and would probably introduce factors which would make the test more difficult to duplicate. The fewer the variable features introduced into laboratory tests, the more consistent the results obtained by different workers. In regulatory work this factor is of considerable importance. If substances prove to be antiseptic under the conditions set forth here, there is every reason to believe they will be efficacious when used in practice."

A PHARMACEUTICAL STUDY OF SYRUP OF FERROUS IODIDE (1840-1927).

BY CATY J. BRAFORD AND H. A. LANGENHAN.

(*Continued from p. 567, June issue.*)

No. IV. ASSAY—QUANTITATIVE AND QUALITATIVE.

(1) *Description.*—The first two revisions of the U. S. P. to contain Syrup of Ferrous Iodide described it as "a transparent liquid of a pale green color." The revisions of 1880 and 1890 elaborate on this a little and read as follows: "A transparent, pale green liquid, odorless, having a sweet, strongly ferruginous taste and a neutral reaction." In the formula given in the Pharmacopœia of 1900, diluted hypophosphorous acid was added which gave the finished syrup a slightly acid reaction. The description was again changed to include this point, by changing the last phrase of the old definition to read "acid in reaction." The last two revisions were changed only in that the reaction was stated as "slightly acid."

(2) *Tests for Iodine and Iodides.*—The revisions of 1860, 1870 and 1880 specified that the syrup should not tinge starch blue, showing the absence of free iodine. It also stated that no sediment should form when the preparation was allowed to stand for some time. Such a sediment was explained by England[1] to be first an oxidation to a ferric compound and then a precipitation of ferric hydrate and iodine. The 1890 revision applied the same test for free iodine as above.

A test for the iodide was introduced in 1880 and has been continued up to the present time with a few slight changes from time to time. The first directions were to add carbon disulphide and chlorine water to the syrup, whereupon the carbon disulphide would become purple or violet due to the iodine which had been liberated by the chlorine. The revisions since that time have followed the same procedure but have used starch as an indicator rather than dissolving the iodine in the carbon disulphide with the subsequent color reaction.

(3) *Addition of Sulphuric Acid.*—The first two revisions containing a formula for this syrup were the only ones to comment on the action of sulphuric acid, which they did in the following manner. "Mixed with sulphuric acid, it becomes brown and the mixture emits violet vapors when heated." This brown color may have been due to caramelization or to the liberation of free iodine. Heat would naturally cause iodine to be given off in the violet vapors.

(4) *Test for Ferrous Iron.*—Each revision since 1880 has included a qualitative test for the ferrous iron, by directing the addition of a few drops of potassium ferricyanide T. S. to the diluted syrup, resulting in the formation of a blue color

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[1] England, *Am. J. Pharm.*, 60, 547 (1888).

or precipitate. The potassium ferricyanide reacts with the ferrous iron to form ferrous ferricyanide (Turnbull's blue) according to the following equation: $2K_3Fe(CN)_6 + 3FeI_2 \longrightarrow Fe_3(Fe(CN)_6)_2 + 6KI$.

(5) *Methods of Assay.*—No method of assay was included in the first two revisions of the Pharmacopœia containing Syrup of Ferrous Iodide. In the 1880 revision an assay was introduced. The following table will offer a brief résumé of the changes that have occurred since that time.

Year.	Syrup used.	Water added.	Amt. used.	$AgNO_3$ $N/10$.	HNO_3.	Indicator.	Residual titration.	% strength.	Remarks.
1880	7.73 Gm.			50 cc.				10	No procedure given
1890	1.55 Gm.	10 cc.	Total	11 cc.	5 cc. dil.	Ferric ammonium sulphate, 5 cc.	KCNS $N/10$, not more than 1 cc.	10	
1900	10 Gm.	q. s. 100 cc.	15.4 cc. mixture 15 cc. water	6 cc.	2 cc. dil.	Ferric ammonium sulphate, 2 cc.	KCNS $N/10$ not more than 1 cc.	5	Shake to precipitate silver iodide; 1 cc. $AgNO_3$ = 1% FeI_2
1910	App. 10 Gm. weighed.	30 mils	Total	50 mils	5 mils	Ferric ammonium sulphate, 2 mils	KCNS $N/10$ q. s.	4.75 to 5.25	Heat to precipitate silver iodide. Yellow color
1920	10 cc.	30 cc.	Total	50 cc.	5 cc.	Ferric ammonium sulphate, 2 cc.	KCNS $N/10$	5, app.	Heat to precipitate silver iodide

The first assay was brief and included no method of procedure. It simply stated that "7.73 Gm. of the syrup should require for complete precipitation 50 cc. of the volumetric solution of nitrate of silver (corresponding to 10% of ferrous iodide)." These amounts were based on the cc. equivalent of the silver nitrate solution when compared to ferrous iodide, which was given as 0.015455. This value multiplied by the number of cc. of silver nitrate used (50) equaled 0.77275 Gm. or 10% of the weight of the sample taken for analysis.

The next revision offered a slightly different method. An excess of silver nitrate (11 cc.) was added to a weighed (1.55 Gm.) and acidulated sample and the excess was determined by titration with $N/10$ potassium thiocyanate, of which not more than 1 cc. was supposed to be required. The potassium thiocyanate reacted with the silver nitrate to form silver thiocyanate and potassium nitrate. Ferric ammonium sulphate which produces a red-brown color with any excess of potassium thiocyanate, was used as an indicator to mark the end of the reaction.

The general procedure was the same in the U. S. P. of 1900; the sample was prepared a little differently, however. Ten Gm. of the syrup were mixed with water q. s. for one hundred cc., and of this mixture fifteen and four-tenths cc. (15.4 cc.) were diluted with fifteen cc. of water. Six cc. of silver nitrate V. S. were added and the excess was determined as above. Not more than one cc. of $N/10$ potassium thiocyanate would be required if the syrup was up to standard. Each cc. of the $N/10$ silver nitrate consumed, represented 1% of ferrous iodide. Assuming that exactly one cc. of the thiocyanate was required, then the actual amount of silver nitrate consumed was five cc. This number multiplied by the cc. equivalent of silver nitrate for ferrous iodide, which was given as 0.015365 in this revision, gives 0.076825 Gm. in the diluted sample which was in turn equivalent to 1.54 Gm. of the original sample. By proportion there would be 4.9 Gm. in one hundred Gm., or approximately 5% by weight. Taking the specific gravity into consideration the strength of the syrup would be about 6.7 Gm. in one hundred cc. as the U. S. P. directed.

In the 1910 edition an accurately weighed sample of approximately ten Gm. was directed to be diluted with thirty mils of water and to the mixture fifty cc. of silver nitrate V. S. were added. After acidifying and heating to precipitate the silver iodide, the residual silver nitrate was determined by titration with $N/10$ potassium thiocyanate. Each mil of silver nitrate consumed corresponded to 0.154844 Gm. of ferrous iodide according to the molecular equivalent and each Gm. of syrup corresponded to not less than 3.07 mils or more than 3.4 mils of $N/10$ silver nitrate V. S. Assuming that the syrup contained an even 5% of ferrous iodide the latter equivalent can easily be determined, since one cc. of silver nitrate is equivalent to 0.015484 then x cc. will be equivalent to one cc. of syrup or 0.05 Gm. of ferrous iodide. Calculating such a proportion the value for x is found to be 3.09.

The last revision directs that the syrup be made up to a given volume and consequently specifies a measured rather than weighed amount of syrup for the assay (10 cc.). Otherwise, the procedure is the same as in 1910; only one equivalent was included and that was the ferrous iodide equivalent for $N/10$ silver nitrate (0.01548).

Ammonium thiocyanate has been used to determine the excess silver nitrate. Bourquelot[1] and Roeder[2] both offered assay processes which were merely modifications of the U. S. P. and used the ammonium rather than the potassium thiocyanate.

A slightly different assay was used by Rupp.[3] His method depended upon the separation of iodine by means of potassium permanganate and sulphuric acid. The excess of permanganate was decomposed by the sugar present and the iodine separated from the clear liquid as a powder. After three hours potassium iodide was added which dissolved the free iodine and reduced the ferric sulphate which liberated a corresponding amount of iodine. Each cc. of $N/10$ thiosulphate required to react with the liberated iodine was equivalent to 0.0020666 of ferrous iodide. The equations which the author gave to explain the reaction are as follows:

$$10FeI_2 + 3K_2Mn_2O_8 + 24H_2SO_4 = 10I_2 + 5Fe_2(SO)_3 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$$
$$5Fe_2(SO_4)_3 + 10KI = 5I_2 + 10FeSO_4 + 5K_2SO_4$$

Korndorfer[4] liberated the iodine by means of hydrogen peroxide and sulphuric acid. His method was as follows:

"5 Gm. of syrup, 5 Gm. of water, and 3 Gm. of commercial hydrogen dioxide are mixed and allowed to stand $^1/_2$ minute; 20 Gm. of chloroform and 10 Gm. of sulphuric acid are added, the flask rotated until the liberated iodine is dissolved in the chloroform. $KMnO_4$ (1–1000) is added to destroy the excess hydrogen dioxide, then add $N/10$ $Na_2S_2O_3$ until the iodine is decolorized (16 to 16.2 cc.); 1 cc. of thiosulphate represents 0.0155 Gm. of ferrous iodide."

Griggi[5] warmed the syrup with a 5% solution of potassium chlorate until the

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[1] Bourquelot, *Jour. de Pharm.*, 6, 170; through "British Year Book of Pharm.," 191 (1895).

[2] Roeder, *Pharm. Zeit.*, 51, 278; from "British Year Book of Pharm.," 43, 75 (1906).

[3] Rupp, *Jour. Soc. Chem. Ind.*; through "British Year Book of Pharm.," 37, 201 (1900).

[4] Korndorfer, *Apoth. Ztg.*, 24, No. 90, 850 (1909); through A. PH. A. YEAR BOOK, 58, 11 (1910).

[5] Griggi, *L'Union Pharm.* (Oct. 1893); through "British Year Book of Pharm.," 31, 202 (1894).

following reaction was completed: $2FeI_2 + KClO_3 \longrightarrow Fe_2O_3 + HCl + 2I_2$. The liberated iodine was dissolved in chloroform and then titrated with sodium hyposulphite. Kubel[1] first precipitated the iron with sodium carbonate and, after filtering, titrated an aliquot part of the filtrate, to which potassium chromate had been added as indicator, with $N/10$ silver nitrate. Parker[2] assayed both the iodine and the iron. He placed the diluted syrup into a retort containing potassium chlorate and distilled the mixture, allowing the distillate to pass into a potassium iodide solution. The distillate was titrated with standard hyposulphite. To determine the iron, he mixed two Gm. of potassium chlorate, sixty cc. of standard hyposulphite and forty cc. of diluted syrup (containing 10 cc. of syrup). After boiling the mixture gently for five or ten minutes, he filtered it through a very fine filter, rinsing both the flask and the filter with boiling water. He then removed the precipitate from the paper by washing, and dissolved it in dilute hydrochloric acid with the aid of heat. The iron was then precipitated with excess ammonium hydroxide and after drying and igniting was weighed as ferric oxide.

Kolthoff[3] devised a new method recently by which both the iodide and iron content can be determined. A diluted sample is prepared by adding eighty cc. of water, ten cc. of phosphoric acid (25%) and five cc. potassium cyanide (10%). Potassium permanganate $N/10$ is delivered into this solution until a permanent pink color appears, when the "iodide is oxidized to iodine cyanide and the ferrous to ferric iron." "The iodine cyanide itself also is an oxidant, and it reacts in acid solution with iodide in forming iodine," as follows: $ICN + I + H \longrightarrow I_2 + HCN$.

Excess iodide is therefore added and the iodine which it liberates is titrated with thiosulphate V. S. The number of cc. of potassium permanganate V. S. minus the number cc. thiosulphate V. S. multiplied by 5.58 mg. gives the ferrous content. The iodide content is determined by multiplying the cc. of thiosulphate V. S. by 12.69 mg.

A method to determine iron in syrups has been outlined by Richmond and Ilson,[4] the efficiency of which, they claim, depends upon the following facts:

"1. In $N/5$ HCl solution iron is completely ionized even if phosphates and organic matter be present.

"2. Permanganates oxidize ferrous ions to ferric ions in the presence of sugars and also destroy the coloring matters used in syrups. In oxidizing ferrous to ferric ions by potassium permanganate the amount used before the color is discharged shows that the oxidation of the ferrous ions takes preference over that of the dye, while sugar is attacked to a still less degree.

"3. A small excess of potassium permanganate is reduced completely by the sugars and practically no Cl is liberated.

"4. Ferricyanides are sensitive indicators for the production and thiocyanates for the removal; $SnCl_2$ reduces ferric to ferrous ions and in an atmosphere of CO_2 the reduction is a measure of the iron present."

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[1] Kubel, *Apoth. Zeit.*, 389 (1895); through "British Year Book of Pharm.," 32, 191 (1895).

[2] Parker, *Pharm. Jour.*, 3rd series, 10, 851; through "British Year Book of Pharm.," 17, 126 (1886).

[3] Kolthoff, JOUR. A. PH. A., 15, 164 (1926).

[4] Richmond and Ilson, *Analyst*, 45, 438 (1920); through "British Year Book of Pharm.," 58, 102 (1921).

To carry out the assay a five- or ten-cc. sample is measured into a one hundred-cc. flask and a few drops of strong hydrochloric acid are added after which potassium permanganate is run into the mixture until a transitory purple color is produced. After this purple has vanished an equal bulk of concentrated hydrochloric and a little sodium bicarbonate are added to give an atmosphere of carbon dioxide. As indicator a drop of $N/10$ $SnCl_2$ and a drop of the mixture are added to a drop of freshly prepared potassium ferricyanide solution on a spot plate. A blue coloration results generally, except in cases where a large excess of potassium permanganate was added. In such a case $SnCl_2$ must be added until a reaction for ferrous iron is given. The solution, which is yellow as is customary for a solution of ferric salts in strong hydrochloric acid, is now titrated until the color becomes faint. The titration is continued until a drop no longer colors a drop of potassium thiocyanate solution on a spot plate. The number of cc. used multiplied by 0.0056 gives the weight of the iron present.

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F. T. C. CITES PEPSODENT FOR RESALE PRICE POLICY.

The Federal Trade Commission has served a complaint on the Pepsodent Company, Chicago, alleging that the practices of the Company in enforcing a policy of resale price maintenance are in violation of the Federal Trade Commission act. The complaint charges that in the sale of its dentifrices the company solicits and secures from customers the names of other dealers who fail to observe and maintain designated resale prices, and seeks and obtains the coöperation of dealers so reported in maintaining such prices through contracts or agreements, expressed or implied. According to the Commission's complaint, also, the Company refuses to sell its products to dealers who fail to maintain prices as a part of its coöperative plan to maintain such prices.

LIBRARY AND MUSEUM ITEMS.

The opening of the new Business Branch of the Newark Public Library at 34 Commerce Street, Newark, N. J., has given to the business people of that city a new house of knowledge—the only institution of its kind in the East. Indianapolis and Minneapolis have business libraries on a smaller scale. The idea had its inception in 1904, when a small part of the Public Library Building in Newark was given over to books dealing with trade and commerce. The plan was gradually extended until now the business branch is established in a home of its own, built by the City of Newark at a cost of $225,000.

The purpose of the library is to provide those interested in business problems with quick, efficient and useful answers to queries. It offers also to the business man an opportunity to profit by the works of specialists in his own line. It makes available for him information as to where, how and when he may most advantageously market his products. Directories are available.

Sixteen fields of research and publication comprise a coöperative program of scholarship outlined for the American Historical Association and made public by the Association's national endowment committee at Columbia University.

History investigation will be conducted, it is declared, on a scale never before attempted in this country. At the outset there will be "a comprehensive survey of the field of American history."

With the dedication of the new building of the Free Library of Philadelphia a dream of many years ago has come true. It is situated on the Parkway, midway between the City Hall and the Art Museum, at the entrance to Fairmount Park. The Library in its present house has a capacity of 1,500,000 volumes not counting the numerous rooms which are set apart for special purposes. One of the modern collections soon to be moved into the main building consists of 7000 talking machine records.