

more frequently. During some titrations it may be necessary to readjust the galvanometer by means of resistance R_1 , especially if an instrument with a small scale is used. Vigorous stirring of the reaction mixture is necessary and is best accomplished by a small motor stirrer. It is well to wait thirty seconds after each addition of reagent to allow the galvanometer reading to become constant. The end-point is characterized by a sudden large deflection, *i. e.*, dE/dV , the rate of change of the E. M. F. of the titration cell with a small change in concentration of the reagent, approaches a maximum. It was observed that concordant results could be obtained when using the graphite or silicon carbide electrodes if, after each titration, the electrodes were immersed in cleaning solution, followed by thorough washing with distilled water. This apparatus is being used at the present time in these laboratories for the titration of alkaloids. A report of the work will appear shortly.

SUMMARY.

1. The use of graphite-platinum, tungsten-platinum and silicon carbide-platinum electrode pairs with a vacuum-tube titration apparatus has been suggested and illustrated.
2. The apparatus has been applied to the titration of some ferrous iron compounds of the U. S. P.

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A NOTE ON THE ASSAY OF REDUCED IRON.*¹

BY MARGARETHE OAKLEY AND JOHN C. KRANTZ, JR.

INTRODUCTION.

Reduced iron has found a place in practically all of the pharmacopœias of the world. In some, the evaluation is expressed in terms of metallic iron and in others, the total iron content is employed. Winter (1) reviewed these various standards in 1913. The eighth revision of the United States Pharmacopœia employed the iodimetric process of assay. The ninth and tenth revisions employed the well-known mercuric chloride method. The British Pharmacopœia specifies the copper sulphate procedure; this method depends upon the displacement of the copper by the iron. In all of these methods, the ferrous or ferric oxide present in reduced iron remains unattacked by the reagents employed. In 1909 Frerichs (2) reviewed

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¹ From the Bureau of Chemistry, Maryland State Department of Health.

the various assays and recommended the copper sulphate method on the basis of its being capable of a greater degree of precision.

Owing to the fact that this method has been continued in the British Pharmacopoeia of 1932, in which only 80 per cent of metallic iron is required, the authors decided to investigate the method and compare it with that of the U. S. P.

EXPERIMENTAL.

Three commercial grades of reduced iron were mixed and sifted through a number 100 sieve. Assays were conducted by the method recommended for the U. S. P. XI and by the following modification of the method of the British Pharmacopoeia. The difference between the U. S. P. X and U. S. P. XI methods lies in the fact that in the latter the mercuric chloride solution and reduced iron are heated together on a water-bath for ten minutes instead of boiling for five minutes.

The modified British Pharmacopoeia method is as follows:

"Transfer to a 100-cc. volumetric flask about 0.6 Gm. of reduced iron accurately weighed. Add 30 cc. of copper sulphate T.S. heated to its boiling point. Shake the mixture frequently and vigorously during ten minutes. Cool to 25° C. and add sufficient distilled water to make 100 cc. Mix thoroughly and filter. To exactly 25 cc. of the filtrate, add 20 cc. of diluted sulphuric acid and titrate with tenth-normal potassium permanganate. Each cc. of tenth-normal potassium permanganate corresponds to 0.005584 Gm. of Fe."

The results obtained on the same sample of reduced iron by each of the two methods are shown in Table I.

No.	Modified B. P. Method.	U. S. P. XI Method.
1	98.30	93.85
2	99.02	95.58
3	99.01	94.55
4	98.62	95.90
5	98.38	95.43
6	98.31	95.38
7	98.85	94.78
8	98.30	96.30
9	98.18	95.50
10	98.32	...
11	98.90	...
12	98.48	...
13	98.00	...
14	98.30	...
Mean	98.49	95.25

The probably error of a single determination of the modified British process calculated by the formula $P.E. = \pm 0.6745 \sqrt{\frac{\sum v^2}{(n-1)}} = 0.23$ per cent. By the U. S. P. XI process the probable error is ± 0.48 per cent.

Obviously the modified British process is less cumbersome than the mercuric chloride method and according to the analysis of the data set forth has advantage of a higher degree of precision. The difference between the mean of the two determinations is approximately 3 per cent. Since the purity of the substance is based upon the elementary iron content, it is manifestly important to determine which of the two procedures more closely approximates the theoretical value.

In order to determine the absolute accuracy of the two methods a sample of powdered electrolytic iron was obtained through the courtesy of Dr. George D. Beal. This iron assayed between 99 and 100 per cent by direct titration with potassium permanganate after acid solution.

With the sample of pure iron both the U. S. P. and the modified British methods gave results between 99 and 100 per cent.

A sample of iron was prepared by thoroughly mixing 95 parts of powdered electrolytic iron with 4 parts of ferric oxide, 0.5 part of ferrous sulphide and 0.5 part of ferrous phosphide. This mixture containing 95 per cent of metallic iron was submitted to analysis by both methods.

The results obtained on this adulterated sample are set forth in Table II.

No.	Modified B. P. Method.	U. S. P. XI Method.
1	98.11	95.10
2	97.57	94.71
3	96.85	96.56
4	98.09	95.17
5	97.28	94.60
6	94.75	94.20
7	97.95	...
8	94.18	...
9	98.00	...
10	98.40	...
11	98.20	...
12	98.20	...
13	98.72	...
14	98.42	...
Mean	97.48	95.06

It is obvious that in the presence of these impurities the modified method of the British Pharmacopœia fails to give results which correspond closely to the absolute content of elementary iron.

CONCLUSION.

1. The presence of ferric oxide, ferrous sulphide and ferrous phosphide in a sample of reduced iron vitiates the results obtained by the copper sulphate method. The mercuric chloride method gives absolute values in the presence of these impurities.

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ASSAY METHODS FOR SALTS OF ORGANIC ACIDS.*

BY RICHARD M. HITCHENS.

The assay methods for alkali salts of organic acids have been for many years the subject of much discussion. A survey of the problems involved is given by Clark.¹

* Scientific Section, A. PH. A., Washington meeting, 1934.

¹ Clark, *JOUR. A. PH. A.*, 15 (1926), 6.