THE RAPID ELECTROMETRIC DETERMINATION OF IRON IN SOME OPTICAL GLASSES.

BY J. B. FERGUSON AND J. C. HOSTETTER.

In the early stages of the development of the optical glass industry in this country, the determination of iron in the materials used, and produced in that industry, was one of the most important chemical analyses made, and was carried out on all raw materials, and frequently also on the glasses. The amounts of iron present in the glasses ranged from 0.01 to 0.02 per cent in the best heavy flints to 0.3 per cent in some experimental glasses, and at times, for purposes of comparison, an accuracy of 0.002 per cent in the determination of this element was desirable. This accuracy can be obtained upon ten-gram samples by the methods based upon the decomposition of the glasses with sulphuric and hydrofluoric acids and subsequent titration of the iron with potassium permanganate, but the use of sulphuric acid solutions necessitates many time-consuming precautions which may not be considered disadvantageous in a complete analysis of a glass with its manifold manipulations, but which should be eliminated if possible when many single determinations for factory control are desired. Fortunately at the time when a need for a more rapid method arose, an investigation of the use of the electrometric method for the determination of the end-points in the stannous chloride-potassium dichromate iron titration was nearing completion at the Geophysical Laboratory and the method was at once applied, first to sands,¹ later to the other raw materials, and finally to the glasses. The information obtained in the last application is presented in this paper.

The description of the electrometric method is in course of publication² but for clarity a few details will be repeated here. The principle is simple; the iron, in acid solution, is first reduced

¹ J. B. Ferguson, *J. Ind. Eng. Chem.*, **9**, 941 (1917).

² J. C. Hostetter and H. S. Roberts, *J. Am. Chem. Soc.* (Sept. No.)

by stannous chloride and then titrated with potassium dichromate, plotting the electromotive force against the volume of the oxidizer instead of using the inaccurate outside indicator.¹ The curve so obtained undergoes two inflections, the first upon the complete oxidation of the excess stannous chloride, and the second when the iron has similarly become all oxidized; from the location of these inflections the amount of the dichromate used up in the oxidation of the iron may readily be found. A typical curve which indicates the titration of the ferrous iron initially present in the glass in addition to the total iron is shown in Fig. 1. The method provides an accurate means of determining the

FIG. 1.—Typical curves obtained in the electrometric determination of ferrous and total iron in an experimental glass.

end-points and makes available for accurate work the dichromate titration with its many advantages over the permanganate titration, not the least of which is the use of hydrochloric acid solutions.

¹ Forbes and Bartlett have shown that the use of potassium ferrocyanide as an outside indicator in the dichromate titration may cause an appreciable error. *J. Am. Chem. Soc.*, 35, 1527 (1913).

The titration is carried out in a flask covered by a "titrating head" which serves the dual purpose of permitting the titrations to be carried out in a current of inert gas and of supporting the calomel half-cell and platinum electrode (see Fig. 2). The elec-

FIG. 2—Flask with "titrating head" in place. The latter carries the electrodes and acts as a cover for the flask during titration.

tromotive force developed is read on a simplified potentiometer designed by Roberts,¹ or by the method used by Hildebrand.²

Interfering Substances in the Glasses.—The optical glasses investigated by us were of the following types: Alkali-lead flint, borosilicate crown, light crown and barium crown, and con-

¹ To be described later.

² J. Hildebrand, *J. Am. Chem. Soc.*, **35**, 847-871 (1913).

tained only arsenic and boric acid among the substances which might be considered possible interfering substances. Antimony and manganese were not present. Arsenic is, however, reduced to the metal in hot concentrated hydrochloric acid solution by stannous chloride and consequently did not interfere with the determination of total iron. On the other hand, arsenic in the arsenious condition is oxidized by dichromate and therefore interferes with the accurate determination of ferrous iron.¹ Tests carried out on ferric chloride solutions indicate that boric acid also does not interfere; titrations of 6.1 and 6.0 cc. of 0.005 N $K_2Cr_2O_7$ were obtained in two experiments which were identical in all respects but one, namely, the addition of one gram of boric acid to one solution.

Preparation of Samples.—Samples should be pulverized with iron-free utensils such as an agate mortar and pestle. For the preliminary crushing the use of a brass cylinder² which loosely fits the pestle materially aids the process and reduces the flying of the glass fragments to a minimum. A powder which will pass 100 mesh is satisfactory.

Hydrofluoric Acid.—Hydrofluoric acid is generally considered responsible for the unsatisfactory end-point often obtained when a permanganate titration is carried out in its presence. To test its effect upon the dichromate titration the following experiments were made. The ferrous iron was determined by titration in solutions containing 100 cc. of 1 : 1 hydrochloric acid, 5 cc. dilute ferrous iron solution, and various amounts of 48-per cent hydrofluoric acid. The solutions were kept in flasks which had by test been shown to yield no appreciable ferrous iron to such solutions under more severe conditions than existed in these experiments and the titrations were made in the cold. The results are given in Table 1.

¹ Smooth curves are obtained when solutions of ferrous iron and arsenious arsenic in 1 : 1 HCl are titrated electrometrically. This is in accord with the well-known ability of certain ferrous salts to reduce arsenic in the higher (arsenic) state of oxidation in hydrochloric acid solution.

² Our standard laboratory practice.

TABLE I.

Cc. 48% hydrofluoric acid added.	Cc. 0.01 N $K_2Cr_2O_7$ solution.
0	6.7
5	6.9
10	6.9
15	6.9
25	7.0

These results indicate that in the cold the acid is without effect. In hot solutions such as were used in the analyses of glasses there was frequently a drifting end-point and since its irregular occurrence precluded the placing of the blame for it upon the acid itself, we were led to believe that there must at times be some impurity in the acid capable of being oxidized in hot hydrochloric acid solution by dichromate. The nature of this impurity is somewhat obscure but may well be organic¹ and volatile, because when the acid in question was evaporated alone in platinum no residue remained, but when evaporated with sulphuric acid an appreciable carbonaceous residue was usually obtained. The so-called C.P. hydrofluoric acid usually carries this impurity, so that its presence must be considered in any procedure that is to be of general use.

Glassware Tests.—Good analyses may be carried out in glass vessels in the place of platinum if pure hydrofluoric acid is available. This is possible because the rate of attack of any reagent, as for instance hydrofluoric acid, upon a glass powder,² is much more rapid than upon the vessel used as a container, and this is especially true when powdered optical glass is decomposed in flasks of chemically-resistant glass. For this purpose, however, the glass vessel most resistant to hydrofluoric acid would naturally be chosen, and to enable us to make a proper selection the following tests were made:

In each of three Erlenmeyer flasks of identical size (Jena, Fry and Pyrex) were placed 25 cc. of 1 : 1 hydrochloric acid, 5 cc. of

¹ The acid did not behave as though impurities such as sulphur dioxide, arsenious acid, etc., were causing the trouble. See "A Treatise in Quantitative Inorganic Analysis," J. W. Mellor, p. 463, (1913).

² Compare the rates of attack found by J. H. Davidson and W. E. S. Turner on glass powders consisting of differently-sized particles. *J. Soc. Glass Tech.* 11, 284 (1918).

48-per cent hydrofluoric acid and 0.5 cc. of concentrated sulphuric acid and the flasks were set on a hot steam bath for twenty minutes. The solutions were then removed from each flask, separately evaporated in platinum to remove the hydrofluoric acid, taken up in 150 cc. of 1 : 1 hydrochloric acid and the iron electrometrically titrated after reduction with stannous chloride. The iron (Fe) values obtained were Jena 1.92 mg., Fry 1.85 mg., and Pyrex 1.26 mg., indicating the superiority of Pyrex over the other two types in this respect. These tests were intended as comparative tests and not intended to be in the nature of blank determinations and were purposely carried out under conditions of much greater severity than those existing during an analysis. However, a blank determination for ferrous iron was made subsequently on a Pyrex flask and gave a negligible result.

Analyses in Glassware.—The analyses in glassware were carried out by first decomposing the glass in a Pyrex Erlenmeyer flask and then reducing the iron and titrating in the same flask without the removal of any precipitate which may have formed. In this manner the determination could be carried out in less than ten minutes and the procedure was applicable to those glasses such as flints, borosilicates and crowns which are either completely soluble in a mixture of hydrochloric and hydrofluoric acids or form insoluble precipitates which carry no appreciable quantities of iron. The procedure necessitates the use of pure acids or at least acids upon which definite blank determinations could be made, and usually a slight excess of glass powder was used which insured a minimum attack upon the flask. Comparative results upon an experimental light flint glass analyzed in glassware and also in platinum ware are as follows: In glassware 0.110 and 0.109 per cent iron (Fe), and in platinum ware 0.111 per cent iron (Fe). Most of the C. P. hydrofluoric acid which we obtained was too impure to be used with this procedure for accurate work, but served for the determination of the approximate value of the iron content if the titrations were rapidly carried out since the iron reacted with the dichromate much more rapidly than did the impurity carried by the hydrofluoric acid and thus made possible the locating of the end-point approximately. The curves A and

B, given in Fig. 3, are typical of the effect of this impurity; curve C is a normal curve.

FIG. 3—Titration of total iron. Curves A and B are the result of impurity in hydrofluoric acid used in decomposing the glass. Curve C is a typically normal curve. The end-points for A and B can still be located within a small error.

Platinum Ware.—The platinum used by us was of the purest grade imported before the war. Ordinary platinum as a rule carries an appreciable amount of iron and cannot be expected to yield a constant blank. For this reason only the purest platinum should be used, thus rendering negligible any errors due to the variable amounts of iron obtained from the platinum during different analyses.

Retention of Iron by Precipitates.—The retention of iron by the insoluble salts formed during the decomposition of a glass may be a source of serious error. Allen and Zies¹ state that in some cases as much as 50 per cent of the iron may be so retained. The following analyses confirm their observations. These analyses were made upon a series of light flint glasses which were decomposed with hydrofluoric and sulphuric acids.

¹ *J. Am. Ceram. Soc.*, 1, 739 (1918).

TABLE 2.

Retention of Iron by Lead Sulphate Precipitated in the Decomposition of Light Flint Glasses.

Glass No.	Total Fe.	Fe in lead sulphate.	Per cent total iron in lead precipitate.
43-1.....	0.105	0.043	41
43-3.....	0.193	0.117	61
43-4.....	0.032	0.003	9
43-5.....	0.099	0.072	73
45-3.....	0.179	0.049	27
45-6.....	0.150	0.091	60

The retention of iron (especially ferric) by barium and lead sulphates has been known for some years.¹ Our results given in Table 2 are of interest chiefly because of the variability in the amount of iron so retained. There was some evidence that indicated that this variability was due to the heat treatment of the precipitates inasmuch as more iron was held in those cases in which the solutions were evaporated to dryness than in those in which the evaporation of the sulphuric acid was not carried so far. Lead chloride, on the contrary, was invariably found to be free from even traces of iron, as might have been expected from the crystalline nature of this precipitate.

Total Iron.

The procedures which follow were used by us in some hundreds of glass analyses. The retention of iron by barium sulphate made necessary a separate procedure for glasses containing barium, and procedure (4) was used in place of procedures (2) and (3) when barium glasses were being analyzed. Procedure (1) was not used by us for these barium glasses because of lack of pure hydrofluoric acid. Since barium fluoride is known to be soluble in strong acids,² there is no good reason why this procedure should not give good results with these barium glasses.

Procedure (1).—For accurate work pure acids are required. Place 10 g. of glass powder in a Pyrex Erlenmeyer flask and cover

¹ Many references to this subject may be found in J. W. Mellor's, "A Treatise on Quantitative Inorganic Analysis," p. 611 (1913).

² Abegg's *Handbuch der Anorganische Chemie* 11, 2, p. 245.

with 25 cc. 1 : 1 hydrochloric acid. Add not quite enough hydrofluoric acid to decompose all the glass (the amount of hydrofluoric acid required may be calculated approximately and later determined more accurately by test). When the reaction ceases, add enough strong hydrochloric acid to bring the volume to about 150 cc. and the acid concentration to a little above the 1 : 1 ratio and then heat to boiling, reduce with stannous chloride, cool a few seconds and titrate electrometrically with 0.01 N dichromate. Wash several times by decantation with hot water¹ any particles of glass which may have escaped decomposition, transfer to suitable dish, dry over flame, weigh roughly and deduct the weight from the initial weight of charge. The whole operation can be carried out in less than ten minutes.

Procedure (2).—For accurate work with impure hydrofluoric acid. Place 5 g. of glass powder in a platinum dish and moisten with 5 cc. of 1 : 1 sulphuric acid. Add cautiously, a little at a time, 10 to 15 cc. concentrated (48%) hydrofluoric acid. Care must be taken in this operation lest a violent reaction take place and cause a loss of much of the sample. When the reaction has apparently ceased, heat, at first gently and then more strongly, until the sulphuric acid fumes copiously and any organic matter present is decomposed. For this evaporation a Hillebrand radiator² may be used to advantage. We used a simpler and cheaper device which worked very satisfactorily. The platinum vessel was placed upon a nichrome triangle which was fitted with silica protecting tubes and the arms of the triangle were bent so that the vessel was held the desired distance above an electric hot plate. Around the triangle and crucible was placed an alundum or similar ring 5–8 cm. in height. After the sulphuric acid has fumed copiously for a few minutes the platinum dish is set aside to cool, and when cold its contents are taken up in 150 cc. of 1 : 1 hydrochloric acid and the iron determined electrometrically in this solution.

Procedure (3).—It sometimes happens when procedure (2) is

¹ This will remove any precipitated lead chloride which may be present.

² W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks." U. S. Geol. Surv. *Bull.*, 422, 31 (1910).

used that the organic matter does not coagulate but is suspended in the hydrochloric acid solution in such a fine state of subdivision that it is able to reduce the dichromate and thereby be a source of error. To avoid this, the contents of the platinum dish may be dissolved in just enough hot 1 : 1 hydrochloric acid to prevent the precipitation of the sulphates. This solution is cooled and the insoluble chlorides filtered off and washed several times with cold water. To the filtrate is added a few cc. of 0.1 N alum solution and the alumina and iron are then precipitated hot with ammonia. The iron and alumina are filtered off, washed with hot water and then dissolved with hydrochloric acid from the filter. The hydrochloric acid solution thus obtained is used for the titration. The organic matter either runs through the filter when the iron and alumina are being filtered, or is left on the filter when these are dissolved. The alumina gives more bulk to the precipitate and if but a little is used materially assists in the operation. Suitable blanks must, of course, be made.

Procedure (4).—Since barium sulphate is not appreciably soluble in hydrochloric acid, the iron in this sulphate is lost if procedures (2) or (3) are used with glasses containing barium. The glass may be decomposed as in procedure (2) and the contents taken up in hydrochloric acid as in procedure (3), with the exception that enough acid is used to dissolve and prevent the precipitation of the sulphates other than barium. The solution is filtered hot and the precipitate washed with hot water. The filtrate is cooled and again filtered. This second filtrate contains part of the iron and little, if any, lead or barium. The rest of the iron is in the barium sulphate. The barium sulphate precipitate is ignited in a platinum crucible, fused with sodium carbonate, leached with water, filtered and washed.¹ The sulphuric acid is thus separated from the barium and iron and these are dissolved in hydrochloric acid. The iron from the glass is thus obtained in two acid solutions which can be used for an electrometric titration. They cannot

¹ According to W. F. Hillebrand, when sulphur is determined in rocks by first fusing with sodium carbonate and then leaching with water, a very little iron is to be found in the filtrate with the sulphates. (*U. S. Geol. Surv. Bull.*, 442, 139 (1910). In our experience with procedure (4) the amount of iron in the filtrate was always negligible.

be mixed, else the barium would again be precipitated as sulphate and might remove some of the iron. The titration may be carried out directly, or the iron may be precipitated as in procedure (3), although this would not be necessary in the case of the iron from the barium sulphate, but might be in the case of the other solution.

Ferrous Iron.—Ferrous iron may be determined in glasses provided no other reducing material is present. For this purpose the following procedure was devised, based upon the experiments given earlier in this paper, which showed that hydrofluoric acid and the impurity it usually carries do not react with 0.01 N solutions of dichromate in the cold.

Procedure: 10 g. of the glass powder (glasses other than barium crown) are placed in a Pyrex Erlenmeyer flask with 50 cc. 1 : 1 hydrochloric acid and the acid boiled to expel all air from the glass. The flask is then covered with a funnel through which a glass tube is inserted and by means of which nitrogen or carbon dioxide (freed from oxygen) can be passed through the flask. After the air has been expelled from the flask, 20 cc. of hot concentrated hydrofluoric acid which has previously been boiled for a few minutes to expel the air is added. A violent reaction takes place, and care must be exercised if an accident is to be avoided at this stage. As soon as the reaction is over, enough freshly boiled hydrochloric acid is added to bring the volume to 150 cc. and the acid concentration to a 1 : 1 value. The solution is then cooled in the atmosphere of nitrogen. When cold, the funnel and tube are removed quickly and the titration head inserted in their place. The titrations are then carried out. With the barium crown glasses the procedure is slightly modified because this glass is slightly decomposed by strong hydrochloric acid. The glass powder is first moistened with water (25 cc.) and no acid is added until all the air has been expelled by boiling for some minutes.

Blank Determinations.—The necessity for careful blank determinations is so apparent that it need not be stressed here. A true blank for the total iron determinations would require the use of an iron-free glass or silica powder. This we did not have, and with procedures (2), (3) and (4) we substituted, for the blank,

the iron value obtained when the procedure was carried out without a glass powder. The blank usually obtained in this manner amounted to from 0.2 to 0.5 cc. of 0.01 N dichromate, although in a few cases the hydrofluoric acid carried sufficient iron to materially raise these figures. The blank with procedure (1) was this blank minus the iron value obtained when the sulphuric acid alone was evaporated in platinum and the residue taken up in hydrochloric acid and titrated electrometrically, from which the hydrochloric acid blank had previously been taken. With our pure platinum we found practically the same blank for procedures (1), (2), (3) and (4).

The chemicals and glassware used in the ferrous iron determinations gave no appreciable titration with dichromate, a fact previously mentioned under the discussion of the ferrous iron determination.

The procedures previously outlined were frequently used by us during the years 1917 and 1918 and some of our results have already been published.¹ Our results upon the ferrous iron content of glasses have not previously been published, nor do we find any record of any one having attempted such analyses in the past. It is true that several investigators² have studied the relation between the total iron content and the color of certain glasses, and therefore it is the more surprising that no previous attempts have been made to determine the ferrous iron content since the green color so often obtained in many glasses containing much iron is generally ascribed to this ferrous iron. The ferrous iron content of good optical glass is so minute a quantity that any investigation of the relation of ferric and ferrous iron to the transmission of such optical glasses must be carried out upon special glasses containing appreciable quantities of iron. A number of these special iron-bearing optical glasses which had been prepared, were analyzed by us for both ferric and ferrous iron. The relative amounts of ferrous iron were found to vary considerably with the composition of the glass and with several other

¹ Hostetter, Roberts and Ferguson, *J. Am. Ceram. Soc.*, **2**, 356-372 (1919).

² C. Dralle, *Chem. Ztg.*, **24**, 1132-6 (1900); R. Zsigmondy, *Ann. d. Phys. u. Chem.*, [4] **4**, 60 (1901).

factors which need not be gone into here but which will be treated in a subsequent paper dealing with these glasses. A few representative analyses will be cited as indicative of the order of magnitude the ferrous iron content may assume in iron-bearing glasses.

TABLE 3.
Total and Ferrous Iron Found in Some Experimental Glasses.

Glass No.	Type of glass.	Total iron as Fe.	Ferrous iron as Fe.	% of total Fe which is in ferrous form.
43-1.....	Light Flint	0.103	0.0112	10.8
43-5.....	Light Flint	0.098	0.0117	12.0
43-6.....	Light Flint	0.101	0.0078	7.7
45-2.....	Light Flint	0.099	0.0207	20.9
45-5.....	Light Flint	0.110	0.0168	15.3
43-2 ^a	Light Flint	0.157 0.158 0.197	0.0224	14.3
41-1.....	Barium Crown ^b	0.138	0.0241	12.3
61-1.....	Barium Crown	0.136	0.0148	8.5
41-2.....	Barium Crown	0.229	0.0334	14.6
61-2.....	Barium Crown	0.230	0.0319	13.8
73-2.....	Barium Crown	0.214	0.0816	38.2
73-4.....	Barium Crown	0.073	0.0280	38.3
49-3.....	Ordinary Crown ^b	0.068	0.0047	6.8
49-4.....	Ordinary Crown	0.078	0.0054	7.0
49-1.....	Ordinary Crown	0.170	0.0109	6.3
85-2.....	Ordinary Crown	0.067	0.0109	16.3
85-5.....	Ordinary Crown	0.125	0.0319	25.5

^a The first three determinations (two ferric and one ferrous) upon glass 43-2 by Ferguson and the last two by Hostetter upon different pieces of glass from the same thread-pot.

^b The values given for the iron in the ferrous condition in the barium crown and ordinary crown glasses may include some arsenious arsenic due to the presence of this element in these glasses, which were prepared upon the assumption that in glasses all the arsenic exists in the arsenic condition. Allen and Zies have since shown that some arsenic may be present in the arsenious condition. (See *J. Am. Ceram. Soc.*, 1, 739-86 (1918).)

Summary.

The results of the application of the electrometric determination of iron with stannous chloride and potassium dichromate are discussed in this paper. The electrometric method enables one to

make rapid and accurate analyses for both ferric and ferrous iron provided interfering substances are absent. Under favorable conditions such an analysis can be made in ten minutes and may be carried out in glassware. Four different procedures are described for total iron and one for ferrous iron. A number of analytical results, including many ferrous iron determinations, are given. The ferrous iron content of the glasses proved to be dependent upon a number of factors and in some cases reached values in excess of 35 per cent of the total iron present.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.
July, 1919.