

ASSAYS OF SOME OFFICIAL IRON PREPARATIONS CONTAINING ORGANIC MATTER.*

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The purpose of the work described herein was to establish reliable methods for the analysis of several official preparations containing iron. Specifically these are Solution of Iron and Ammonium Acetate, U. S. P. X (1), Solution of Peptonized Iron and Manganese, N. F. V (2), and Solution of Albuminized Iron, N. F. V (2). Of these only Solution of Iron and Ammonium Acetate, U. S. P. X (1), is required to be assayed, and this assay is not satisfactory for several reasons discussed later.

The objections to the U. S. P. X (1) method for the analysis of Solution of Iron and Ammonium Acetate are: 1, The solution tends to foam when heated, frequently splattering, with a resultant loss of iron, 2, it is practically impossible to completely burn all of the organic matter present, and 3, when the residue is treated with hydrochloric acid some of the iron is held in the charred mass, thus giving low results.

The method of the German Pharmacopœia VI (3); of W. Gruning (4); of the *Druggists Circular* (5); of J. L. Mayer (6); boiling with concentrated hydrochloric acid and extracting the ferric chloride with ether; evaporating the solution to dryness in a Kjeldahl flask; evaporating to dryness after the addition of sodium borate were tried, in addition to the one given in the U. S. P. X (1), but were found to be unsatisfactory.

Method of the German Pharmacopœia VI (3).—This method which is essentially that abstracted by the *Druggists Circular* (5) from Riedel's *Berichte*, for the estimation of Solution of Iron Albuminate, requires the alcohol to be expelled from the solution, solution of hydrogen dioxide added, followed by diluted sulphuric acid, and the mixture heated on a water-bath until the froth produced by the albumin has disappeared. The excess of solution of hydrogen dioxide is then removed by the careful addition of a solution of potassium permanganate. Water is added until the mixture measures 100 cc., filtered and potassium iodide is added to an aliquot part of the filtrate and the liberated iodine is determined with tenth-normal sodium thiosulphate.

This method was tried with each of the three solutions under consideration but proved entirely unsatisfactory for both Solution of Iron and Ammonium Acetate, U. S. P. X (1), and Solution of Peptonized Iron and Manganese, N. F. V (2). Fairly consistent results, however, were obtained for Solution of Albuminized Iron, N. F. V (2) and a detailed method, table of results and criticisms of this method will be found on page 15 of this report.

Method of Gruning (4).—This method, which consists of the iodometric titration of the ash obtained by incinerating the precipitated iron albuminate obtained by adding sodium chloride and acetic acid to the solution, is open to the objection that the ashing is not complete and the subsequent solution of the ash in hydrochloric acid does not contain all of the iron.

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Mayer's Method (6).—Mayer proposes a method developed especially for the determination of iron in Solution of Iron and Ammonium Acetate, U. S. P. X (1), in which hydrochloric acid and potassium iodide are added to the sample, the mixture kept at 40° C. for half an hour and after cooling titrated with tenth-normal sodium thiosulphate. Repeated experiments with this method showed that while fairly consistent results may be obtained the results are invariably low. It is believed that the glycerin interferes with the reactions since solutions which do not contain glycerine can be accurately determined by this method.

Ether Extraction Method.—Since ferric chloride is soluble in ether and glycerin is insoluble an attempt was made to convert the salt to the chloride by boiling with concentrated hydrochloric acid and then removing the ferric chloride with ether, allowing the ether to evaporate, dissolving the residue in hydrochloric acid and determining the iron in the usual way. The principal difficulty encountered was due to the caramelization of the sugar, which colors the solution brown and renders it extremely difficult to determine when all of the ferric chloride has been extracted.

Evaporation in Kjeldahl Flask.—In evaporating the solutions to dryness in a Kjeldahl flask it was found to be impossible to completely ignite all of the organic matter. By the use of a Kjeldahl flask the loss of iron by splattering is prevented but the addition of hydrochloric acid does not completely remove the iron from the charred mass. Furthermore when the solution contains manganese, as in Solution of Peptonized Iron and Manganese, N. F. V (2), the flask invariably cracks when it is attempted to heat the material to dryness.

Addition of Sodium Borate.—The use of sodium borate to decompose the glycerin proved unsuccessful since on every attempt a hard charred mass remained which could not be completely ignited.

Of all the methods tried, one which was originated by Mayer (6) but not recommended by him proved the most successful. In this method the organic matter is destroyed by heating the material in a Kjeldahl flask with the aid of concentrated sulphuric acid, concentrated nitric acid and solution of hydrogen dioxide added successively, the latter serving also to oxidize the iron and manganese. The iron may then be precipitated as ferric hydroxide and after filtering may be dissolved in hydrochloric acid and estimated in the usual way.

The methods which follow for the assay of Solution of Iron and Ammonium Acetate, U. S. P. X (1), Solution of Peptonized Iron and Manganese, N. F. V (2) and Solution of Albuminized Iron, N. F. V (2) are essentially modifications of the method originally tried by Mayer (6).

EXPERIMENTAL DATA.

1. Solution of Iron and Ammonium Acetate, U. S. P. X (1).

For Solution of Iron and Ammonium Acetate the U. S. P. X (1) states: "Solution of Iron and Ammonium Acetate contains, in each 100 cc., ammonium acetate corresponding to not less than 0.6 Gm. and not more than 0.8 Gm. of NH₃, and not less than 0.16 Gm. and not more than 0.20 Gm. of Fe."

The following method proved satisfactory for this preparation:

Assay for Iron.—Transfer exactly 25 cc. of Solution of Iron and Ammonium Acetate to a 500-cc. Kjeldahl flask and heat gently until the material begins to char, remove the heat, allow

the flask to cool, add 25 cc. of concentrated sulphuric acid and heat strongly for one hour, remove the heat and add 25 cc. of concentrated nitric acid and again heat strongly for about twenty minutes, again remove the heat, add 25 cc. of solution of hydrogen dioxide and again heat strongly until the solution assumes a pale yellow color. Dilute this solution with about 100 cc. of distilled water, and then add ammonia water until the solution is alkaline to litmus, filter, and wash the precipitated ferric hydroxide upon the filter with distilled water, and discard the filtrate and washings. Dissolve the precipitate upon the filter in hydrochloric acid, and then wash the filter, with distilled water, until free from color. Dilute the solution to about 100 cc., add about 2 Gm. of potassium iodide, allow to stand about fifteen minutes, cool, and titrate the liberated iodine with tenth-normal sodium thiosulphate, using starch T.S. as indicator. Each cc. of tenth-normal sodium thiosulphate corresponds to 0.005584 Gm. of Fe.

If the concentrated sulphuric acid is added to the solution before evaporating the foaming is very violent. By evaporating until the mass begins to char and then adding the acid the tendency to foam is practically eliminated. It was found that better results were obtained if the iron was first precipitated from the strong sulphuric acid solution and then dissolved in hydrochloric acid before titrating.

The following equations explain the several reactions occurring in this analysis:

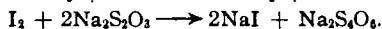
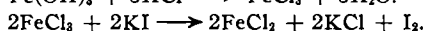
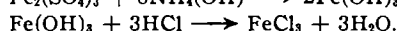
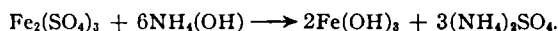


Table I shows the results obtained using this method.

TABLE I.—SOLUTION OF IRON AND AMMONIUM ACETATE, U. S. P. X (1).**

Number of sample.	Amount used.	*N/10 $\text{Na}_2\text{S}_2\text{O}_3$ consumed.	Gm. of Fe per 100 cc.
1	25 cc.	7.9 cc.	0.172 Gm.
2	25 cc.	7.85 cc.	0.171 Gm.
3	25 cc.	8.0 cc.	0.174 Gm.
4	25 cc.	8.1 cc.	0.176 Gm.
5	25 cc.	7.95 cc.	0.173 Gm.
6	25 cc.	8.15 cc.	0.177 Gm.
7	25 cc.	8.1 cc.	0.176 Gm.
8	25 cc.	8.15 cc.	0.177 Gm.
9	25 cc.	8.1 cc.	0.176 Gm.
10	25 cc.	8.2 cc.	0.178 Gm.

Average: 0.175 Gm. of Fe per 100 cc.

Percentage of error from the theoretical: 1.68%.

** Analysis of the Tincture of Ferric Chloride used in preparing this solution showed an average content of 4.452% Fe, therefore the solution analyzed, upon which Table I is based, should contain 0.178 Gm. of Fe in each 100 cc.

* Exactly 0.0976 N.

2. Solution of Peptonized Iron and Manganese, N. F. V (2).

In the absence of assay requirements for Solution of Peptonized Iron and Manganese, N. F. V (2), the following standard, based upon the present requirements for Peptonized Iron, N. F. V (2) and Soluble Manganese Citrate, N. F. V (2) is proposed:

Solution of Peptonized Iron and Manganese contains in each 100 cc. Peptonized Iron, corresponding to not less than 0.266 Gm. and not more than 0.325

Gm. of Fe, and Soluble Manganese Citrate, corresponding to not less than 0.114 Gm. and not more than 0.136 Gm. of Mn.

This proposed standard allows for a 5% variation of iron and manganese using the official chemicals.

This solution exhibits a marked tendency to foam when heated, but this condition can be remedied by evaporating in a Kjeldahl flask. As previously stated solutions which contain manganese, when evaporated to dryness, tend to crack the flasks. This can be avoided by evaporating gently until the material begins to char and then adding sulphuric acid. The acid not only greatly assists in destroying the organic matter but also prevents the flasks from cracking. If the acid be added to the solution before it has been evaporated the tendency to foam is greatly increased. Nitric acid and solution of hydrogen dioxide are also added to hasten the decomposition of the organic matter as well as to oxidize the iron and manganese.

The method of Kolle (7) for the separation of iron and manganese, which depends upon the precipitation of the iron from an acid solution by hexamethylenamine, was tried but was found to be unsatisfactory. The precipitation of the iron as hydroxide is not complete quantitatively and in addition very large quantities of hexamethylenamine are required.

Next it was attempted to precipitate the iron as ferric hydroxide using ammonia water. Ammonium nitrate was added to the solution before the addition of the alkali to prevent the precipitation of the manganese. It is believed that the manganese was not precipitated under these conditions but in every case about one-half of the manganese was held, apparently mechanically, by the ferric hydroxide.

Finally no attempt was made to separate the elements but aliquot parts of the solution containing both iron and manganese were used for the determination of each element. Neither iron nor manganese interferes with the determination of the other element by the process here given.

No effort was made to determine the iron or manganese gravimetrically since volumetric methods, being more rapid, are generally preferred.

The iron content of Solution of Peptonized Iron and Manganese, N. F. V (2) can be determined in exactly the same manner as in Solution of Iron and Ammonium Acetate, U. S. P. X (1).

The most accurate method for the determination of manganese was found to be the so-called bismuthate method (8). This method originally proposed by Schneider (9) in 1888, depends upon the property of bismuth tetroxide in the presence of large quantities of nitric acid, to oxidize manganous salts to permanganic acid. In 1895, Reddrop and Ramage (10) improved the method by substituting for bismuth tetroxide, which frequently contained some chloride, sodium bismuthate. Later, in 1904, Blair (11) found that even traces of hydrochloric acid vitiated the results when using a bismuth compound. The sodium bismuthate of Reddrop and Ramage (10), as well as the article supplied at present is free from even traces of chloride. Lundell (12) reported that the method was accurate to within 1 part in 500 and that the temperature of the solution may vary from 5° C. to 25° C. However, it was found that less opportunity for error is offered if the nitric acid mixture is cooled in an ice bath before adding the sodium bismuthate.

In the method originally proposed by Schneider (9) the permanganic acid was treated with a slight excess of tenth-normal hydrogen dioxide and the excess determined with tenth-normal potassium permanganate. The same technic was employed by Reddrop and Ramage (10). Ibbotson and Brearley (13) in 1901 recommended the use of tenth-normal ferrous sulphate in place of the tenth-normal hydrogen dioxide for the reason that ferrous sulphate does not react with ferric nitrate as does hydrogen dioxide. This modification can be applied to the particular conditions of this assay since the filtrate of sodium permanganate will also contain some ferric nitrate. Blum (14) recommended that the nitric acid concentration of the solution to which the sodium bismuthate was to be added should contain 20% to 40% of nitric acid by volume. He also compared the relative value of tenth-normal ferrous sulphate and tenth-normal ferrous ammonium sulphate and found that the solutions possessed about the same stability and that therefore they could be used indiscriminately.

The following method proved satisfactory for this preparation:

Assay for Iron.—Transfer exactly 25 cc. of Solution of Peptonized Iron and Manganese to a 500-cc. Kjeldahl flask and heat gently until the material begins to char, remove the heat, allow the flask to cool, add 25 cc. of concentrated sulphuric acid, and heat strongly for one hour. Remove the heat and add 25 cc. of concentrated nitric acid and heat strongly for about twenty minutes, again remove the heat, add 25 cc. of solution of hydrogen dioxide and again heat strongly until the solution assumes a pale yellow color. Dilute this solution and transfer to a 250-cc. volumetric flask, carefully washing the first flask with distilled water. If any undissolved material remains, add a slight excess of ammonia water and then nitric acid until the precipitate dissolves, transfer all of this solution to the volumetric flask, and add distilled water until the mixed liquids measure exactly 250 cc. and mix thoroughly. Allow to cool to room temperature, and then transfer exactly 100 cc. of this solution to a 250-cc. beaker, add about 5 Gm. of ammonium nitrate and then ammonia water until the mixture is alkaline. Filter off the ferric hydroxide, wash the precipitate once with distilled water, and discard the filtrate and washings. Dissolve the precipitate in hydrochloric acid, carefully washing the filter with distilled water until free from color. To this solution add about 2 Gm. of potassium iodide, and allow to stand about fifteen minutes, cool and titrate the liberated iodine with tenth-normal sodium thiosulphate, using starch T.S. as indicator. Each cc. of tenth-normal sodium thiosulphate corresponds to 0.005584 Gm. of Fe. This number multiplied by 10 gives the Gm. of Fe in each 100 cc. of solution of peptonized iron and manganese.

Assay for Manganese.—Transfer exactly 100 cc. of the solution contained in the volumetric flask, as prepared for the assay for iron, to a 250-cc. beaker, add 50 cc. of concentrated nitric acid, cool to about 5° C., and add from 0.5 to 1 Gm. of sodium bismuthate, mix thoroughly and allow to stand for one minute. Filter through asbestos, using a Buechner funnel, and wash the residue on the filter with distilled water until the washings are colorless. To this solution add exactly 20 cc. of tenth-normal ferrous sulphate, and titrate the excess of tenth-normal ferrous sulphate with tenth-normal potassium permanganate. Each cc. of tenth-normal ferrous sulphate consumed corresponds to 0.001098 Gm. of Mn. This number multiplied by 10 gives the Gm. of Mn in 100 cc. of solution of peptonized iron and manganese.

The following equations explain the several reactions occurring in this analysis.

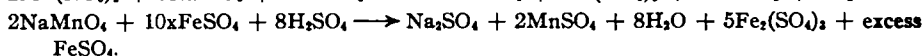


Table II shows the results obtained using this method.

TABLE II.—SOLUTION OF PEPTONIZED IRON AND MANGANESE, N. F. V (2).****

Assay for Iron.				
Number of sample.	Amount used.	Aliquot equivalent to.	*N/10 Na ₂ S ₂ O ₄ consumed.	Gm. of Fe per 100 cc.
1	25 cc.	10 cc.	6.2 cc.	0.337 Gm.
2	25 cc.	10 cc.	6.35 cc.	0.345 Gm.
3	25 cc.	10 cc.	6.1 cc.	0.332 Gm.
4	25 cc.	10 cc.	6.1 cc.	0.332 Gm.
5	25 cc.	10 cc.	6.2 cc.	0.337 Gm.
6	25 cc.	10 cc.	5.9 cc.	0.321 Gm.
7	25 cc.	10 cc.	6.2 cc.	0.337 Gm.
8	25 cc.	10 cc.	6.1 cc.	0.332 Gm.
9	25 cc.	10 cc.	6.2 cc.	0.337 Gm.
10	25 cc.	10 cc.	6.0 cc.	0.326 Gm.

Average: 0.3336 Gm. of Fe per 100 cc.

Percentage of error from the theoretical: 0.80%.

Assay for Manganese.				
Number of sample.	Aliquot equivalent to.	**N/10 FeSO ₄ added.	***N/10 KMnO ₄ required.	Gm. of Mn per 100 cc.
1	10 cc.	20 cc.	4.1 cc.	0.152 Gm.
2	10 cc.	20 cc.	4.15 cc.	0.152 Gm.
3	10 cc.	20 cc.	4.1 cc.	0.152 Gm.
4	10 cc.	20 cc.	4.2 cc.	0.151 Gm.
5	10 cc.	20 cc.	3.8 cc.	0.155 Gm.
6	10 cc.	20 cc.	4.2 cc.	0.151 Gm.
7	10 cc.	20 cc.	4.1 cc.	0.152 Gm.
8	10 cc.	20 cc.	4.1 cc.	0.152 Gm.
9	10 cc.	20 cc.	4.0 cc.	0.153 Gm.
10	10 cc.	20 cc.	4.15 cc.	0.151 Gm.

Average: 0.1519 Gm. of Mn per 100 cc.

Percentage of error from the theoretical: 0.39%.

* Exactly 0.0976 N.

** Exactly 0.0913 N.

*** Exactly 0.1077 N.

**** Analysis of the Peptonized Iron and Soluble Manganese Citrate used in preparing this solution showed an average content of 19.22% of Fe, and 17.435% of Mn, respectively; therefore this solution, upon which Table II is based should contain 0.3363 Gm. of Fe and 0.1525 Gm. of Mn per 100 cc.

3. Solution of Albuminized Iron, N. F. V (2).

In the absence of assay requirements for Solution of Albuminized Iron, N. F. V (2), the following standard, based upon the present requirements for Albuminized Iron, N. F. V (2) is proposed:

Solution of Albuminized Iron contains in each 100 cc. Albuminized Iron, corresponding to not less than 0.808 Gm. and not more than 0.997 Gm. of Fe.

This proposed standard allows for a 5% variation of iron using the official chemical.

Efforts to obtain Albuminized Iron, N. F. V (2) disclosed the fact that no manufacturer lists this item. It was possible, however, to obtain a similar product, namely, Iron Albuminated, Merck, containing 5% of Fe₂O₃. This contains approximately one-fifth as much iron as does the N. F. V (2) item. The solution was prepared using Iron Albuminated, Merck, but with the N. F. V (2) quantities.

The finished product differed from the official product only in the quantity of iron present. While this solution was not identical with that of the N. F. V (2) it is believed that, since the difference is only one of quantity of iron, the methods which follow could be used satisfactorily for the Solution of Albuminized Iron, N. F. V (2).

This solution exhibits the tendency to foam noted under the preceding preparations. Treatment similar to that used for Solution of Iron and Ammonium Acetate, U. S. P. X, (1) yielded satisfactory results. It was found that this preparation could also be assayed with a fair degree of accuracy by the method of the German Pharmacopœia VI (3). The latter method while apparently very simple does not yield consistent results unless very carefully controlled, because the excessive foaming frequently causes loss of iron. It will be observed that of the three preparations discussed in this report, Solution of Albuminized Iron, N. F. V (2) is the only one which does not contain glycerin. This probably explains the fact that this solution alone can be successfully assayed by the method of the German Pharmacopœia VI (3) for the determination of iron in Liquor Ferri Albuminati, P. G. VI (3).

The following method proved most satisfactory for this preparation.

Assay for Iron.—Transfer exactly 25 cc. of Solution of Albuminized Iron to a 500-cc. Kjeldahl flask and heat gently until the material begins to char, remove the heat, allow the flask to cool, add 25 cc. of concentrated sulphuric acid and heat strongly for one hour. Remove the heat and add 25 cc. of concentrated nitric acid and heat strongly for about twenty minutes, again remove the heat, and add 25 cc. of solution of hydrogen dioxide and again heat strongly until the solution assumes a yellow color. Dilute this solution with about 100 cc. of distilled water, and then add ammonia water until alkaline, filter, and wash the precipitated ferric hydroxide upon the filter with distilled water, and discard the filtrate and washings. Dissolve the precipitate upon the filter in hydrochloric acid, and then wash the filter with distilled water until free from color. Dilute the solution to about 100 cc., add about 2 Gm. of potassium iodide, allow to stand about fifteen minutes, cool, and titrate the liberated iodine with tenth-normal sodium thiosulphate, using starch T.S. as indicator. Each cc. of tenth-normal sodium thiosulphate corresponds to 0.005584 Gm. of Fe.

Table III shows the results obtained using this method.

TABLE III.—SOLUTION OF ALBUMINIZED IRON, N. F. V (2).*

Number of sample.	Amount used.	**N/10 Na ₂ S ₂ O ₃ consumed.	Gm. of Fe per 100 cc.
1	25 cc.	7.9 cc.	0.172 Gm.
2	25 cc.	7.85 cc.	0.171 Gm.
3	25 cc.	7.9 cc.	0.172 Gm.
4	25 cc.	8.0 cc.	0.174 Gm.
5	25 cc.	7.95 cc.	0.173 Gm.

Average: 0.172 Gm. of Fe per 100 cc.

Percentage of error from the theoretical: 1.71%.

* Analysis of the Albuminated Iron used in preparing this solution showed an average content of 3.50% of Fe, therefore the solution analyzed, upon which Table III is based, should contain 0.175 Gm. of Fe in each 100 cc.

** Exactly 0.0976 N.

The following method proved fairly satisfactory for this preparation.

Assay for Iron.—Evaporate the alcohol from 20 cc. of Solution of Albuminized Iron and add to the residual liquid while hot 20 cc. of solution of hydrogen dioxide. Shake and allow to

stand until the evolution of gas ceases. Add 30 cc. of diluted sulphuric acid and heat on a water-bath until the froth produced by the albumin has disappeared. Remove the excess of solution of hydrogen dioxide by carefully adding a solution of potassium permanganate (2% to 5%) until a faint but persistent pink color appears. Filter and add about 2 Gm. of potassium iodide to the filtrate, allow to stand about half an hour, and then titrate the liberated iodine with tenth-normal sodium thiosulphate, using starch T.S. as indicator. Each cc. of tenth-normal sodium thiosulphate corresponds to 0.005584 Gm. of Fe.

Table IV shows the results obtained using this method.

TABLE IV.—SOLUTION OF ALBUMINIZED IRON, N. F. V (2).*

Number of sample.	Amount used.	**N/10 $\text{Na}_2\text{S}_2\text{O}_3$ consumed.	Gm. of Fe per 100 cc.
1	20 cc.	6.45 cc.	0.175 Gm.
2	20 cc.	6.3 cc.	0.172 Gm.
3	20 cc.	6.35 cc.	0.173 Gm.
4	20 cc.	6.35 cc.	0.173 Gm.
5	20 cc.	5.9 cc.	0.160 Gm.

Average: 0.173 Gm. of Fe per 100 cc. (rejecting No. 5).

Percentage of error from the theoretical: 1.12%.

* Analysis of the Albuminized Iron used in preparing this solution showed an average content of 3.50% of Fe, therefore the solution analyzed, upon which Table IV is based, should contain 0.175 Gm. of Fe in each 100 cc.

** Exactly 0.0976 N.

SUMMARY.

Satisfactory methods have been devised for the analysis of Solution of Iron and Ammonium Acetate, U. S. P. X (1), Solution of Peptonized Iron and Manganese, N. F. V (2) and Solution of Albuminized Iron, N. F. V (2).

The method given in the U. S. P. X (1) for the assay for iron in Solution of Iron and Ammonium Acetate, U. S. P. X (1) does not yield true results and should be replaced by a more accurate and dependable method.

Albuminized Iron, N. F. V (2) cannot be obtained at present on the drug market and it seems advisable to change the requirements for this item or to devise a new formula for preparing the Solution of Albuminized Iron, N. F. V (2).

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