

fully corroborate the conclusions drawn from the experiments with casein, ovalbumin and gelatin.

TABLE III.—NITROGEN DISTRIBUTION IN SPINACH.

Magnesium oxide used for distillation. G.	Nitrogen of acid amides.		Nitrogen in magnesium oxide ppt.		Basic nitrogen.		Non-basic nitrogen.	
	Oven-dried Spinach. %	Spinach nitrogen. %.	Oven-dried Spinach. %.	Spinach nitrogen. %.	Oven-dried Spinach. %.	Spinach nitrogen. %.	Oven-dried Spinach. %.	Spinach nitrogen. %.
4.0	0.88	17.61	0.26	5.28	0.79	15.81	3.06	61.30
2.0	0.89	17.77	0.19	3.77	0.81	16.22	3.11	62.24
1.0	0.88	17.68	0.11	2.13	0.85	16.98	3.16	63.21

An attempt to distill the evaporated hydrolyzed spinach with 0.5 g. of magnesia was unsuccessful, the amount of the latter being insufficient to render the substance alkaline.

Summary.

1. The proportion of acid amide nitrogen obtained by Hausmann's method, as modified by Osborne and Harris, is constant and does not depend upon the quantity of magnesium oxide applied to the distillation.

2. The percentage of nitrogen contained in the magnesium oxide precipitate is the higher, the greater the quantity of magnesium oxide employed in distillation.

3. Conversely, the proportion of monoamino and diamino nitrogen is the smaller, the larger the amount of magnesium oxide used in distillation.

4. In order to obtain uniform results and a minimum of "humins" nitrogen it is necessary to use the least possible amount of magnesia which is sufficient to render the substance to be distilled alkaline. In the case of plant and animal materials the uniform application of one g. of magnesium oxide seems to be satisfactory, while in the case of proteins 0.5 g. suffices.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE HYDROCHLORIC ACID COLOR METHOD FOR DETERMINING IRON.

BY J. C. HOSTETTER.

Received August 2, 1919.

Iron occurs in determinable amounts in a surprisingly large number of materials. In the course of work on the raw materials for optical glass the determination of this element soon became the most pertinent criterion of quality, inasmuch as iron introduced into the glass produces color, with a corresponding absorption of light, and lowering of the usefulness of the glass.

In the preparation of solutions of these raw materials for the determina-

tion of iron it was observed that the color of the hydrochloric acid solution was a convenient index to the amount of iron actually present. The iron in these solutions was subsequently titrated electrometrically and experience soon indicated that a method for iron based on this color could be made to yield results sufficiently accurate for average control work. The subject was later studied somewhat more in detail and the present note gives the results of experiments undertaken to establish conditions for the development of this color, the effects of acids and salts, the precision attainable, and also certain applications of the method as finally developed. Several interesting lines of research were suggested by these experiments but, unfortunately, time was not available for other investigation than that necessary for the development of an analytical procedure.

The yellow color developed by ferric chloride in hydrochloric acid solution has been used as an indicator in the direct determination of iron by titration with stannous chloride,¹ the disappearance of the color indicating complete reduction of the iron. Similarly, the appearance of the yellow color is used as an indicator in the determination of tin by titration with ferric chloride.² Advantage has also been taken of the color of ferric chloride solutions in the development of color standards for use in drug assays.³ The application of this color to the determination of iron was proposed by Hüttner in 1914,⁴ but has received very little, if any, recognition; his results will be presented later. Reference will also be made in the course of the text to the older investigations of Müller on the change of color of ferric chloride solutions under different conditions. The researches of Schaer on the color of solutions of iron salts should also be noted here.⁵

The color produced by ferric chloride in hydrochloric acid solution has been investigated by Donnan and Bassett, who attribute it to the formation of some negative ion since, under electrolysis, the color moves toward the anode.⁶ Three colored crystalline hydrates of $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl}$ have been described by Roozeboom and Schreinemakers⁷ and probably the color developed in solution arises from these, or similar, compounds.

Method of Study.

The colors developed by ferric iron in hydrochloric acid under definite conditions were compared with the color produced by a certain quantity

¹ W. W. Scott, *Standard Methods of Chemical Analysis*, 1917, p. 221.

² C. Mene, *Compt. rend.*, 31, 82 (1850).

³ H. V. Arny and C. H. Ring, *J. Ind. Eng. Chem.*, 8, 309-317 (1916).

⁴ *Z. anorg. Chem.*, 86, 341-357 (1914).

⁵ *Arch. Pharm.*, 239, 257-283, 340-353 (1901).

⁶ *J. Chem. Soc.*, 81, 955 (1902).

⁷ *Z. physik. Chem.*, 15, 591 (1894).

of iron under known conditions, taken as the standard. After a series of comparisons had been made the results, of course, could be transferred by calculation to any other basis and this was done in certain experiments. The standard ferric solution first used was made up from ferric alum, the actual iron content being determined by electrometric titration with 0.01 *N* potassium dichromate solution and also by precipitation with ammonia. Later, standard solutions were made up determinate by dissolving ferric oxide in 1 : 1 hydrochloric acid.

In the earlier work the color comparisons were carried out in test tubes or small cylinders, no optical devices being used to facilitate the comparison or to make it more sensitive. Later a color comparator developed by H. E. Merwin of this Laboratory, and soon to be described by him, was used to good advantage and all of the comparisons were repeated with the new device. The heights of the solutions compared varied from 10 to 100 mm. and settings could be made to 0.5 mm. in the lower range and to 2 or 3 mm. at the greatest height.

Sensitivity of Method.

The amounts of iron which were present in our materials ranged from 0.001% to 0.1% Fe_2O_3 . The iron content for the most part fell within the range of 0.005 to 0.02% and an accuracy of 25% on the lower, and of 10 to 15% on the higher amount was satisfactory. On a 10 g. sample, 0.01% corresponds to 1 mg. of ferric oxide; this amount of oxide in 25 cc. of acid can be readily determined colorimetrically within 10%.

Hüttner¹ states that a solution containing 1 part iron in 100,000 possesses a significant yellow color.²

It has been found in this study of the color that a solution of 0.02 mg. of ferric iron in 50 cc. of 1 : 1 hydrochloric acid shows a detectable color when viewed lengthwise against a white background through a layer 18 mm. in height. The color developed by $\frac{1}{2}$ this quantity of iron under the same conditions is barely perceptible even when compared with pure acid (1 : 1). This sensitivity is ample for most work, but when necessary it may be increased by using more concentrated acid, or by adding calcium chloride.³

A good idea as to the intensity of this coloration may be had from the fact that the color intensity of a peroxidized titanium solution (developed

¹ *Loc. cit.*, p. 346.

² Morgan, in a study of Mene's method for tin, has shown that the amount of ferric chloride necessary to produce a coloration at the end-point may be lessened by viewing a Bunsen flame through the solution; under these conditions the flame takes on a greenish color as soon as a trace of ferric iron in excess is added, and 0.035 mg. of ferric iron in 25 cc. may be detected in this manner. (*J. Anal. App. Chem.*, 2, 169 (1888). Taken from Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 310.)

³ Cf. *postea*.

under standard conditions¹) is, approximately, 16 times the intensity of color developed by an equal weight of iron in 1:1 hydrochloric acid when the height of the iron solution (containing 0.5 mg. of ferric oxide per cc.) is about 100 mm. This test was very kindly made by my colleague, Dr. H. E. Merwin. Exact comparison, however, could not be made since the hue of the iron solution was slightly yellower than that of the titanium solution. Both solutions were orange-yellow.

Permanency of Color.

Arny and Ring¹ state that the original acidulated solution of ferric chloride neither fades nor precipitates to a perceptible degree within two years. Experiments carried out in the course of this study showed definitely that no change of color took place within 2 or 3 weeks, and although longer time tests were not made it is probable that the colors of acidified ferric chloride solutions are fully as stable as stated by the above mentioned authors.

Relative Color Intensity.

The term "relative color intensity" used here is defined as the ratio of the depth of the standard solution to the depth of the test solution when matched. Expressed otherwise, it is the color intensity developed by a quantity of iron under certain conditions, as compared to the color intensity developed by the same amount of iron under the standard conditions. The solution used as a standard is defined by the concentrations of iron and of acid at a given temperature; these conditions are expressed on the graphs in Figs. 1 to 4.

Effect of Temperature upon Color Intensity.

The effect of temperature upon the color developed by ferric iron in hydrochloric acid was studied by comparing the color developed in a standard acid solution held at 30° with the color of another portion of the same solution heated, or cooled, to some other temperature. The color intensity increases with elevation of temperature and it was also found that the relative increase depends upon the concentration of iron in the solution—the more concentrated the iron solution the greater the increase produced by a given temperature rise until a concentration of 0.5 mg. of iron per cc. is reached, after which doubling the concentration causes very little, if any, change in the temperature coefficient. The measurements made in this series of tests are subject to two errors which could have been avoided only by the development of special apparatus. The first error was that caused by the temperature changing during a comparison, and the second was the formation of a mist in the tube above the hot solution developed by the condensation of hydrochloric acid and

¹ H. E. Merwin, *Am. J. Sci.*, 28, 119-125 (1909).

² *Loc. cit.*

moisture. The curves shown in Fig. 1 are the most representative that could be passed through points deviating by as much as 15% (maximum). The standard color for each series was the color produced by the same amount of iron in hydrochloric acid (18.8% HCl) held at 30°.

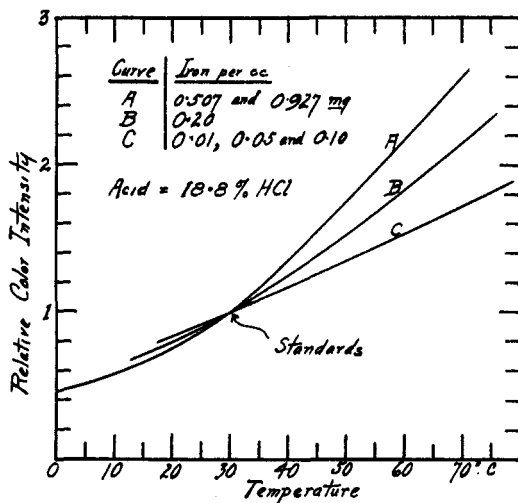


Fig. 1.—Showing the change of color intensity with temperature for hydrochloric acid solutions of ferric chloride containing different concentrations of iron. The color developed at 30° is taken as the standard for each solution studied. The temperature coefficient increases with the iron concentration. All solutions were made up in 18.8% HCl.

From the slopes of the curves near 30° the temperature coefficient is found to be approximately 1.7% per degree for dilute solutions containing up to 0.1 mg. of iron per cc.; that for solutions containing 0.2 mg. of iron per cc. the coefficient is 2.3% per degree, while for solutions containing 0.5 mg. or more per cc. the coefficient rises to 2.9% per degree.

The coefficients just given are approximate values obtained under the conditions described and apply only to these conditions. It is quite probable that the coefficient changes with acid concentration and the curves of Fig. 2 shortly to be described support this view. It is also probable that there is a time lag in the change of color on heating or cooling.

We may note here that Müller¹ found that an elevation of 30° increased the color intensity of a ferric chloride solution from 1 to 1.4 or 1.5, a result which agrees well with those plotted in Curve B.

Dependence of Color Intensity upon Acid Concentration.

Effect of Hydrochloric Acid.—It is a matter of common observation that the intensity of the color developed by a certain amount of ferric

¹ A. Müller, *Pogg. Ann. Ergänzungs-b.*, 6, 123-141 (1874).

iron in hydrochloric acid depends upon the concentration of the acid. Müller¹ pointed out in 1874 that the color intensity of a feebly acidified solution of ferric chloride decreases by dilution with water more rapidly than in a strictly inverse proportion to the increase of volume. He also showed that hydrochloric acid increases the "specific intensity" of ferric chloride solutions. Hüttner made a study of the effect of acid concentration on the color intensity and found that the intensity passed through a maximum at about 28% HCl. He carried out this test at 18°, using a solution containing 1 part of iron to 20,000. His results, recalculated to another acidity basis, are shown in the dotted curve on Fig. 2, which also gives some values obtained in my repetition of his work. The agreement is quite satisfactory.² It is interesting to call attention here to the lower intensification obtained at a higher temperature as shown by the curve for 27°.

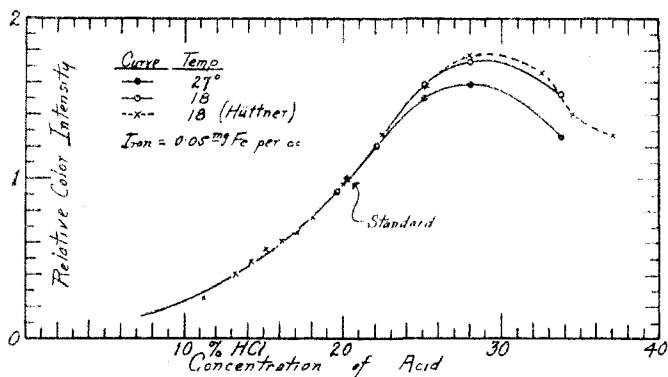


Fig. 2.—Showing the change of color intensity as the concentration of hydrochloric acid increases. The broken line gives the results obtained by Hüttner recalculated to a different standard. Note the change of relative intensification produced by a change of temperature. The color produced in acid of constant-boiling composition is taken as the standard.

In this detailed study of the effect of hydrochloric acid on the color intensity, iron solutions containing various concentrations of acid were matched against an iron solution made up in constant-boiling hydrochloric acid (20.24% HCl)³ containing the same amount of iron. The results obtained in this test are shown in Fig. 3; they may be summarized as follows: (1) The relative color intensity increases from about 0.20 at 9% acid to 1.4–2.4 at higher acidities (26 to 30% HCl) and then decreases

¹ *Loc. cit.*

² The acid available was, unfortunately, not sufficiently concentrated to permit the covering of the entire range studied by Hüttner. The label on the bottle claimed a sp. gr. of 1.18 to 1.19 and an acid content of 35.5 to 37.5 HCl, but actually the sp. gr. (15/15) was found to be only 1.172 corresponding to about 33.8% HCl.

³ Hulett and Bonner. *THIS JOURNAL*, 31, 390–393 (1909).

as the acid reaches its maximum concentration. (2) Below 20.24% HCl (taken as the standard), the relative intensity change is independent of the iron concentration, but above this concentration the change produced depends upon the amount of iron present. A solution containing 0.5 mg. of iron per cc. reaches a maximum color intensity of 2.4; a solution containing 0.2 mg. iron per cc. goes through a maximum of 1.9, while a dilute solution containing 0.007 mg. per cc. rises only to 1.5 in comparison with the color developed by these amounts of iron in 20.24% HCl. (3) The acid concentration at which the maximum development of color intensity takes place likewise depends upon the concentration of iron. For the dilute solution containing only 0.007 mg. iron per cc. the maximum is reached at about 26% acid; with higher iron concentrations the maximum takes place at successively higher acid concentrations reaching over 30% when the iron present amounts to 0.5 mg. per cc.

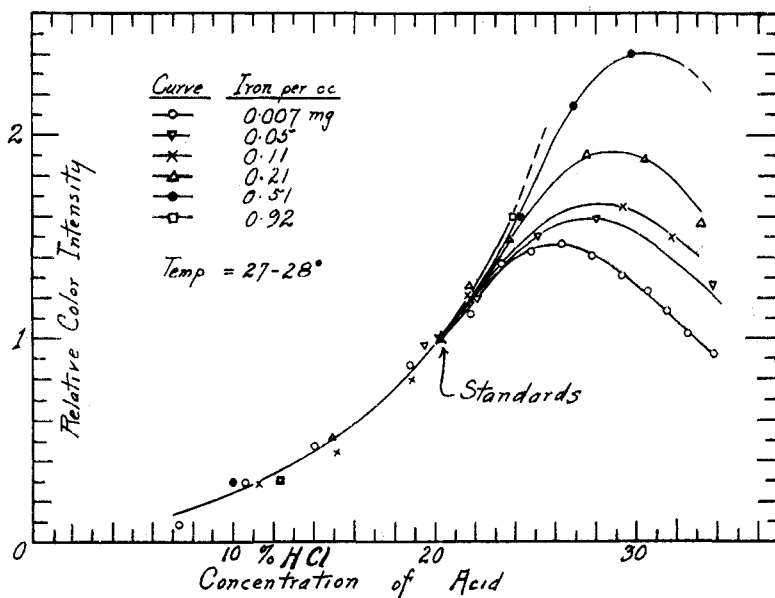


Fig. 3.—Showing how the intensification caused by increase of acidity depends upon the concentration of iron. The standard color is that produced by the given concentration of iron in constant-boiling hydrochloric acid.

The advantage of the increase of intensity gained by working at high acidities is only apparent because of the fact that the relative intensification is a function of the iron concentration. However, at 20% acid concentration this criticism no longer applies and this is the acid composition actually used in the final method. The disadvantage of working in a region where the color intensity is changing rapidly with acid concentration—as in the neighborhood of 20% acid—is more than coun-

terbalanced by the fact that such solutions of hydrochloric acid are very near the constant-boiling ratio and consequently may be boiled with little change in concentration. Inasmuch as solutions of materials must almost invariably be boiled in order to insure the complete solution of particles of iron scale, the use of this acid is decidedly advantageous.

The composition of constant-boiling hydrochloric acid changes very little with factors affecting the boiling point such as change of barometric pressure.¹ Furthermore, hydrochloric acid of the constant-boiling composition has very little odor compared to the more concentrated acid, the use of which may be extremely disagreeable, especially when the humidity is high.

While 1:1 acid made up from the usual concentrated acid is sufficiently near the constant-boiling composition for practical purposes, the concentration of the acid used should be checked by actual test, and failure to do so may lead to large errors. A very convenient method for doing this is to determine the density of the acid. Hulett and Bonner² give [D_4^{25}] as 1.09620, and the concentration as 20.242% HCl. The table of W. C. Ferguson³ gives the specific gravity corresponding to this concentration as 1.1012 at 15.55° referred to water at 15.55°.

Effect of Sulfuric Acid.—Inasmuch as sulfuric acid might conceivably be present in many test solutions the effect of this acid on the color of ferric iron in 1:1 hydrochloric acid was studied. Ferric sulfate solutions are not so highly colored as those of the chloride, and a bleaching effect from the addition of sulfuric acid would not have been unexpected. It was found, however, that the influence of sulfuric acid was similar to that of more hydrochloric acid, namely, to intensify the color up to a certain region and then to cause a fading, the maximum intensity appearing within the range 10 to 15 cc. of conc. sulfuric acid added to a solution of ferric iron in 1:1 hydrochloric acid contained in a total volume of 50 cc. It is probable that the change in relative color intensity caused by addition of sulfuric acid is a function of the iron concentration, and the temperature.

Dil. sulfuric acid was also added to the 1:1 hydrochloric acid solution and the increase of color developed under these conditions was found to be approximately equal to the intensity developed by equivalent additions of concentrated acid.

Effect of Acetic Acid.—It was not necessary, for our purposes, to study the effect on this color produced by acetic acid. An observation on this effect by Müller may be mentioned here, however. He states that the specific intensity of the color of a ferric chloride solution is increased by

¹ *J. Chem. Soc.*, 12, 128 (1860).

² *Loc. cit.*

³ Van Nostrand's *Chemical Annual* (Olsen), 1913, p. 403.

the addition of acetic acid by about $\frac{1}{10}$ of the increase caused by the addition of hydrochloric acid.¹

Effect of Boric Acid.—A solution of iron in 1:1 hydrochloric acid saturated with boric acid showed no measurable change of color when compared to another portion of the same iron solution free from boric acid. The iron solution contained 2 mg. of Fe per cc.

Effect of Salts on the Color Intensity.

The effect of salts on the color of hydrochloric acid solution of ferric chloride was studied by adding the salts to the iron solution (made up in 1:1 hydrochloric acid) and comparing the color of the resulting solution with that of the original. The salts so studied were those which would form in making a solution of the common raw materials for optical glass in hydrochloric acid, or which might be added in the course of an analysis. Owing chiefly to the limited solubility in 1:1 hydrochloric acid of some of the salts selected the effects obtained vary considerably. If conclusions may be drawn from such limited data we may say that the chlorides used tend to increase the color intensity;² sulfates decrease it, whereas acid sulfates cause very little change—the effect of the acid neutralizing the bleaching effect of the sulfate. The iron solution contained 2 mg. of Fe per cc.

TABLE I.
Effect of Salts on Color Intensity of Ferric Chloride in (1:1) Hydrochloric Acid.
(Iron present, 2 mg. per cc.)

Salt.	Concentration of salt, g. per 50 cc.	Color intensity of solution containing salt. (Standard = 1.)
CHLORIDES:		
Ammonium.....	5 ⁵	1.3
Barium.....	Saturated	1.0
Calcium ³	10	1.9
Lead.....	Saturated	1.3
Potassium.....	Saturated	1.2
Sodium.....	Saturated	1.2
SULFATES:		
Potassium.....	Saturated	0.7
Potassium pyro- (acidity ⁴ 34.6%)....	Saturated	1.0
Sodium acid (acidity 33.4).....	Saturated	1.0

Effect of Calcium Chloride.—The large intensifying effect found for calcium chloride may be attributed primarily to the fact that this salt is extremely soluble. Advantage was taken of this fact to investigate

¹ A. Müller, *Pogg. Ann. Ergänzungs-b.*, 6, 262-275 (1874).

² Donnan and Bassett (*Loc. cit.*) found (qualitatively) an intensification with calcium and magnesium chlorides but a bleaching effect with zinc and mercuric chlorides.

³ Hydrated, containing about 75% CaCl₂.

⁴ Expressed as sulfuric acid; values taken from label.

⁵ Nearly saturated. A saturated solution could not be used on account of the separation of mixed crystals of ferric and ammonium chloride.

in further detail the effect of a high concentration of chloride on the color being studied. This was done by adding successively larger quantities of the salt to portions of a standard iron solution and comparing the resulting colors. The calcium chloride was hydrated to the extent of 25% and this additional water content was considered in calculating the acidity of the final solution. Some of the effects found in the earlier experiments indicated that the intensifying effect brought about by calcium chloride is a function of the acid concentration and this was confirmed by the final series, the results of which are shown in Fig. 4. The

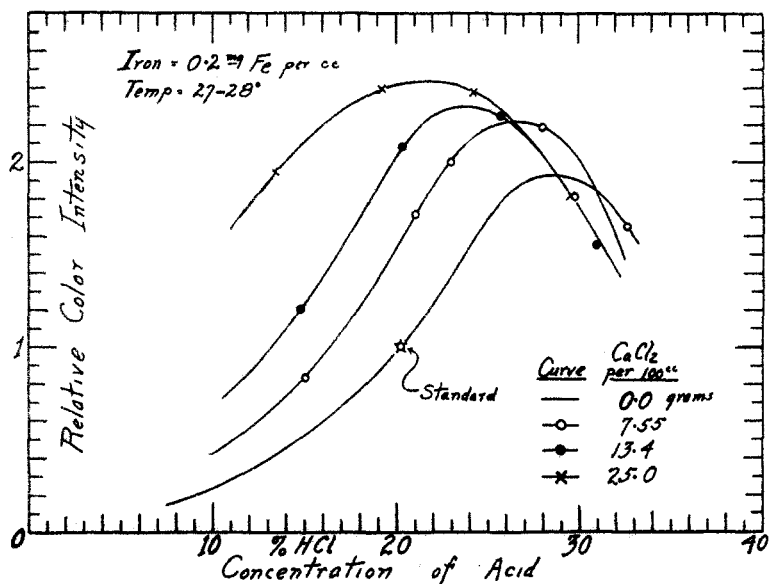


Fig. 4.—Showing the effect of calcium chloride on the change of color intensity caused by varying the concentration of acid. All the curves have been made by comparison with the color produced by 0.2 mg. of ferric iron per cc. of constant-boiling hydrochloric acid.

curves show the maxima which seem to be characteristic of the effect of acid on the color but the maximum occurs in more dilute acid as the concentration of calcium chloride is increased. It is quite probable that the increase of intensification caused by the chloride depends also on the iron concentration.

The results obtained on the action of salts on the color intensity of ferric chloride solutions indicate that correction should be made for the change of intensity caused by the salt, or, more accurately, the standard should be made up with equivalent quantities of the salt. The results given by Hüttner on the iron contents of certain metals, such as tin and zinc which form very soluble chlorides, may be too high because of the

intensifying effect of the chlorides, which apparently was not recognized by Hüttner. The addition of calcium chloride, if iron-free material is available, furnishes a simple method of increasing the color intensity for a given amount of iron, which may be useful in certain cases.

Interfering Substances.

It is obvious that colored metallic chlorides must be absent from the solution to be compared for color. In such cases the iron must first be separated from such metals and the procedure to be used for this separation will depend upon the nature of the interfering substance. The iron must also be separated from nitrates before color comparison can be made since the interaction between strong hydrochloric acid and the nitrate would form colored products which would obviously interfere. In these cases the iron is conveniently precipitated from the solution by ammonia after the addition of alum solution. The aluminous precipitate carries the iron hydroxide with it; the precipitate is readily filtered off and is dissolved in 1 : 1 hydrochloric acid.

It has also been found that samples of salts will frequently contain organic matter, sometimes in the form of wood fibers, or chips, which will develop a deep yellow color when boiled with hydrochloric acid. To avoid this difficulty the iron should be precipitated with ammonia after all the iron-bearing scale has been dissolved in acid; the precipitate is dissolved off the filter in cold acid which, for the short time of contact, does not acquire color from the organic matter caught on the filter.

If the iron is not fully oxidized it must be changed to the ferric condition by treatment with an oxidizing agent. Unfortunately, this adds another complication since, if excess of oxidizer is added, other products, such as chlorine, are liberated which interfere with the colorimetric determination because of the additional color produced thereby.

In case it is necessary to oxidize the iron it may be done with nitric acid, hydrogen peroxide, etc., after which the iron must be precipitated with ammonia, alum solution having previously been added. Hüttner treats the solution with potassium chlorate, boiling off the excess of free chlorine.

Solution of Iron Scale.

Iron may exist as an impurity in salts and oxides in several forms, and failure to recognize the nature of the iron-bearing material may lead to large errors in the determination of this element. Precautions similar to those found to be necessary in an exact determination of iron in sand¹ for instance, are not confined to mineral products and may be used to illustrate the importance of knowing the nature of the iron-bearing materials, if these are to be decomposed and the iron content determined. In most salts and oxides iron was found to be present to a greater or less

¹ J. B. Ferguson, *J. Ind. Eng. Chem.*, 9, 941-943 (1917).

extent as "scale" derived from iron apparatus used in the manufacturing processes. This scale is essentially an oxide of iron and is very resistant to the action of sulfuric and nitric acids which dissolve it very slowly. Hydrochloric acid, on the other hand, will dissolve this scale if the action takes place at an elevated temperature and is sufficiently prolonged. The presence of this scale can be readily demonstrated in many salts by dissolving from 10 to 100 g. of the salt in water or in dil. acid and examining the slight residue which usually remains. This is a severe test and many highly purified chemical reagents will show in a concentrated solution of this kind foreign material suspended throughout the solution or on the bottom of the beaker. The iron scale is usually magnetic and test with a hand magnet will demonstrate its presence.

The fact that iron scale of this sort is not readily dissolved by nitric or sulfuric acids indicates at once that analytical methods which decompose the sample with these acids will give low results for iron if no further precautions are taken. This has actually been found to be the case in certain materials—our results, obtained in hydrochloric acid solution, being higher, frequently by many times, than those found by the manufacturer of the chemical.

Iron occurring as the salt of the acid present in the chemical may in general be brought into solution by acids other than hydrochloric but our experience indicates that one must always assume the presence of iron scale and consequently take precautions to insure its decomposition.

Results Obtained with this Colorimetric Method.

A few results may be quoted here to show the agreement obtained with the hydrochloric acid color method for total iron and the electrometric method¹ on the same material. It is a pleasure to acknowledge here the assistance of Mr. E. C. Baum, of the Armour Fertilizer Works, in making these analyses.

TABLE II.
Total Iron as Fe_2O_3 .

Material.	Electrometric.	Colorimetric.
	0.046%	
Potassium carbonate.....	0.041	0.040%
	0.042	
Potassium carbonate.....	0.032	0.030
Potassium carbonate.....	0.022	0.020
Potassium carbonate.....	0.0276	0.028
Potassium carbonate.....	0.0090	0.010
Precipitated silica.....	0.251	0.250

Summary.

Conditions have been found under which the yellow color developed by dissolving ferric iron in hydrochloric acid may be used for the deter-

¹ J. C. Hostetter and H. S. Roberts, *THIS JOURNAL*, 41, 1337-1357 (1919).

mination of iron. The temperature coefficient for this color varies from 2 to 3% per degree depending on the concentration of iron and probably also on the acidity. The color developed by a given amount of iron varies with the acid concentration, reaching the maximum intensity at from 26 to 28% HCl. The relative increase produced by acid is greater the higher the concentration of iron; this is especially true above 20% HCl, but below this concentration the relative change is independent of the iron content. Inasmuch as solutions must frequently be boiled in order to insure the complete solution of iron present as "scale" the use of constant-boiling acid is recommended and its use has been found to be altogether satisfactory. The effects of salts on the color indicate that sulfates cause bleaching, and chlorides intensification; detailed study of the effect of the very soluble calcium chloride shows that an intensification of 2.5 may be attained by the addition of this salt, consequently when testing for iron in a very soluble chloride the standard iron solution must be made up to possess the same salt concentration.

Some applications of the method are given and certain results presented.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

ISOMORPHISM, ISOSTERISM AND COVALENCE.

BY IRVING LANGMUIR.

Received June 30, 1919.

In recent papers¹ I have described a theory of valence which I have called the octet theory. This theory is based upon and is essentially an extension of G. N. Lewis' theory of the "cubical atom."² According to this theory each bond between adjacent atoms in organic compounds corresponds to a pair of electrons held in common by the two atoms. Since in other types of compounds the number of pairs of electrons held in common is not always the same as the number of valence bonds that have usually been assumed I proposed that the number of pairs of electrons which any given atom shares with the adjacent atoms be called the covalence of that atom. It was then shown that the covalence of carbon is always 4, that of nitrogen is usually 3 or 4, while that of oxygen is 1, 2 or sometimes 3, etc.

The octet theory indicates that the number and arrangement of electrons in the nitrogen molecule, the carbon monoxide molecule, and the

¹ A simpler exposition of the theory and its applications is given by Elwood Hendrick, *Met. Chem. Eng.*, 21, 73 (1919), July 15th; Langmuir, *J. Frank. Inst.*, 187, 359 (1919); *THIS JOURNAL*, 41, 868-934 (1919); *Proc. Nat. Acad. Sci.*, 5, 252 (1919).

² G. N. Lewis, *THIS JOURNAL*, 38, 762 (1916).