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STANDARDS FOR CHECKING THE
CALIBRATION OF SPECTROPHOTOMETERS
(200 to 1000 $m\mu$)Contents

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1. Introduction.

In continuation of a type of activity carried on with expanding scope for many years at the National Bureau of Standards, there is described in this letter circular the various types of standards that are now 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.

The appearance of this letter circular coincides closely with the announcement of new test fee schedules in spectrophotometry. These new schedules are: 215.505, Spectrophotometric Standards, and 215.506, Spectrophotometric Measurements. The

information in the letter circular and in the fee schedules is consistent and supplementary. Copies of the new test fee schedules are obtainable from the National Bureau of Standards on request.

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 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 $m\mu$ throughout the ultraviolet and visible spectrum. However, if one wishes the uncertainties in his wavelength settings to be of the order of 0.1 $m\mu$, a careful check of these direct-reading scales is necessary.

The best procedure to use for checking the wavelength scale of a spectrophotometer depends on whether it is a non-recording or a recording spectrophotometer.

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 $m\mu$. 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 $m\mu$ for spectrophotometric calibration.

Two of the most suitable sources for wavelength calibration of spectrophotometers are the quartz or glass mercury arc and the ordinary helium vacuum tube in glass. If the range from 205 to 1014 $m\mu$ is of interest the quartz-Hg arc is by far the best single source. A glass-Hg arc gives the same wavelengths as the quartz arc above 300 $m\mu$.

The helium lines are especially well placed for wavelength calibration in the visible spectrum, and the strong lines at 388 and 1083 $m\mu$ are also often very useful. Many other sources, flame or arc, are available for visual wavelength calibration (1, 2)*but most of these are too unstable for accurate

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

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 $m\mu$ the series of doublets obtained from the aluminum spark in air is very useful because they are so readily recognized.

The wavelengths characteristic of the above sources, with a few others that have proved useful, are noted in table 1. All values are consistent with those published in the M.I.T. wavelength tables (2). Not all of the lines for any of the sources are given in table 1 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. Take the mercury arc in quartz, for 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. And all of the lines from 404.7 to 690.7 $m\mu$ 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 $m\mu$ (3). From table 1 it is apparent that suitable lines between 706.5 and 1014.0 $m\mu$ are otherwise mostly unavailable, particularly from steady sources necessary or desirable in the calibration of photoelectric spectrophotometers. The neon discharge tube gives many lines between 750 and 1000 $m\mu$ (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 (4) if the sensitivity is such that very narrow slits can be used. The relative intensities given (5) will help in case of overlapping.

The best technique to use in wavelength calibration of non-recording spectrophotometers, given a suitable source, will vary

Table 1. Sources and Wavelengths Suitable for the Calibration of Spectrophotometers. Wavelengths given in millimicrons.

Mercury Arc in Quartz (Same Wave- lengths in glass above 300 mμ)		Aluminum Spark in Air	Helium Discharge Tube in Glass	
<u>Wave- length</u>	<u>Remarks</u>	<u>Wave- length</u>	<u>Wave- length</u>	
205.29		216.88	318.77	
222.47		217.40	361.36	
223.41			363.42	
225.88		220.46	370.50	
230.21		221.00	381.96	
232.32			388.86	
235.25		226.35	396.47	
237.83		226.91	402.62	
239.94	1		412.08	
239.97		236.71	414.38	
244.69		237.21	438.79	
246.41		237.31	443.75	
248.20	2	237.34	447.15	
248.27		237.84	471.31	
248.38			492.19	
253.48	3	256.80	501.57	
253.65		257.51	504.77	
257.63		257.54	587.56	
260.32			667.81	
265.20	4	263.16	706.52	
265.37			728.13	
265.51		265.25	1083.0	
269.95		266.04		
275.28				
275.97		281.62		
280.35	5			Neon Discharge Tube
280.45		308.22		
284.78		309.27		<u>Wave- length</u> <u>Relative Intensity</u>
289.36				
292.54		358.69		
296.73			585.25	5.2
302.15	6	394.40	588.19	3.9
302.35		396.15	594.48	7.7
302.56			597.55	1.7
302.75			603.00	2.3
312.57			607.43	7.8
313.15	7		609.62	13.0
313.18			614.31	24.6
334.15			616.36	5.9
349.28			621.73	3.9

Table 1. (Continued)

Mercury Arc in Quartz (Same Wave- lengths in glass above 300 mμ)		Hydrogen Sodium Cesium Arcs	Neon Discharge Tube
Wave- length	Remarks		Wave- length Relative Intensity
365.01	8	H 434.05	626.65 11.4
365.48		H 486.13	630.48 4.3
366.29		Na 589.00	633.44 19.9
366.33		Na 589.59	638.30 22.8
390.64		H 656.28	640.22 100.0
398.40		Cs 852.11	650.65 38.6
400.63		Cs 894.35	653.29 7.9
404.66			659.90 11.8
407.78		667.83 23.4	
435.83		671.70 14.0	
491.60		692.95 23.0	
546.07		702.41 2.	
576.96	9		703.24 44.9
579.07			705.91 --
623.44			717.39 4.9
671.62			724.52 17.3
690.72			743.89 4.5
1014.0			748.89 --
1128.7			753.58 --
			754.40 --

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 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.

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, for highest precision, it usually is necessary 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 on the König-Martens visual spectrophotometer (6). At the slit widths used the overlapping of the two lines gives a central brighter "line" taken as 578.0 $m\mu$ 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 (7) 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 probable 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.

On the Beckman spectrophotometer the same method has been used (8), but at the Bureau it has seemed preferable and is much more rapid, to calibrate with a narrow slit and note the farthest throw to the left (of the rapidly responding 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 $m\mu$ (4).

2.2 General Electric 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 many kinds of work to have this calibration appear on the graph sheet so that worries 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) Didymium glasses have been used for many years at the National Bureau of Standards (9), (b) quartz-Polaroid combinations have been proposed (10) and may prove useful for such work.

The use of a didymium glass in this manner would not in general be accurate unless it is calibrated at closely the same slit widths at which it is 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 a previous publication (9).

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 4, 8, 10 and 20 millimicron slits used on the NBS General Electric spectrophotometers. Some of these values have been published (11).

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 ($m\mu$)	Approximate Spectrum Interval Transmitted by Slits ($m\mu$)
441.0	10
475.5	10
528.7	10
585.0	10
684.0	10
743.8	10
745.5	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 215.505, items d to h. 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 $\pm 1 m\mu$ from 441.0 $m\mu$ to 743.5 $m\mu$, and not greater than $\pm 2 m\mu$ from 745 to 1067 $m\mu$.

Methods of use of a calibrated didymium glass on a G.E. recording spectrophotometer are described in references (9) and (11).

While the use of a didymium glass for checking the wavelength calibration of G.E. recording spectrophotometers is highly recommended, as noted above, there are two other uses of the didymium glass which are not recommended. First, the didymium glass is 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 (9). Second, the use of a didymium glass to check the wavelength calibration of a non-recording spectrophotometer is considered much inferior from the standpoints of time, convenience, and reliability to the direct use of line sources as described above. The National Bureau of Standards has consistently refused to accept didymium glasses for calibration for either of these two purposes.

3. Check of 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. No such glasses or other materials are available, however.

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, however. 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.

On photoelectric spectrophotometers, however, the use of rotating sectors to check the reliability of the photometric scale is usually either impossible or 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 (12). To date, about 130 of these filters have been issued with accompanying certificates.

Three of the four types of filters used for this purpose are of moderate selectivity, covering a large part of the transmittance scale. In one sense these are inferior to strictly neutral filters in that a deviation from the true value may be due to other causes 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". The copper green filters are approximately 25 mm square and 2 mm thick; the others are approximately 30 mm in diameter and 2, 3, and 2 mm thick, respectively. They are issued in accordance with NBS test fee schedule 215.505, item a. The transmittances

by wavelength

reported are for 25°C and are usually obtained by measuring wavelength on the Beckman spectrophotometer, the ratio of transmittance of test glass to standard. The standards have been calibrated by extensive measurements on the Beckman, König-Martens and Gibson spectrophotometers (4), 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 other wavelengths than those given will be determined on request from 365 $m\mu$ to 1000 $m\mu$ in accordance with item c of NBS test fee schedule 215.505. Values will be obtained for temperatures of 25°C. The effect of change of temperature has not been determined for these glasses outside the range from 390 to 750 $m\mu$. It is known, however, that for all four types of glass the temperature effects are very small from 750 to 1000 $m\mu$, 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, so that increasingly large temperature effects may be expected for these filters in the ultraviolet.

3.2 Solution Standards of Spectral Transmittancy.

The photometric scale of spectrophotometers may be checked by means of solutions of known spectral transmittancies, instead of by means of the standard glasses, if one prefers. For this purpose the following 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 (13).

The published values for absorbancy and transmittancy are given in tables 4 and 5, together with the composition and certain other pertinent information. Many additional details are given in M1143 (13) including the changes in absorbancy with temperature. Both solutions obey Beer's law over a considerable range. 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.

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 m μ	Transmittance for glasses designated as			
	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	0.0000
570	---	---	---	.0002
578	.636	.0273	.473	.0056
587.6	.668	---	---	.195
600	.699	.0074	.350	.70
620	.731	.0100	.256	.890
640	.747	.0074	.187	.907
660	.754	---	---	.911
667.8	---	.034	.122	---
680	---	.14	---	---
690	.755	.34	---	.912
706.5	---	.713	---	---
710	---	---	.074	---
720	.748	.845	---	.912
750	.730	.901	.057	.912

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 ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)*	20.000 grams
Sulphuric Acid (specific gravity 1.835)	10.0 cc
Water (distilled) to make	1000. cc

Wave-length $m\mu$	A_s	T_s^{**}	Wave-length $m\mu$	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	Hg 404.7	.0021	.995
20	.0055	.987	Hg 435.8	.0013	.997
30	.0079	.982	Hg 491.6	.0019	.996
40	.0111	.975	He 501.6	.0028	.994
550	.0155	.965	Hg 546.1	.0135	.969
60	.0216	.951	Hg 578.0	.0368	.919
70	.0292	.935	He 587.6	.0487	.894
80	.0390	.914	He 667.8	.319	.480
90	.0518	.888			

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

**values of T_s are derived from 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 ($\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$)** 14.481 grams
 Sulphuric acid (specific gravity 1.833) 10.0 cc
 Water (distilled) to make 1000. cc

Wave-length $m\mu$	A_s	T_s	Wave-length $m\mu$	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	.1051	.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	Hg 404.7	.0144	.967
20	.1689	.678	Hg 435.8	.0437	.904
30	.1452	.716	Hg 491.6	.1497	.708
40	.1113	.774	He 501.6	.1661	.682
550	.0775	.837	Hg 546.1	.0901	.813
60	.0496	.892	Hg 578.0	.0219	.951
70	.0308	.932	He 587.6	.0167	.962
80	.0207	.953	He 667.8	.0089	.980
90	.0158	.964			

*These data apply accurately also from 400 to 750 $m\mu$ to a similar solution made up with 10.3 grams of cobalt sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$)

**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.

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, for example, Hogness, Zscheile, and Sidwell (14), and is considered one of the most suitable as a standard of spectral transmittancy and absorbancy in the ultraviolet. Its 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. Accordingly, an extensive series of measurements was initiated here in 1940 which it was hoped would result in a set of standard spectral transmittancy and absorbancy data for a specified potassium chromate solution of known stability. Unfortunately this work was interrupted before completion by diversion to war activities, and has not since been finished. Sufficient data had been obtained, however, that a tentative set of spectral transmittancy values could be adopted. These values are given in table 6. It is hoped that this work may be completed and final values published. Pending this, the following details are of interest and importance in connection with the use of table 6.

All of the potassium chromate solutions were prepared in the Chemistry Division of the National Bureau of Standards. The data of table 6 were obtained from solutions prepared in the following ways:

(1) A solution of K_2CrO_4 , stock material, reagent grade, 0.0400 grams 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 grams of $K_2Cr_2O_7$, which when neutralized gave 0.0400 grams of K_2CrO_4 per liter.

Both solutions were found to remain stable (in transmittancy) for the two years during which the measurements were being made, if 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.

The data of table 6 are based on extensive measurements made with the Hilger sector-photometer photographic spectrophotometer, supplemented by data obtained by photoelectric and (above 400 $m\mu$) visual methods. Temperature control was not used but room temperatures were usually close to 25°C. In the values of T_s given in table 6 there is considerable uncertainty in the third decimal where three significant figures are used. Where but two significant figures are used there is slight uncertainty in the last figure. These uncertainties are estimated from the degree of agreement of results by the different methods.

Table 6. Values of Spectral Transmittancy, T_s , and Absorbancy, A_s , for Standard Potassium Chromate Solution, Unfiltered, Thickness 10.00 mm, Room Temperatures (usually close to 25°C), having the following composition:

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

Wave-length m μ	T_s **	A_s ***	Wave-length m μ	T_s **	A_s ***
210	0.000	--	325	0.810	0.0915
15	.037	1.4318	30	.715	.1457
20	.35	.4559	35	.605	.2182
			40	.485	.3143
225	.60	.2218	45	.385	.4202
30	.68	.1675			
35	.62	.2076	350	.28	.5528
40	.509	.2933	55	.202	.6946
45	.408	.3893	60	.148	.8297
			65	.115	.9393
250	.319	.4962	70	.102	.9914
55	.268	.5719			
60	.232	.6345	375	.103	.9872
65	.201	.6968	80	.118	.9281
70	.180	.7447	85	.152	.8182
			90	.207	.6840
275	.173	.7620	95	.30	.5229
80	.189	.7235			
85	.254	.5952	400	.41	.3872
90	.372	.4295	404.7	.52	.2840
95	.527	.2782	410	.635	.1972
			20	.748	.1261
300	.705	.1518	30	.824	.0841
05	.835	.0809	435.8	.861	.0650
10	.90	.0458	40	.884	.0535
15	.905	.0434			
20	.867	.0620	450	.928	.0325
			60	.961	.0173
			70	.981	.0083
			80	.992	.0035
			90	.998	.0009
			500	1.000	.0000

*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.

**Tentative values. See text.

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

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

As a fundamental standard of spectral directional reflectance 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 directional reflectance, $R_{0,45}$, is 1.00, and its spectral selectivity throughout the visible spectrum appears to be less than 1 percent. These data are based on work by Priest (15), McNicholas (16), and Preston (17) and are summarized in National Bureau of Standards letter circular LC-547 (18). In recent publications, Benford and others (19, 20) give the spectral reflectance of MgO and MgCO₃ in the ultraviolet and visible spectrum obtaining a value of about 0.99 for the luminous reflectance of MgO, with a selectivity of about 2 percent in the visible spectrum.

Other agencies besides the Bureau have also recommended MgO for the same or similar purpose. In 1931, the International Commission on Illumination adopted a resolution (3a) 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". (21). In 1944, this method was incorporated in ASTM Standard Method of test for spectral characteristics and color of objects and materials (22).

While the characteristics above noted make fresh MgO an excellent fundamental 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 550m μ . Furthermore the nature and extent of the changes seem somewhat variable. A third reason for use of a 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 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 working 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 now calibrated and issued for either the General Electric recording spectrophotometer or the Beckman quartz 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 215.505, items i to k. Item i refers to data taken with the earlier model of the recording spectrophotometer where the radiant energy is incident upon the sample in a slightly diverging beam whose axis is perpendicular to the sample. The specular component of the reflected energy from the polished surface thus returns towards the entrance aperture, part of it passing out through this aperture and being lost, and part being intercepted by the sphere and contributing to the measurements. The values obtained and reported are strictly valid on another spectrophotometer only if the same fraction of the specular component of the reflected energy is intercepted by the sphere.

In the later models 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 surface. 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 the specular component may be respectively "included" in, or (for plane surfaces) "excluded" from, the measurements. This is covered in test fee items j and k.

To give one a better idea of the spectral directional reflectance relative to MgO for the Vitrolite standards thus issued, there is given in table 7 a set of values from 400 to 1080 m μ 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. Under item i, with specular component partly included and partly excluded, the values are of course intermediate between the other two sets.

Only one Vitrolite working standard is needed for the measurement of spectral directional reflectance 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 as MgO or MgCO₃ may be used at the comparison aperture provided the material to be tested does not reflect more than the comparison material.

The directional reflectances of the test samples relative to freshly prepared MgO are then obtained by multiplying (at the respective corrected wavelengths) the values for these samples read from the curve sheet, by the ratios of (a) the standard Vitrolite values reported to (b) the values for the Vitrolite read from the curve sheet.

Table 7. Spectral Directional Reflectance of NBS Standard Vitrolite V1-G4 Relative to Freshly Prepared Magnesium Oxide for Excluded Specular Component of Reflected Radiant Energy on a General Electric Recording Spectrophotometer.

Wave-length (m μ)	For Visible Spectrum (400 to 750 m μ) (black velvet port) (10 m μ slits)	Wave-length (m μ)	For Near Infrared Spectrum (730 to 1080 m μ) (black cavity port) (20 m μ slits)
400	0.875	730	0.861
10	.865	40	.858
20	.859		
30	.858	750	.856
40	.856	60	.854
		70	.851
450	.863	80	.849
60	.871	90	.848
70	.874		
80	.876	800	.845
90	.878	10	.843
		20	.841
500	.880	30	.839
10	.883	40	.836
20	.885		
30	.887	850	.834
40	.888	60	.832
		70	.830
550	.888	80	.828
60	.888	90	.826
70	.887		
80	.885	900	.824
90	.883	10	.822
		20	.821
600	.880	30	.819
10	.877	40	.817
20	.874		
30	.871	950	.817
40	.869	60	.816
		70	.814
650	.868	80	.814
60	.867	90	.814
70	.867		
80	.866	1000	.813
90	.866	10	.812
		20	.812
700	.865	30	.811
10	.865	40	.811
20	.864		
30	.863	1050	.810
40	.862	60	.810
		70	.810
750	.862	80	.810

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 (Non-Recording) Spectrophotometer.

The Vitrolite standards issued for use with the Beckman spectrophotometer are about 1 1/2 by 2 inches and 5/16 inch thick. They are covered in NBS test fee schedule 215.505, items L and M. 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 and reported do not differ greatly from those shown in table 7. At 400 m μ and below, these values as obtained on NBS standard V2-B4 for the Beckman spectrophotometer are:

350	0.753
360	.812
370	.826
380	.809
390	.852
400	.868

It should be noted, however, that the values of spectral directional reflectance obtained and reported for use on the Beckman quartz 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.

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