

# Determination of Iodide in the Presence of Interfering Substances\*

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Inorganic iodides in simple solution may be accurately and conveniently determined, but the determination of iodides in heterogeneous mixtures has long been a source of difficulty. Since Pills of Ferrous Iodide, N. F. VI, contain troublesome vegetable material and have no recognized method of assay, this preparation was selected to serve as basis for the development of a procedure which would enable satisfactory determination of iodide in this and other complex mixtures. The work presented here is divided into two parts: first, investigation of efficiency of methods proposed in the literature; and, second, development of a practical and accurate quantitative procedure as applied to ferrous iodide pills.

## EXPERIMENTAL

### PART I

*Standard Reference.*—In order to evaluate the efficiency of existing methods of assay, mass of ferrous iodide of known iodide content was used as reference. The mass was freshly prepared before each determination in the following manner:

One-half gram of iodine was accurately weighed in a glass-stoppered weighing bottle, and to it were added 0.4 Gm. of reduced iron and about 1 cc. of distilled water. The weighing bottle was quickly stoppered and rapidly rotated until the pale green solution of ferrous iodide formed. The following previously mixed powders were then added and incorporated: glycyrrhiza, 0.4 Gm.; sugar, 0.4 Gm.; extract of glycyrrhiza, 0.1 Gm.; and acacia, 0.1 Gm.

Standard sodium thiosulfate solution, required in assays to follow, was standardized against iodine taken from the same container as that used in the preparation of the mass. This obviated the necessity of determining the purity of iodine and assured an experimental recovery equal to the theoretical amount.

Two methods, that of François and Lormand (1), and the method of Lansberg (2), were not tested

\* Presented to the Scientific Section of the A. Ph. A., Detroit meeting, 1941.

† Submitted in partial fulfillment of the requirements for the degree of Master of Science in Pharmacy.

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because the former was admittedly lacking in accuracy and the latter, which required extraction in a Soxhlet, filtration, and distillation, appeared to be too laborious and time-consuming to be practical. Following are summaries of those methods which were applied to the analysis of the standard reference.

*Method of Fullerton, Watkins and Graham (3).*—Weigh enough of the freshly powdered material to represent approximately 5 grains of potassium iodide (or an equivalent amount of iodine), and transfer to a separatory funnel. Add 50 cc. of water and, if alkaline, neutralize with phosphoric acid, finally adding 5 cc. in excess. Add 25 cc. of hydrogen peroxide and agitate thoroughly. Allow to stand a few minutes to be sure the reaction is complete and extract the liberated iodine with several portions of chloroform until the iodine has been removed, as can be told from the color. Collect the chloroform extracts in an iodine flask containing 4 Gm. of potassium iodide in 25 cc. of water. Titrate with 0.1 *N* sodium thiosulfate solution, using starch indicator.

*Method of Sheringa (4).*—Triturate 10 pills with water and make alkaline with sodium hydroxide solution. Transfer to a 100-cc. volumetric flask with the aid of water and dilute to the mark. Filter and to a 20-cc. aliquot of the filtrate add 50 cc. of water, 10 cc. of dilute sulfuric acid, 7 cc. of 0.1 *N* silver nitrate and 2 cc. of ferric alum indicator. Titrate the excess of silver nitrate with 0.1 *N* potassium thiocyanate.

*Method of Kolthoff (5).*—Triturate 10 pills with water and rinse into a 100-cc. volumetric flask. Add 2 to 5 cc. of 0.1 *N* sodium thiosulfate followed by 20 cc. of 0.2 *N* barium hydroxide solution; dilute to exactly 100 cc., allow the precipitate to settle, and decant the supernatant liquid through a filter. To a 10-cc. aliquot of the filtrate add 5 to 10 cc. of 4 *N* phosphoric acid and an excess of freshly prepared calcium hypochlorite solution, dilute with about 100 cc. of water and boil off the excess chlorine. Cool, add 5 cc. of 1 *N* potassium iodide solution and titrate the liberated iodine with 0.1 *N* sodium thiosulfate.

Each of the procedures was applied to analysis of standard mass of ferrous iodide. The results of the analyses, recorded in Table I, show that the existing methods gave neither accurate nor consistent recoveries of iodine and they were, therefore, unsatisfactory for the determination of iodide in mixtures.

*Modified Kolthoff's Method.*—The discordant and low recoveries of iodine with Kolthoff's method were thought to be due to the fact that the precipitate obtained upon the addition of barium hydroxide,

Table I.—Recovery of Iodine by Various Methods of Analysis

Method	No. of Detns.	Iodine Weighed		Iodine Recovered		Per Cent Error	
		Mean	Range	Mean	Range	Mean	Range
Fullerton	5	0.3005	0.3827-0.2163	0.2922	0.3754-0.2065	3.0	1.5-4.8
Sheringa	6 <sup>a</sup>	0.4693	0.5121-0.4051	0.4606	0.5013-0.3934	1.9	1.0-3.1
Kolthoff	7 <sup>a</sup>	0.4433	0.5285-0.3435	0.4314	0.4996-0.3278	2.7	1.5-5.5

<sup>a</sup> Each determination checked by duplicate.

Table II

Method	No. of Detns.	Iodine Weighed		Iodine Recovered		Per Cent Error	
		Mean	Range	Mean	Range	Mean	Range
Modified Kolthoff	6 <sup>a</sup>	0.4890	0.5375-0.4289	0.4856	0.5326-0.4264	0.6	0.5-0.9

<sup>a</sup> Each determination checked by duplicate.

plus other insoluble material, was not removed before the volume was diluted to 100 cc. Since the volume occupied by the insoluble matter was relatively large and varied in amount with each determination, the aliquot did not represent a proportionate part of the whole. Also, gelatinous precipitates are known to cause serious coprecipitation of ions; it is, therefore, possible that low and inconsistent recoveries were due to adsorption of iodide by the precipitate. With these thoughts in mind, Kolthoff's procedure was modified as follows:

Mass of ferrous iodide (corresponding to the pills) was quantitatively prepared and rinsed into a beaker. After the addition of 2 to 5 cc. of 0.1 *N* sodium thiosulfate and 20 cc. of 0.2 *N* barium hydroxide, the mixture was filtered, receiving the filtrate in a 250-cc. volumetric flask. The beaker and precipitate were washed with successive portions of distilled water until a test portion showed no indication of iodide. The filtrate and washings were then diluted to the mark. A 25-cc. aliquot was taken and treated as described in the original method.

Results of analyses, recorded in Table II, show that the change in procedure produced recoveries which were more uniform and nearer the theoretical amounts. The revised method, however, was time-consuming because the gelatinous character of the precipitate made filtration exceedingly slow and tedious and repeated washings were required to remove the last trace of iodide. Use of suction was not practical because of frothing.

#### PART II

Results of analyses have shown that earlier methods for the determination of iodide in heterogeneous mixtures are unsatisfactory. We have here attempted to devise a procedure which would permit accurate and concordant recoveries of iodine and at the same time avoid expenditure of excessive time and labor.

Scott (6) gives a method for estimation of iodine by addition of hydrogen peroxide to a solution acidulated with phosphoric acid and subsequent distillation of the iodine into a series of two absorption vessels, each containing a solution of potassium iodide. Serious difficulties were encountered when this method was applied to analysis of mass of

ferrous iodide. First, a portion of the iodine condensed in the neck of the distillation flask and could not be recovered; second, all exposed rubber fittings were discolored by iodine; third, steam caused vaporization of iodine from the absorption vessels; and, fourth, excessive frothing of the reaction mixture made quantitative distillation impossible.

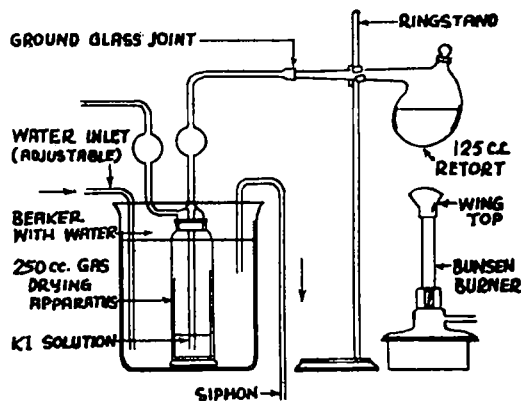


Fig. 1.—Apparatus for Quantitative Distillation of Iodine.

Modifications in the apparatus and procedure overcame the difficulties. A retort having a ground glass opening was substituted for the distillation flask. A Dreschel gas drying apparatus made an excellent receiver and eliminated the necessity of rubber stoppers. A ground glass joint was made to connect the retort to the receiver. Volatilization of iodine from the receiver was prevented by immersing the receiver in a beaker of cold, circulating water. After many futile attempts to overcome or reduce frothing of the boiling mixture, it was found that ferric chloride (or ferric alum) in dilute sulfuric acid was efficient in this respect. The ferric salt, at the same time, served as a mild oxidant for the iodide. Details of the set-up are shown in Fig. 1. The procedure is as follows:

Transfer quantitatively prepared mass of ferrous iodide (or 10 pills of ferrous iodide, if this preparation is to be assayed) to the retort and dilute with water to about 40 cc. Add 10 cc. of 10% sulfuric acid and heat gently to dissolve excess iron. Allow the retort to cool somewhat and connect the retort by means

of the ground glass joint to the Dreschel gas drying apparatus containing 30 cc. of 20% potassium iodide solution. Keep the receiver cold in a beaker of circulating water. Add an excess of ferric chloride (about 5 Gm.) to the retort and gently heat to boiling. Continue the distillation for about 30 min. in such manner as to cause the gases to bubble continuously into the potassium iodide solution. Disconnect the apparatus at the ground glass joint, wash the delivery tube with water and titrate the liberated iodine with 0.1 *N* sodium thiosulfate solution using starch indicator.

The accuracy of the method is evidenced by recoveries of iodine recorded in Table III.

Table III.—Recoveries of Iodine

Detn.	Iodine Weighed	Iodine Recovered	Per Cent Recovery
1	0.3937	0.3914	99.42
2	0.2814	0.2813	99.96
3	0.4483	0.4480	99.93
4	0.3169	0.3162	99.78
5	0.3916	0.3905	99.72
6	0.4396	0.4393	99.93
7	0.3608	0.3589	99.61
8	0.3627	0.3615	99.67
9	0.4408	0.4406	99.95
10	0.3449	0.3448	99.97
11	0.4379	0.4383	100.09
Average			99.82

Blank determinations were made using the same procedure but with omission of the iodine. Results showed that the vapors from the flask had very little or no reducing action upon the potassium iodide in the receiver. Other experiments were made showing that gelatin (commonly used as pill coating) did not decrease the efficiency of the method.

Table IV.—Analysis of Commercial Brands of Pills of Ferrous Iodide

Company	No. of Detns.	Labeled FeI <sub>2</sub> , Gm. per 2 Pills	Determined FeI <sub>2</sub> , Gm. per 2 Pills
P. D. & Co.	3	0.122	0.125
Foreign	3	0.09	0.10
Upjohn	3	0.067	0.065

The procedure was applied to analysis of commercial brands of ferrous iodide pills and gave results recorded in Table IV.

## SUMMARY

The efficiency of methods proposed in the literature for determining iodide content of mixtures was determined by applying the procedures to analysis of quantitatively prepared mass of ferrous iodide. None of the methods gave accurate or consistent recoveries of iodine.

Kolthoff's method was modified to give satisfactory recoveries of iodine, but the procedure was time-consuming.

A method for the determination of iodide in the presence of interfering substances has been developed by the authors. It is based on the release of iodine with ferric chloride in a specially designed distillation apparatus. The procedure proved to be convenient and it gave accurate recoveries of iodine from samples of quantitatively prepared mass of ferrous iodide.

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## A Study of Antiseptics in Various Ointment Bases\*

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As early as 1881 Koch observed that phenol, when dissolved in oil or alcohol, showed less bactericidal action than it did

in aqueous solution. In 1895 Breslauer (1) reported upon the bactericidal effects of ointments, and concluded that cold cream and lanolin were the best ointment bases for antiseptics. A few years later Eldred (2) showed the presence of bacteria or molds in thirty of the fifty samples of official ointments and bases which he tested.

\* Submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, 1941.

Presented to the Scientific Section of the A. Ph. A., Detroit meeting, 1941.

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