

colorimeter. The results of this critical comparison are tabulated below.

TABLE XI
PRIME WHITE No. 2

In 1-oz. round bottles matched 39a
In Lovibond apparatus matched 39a
In Kober colorimeter matched (30 mm. layer against 30 mm. layer) 39a

CHOICE SUMMER YELLOW No. 2

In 1-oz. round bottles matched 2c and 4c
In Lovibond apparatus matched 2c
In Kober colorimeter matched 2c (30 mm. layer against 30 mm. layer) and 4c (30 mm. layer against 28 mm. layer)

OFF. SUMMER YELLOW No. 2

In 1-oz. round bottles matched 11b and 14b
In Lovibond apparatus matched 14b
In Kober colorimeter matched 19b (30 mm. layer against 30 mm. layer)

PRIME WHITE No. 3

In 1-oz. round bottles matched 42a
In Lovibond apparatus matched 42a
In Kober colorimeter matched 42a (30 mm. layer against 30 mm. layer)

CHOICE SUMMER YELLOW No. 3

In 1-oz. round bottles matched 27c
In Lovibond apparatus matched 27c
In Kober colorimeter matched 27c (30 mm. layer against 30 mm. layer) and 28c (30 mm. layer against 28 mm. layer)

OFF. SUMMER YELLOW No. 3

In 1-oz. round bottles matched 20b and 21b
In Lovibond apparatus matched 21b
In Kober colorimeter matched 21b (30 mm. layer against 30 mm. layer)

In most of the Kober readings matching of 40 mm. layers gave same results as 30 mm. layers.

SUMMARY AND CONCLUSIONS

I—The greatest difficulty in standardizing the color of cottonseed oil is the variation of the tint of commercial samples. This is shown by the matched difference in the Lovibond readings (using the same Lovibond glasses in each case) of Samples 1, 2, and 3 as given in Tables I, VIII, and IX, which is all the more surprising as the color values (expressed in the now accepted Lovibond units) given by those kindly furnishing the samples are in practical agreement as far as Prime White and Choice Summer Yellow are concerned.

II—This discrepancy may be due to the variation in the tint of the supposed standard Lovibond glasses (as pointed out by Mr. Priest) or to alteration of the color of the oil samples (see Table I) or to both causes.

III—Further study of the "Co-Fe-Cu" standardized colored fluids confirms the stability of the tints obtained on blending.

IV—The facts that they can be prepared by anyone competent to conduct quantitative analysis, that when made of proper strength their color values are uniform, and that their employment saves the cost of expensive appliances commend them to the practical men.

V—In matching cottonseed oil with these standardized fluids (as shown in Table XI) approximately good matches are obtained when the oil samples and the fluids are compared in 1-oz. round bottles, while practically perfect results are secured by comparing the oil samples with the fluids in 1/2-in. cells placed side by side in the Lovibond instrument. In fact, in our work we found such matches not only more easily secured, but in some respects even more satisfactorily obtained, than when the more expensive colorimeter was used.

VI—As shown in Tables III, V, VII, and XI, the Prime White samples were matched by blends ranging from 6 cc. $N/2$ acidulated ferric chloride solution, 0.4 cc. $N/2$ acidulated cobalt chloride solution, and water enough to make 50 cc. to 16 cc. $N/2$ acidulated ferric chloride solution, 1.4 cc. $N/2$ acidulated cobalt chloride solution, and water enough to make 60 cc.; Choice Summer Yellow samples were matched by blends ranging from 22 cc. N acidulated ferric chloride solution, 3.4 cc. $N/2$ acidulated cobalt chloride solution, and water enough to make 50 cc. to 33.3 cc. N acidulated ferric chloride solution, 3.3 cc. $N/2$ acidulated cobalt chloride solution, and water enough to make 50 cc., while Off. Summer Yellow samples were matched by blends ranging from 42 cc. N acidulated ferric chloride solution, 6.2 cc. $N/2$ acidulated cobalt chloride solution, and water enough to make 60 cc. to 39 cc. N acidulated ferric chloride solution, 7.2 cc. $N/2$ acidulated cobalt chloride solution, and water enough to make 50 cc. Whether the limits of color should be fixed between narrower boundaries is a problem to be decided by the standards committee of the Society of Cotton Products Analysts.

In closing, the authors wish to extend their thanks to Messrs. David Wesson, F. N. Smalley, and G. Worthen Agee for samples of oil and for suggestions kindly given.

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THE TINCTURE OF VANILLA OF THE NATIONAL FORMULARY

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Tincture of vanilla was discontinued in the 9th Edition of the Pharmacopoeia, being transferred to the 4th Edition of the National Formulary. The method of the 8th Edition of the Pharmacopoeia called for the use of 65 per cent alcohol, which is generally recognized as being higher than is necessary to produce the best vanilla extract, but otherwise the procedure was practicable and workable. The same cannot be said of the substituted method, which is as follows:

TINCTURE OF VANILLA

(U. S. P. VIII)

Tr. Vanill.

Vanilla, cut into small pieces, one hundred grams.....	100 g.
Sugar, in coarse granules, two hundred grams.....	200 g.
Alcohol.....
Diluted Alcohol.....
Water, each, a sufficient quantity.....

To make one thousand milliliters..... 1000 mls.

Macerate the vanilla with five hundred milliliters of alcohol in a stoppered container, in a moderately warm place, for two days with frequent agitation; then transfer it to a plain filter and reserve the filtered liquid. Spread out the drug on the filter and expose it to the air until all of the alcohol has evaporated. Then grind the vanilla and sugar to a uniform powder, pack this in a percolator and slowly percolate it with a mixture of the reserved filtrate and an equal volume of water. When the liquid ceases to drop, continue the percolation slowly, gradually

adding the remainder of the prepared menstruum and then sufficient diluted alcohol to make the product measure one thousand milliliters.

It will be noticed that the new method calls for a preliminary extraction with alcohol which contains not less than 94.9 per cent of alcohol by volume; in other words, "Cologne spirits" of commerce. Alcohol of this strength removes a resinous extractive from the beans which is precipitated in the form of a persistent cloud when the menstruum is diluted and which is not subsequently removed by percolation or by any ordinary method of filtration. This colloidal material adds nothing to the flavor of the extract, but on the other hand renders it unsightly and unsalable.

Another obvious disadvantage of the proposed method is the loss of alcohol which its use entails. Vanilla beans of average moisture content will retain 10 per cent of the alcohol used when placed upon a filter to drain, which is lost if the directions are followed to expose the drug "to the air until all of the alcohol has evaporated."

The method would seem to be of greater academic interest than of practical value, which is unfortunate, inasmuch as the authorities having the enforcement of the food and drug laws in charge naturally attach great importance to official methods of procedure.

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THE DETERMINATION OF BROMIDE IN MINERAL WATERS AND BRINES¹

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The chief sources of bromine in the United States are natural and artificial brines in which it is present as bromide associated frequently with small amounts of iodide. Bromine is obtained by appropriate treatment of the mother liquor, or "bittern," obtained as a by-product in the manufacture of common salt. Owing to the increased demand for bromine resulting in a greatly increased market value during the period of the war, search has been made for new supplies of brine rich in bromide. The authors had occasion to examine a number of samples of brines and desired to determine their bromide content.

The colorimetric methods have been studied by the Association of Official Agricultural Chemists² and by Sweeney and Withrow,³ but are not entirely satisfactory. In these methods the bromide solution is treated with chlorine water or some other oxidizing agent and the liberated bromine absorbed in carbon disulfide, chloroform, carbon tetrachloride, etc., and compared with suitable standards. Where the bromine present in the sample taken for the determination is greater than 5 mg., however, only approximate results can be obtained by these methods.

A search of the literature revealed no method which could confidently be relied upon to give correct results for bromine associated with the other constitu-

ents usually found in brines, and it was necessary to attempt the development of a satisfactory method.

The literature contains many methods for the selective oxidation of bromides in the presence of chlorides and the subsequent removal of the liberated bromine by steam distillation or by aspiration. Vortman¹ recommended the use of lead peroxide (PbO_2) and acetic acid, the liberated bromine being removed by distillation. Cavazzi² recommended barium dioxide (BaO_2) and dilute sulfuric acid. Engel³ made the assertion that ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) will liberate bromine and not chlorine at a temperature of 70–80° C. Berglund⁴ used a mixture of potassium bisulfate (KHSO_4) and potassium permanganate (KMnO_4) in the cold, and removed the bromine by aspiration. He found, however, that if sodium chloride were present in excess of 1 g., a small amount of chlorine would be set free along with the bromine. To overcome this difficulty he recommended two aspirations, the first to concentrate the bromine content in a suitable absorbing solution from which the bromine is again liberated by potassium bisulfate and potassium permanganate and removed by aspiration, resulting in pure bromine being obtained. Baubigny and Rivals⁵ stated that copper sulfate (CuSO_4) and potassium permanganate (KMnO_4) will liberate at room temperature bromine and not chlorine unless chloride is present in too large amount. Wyss⁶ used ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) and potassium permanganate (KMnO_4). White⁷ used aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and potassium permanganate (KMnO_4). Jannasch and Aschoff⁸ used acetic acid and potassium permanganate (KMnO_4). Bugarsky,⁹ Benedict and Snell,¹⁰ and Andrews¹¹ suggested the use of iodic acid. Gooch and Blumenthal¹² used selenic acid, and Gooch and Cole¹³ telluric acid.

The possibility of obtaining a clean separation of bromine and chlorine by the use of most of these methods is dependent upon the concentration of the chloride or of the oxidizing agent, or of the acidity of the solution. They are effective, therefore, only within narrow limits of concentration of the reacting solution and the possibility always exists that either owing to the addition of too much acid or oxidizing agent, or from the solution becoming too concentrated during distillation, some chlorine will be set free, or, the contrary conditions prevailing, all of the bromine will not be liberated.

The double aspiration recommended by Berglund disposes of the possibility of bromine being contaminated with chlorine, but it seems to have been overlooked or not approved by later investigators who

¹ *Z. anal. Chem.*, **25** (1886), 172.

² *Gazz. chim. ital.*, **13**, 174.

³ *Compt. rend.*, **118** (1894), 1263.

⁴ *Z. anal. Chem.*, **24** (1885), 184.

⁵ *Compt. rend.*, **125** (1897), 527, 607.

⁶ *Repert. anal. chem.*, **5** (1885), 238.

⁷ *Chem. News*, **57** (1888), 233.

⁸ *Z. anorg. Chem.*, **1** (1892), 144.

⁹ *Ibid.*, **10** (1893), 387.

¹⁰ *J. Am. Chem. Soc.*, **25** (1903), 809.

¹¹ *Ibid.*, **29** (1907), 275.

¹² *Am. J. Sci.*, **35** (1913), 54.

¹³ *Ibid.*, **37** (1914), 257. See also Cole, *Ibid.*, **38** (1914), 265.

¹ Read before the Division of Water, Sewage, and Sanitation of the American Chemical Society, at the 57th Meeting, Buffalo, April 7 to 11, 1919.

² *J. A. O. A. C.*, [I] **1** (1915), 97.

³ *THIS JOURNAL*, **9** (1917), 671.