SOLUTIONS FOR COLORIMETRIC STANDARDS. VIII. ARNY'S SERIES.[1]

BY C. T. KASLINE* AND M. G. MELLON.

Various uses have been found (1) for Arny's "Co-Fe-Cu" and "Co-Cro-Cu" series of colorimetric solutions. Specifications for the preparation and use of the former, or acidic, series are contained in the 1935 issue of the Pharmacopœia of the United States (9).

In view of the value which these systems have for certain work, it has seemed worth while to reëxamine their colorimetric characteristics. A more precise knowledge of their absorptive capacity is desirable from the standpoint of knowing their limitations, and of providing a basis for adapting different combinations of them to other uses.

Measurements were reported from this Laboratory several years ago (8) for the stock solutions and several dilutions of them. The data were obtained by means of a visual spectrophotometer. Unfortunately, some of the transmittancy values below 450 mμ and above 650 mμ are not reliable. The sensitivity of the eye is low in these regions and the type of instrument used in the earlier work is not capable of sufficient precision in the red and the blue portions of the spectrum. In the present work the stock solutions have been re-measured, together with the 20 mixtures of the acidic series described in the Pharmacopœia.

EXPERIMENTAL WORK.

Materials.—With the exceptions noted, the same methods of preparation of salts and solutions were followed as reported previously (8).

It may be noted that the directions given by Arny and Ring (2) for the preparation of the roseo-compound, aquo-pentammine cobaltic chloride $[Co(NH_3)_5H_2O]Cl_3$, yield instead the purpureo-compound, chloro-pentammine cobaltic chloride $[Co(NH_3)_5Cl]Cl_2$ (10). The latter compound was prepared, both according to these directions and those of Willard (12). Solutions of the two products yielded identical spectral transmission curves. The "aquo" compound, prepared according to the direction of Biltz (3), has a different hue as a solid and gives a different transmission curve immediately after dissolution, although Biltz states that the "chloro" compound dissolves in ammonia to form the "aquo" compound.

Since potassium dichromate is a primary standard, it was used to prepare the chromate solution.

Apparatus.—All the transmittancy data were obtained by means of a General Electric photoelectric spectrophotometer, a recording model of which has been described recently by Hardy (4). The method of operation and characteristics of the instrument have been described by the authors in another place (7). It is sufficient here to state that repeated checking against three glasses calibrated by the U. S. Bureau of Standards, and with lines from a mercury arc and a helium tube, led to the belief that the reliability of the wave-length values from 400mμ to 700 mμ is within 1 mμ and that of the transmittancies within one per cent. The latter values could be checked repeatedly within 0.1–0.2 per cent.

Data.—Since spectral transmission curves reveal the colorimetric characteristics of a system more quickly than tabular data, the graphical method was used, plotting per cent transmittancy as ordinates and wave-length as abscissas. All data were calculated to a basis of 10.0-mm. cell thickness by means of a special slide rule based on Bouguer's law. Figure 1 shows the results obtained for the acidic and basic series of stock solutions, and Figs. 2–6 show those for the acidic blends recommended in the Pharmacopœia. The composition of the latter solutions is given in Table I.

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TABLE I.—COMPOSITION OF INORGANIC SOLUTIONS.

		$CoCl_2$.	$FeCl_3$.	$CuSO_4$.	H_2O.
Grayish	A	0.1 ml.	0.4 ml.	0.1 ml.	4.4 ml.
	B	0.3	0.9	0.3	8.5
	C	0.1	0.6	0.1	4.2
	D	0.3	0.6	0.4	3.7
Fawn	E	0.4	1.2	0.3	3.1
	F	0.3	1.2	0.0	3.5
	G	0.5	1.2	0.2	3.1
Yellow	H	0.2	1.5	0.0	3.3
	I	0.4	2.2	0.1	2.3
	J	0.4	3.5	0.1	1.0
	K	0.5	4.5	0.0	0.0
	L	0.8	3.8	0.1	0.3
Green	M	0.1	2.0	0.1	2.8
	N	0.0	4.9	0.1	0.0
	O	0.1	4.8	0.1	0.0
Pink	P	0.2	0.4	0.1	4.3
	Q	0.2	0.3	0.1	4.4
	R	0.3	0.4	0.2	4.1
	S	0.2	0.1	0.0	4.7
	T	0.5	0.5	0.4	3.6

$CoCl_2$ = 0.2500 M (1 ml. contains 0.05944 Gm. $CoCl_2.6H_2O$).
$FeCl_3$ = 0.1668 M (1 ml. contains 0.04505 Gm. $FeCl_3.6H_2O$).
$CuSO_4$ = 0.2500 M (1 ml. contains 0.06243 Gm. $CuSO_4.5H_2O$).

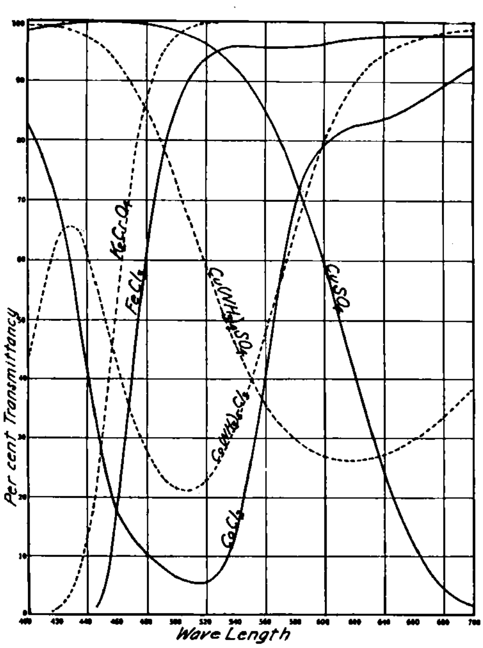

Fig. 1.—Spectral transmission curves for Arny's stock solutions.

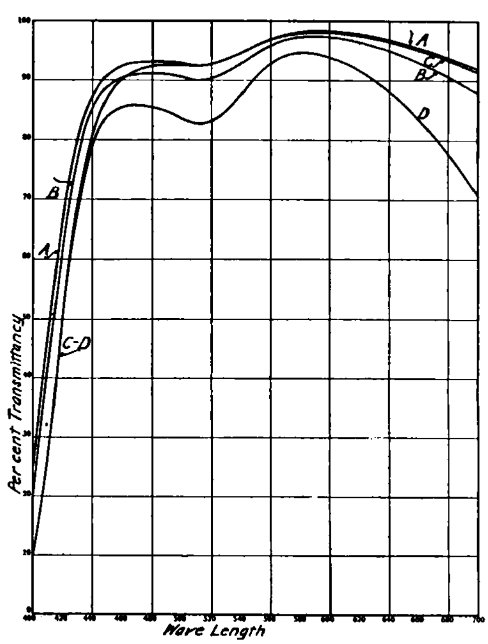

Fig. 2.—Spectral transmission curves for grayish blends.

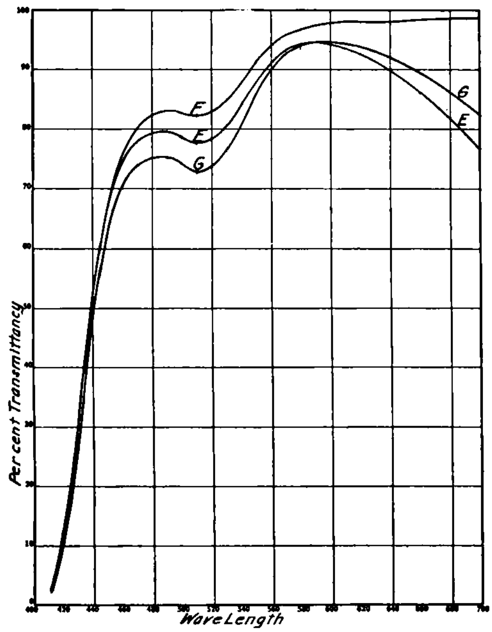

Fig. 3.—Spectral transmission curves for fawn blends.

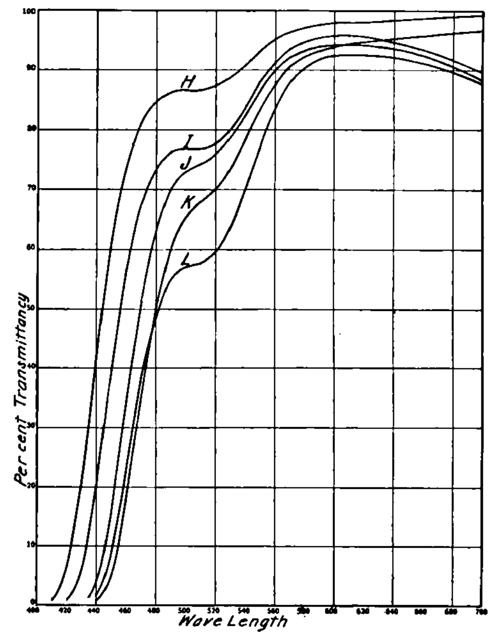

Fig. 4.—Spectral transmission curves for yellow blends.

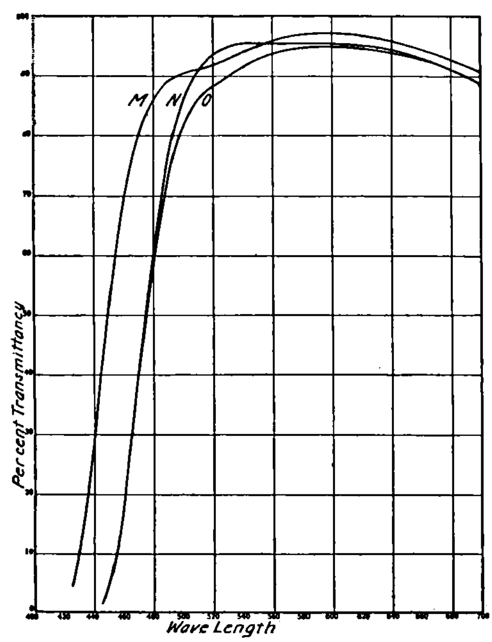

Fig. 5.—Spectral transmission curves for green blends.

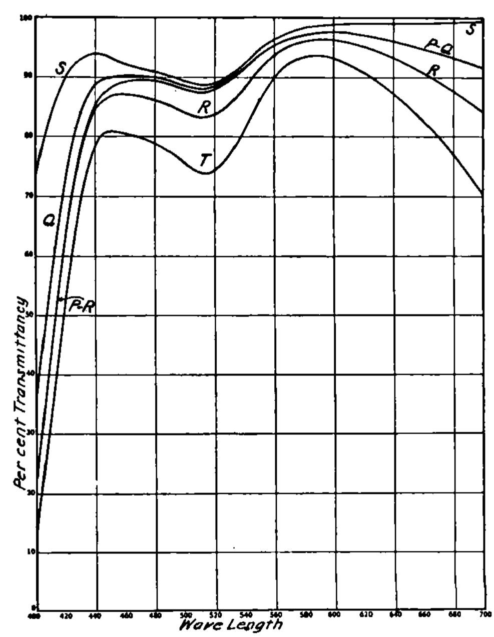

Fig. 6.—Spectral transmission curves for pink blends.

Discussion.—The curves as such require no comment. Each one represents a physical characteristic of a system just as a solubility or melting point of a compound.

In using such systems for colorimetric matching it should be kept in mind that materials matching in color under daylight may not match under artificial illumination. The curves for the two materials appearing to match may be quite different (6). But two materials having identical spectro-photometric curves will always match in color regardless of the type of illumination. It is preferable, therefore, to have an unknown which is to be matched possess a curve agreeing closely with that of the standard (11).

In view of the recommendations that have been made for employing combinations of these solutions for permanent color standards (1), the curves of Fig. 1 were used to calculate the trichromatic and monochromatic values of each stock solution. The selected ordinate method of calculation is described by Hardy (4, 5) and the values obtained are shown in Table II. An inspection of the location of the tristimulus values of these solutions in the color triangle shows that the area included by them is only a minor proportion of the total area. It is obvious, therefore, that these solutions can serve to match only a small portion of the possible colored systems. In order to extend the range one needs solutions which are redder than those of the cobalt compounds and bluer than those of the cupric compounds.

TABLE II.—COLORIMETRIC ANALYSES.

Trichromatic Values.

	Red.	Green.	Violet.
$CuSO_4$	25.3%	30.1%	44.6%
$Cu(NH_3)_4SO_4$	21.8	22.1	56.1
$CoCl_2$	43.7	30.1	26.2
$Co(NH_3)_5Cl_3$	38.3	29.1	32.6
$FeCl_3$	39.8	47.1	13.1
K_2CrO_4	36.4	42.3	21.3

Monochromatic Values.

	Brightness.	Dominant Wave-Length.	Purity.
$CuSO_4$	79.5%	487.7 mμ	22.5%
$Cu(NH_3)_4SO_4$	43.1	477	44
$CoCl_2$	40.7	700	30
$Co(NH_3)_5Cl_3$	49.8	495c	24
$FeCl_3$	92.4	570	65
K_2CrO_4	98.5	568.5	43

REFERENCES.

(1) Arny, *Am. J. Pharm.*, 104, 272 (1932).
(2) Arny and Ring, *J. Franklin Inst.*, 180, 199 (1915).
(3) Biltz-Hall and Blanchard, "Laboratory Methods of Inorganic Chemistry," page 172 (1928), J. Wiley and Sons, N. Y. (4) Hardy, *J. Optical Soc.*, 25, 305 (1935).
(5) Hardy, "Handbook of Colorimetry" (1936). Technology Press, Boston.
(6) Mehlig and Mellon, *J. Phys. Chem.*, 35, 3397 (1931).
(7) Mellon and Kasline, *Ind. Eng. Chem., Anal. Edit.*, 7, 187 (1935).
(8) Mellon and Martin, *J. Phys. Chem.*, 31, 161 (1927).
(9) Pharmacopœia of the United States, 11, 557 (1935).
(10) Swank, Unpublished thesis, Purdue University (1936).
(11) Swank and Mellon, *Ind. Eng. Chem., Anal. Edit.*, 6, 348 (1934).
(12) Willard, *J. Am. Chem. Soc.*, 44, 2220 (1920).