

QUININAE SULPHAS.—Solutions in water are usually slightly alkaline to litmus. It is advisable, in making the test for other cinchona alkaloids, to choose a water-bath of considerable size for the macerations, so that an even temperature can be maintained more readily. There is no reason for deviating 1 or 2 degrees from the specified temperatures and the portion of the official text allowing this is better omitted, as it is likely to lead to careless manipulation. For further comments see under *Quinina*.

(To be continued.)

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## INTERNATIONAL STANDARDS FOR COLORED FLUIDS.\*

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*Introduction:* That the color of certain fluids is a distinct factor in pure chemistry is evident from the employment of such colorimetric tests as that of Wessler, and when we turn to applied chemistry, we find the color of liquid products of such esthetic influence to the consumer as to be of vital commercial value to the manufacturer. This is the philosophy of use of coloring agents in pharmacy and furthermore explains the call for uniformity in the tint of natural colored products. So it is that manufacturers of oils, beer and whiskey seek uniformity in color of their products by the use of colorimeters; that is why Professor Felix Ehrlich (*Zeitschrift Ver. Zuckerind* 59) (1909) (746) has advocated international standardization of caramel by use of the definite brown substance, *Saccharan*, which he prepared from sugar. Professor Ehrlich's effort to establish an international standard for caramel is the partial expression of a still broader need of international uniformity of colors, this need being fittingly expressed by Hans Moeller at the International Pharmaceutical Congress of 1910 (*Berichte der Deutschen Pharmazeutischen Gesellschaft*, 10, 1910, 358), as follows:

“Ein neues Gebiet, auf dem—meiner Meinung nach—jetzt internationale Regeln fest gesetzt werden solten is zweifelsohn das der exakten Farben bestimmungen.”

The subject was brought to the writer in his capacity as member of the Committee on Revision of the National Formulary, there being entrusted to a subcommittee of which he was a member, the problem of standardizing tincture of caramel (*Saccharum ustum*) and tincture of cudbear (*Persionis*) which is proposed to recognize in the forthcoming edition of that work. It is needless to repeat the numerous and practically fruitless efforts toward standardization already reported by the writer (*American Druggist* 59, 1912, 35) except to say that while some of the plans tried out were satisfactory, each possessed the in-

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superable objections of uncertainty of strength or instability of tint. So it was that such standards for cudbear as stained glass, alkaline phenolphthalein solution and solution of commercial orcein, and such for caramel as amber glass and carefully prepared burnt sugar solution were abandoned and after experimentation with tintometers, the following simple, accurate and inexpensive method was devised.

*Suggested Basis of Standardization:* From the Lovibond tintometer with its blendings of red, yellow and blue glass slides, it was a simple step to the mixing of standard and stable, red, yellow and blue solutions and the chemical solutions adopted, because of stability and comparative ease of standardization were slightly acidulated solutions of cobalt chloride, ferric chloride and cupric sulphate. Since starting the work, examination of the literature has shown that Hazen (American Chemical Journal 14, 1892, 300), prepared diluted water-testing solutions from potasso-platinic chloride and cobalt chloride and that Crookes, Odling and Tidy (Chemical News 34, 1881, 174), used for similar water-testing purposes a ferric chloride-cobalt chloride solution in conjunction with a cupric sulphate solution, the two solutions operated in two wedge-shaped flasks. But in both of these plans empiric solutions were employed and for the limited scope of matching colors of water samples, whereas the investigation here recorded, standardized volumetric solutions were used and the wide range of hues here exhibited are produced.

*Operation:* For the blending, half-normal volumetric solutions based on the atomic weights of 1912 were employed.

*Standard Red* contains 14.74 gm. cobalt to the liter.

*Standard Yellow* contains 9.308 gm. ferric iron to the liter.

*Standard Blue* contains 15.8925 gm. copper to the liter.

Three sets of these standard red, yellow and blue solutions have thus far been prepared. The first set was unacidulated and empirically prepared by dissolving the exact molecular proportion of C. P. crystalline chemicals, ferric alum, cobalt chloride and cupric sulphate in water to a half-normal solution; but as the iron solution either alone or in combination with the cobalt or copper solution precipitated after standing a few weeks, slight acidulation was necessary to secure permanent solutions and to aid uniformity, all the colored solutions were subsequently prepared with a fluid consisting of 25 cc. of 31% hydrochloric acid and 975 cc. of water; while for the iron solution, ferric chloride was substituted for ferric alum.

While the addition of the small amount of acid did not affect the tint of the cobalt or copper solution, it of course changed materially the color of the ferric solution, and hence the blends of the three solutions. In passing, it might be said that the blending of neutral solutions strongly pointed to the interesting fact that *equal volumes of equimolecular solutions of ferric iron, copper and cobalt, give a practically colorless fluid corresponding closely with the "neutral tint" of Lovibond.* (Measurement of Light and Color Sensations, p. 32.)

As will be noted below when acid is added to the three solutions, the color preponderance is so affected that the neutral gray tint is found in a blending of red 5, yellow 2, and blue 5, the mixture of equal parts of the three solutions being distinctly yellow. The other two sets of red, yellow and blue solutions were made strictly half-normal as per specifications given below.

*Red:* 59.4965 gm.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  diluted to 1000 cc. with a mixture of 25 cc. 31% HCl and 975 cc. water.

*Yellow:* 45.054 gm.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  diluted to 1000 cc. with a mixture of 25 cc. 31% HCl and 975 cc. water.

*Blue:* 62.43 gm.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  diluted to 1000 cc. with a mixture of 25 cc. 31% HCl and 975 cc. water.

Of course, the original solutions were prepared from larger amounts of the three salts and were then diluted to the above specified half-normal strength with acidulated water; new assays being made after each dilution until exact strength was attained. The iron solution was standardized volumetrically by the potassium iodide-thio-sulphate method, while the copper and cobalt solutions were assayed gravimetrically. Analytical data as to these assays will be published later in a more extended report on this line of investigation.

One of these sets of assayed solutions was prepared from Kaulbaum's C. P. "Analyse" copper sulphate; Kaulbaum's C. P. "Nickel-frei" cobalt chloride and Merck's "Reagent" ferric chloride; while the other set, equally carefully assayed, was prepared from the usual C. P. chemicals as found in stock, the idea being to see if trifling deviations from absolute purity would seriously affect the tint of the mixed solutions. Comparison of products of combinations of these two sets of red, yellow and green fluids and that as "unknowns" showed no deviation save in one isolated case out of the 88 hues tried and this, very likely, was due to some error in mixing.

*The Mixing:* The production of the 88 hues mentioned above from the standard red, yellow and blue solutions was the result of mixing all possible combinations of the three fluids that would lead to a finished volume of 12 cc. when each fluid was used only in cubic centimeter amounts; that is, when fractional parts of the cubic centimeter were not selected. As a full list of these 88 blendings is given below, we need here only mention that the 88 series of combinations of these fluids to make 12 cc. was empirically chosen as a convenient number and that it goes without saying that an indefinite number of hues are possible, if larger volumes are prepared or fractional parts of the cubic centimeter are used as basis of mixing. It might also be added that in the 88 hues, the combinations of any two of the three colors are included. The result of these 88 blends are exhibited with this and show a range of hues covering the entire spectrum from the red of cobalt chloride solution to the blue of copper sulphate solution. This, of course, eliminates the cardinal reds and crimsons and the azures and navy blues. A number of the hues, it will be noted, are of a neutral tint, due undoubtedly to the absorption of the light ray by the chemicals, under certain con-

ditions of blending. These "neutrals" will be the subject of further study on physical lines.

For convenience sake, the 88 hues have been classified by eye into the following tentative groupings:

THE R. Y. B. HUES.

(In this tabulation "R" means  $\frac{1}{2}$  N—CoCl<sub>2</sub>·6H<sub>2</sub>O; "Y" means  $\frac{1}{2}$  N—FeCl<sub>3</sub>·6H<sub>2</sub>O, and "B" means  $\frac{1}{2}$  N—CuSO<sub>4</sub>·5H<sub>2</sub>O; while in the order from top to bottom of the columns the sequence of the solar spectrum is followed. The interrogation point after some of the blendings means a hue which does not fit satisfactorily into the sequence and which, however, is not "gray" enough to place among the neutral tints.)

Red Orange Group.			Yellow Group.			Green Group.			Blue Green Group.			Neutral Group.		
R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.
11	1	0	5	5	2	1	8	3	0	4	8			
10	2	0	4	7	1	0	10	2	1	2	9	10	1	1
9	3	0	3	9	0	2	5	5 ?	3	2	7 ?	9	1	2
9	2	1	4	8	0	1	7	4	3	1	8 ?	8	2	2
8	4	0	3	8	1	0	9	3	2	1	9 ?	7	2	3
8	3	1	2	10	0	0	8	4	2	2	8 ?	8	1	3
7	5	0	1	11	0	1	6	5	1	1	10	7	1	4
7	4	1	Green Yellow Group.			0	7	5	0	1	11	6	1	5
6	6	0	3	7	2	1	5	6	Blue Violet Group.			(Yellowish)		
6	5	1	2	9	1	2	4	6	1	0	11	6	2	4
6	4	2	1	10	1	2	3	7	2	0	10	6	3	3
7	3	2	2	8	2	0	6	6	1	0	9	5	4	3
5	7	0	3	6	3	1	4	7	3	0	9	4	6	2
5	6	1	2	8	2	1	3	8	4	0	8	5	3	4
			Yellow Green Group.			0	5	7	5	0	7	4	5	3
			2	7	3	0	3	9	6	0	6	(Greenish)		
			1	9	2	0	2	10	7	0	5	4	4	4
			0	11	1				8	0	4	4	3	5
			2	6	4				9	0	3	4	2	6
			3	5	4 ?				10	0	2	(Grayish)		
			3	4	5				11	0	1	5	2	5
			3	3	6							5	1	6
												(Bluish)		
												4	1	7

*Using the Hues:* It will be seen from the foregoing table that the 88 combinations afford an excellent range of tints covering most of those required in pharmacy and commerce. The investigation has not, as yet, sufficiently progressed to report an extended line of color values and in this paper mention will only be made of the matching of the two colors entrusted to the writer by the National Formulary Committee.

Before discussing the individual matchings, it might be well to say that the writer has found that a very satisfactory way to match colored fluids is by use of those oblong flint glass prescription bottles known in American commerce as "Tall Blakes," but Nessler tubes give excellent results and for very accurate work the Rowntree Garachty colorimeter is best. Details of this phase of the matter are found in a paper in the (Practical Druggist, 30, 1912, 24).

As to caramel, a typical solution made by carefully carmelizing 1 gm. cane sugar and diluting to 500 cc. was found by two observers to match exactly the half-normal standard solution "R. Y. B. 4-7-1." As to cudbear, a purified extract (made by percolation of the drug with acetone after previous extraction with chloroform) was dissolved in alcohol containing a trace of ammonia and then diluted with water. The purple tint of this dilution did not match any of the "R. Y. B." samples but when the dilution was faintly acidulated with citric acid, similar tints were obtained; although the acidulated cudbear dilution was a trifle more transparent. Since there was some variation, the cudbear dilution and the "R. Y. B." hues were submitted to five observers as "unknowns" and the reports of these observers are tabulated below in sequence from darkest to

lightest. The "R. Y. B." fluids were the assayed half-normal blends, "a" and "b" being the two different samples described above. Two cudbear dilutions 1-50,000 were employed; one being distinctly acid (a), and the other just past the neutral point (b), the intention being to see if difference in degree of acidity would make a difference in tint.

MATCHING CUDBEAR DILUTIONS WITH "R. Y. B." HUES.

I and II	
a. "R. Y. B. 9-0-3"	
a. "R. Y. B. 10-0-2"	
b. "R. Y. B. 10-0-2"	
Cudbear dilution	1-50,000 "b"
" "	1-50,000 "a"
" "	1-60,000
" "	1-75,000

IV	
a. "R. Y. B. 9-0-3"	
Cudbear	1-50,000 "b"
b. "R. Y. B. 10-0-2"	
Cudbear	1-50,000 "a"
a. "R. Y. B. 10-0-2"	
Cudbear	1-60,000
" "	1-75,000

III	
a. "R. Y. B. 9-0-3"	
b. "R. Y. B. 10-0-2"	
a. "R. Y. B. 10-0-2"	
Cudbear dilution	1-50,000 "b"
" "	1-50,000 "a"
" "	1,60,000
" "	1-75,000

X	
a. "R. Y. B. 9-0-3"	
Cudbear	1-50,000 "a"
b. "R. Y. B. 10-0-2"	
a. "R. Y. B. 10-0-2"	
Cudbear	1-50,000 "b"
" "	1-60,000
" "	1-75,000

From these five reports, one is justified in reporting that the dilution of 1 to 50,000 of that particular extract of cudbear matched the hue produced by blending 10 volumes of half-normal cobalt solution and 2 volumes half-normal copper solution.

*General Remarks:* From the foregoing paragraphs it will be seen that the writer has adopted a nomenclature for the hues covered by the cobalt-ferric iron-copper blends; "R. Y. B. 10-1-1" meaning that proportion of the three half-normal colored fluids. This nomenclature is purely tentative and as further experimentation may show the advisability of using other ionic colors, it might be well, in the beginning to call the above cited combination "Co-Fe-Cu 10-1-1."

Soon after beginning the work, platonic chloride was tried out as the yellow fluid and there was prepared a carefully standardized solution which when based on the quadrivalent platinum cation was exactly fifth-normal (9.76 gm. pt. to liter). Blending this with fifth-normal solutions of cobalt chloride and of cupric sulphate showed that the platonic chloride had much more color than did the cobalt and copper solutions; two blends of 1 volume of platinum and 11 volumes of copper solution giving the normal green that is shown in the iron-copper blend, 1-5-6.

The pink manganese solutions (chloride and sulphate) were considered, but the prepared half-normal solutions were too light to be of service.

In conclusion, the writer wishes to admit that his plan is still in the experimental stage and in its present state has its limitations. While the demonstrated samples show a fine range of orange and green tints, it is weak in reds and blues. But in his opinion, the plan is the only one by which after more extended work, the color standard problem will be eventually solved, possibly by construction of a red-yellow-blue series of anions.