
745.	20
808.	20
883.	20
1067.	20

For those who wish greater certainty, however, the Bureau has obtained a supply of Corning 5120 glass in 2-inch polished squares and of 3.0 mm thickness. These are measured and the values reported in accordance with NBS test fee schedule 202.105, items d to f. The measurements consist of recording a curve of the test glass on the same sheet as the curve of the NBS standard glass and deriving values of the wavelengths of minimum transmittance of the former relative to

those of the latter. The over-all uncertainties of the values so reported are considered to be not greater than ±1 nm from 441.0 nm to 743.5 nm, and not greater than ± 2 nm from 745 to 1067 nm.

Methods of use of a calibrated didymium glass on a G. E. recording spectrophotometer are described in references (1), (10), and (13).

2.2.2. Cary Model 14 recording spectrophotometer.

The NBS holmium oxide glass standards were carefully calibrated by using a Cary Model 14 recording spectrophotometer, the wavelength indicating dial of which had previously been calibrated by means of a number of sources having wavelengths throughout the ultraviolet and visible spectral regions. Measurements of the wavelengths of minimum transmittance were made as functions of slit width over the range 0.06 to 5.0 nanometers of spectral width. Eleven sharp absorption bands were found to be sufficiently symmetrical that the wavelengths of minimum transmittance indicated by the recorder remained constant for slit widths up to about 2 nanometers.

The most suitable holmium oxide glass for the purpose is a Corning 3130 glass of approximately 2.5 mm thickness. It is not known how much the wavelengths of minimum transmittance of this 3130 glass might very from melt to melt. It is known that, for some 3130 glasses, the absorption of the base glass prevents the use of the glass for wavelength calibration in the ultraviolet near 241 nanometers. For much work it is probably safe to use the values given in the following table.

Wavelengths of minimum transmittance for Corning 3130 glasses of 2.5 mm thickness as obtained at the National Bureau of Standards for slit widths less than 2 nm.

Useful wavelengths between 240 and 370 nm	Useful wavelengths between 360 and 650 nm
241.5	360.8
279.3	385.8
287.6	418.5
333.8	453.4
360.8	459.9
	536.4
	637.5

For those who require that the base glass of the standard transmit sufficiently for the standard to be useful at 241 nanometers, the Bureau has obtained a supply of Corning 3130 glass in 2-inch polished squares and of 2.5 mm thickness. These are measured and the values reported in accordance with NBS test fee schedule 202.105, items g to i.

The measurements consist of recording a curve of the test glass on the same sheet as the curve of the NBS standard glass and deriving values of the wavelengths of minimum transmittance of the former relative to those of the latter. The over-all uncertainties of the values so reported are considered to be not greater than $\pm$ 0.5 nm. The present supply of holmium oxide glass contains striae, and in some cases strains, which have not appreciably altered the wavelengths of minimum transmittance.

The methods of use of a calibrated holmium oxide glass on a Cary Model 14 recording spectrophotometer are similar to those described in references (1), (10), and (13) relating to the method of use of a didymium glass on a G. E. recording spectrophotometer.

3. Checking the Photometric Scale.

A check of the photometric scale of a spectrophotometer independent of all other sources of error is difficult or impossible to make on most spectrophotometers. Useful for this purpose would be a series of samples whose respective transmittances do not vary with wavelength, which will not displace the beam, which do not reflect strongly, and for which the transmittances can be independently determined with high accuracy. However, no such glasses or other materials are available.

On a visual spectrophotometer such a check is possible by means of rapidly rotating sectors. If such sectors are properly made, the angle of the total opening relative to 360°, that is, the effective transmittance of the sector, can be measured on a circular dividing engine with uncertainties only in the fifth decimal place. Of course, the use of such rotating sectors is based on the validity of Talbot's law. Throughout the spectrum, no certain deviations from this relation are known. As a matter of fact, average values obtained over a period of years in measuring the "transmittances" of accurately calibrated rotating sectors on the NBS König-Martens spectrophotometer prove both the validity of Talbot's law at various wavelengths and the reliability of the instrument over most of the photometric scale, or else there is a remarkable balancing of errors.

3.1 Glass Standards of Spectral Transmittance.

Usually on photoelectric spectrophotometers the use of rotating sectors to check the reliability of the photometric scale either is impossible or is attended with too much uncertainty for one reason or another.

Accordingly, shortly after the advent of commercial photoelectric spectrophotometers, the National Bureau of Standards instituted the service of issuing glass standards of spectral transmittance (14). To date, about 700 of these filters have been issued with accompanying certificates. Further information about these filters, particularly with reference to their permanence, may be found in several publications (15, 16).

All of the filters offered for this purpose have transmittances varying through the visible spectrum from high (0.75 or more) to low (0.06 or less). In one sense these might be considered inferior to strictly neutral filters in that a deviation from the true value may be attributed to causes other than inaccuracy of the photometric scale. On the other hand, they are superior to the neutral filters in detecting stray-energy, slit-width, and gross wavelength errors.

The four types of glass filters are designated as "carbon yellow", "cobalt blue", "copper green", and "selenium orange". They are available in either discs approximately 30 mm in diameter or 2-inch squares and are approximately 3, 3, 2, and 2.5 mm thick, respectively. They are issued in accordance with NBS test fee schedule 202.105, item a. The transmittances reported are for 25°C and are usually obtained by measuring, wavelength by wavelength on the Beckman DU spectrophotometer, the ratio of transmittance of test glass to standard. The standards have been calibrated (5, 16) by extensive measurements on the Beckman DU, König-Martens, Gibson, and Cary Model 14 spectrophotometers, from which also are derived the effects of temperature change on the transmittances and the major part of the uncertainties reported for the values.

To give the reader a better idea of the transmittances he may expect on the standards issued, there are given in table 3 the transmittances of the respective NBS standards at the wavelengths used and reported. The transmittances of the standards issued will not in general be identical with those of table 3 but will not be greatly different from them.

Transmittances of these filters at wavelengths other than those given will be determined on request from 365 nm to 1000 nm in accordance with item c of NBS test fee schedules 202.105. Values will be obtained for temperatures of 25°C. The effect of change of temperature has not been determined at the Bureau for these glasses outside the range from 390 to 750 nm. It is known, however, that for all four types of glass the temperature effects are very small from 750 to 1000 nm, and are probably negligible for the usual room temperature variations. On the other hand, temperature effects are always large for these kinds of glass when the transmittance curve is decreasing rapidly towards shorter wavelengths (1, Figs. 29 and 30), so that increasingly large temperature effects may be expected for these filters in the ultraviolet.

Table 3. Values of Spectral Transmittance of NBS Glass Standards for Checking the Photometric Scale of Spectrophotometers. The transmittances of glasses issued by the Bureau will not, in general, be identical with those of table 3 but will not be greatly different from them.

Wavelength	Transmittance for glasses designated as			
(nm)	carbon yellow	cobalt blue	copper green	selenium orange
390	0.025	0.895	0.862	
404.7	.020	.884	.877	
420	.019	----	----	
435.8	.0240	.806	.893	
471.3	.081	.612	.894	
491.6	----	.344	----	
501.6	.208	.245	.859	
520	.316	.091	----	
530	.379	----	.760	
540	----	.0308	----	
546.1	.479	.0335	.671	
560	.557	.064	.585	
570	----	----	----	
578	.636	.0273	.473	0.0042
587.6	.668	----	----	.118
600	.699	.0074	.350	.55
620	.731	.0100	.256	.852
640	.747	.0074	.187	.904
660	.754	----	----	.914
667.8	----	.034	.122	----
680	----	.14	----	----
690	.755	.34	----	.919
706.5	----	.713	----	----
710	----	----	.074	----
720	.748	.845	----	.918
750	.730	.901	.057	.917

3.2. Solution Standards of Spectral Transmittancy.

The photometric scale of spectrophotometers may be checked, if one prefers, by means of solutions of known spectral transmittancies, instead of by means of the standard glasses. For this purpose the following solutions are recommended:

1. The aqueous solutions of copper sulphate and cobalt ammonium sulphate used in the series of filters developed at the National Bureau of Standards for reproducing the colors of sunlight and daylight and for the determination of color temperatures (17).

The published values for absorbancy and transmittancy are given in tables 4 and 5 herein, together with the composition and certain other pertinent information. Many additional details are given in M114 (17) including the changes in absorbancy (A_s) with temperature. Both solutions obey Beer's law over a considerable range of concentrations. The values given for the eight Hg and He wavelengths are considered the most reliable, with an uncertainty in A_s not exceeding 0.001 for the particular chemicals used. Spectrophotometric reproducibility of the chemicals is also considered in the paper. By increasing the thickness or concentration a wide range of the photometric scale can be covered, except at the shorter wavelengths.

2. An aqueous solution of potassium chromate, K_2CrO_4 (0.04g/l) in 0.05N KOH. This solution has been studied by many investigators here and abroad, and is considered one of the most suitable as a standard of spectral transmittancy and absorbancy in the ultraviolet. The absorption in the violet is also useful because the copper and cobalt solutions have too little absorption in this region to be of much value. The most recent determination is given in NBS Research Paper 2331 (18), which also notes most of the previous work. This solution has also been used in a recent comparative survey of photoelectric spectrophotometers (19). The values adopted in RP2331 are given in table 6. These data were obtained from solutions prepared in the following ways:

(1) A solution of K_2CrO_4, stock material, reagent grade, 0.0400 gram per liter, in 0.05N KOH.

(2) A solution of K_2CrO_4 of the same concentration and alkalinity as (1) but prepared from 0.0303 gram of $K_2Cr_2O_7$ which when converted gave 0.0400 gram of K_2CrO_4 per liter.

At wavelengths greater than 260 nm both solutions were found to remain stable (in transmittancy) for 5 or 6 years when stored in ordinary storeroom glass bottles. "Flaking" may occur during this time and any sediment should be allowed to settle to the bottom of the bottle. It is recommended that alkali-resistant ware, now available, be used for storing the solutions. At wavelengths less than 260 nm, it is recommended that solutions not over 6 months old prepared from chemicals of the highest purity be used.

Table 4. Values of Spectral Absorbancy, A_s, and Transmittancy, T_s for Standard Copper Sulphate Solution as Specified, Unfiltered, Thickness 10.00 mm. Temperature 25°C, Having the Following Composition:

Copper Sulphate ($CuSO_4.5H_2O$)*	20.000 grams
Sulphuric Acid (specific gravity 1.835)	10.0 cc
Water (distilled) to make	1000. cc

Wavelength (nm)	A_s	T_s**	Wavelength (nm)	A_s	T_s**
350	0.0090	0.979	600	0.0680	0.855
60	.0063	.986	10	.0885	.816
70	.0046	.989	20	.1125	.772
80	.0035	.992	30	.143	.719
90	.0028	.994	40	.180	.661
400	.0023	.995	650	.224	.597
10	.0019	.996	60	.274	.532
20	.0016	.996	70	.332	.466
30	.0014	.997	80	.392	.406
40	.0012	.997	90	.459	.348
450	.0011	.997	700	.527	.297
60	.0011	.997	10	.592	.256
70	.0012	.997	20	.656	.221
80	.0014	.997	30	.715	.193
90	.0018	.996	40	.768	.171
500	.0026	.994	750	.817	.152
10	.0038	.991			
20	.0055	.987	Hg 404.7	.0021	.995
30	.0079	.982	Hg 435.8	.0013	.997
40	.0111	.975	Hg 491.6	.0019	.996
			He 501.6	.0028	.994
550	.0155	.965			
60	.0216	.951	Hg 546.1	.0135	.969
70	.0292	.935	Hg 578.0	.0368	.919
80	.0390	.914	He 587.6	.0487	.894
90	.0518	.888	He 667.8	.319	.480

*Analysis showed the copper sulphate to have 99.7 percent of the theoretical copper content.

**These values of T_s are derived from the values of A_s.

$A_s = -\log_{10} T_s$

Table 5. Values of Spectral Absorbancy, A_S, and Transmittancy, T_S for Standard Cobalt Ammonium Sulphate Solution, Unfiltered, Thickness 10.00 mm, Temperature 25°C having the following composition:*

Cobalt ammonium sulphate ($CoSO_4.(NH_4)_2SO_4 .6H_2O$)** 14.481 grams
Sulphuric acid (specific gravity 1.835) 10.0 cc
Water (distilled) to make 1000. cc

Wavelength (mμ)	A_S	T_S***	Wavelength (mμ)	A_S	T_S***
350	0.0038	0.991	600	0.0137	0.969
60	.0040	.991	10	.0124	.972
70	.0050	.989	20	.0115	.974
80	.0065	.985	30	.0112	.975
90	.0088	.980	40	.0110	.975
400	.0125	.972	650	.0105	.976
10	.0168	.962	60	.0097	.978
20	.0224	.950	70	.0087	.980
30	.0340	.925	80	.0076	.983
40	.0522	.887	90	.0066	.985
450	.0773	.837	700	.0054	.988
60	.1031	.789	10	.0046	.989
70	.1213	.756	20	.0038	.991
80	.1349	.733	30	.0032	.993
90	.1472	.713	40	.0030	.993
500	.1635	.686	750	.0028	.994
10	.1742	.670			
20	.1689	.678	Hg 404.7	.0144	.967
30	.1452	.716	Hg 435.8	.0437	.904
40	.1113	.774	Hg 491.6	.1497	.708
			He 501.6	.1661	.682
550	.0775	.837			
60	.0496	.892	Hg 546.1	.0901	.813
70	.0308	.932	Hg 578.0	.0219	.951
80	.0207	.953	He 587.6	.0167	.962
90	.0158	.964	He 667.8	.0089	.980

* These data apply accurately also from 400 to 750 mμ to a similar solution made up with 10.3 grams of cobalt sulphate ($CoSO_4.7H_2O$).

**Chemical analysis showed a cobalt (plus nickel) content of 100.0 percent of the theoretical, the ratio of nickel to cobalt (metals) being 1 to 200.

***These values of T_S are derived from the values of A_S. $A_S = -\log_{10}T_S$.

The data of table 6 are based on extensive measurements made with the Hilger sector-photometer photographic spectrophotometer, and the Beckman DU photoelectric spectrophotometer, supplemented with data obtained with the Brackett quartz photoelectric spectrophotometer and, above 400 nm, with data obtained on the König-Martens visual spectrophotometer and the General Electric recording spectrophotometer. The temperatures were kept close to 25°C. In the values of T_s given in table 6 there is considerable uncertainty in the third decimal.

4. Reference Standards of Spectral Reflectance Factor Relative to Freshly Prepared Magnesium Oxide.

In 1957 the International Commission on Illumination (CIE) adopted a resolution concerning the use of a perfect diffuser for colorimetry (20). The resulution reads, "For colorimetric specification of opaque specimens the perfect diffuser is recommended for ultimate adoption as the reference standard." They note that this action will result in a "recommended set of absolute spectral reflectances of magnesium oxide or other working standards". The absolute spectral reflectance values of MgO adopted by NBS are based on work reported by Goebel et al (21). These adopted values are given in table 7.

As a working standard of spectral reflectance factor nothing has as yet been found more suitable than freshly prepared magnesium oxide. Its (total) luminous reflectance is high, 0.97 or 0.98, and nothing has been found of certainly higher reflectance. Its luminous factor, R_0, 45, is 1.00, and its spectral selectivity throughout the visible spectrum appears to vary by less than 1 percent. These data are based on work by Priest (22), McNicholas (23), and Preston (24) and are summarized in National Bureau of Standards letter circular LC-547 (25). More recent work by Benford and others (26, 27) and by Middleton and Sanders (28, 29) closely confirm these results and extend the data into the ultraviolet and infrared.

Other agencies besides the Bureau have also recommended MgO for the same or similar purposes. In 1931, the International Commission on Illumination adopted a resolution which may be translated as follows: "For the colorimetric measurement of opaque materials the luminance of the specimen studied ought to be expressed as a function of the luminance of a surface of the oxide of magnesium considered under the same conditions of illumination and observation" (30). In 1944, this method was incorporated in ASTM Standard Method of test for spectral characteristics and color of objects and materials (31).

Table 6. Values of Spectral Transmittancy, T_s, and Absorbancy, A_s, for Standard Potassium Chromate Solution, Unfiltered, Thickness 10.00 mm, Temperature 25°C, having the following composition:

0.0400 gram per liter of potassium chromate (K_2CrO_4) in 0.05 normal potassium hydroxide solution*

Wavelength (nm)	T_s	A_s**	Wavelength (nm)	T_s	A_s**
220	0.358	0.446	335	0.600	0.222
25	.601	.221	40	.483	.316
30	.674	.171	45	.373	.428
			50	.276	.559
35	.616	.210	55	.199	.701
40	.507	.295			
45	.402	.396	60	.148	.830
50	.319	.496	65	.116	.936
53.6	.279	.554	70	.103	.987
			75	.102	.991
55	.268	.572	80	.117	.932
60	.233	.633			
65	.202	.695	85	.150	.824
70	.180	.745	90	.202	.695
75	.175	.757	95	.294	.532
			400	.402	.396
80	.194	.712	04.7	.515	.288
85	.257	.590			
90	.373	.428	10	.632	.199
95	.533	.273	20	.751	.124
96.7	.598	.223	30	.824	.084
			35.8	.859	.066
300	.709	.149	40	.882	.054
02.2	.771	.113			
05	.834	.079	50	.927	.033
10	.895	.048	60	.960	.018
13.2	.905	.043	70	.980	.009
			80	.991	.004
15	.900	.046	90	.997	.001
20	.864	.064	500	1.000	.000
25	.804	.095			
30	.710	.149			
34.2	.620	.208			

* This solution of potassium hydroxide can be prepared with sufficient accuracy by dissolving 3.3 grams of potassium hydroxide sticks (85% KOH) of reagent quality in sufficient distilled water to make 1 liter.

**These values of A_s are derived from the values of T_s, $A_s = -\log_{10} T_s$

Note: Distilled water only was used in the reference cell.

Table 7 Absolute 6°-Hemispherical Reflectance, ρ

of Smoked MgO 1-mm thick

Wavelength (nm)	ρ	Wavelength (nm)	ρ	Wavelength (nm)	ρ	Wavelength (nm)	ρ
400	0.989	600	0.992	800	0.983	1000	0.978
10	.990	10	.991	10	.983	10	.978
20	.990	20	.991	20	.982	20	.977
30	.991	30	.991	30	.982	30	.977
40	.991	40	.990	40	.981	40	.977
50	.992	50	.990	50	.981	50	.976
60	.992	60	.990	60	.981	60	.976
70	.993	70	.989	70	.981	70	.976
80	.993	80	.989	80	.980	80	.976
90	.993	90	.988	90	.980		
500	.993	700	.988	900	.980		
10	.993	10	.988	10	.980		
20	.993	20	.987	20	.980		
30	.993	30	.987	30	.979		
40	.993	40	.986	40	.979		
50	.993	50	.986	50	.979		
60	.992	60	.985	60	.979		
70	.992	70	.985	70	.979		
80	.992	80	.984	80	.978		
90	.992	90	.984	90	.978		

While the characteristics above noted make fresh MgO an excellent working standard, it has other characteristics that are undesirable and that make the calibration and use of a secondary working standard a very advisable procedure. An MgO surface is extremely fragile and thus is not very suitable for continued handling. A more serious defect is that its spectral reflectance may change by slight but definite amounts within a short time (sometimes in a day) after preparation, the reflectance decreasing below 550 nm. Furthermore, the nature and extent of the changes seem somewhat variable (1, Fig. 33; 28). A third reason for use of a secondary working standard is that slight variations in reflectance (0.1 or 0.2 percent) have been noted for different preparations of freshly prepared MgO. By calibrating the secondary working standard against several different MgO preparations a more representative standard is obtained than would be any single MgO surface by itself.

White structural glass by the name of Vitrolite, with one surface polished, has proved the most suitable for secondary standards of spectral directional reflectance, although the material is not uniformly good for this purpose and must be selected with care. A considerable supply of suitable Vitrolite has been obtained by the National Bureau of Standards, and standards are calibrated and issued for either the General Electric recording spectrophotometer or the Beckman DU spectrophotometer.

4.1 For the General Electric Recording Spectrophotometer.

The Vitrolite standards issued for use with the General Electric recording spectrophotometer are about 4 inches square and 5/16 inch thick. They are covered in NBS test fee schedule 202.105, items j and k.

In the present model of the spectrophotometer, the design is such that the radiant energy is incident in a slightly diverging beam whose axis is at 6° to the perpendicular to the sample. The specular component of the reflected energy is thus diverted away from the entrance aperture towards a port on the side. This port may be filled with MgO or with a black material, so that for plane glossy surfaces the measurement can be made with the specular component "included" or "excluded".

To give one a better idea of the spectral reflectance factor relative to the perfect diffuser and relative to MgO for the Vitrolite standards thus issued, there is given in table 7 two sets of values from 400 to 1080 nm with specular component excluded that apply to one of the NBS standards. Values reported under test fee items j and k with specular component excluded will probably be closely similar to these. With specular component included, the values are greater by roughly 0.04.

Only one Vitrolite working standard is needed for the measurement of spectral reflectance factor on the General Electric recording spectrophotometer. This calibrated Vitrolite standard and the samples to be tested are in turn placed at the sample aperture of the integrating sphere, and any highly reflecting substance such a MgO, $BaSO_4$, or $MgCO_3$ may be used at the comparison aperture provided the material to be tested does not reflect more than the comparison material.

The reflectance factors of the test samples relative to the perfect diffuser and relative to freshly prepared MgO are obtainable by use of correction factors derived from the ratios between the standard Vitrolite values and the values for the Vitrolite read from the curve sheet. This is explained in detail in the report accompanying each standard.

By this procedure only one Vitrolite standard is necessary and the Bureau does not issue these standards in pairs, as some have requested. For transmittance measurements any two nearly identical white surfaces are suitable and no standard reflecting surface is necessary.

4.2 For the Beckman Quartz (DU, Non-Recording) Spectrophotometer.

The Vitrolite standards issued for use with the Beckman DU spectrophotometer are about 1 1/2 by 2 inches and 5/16 inch thick. They are covered in NBS test fee schedule 202.105, items L to n. In this case the radiant energy is incident upon the sample in a nearly parallel beam whose axis is perpendicular to the sample. The reflected energy accepted for measurement is taken in an annular "beam" whose axis is closely 45° to the perpendicular in all directions, but the parts of which may vary in direction roughly from 35° to 55°. The specular component is thus excluded from the measurements and the values obtained relative to magnesium oxide and reported do not differ greatly from those shown in the columns headed R' in table 8.* At 400 nm and below, these values as obtained on NBS standard V2-B4 for the Beckman spectrophotometer are:

Wavelength (nm)	Spectral Reflectance Factor R'
350	0.753
360	.812
370	.826
380	.809
390	.852
400	.868

* See note on page 22.

Table 8. Spectral Reflectance Factor of NBS Standard Vitrolite V1-G4 Relative ao a Perfect Diffuser, R, and Relative to Freshly Prepared Magnesium Oxide, R', for Excluded Specular Component of Reflected Radiant Energy on a General Electric Recording Spectrophotometer.

Wavelength (nm)	For Visible Spectrum (400 to 750 nm) (black velvet port) (10 nm slits)		Wavelength (nm)	For Near Infrared Spectrum (730 to 1080 nm) (black cavity port) (20 nm slits)	
	R	R'		R	R'
400	0.865	0.875	730	0.850	0.861
10	.856	.865	40	.846	.858
20	.850	.859			
30	.850	.858	750	.844	.856
40	.848	.856	60	.841	.854
			70	.838	.851
450	.856	.863	80	.835	.849
60	.864	.871	90	.834	.848
70	.868	.874			
80	.870	.876	800	.831	.845
90	.872	.878	.10	.829	.843
			20	.826	.841
500	.874	.880	30	.824	.839
10	.877	.883	40	.820	.836
20	.879	.885			
30	.881	.887	850	.818	.834
40	.882	.888	60	.816	.832
			70	.814	.830
550	.882	.888	80	.811	.828
60	.881	.888	90	.809	.826
70	.880	.887			
80	.878	.885	900	.808	.824
90	.876	.883	10	.806	.822
			20	.805	.821
600	.873	.880	30	.802	.819
10	.869	.877	40	.800	.817
20	.866	.874			
30	.863	.871	950	.800	.817
40	.860	.869	60	.799	.816
			70	.797	.814
650	.859	.868	80	.796	.814
60	.858	.867	90	.796	.814
70	.857	.867			
80	.856	.866	1000	.795	.813
90	.856	.866	10	.794	.812
			20	.793	.812
700	.855	.865	30	.792	.811
10	.855	.865	40	.792	.811
20	.853	.864			
30	.852	.863	1050	.791	.810
40	.850	.862	60	.791	.810
			70	.791	.810
750	.850	.862	80	.791	.810

It is important to note that the values of spectral reflectance factor relative to MgO obtained and reported for use on the Beckman DU spectrophotometer are not valid for use on the General Electric spectrophotometer, and vice versa, because of the notably different irradiation-reception conditions of the two types of instrument. Similarly the values reported for either instrument should not be used for other types of instrument, unless the geometrical conditions are sufficiently similar as to make the values valid for such purpose.*

---

* In any comparison of results of reflectance factor measurements on instruments with differing geometries of irradiation and reception, it should be remembered that the reflectance factor of MgO also varies with the geometrical conditions. See second paragraph of Section 4, above.

---

5. References.

1. Kasson S. Gibson, Spectrophotometry (200 to 1000 millimicrons) NBS Circular 484 (1949).

2. Massachusetts Institute of Technology Wavelength Tables, measured and compiled under the direction of George R. Harrison (John Wiley & Sons, Inc., New York, 1939).

3. Spectrophotometry, report of O.S.A. Progress Committee for 1922-23, K. S. Gibson, Chairman, J. Opt. Soc. Am. & Rev. Sci. Inst. 10, 169 (1925).

4. N. C. Beese, Cesium vapor lamps, J. Opt. Soc. Am. 36, 555 (1946).

5. Kasson S. Gibson and Margaret M. Balcom, Transmission measurements with the Beckman quartz spectrophotometer, J. Research NBS 38, 601 (1947) RP1798; also J. Opt. Soc. Am. 37, 593 (1947).

6. M. Garbuny, Relative Intensitäten und Übergangswehrscheimlichkeiten der rotgelben Neonlinien, Zeit. Physik 107, 362 (1937).

7. H. J. McNicholas, Equipment for routine spectral transmission and reflection measurements, BS J. Research 1, 793 (1928) RP30.

8. K. S. Gibson, Direct-reading photoelectric measurement of spectral transmission, J. Opt. Soc. Am. and Rev. Sci. Inst. 7, 693 (1923); also described in J. Opt. Soc. Am. 21, 564 (1931).

9. H. H. Cary and Arnold O. Beckman, A quartz photoelectric spectrophotometer, J. Opt. Soc. Am. 31, 682 (1941).

10. Kasson S. Gibson and Harry J. Keegan, Calibration and operation of the General Electric recording spectrophotometer of the National Bureau of Standards, J. Opt. Soc. Am. 28, 372 (1938).

11. H. J. Keegan, J. C. Schleter, and V. R. Weidner, Ultraviolet wavelength standard for spectrophotometry, J. Opt. Soc. Am. 51, 1470 (1961).

12. George L. Buc and E. I. Stearns, Uses of retardation plates in spectrophotometry, II, Calibration of wavelength, J. Opt. Soc. Am. 35, 465 (1945).

13. Harry J. Keegan and Kasson S. Gibson, On the use of working standards of didymium and Vitrolite glasses for spectrophotometric measurements, J. Opt. Soc. Am. 34, 770 (1944).

14. K. S. Gibson, Geraldine K. Walker, and Mabel E. Brown, Filters for testing the reliability of spectrophotometers, J. Opt. Soc. Am. 24, 58 (1934).

15. Kasson S. Gibson and Marion A. Belknap, Permanence of glass standards of spectral transmittance, J. Research NBS 44, 463 (1950) RP2093; also (condensed) J. Opt. Soc. Am. 40, 435 (1950).

16. H. J. Keegan, J. C. Schleter, and M. A. Belknap, Recalibration of the NBS glass standards of spectral transmittance, J. Research NBS 67A, 577 (1963); also (condensed) J. Opt. Soc. Am. 54, 69 (1964).

17. Raymond Davis and K. S. Gibson, Filters for the reproduction of sunlight and daylight and the determination of color temperature, B. S. Miscellaneous Publication No. 114 (1931) M114.

18. Geraldine W. Haupt, An alkaline solution of potassium chromate as a transmittancy standard in the ultraviolet, J. Research NBS 48, 414 (1952) RP2331; also (condensed) J. Opt. Soc. Am. 42, 441 (1952).

19. Wallace R. Brode, John H. Gould, James E. Whitney, and George M. Wyman, A comparative survey of spectrophotometers in the 210-760 mμ region, J. Opt. Soc. Am. 43, 862 (1953).

20. Proceedings, C. I. E., 14th Session, Brussels, Vol.A, p. 36, 1959.

21. D. G. Goebel, B. P. Caldwell, and H. K. Hammond III, Use of an Auxiliary Sphere with a Spectroreflectometer to Obtain Absolute Spectral Reflectance, J. Opt. Soc. Am., 56, 783 (1966).

22. Irwin G. Priest and J. O. Riley, The selective reflectance of magnesium oxide, J. Opt. Soc. Am. 20, 156 (1930).

23. H. J. McNicholas, Absolute methods in reflectometry, BS J. Research 1, 29 (1928) RP3.

24. J. S. Preston, The reflection factor of magnesium oxide, Trans. Opt. Soc. (London) 31, 15 (1929-30).

25. Preparation and colorimetric properties of a magnesium-oxide reflectance standard, NBS letter circular LC-547 (1939).

26. Frank Benford, Gwen P. Lloyd, and Sally Schwarz, Coefficients of reflection of magnesium oxide and magnesium carbonate, J. Opt. Soc. Am. 38, 445 (1948).

27. Frank Benford, Sally Schwarz, and Gwen P. Lloyd, Coefficients of reflection in the ultraviolet of magnesium carbonate and oxide, J. Opt. Soc. Am. 38, 964 (1948).

28. W. E. K. Middleton and C. L. Sanders, The absolute spectral diffuse reflectance of magnesium oxide, J. Opt. Soc. Am., 41 419 (1951).

29. C. L. Sanders and W. E. K. Middleton, The absolute spectral diffuse reflectance of magnesium oxide in the near infrared, J. Opt. Soc. Am. 43, 58 (1953).

30. Proceedings, C.I.E., 8th Session, Cambridge, p. 23, 1931.

31. A.S.T.M. standard method of test for spectral characteristics and color of objects and materials, ASTM D-307-44.

Letter Circular 1017
(Supersedes LC 929 dated 11/26/48)
Prepared by: KSG:HJK:JCS/
Colorimetry and Spectrophotometry Section
Metrology Division
Institute for Basic Standards
National Bureau of Standards