flexible tin or lead pipe where such material can be used. The small unevenness commonly found in the quartz tubes does not seem to interfere with the expansion.

Durability of Copper Combustion Tube.—Copper tubes such as have been described have been in use with the gas furnace for as many as 1100 hours before being renewed. With the electric furnace, where the heat is much more uniform, the tube, which in this case is nickel-plated on the outside, may last even longer.

Advantage of Electric Furnace over the Gas Furnace.—By the electric furnace a source of probable error—that of combustible gases under certain atmospheric conditions contaminating the air supply of the respiration calorimeter—has been removed. It supplies more uniform heat. It is more economical than gasoline gas since even with much outside resistance the amount of heat lost is only a very small fraction of that wasted by a large gas furnace. There is no trouble in regulating the heat as there is with a varying gas supply.

THE PRECIPITATION OF THE IRON GROUP AND THE COMPOSITION OF CERTAIN FERRIC FORMATES.

By O. F. Tower.

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The difficulties of precipitating the metals of the iron group, *viz.*, iron, aluminium and chromium are well known. Many prefer to attempt no independent separation, but to precipitate them along with the zinc group by using both ammonium hydroxide and ammonium sulphide. This, however, entails a complex and rather tedious method of analysis, unless chromium is known to be absent. In case manganese is absent the metals of the iron group may be separated rather sharply by repeating the process of precipitation. After the first precipitation with ammonium hydroxide, the precipitate is dissolved in hydrochloric acid and the metals reprecipitated with ammonium hydroxide as before. In this way any zinc or nickel dragged down in the precipitation are fairly completely removed. The most complete method of separation, however, no matter what other common metals may be present, is to precipitate them as basic acetates. Furthermore, the presence of PO_4''' causes no complications when the basic acetate process is employed, provided sufficient $\overset{\cdots}{Fe}$ is present. In addition to causing the removal of the PO_4''', $\overset{\cdots}{Fe}$ is required to insure the precipitation of chromium. The great objection to the use of the method, however, is the great difficulty experienced in filtering and washing the precipitate of basic acetates.

On this account, in 1861, F. Schulze[1] recommended the use of ammonium formate for precipitating iron and aluminium, claiming that the basic formates are much easier to filter and wash than the corresponding acetates. This paper contains an account of an investigation of this point together with a few matters closely related to it.

Schulze's conclusions, in the main, have been confirmed. Both iron and aluminium can be practically completely precipitated by boiling with ammonium formate provided the solution is sufficiently dilute. The boiling need be continued only for a moment. The precipitate has a flocculent appearance and looks as if it could be filtered with great ease. Filtration is, however, not so rapid as Schulze describes, but can be accomplished in less time than in the case of the basic acetates. Chromium by itself is not precipitated by boiling with ammonium formate, but is carried down by basic ferric formate, hence the presence of Fe is required for the complete precipitation of the group. The presence of ammonium chloride is desirable, as it causes the precipitate to be thrown down in larger flakes, which facilitates filtration.

The procedure found to give the best results follows: After hydrogen sulphide has been expelled from the filtrate of the copper-tin group and iron, if present, has been oxidized (if Fe is not present, 5–10 cc. molar $FeCl_3$ must be added), add ammonium chloride, and then dilute the solution until the concentration of any one of the metals of the iron group does not exceed 1/100 molar, and heat the whole to boiling. Add about 10 cc. 4 *N* ammonium formate and continue to boil for about one minute. Filter hot, preferably with the suction pump. The group is then analyzed as usual, except that, of course, iron must be tested for in the original solution, or at least before the precipitation of the group.

The question arose as to the nature of the precipitate and the composition of the ferric formates in general. This is especially interesting in view of the recent work of Werner and his associates on the acetates of the metals of this group[2] and on the formates of chromium.[3] For example, Weinland and Gussmann[4] have been unable to isolate ferric triacetate by any of the methods given for its preparation. There crystallizes usually from strongly acid solutions containing ferric hydroxide and acetic acid a basic salt of a triferric base, *viz.*, $Fe_3(C_2H_3O_2)_6{}^{C_2H_3O_2}_{(OH)_2}$. H_2O, the formula indicating that only one acetate radical is replaceable. Another acetate containing one less hydroxyl group than this was also

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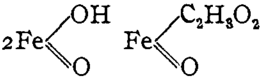
[1] *Chem. Centralblatt*, 1861, 3.

[2] See *Ber.*, 41, 3236 and 3447 (1908); 42, 2997 and 3881 (1909); *Z. anorg. Chem.*, 66, 157 (1910).

[3] Werner, *Ber.*, 41, 3449 (1908).

[4] *Ber.*, 42, 3881 (1909); and *Z. anorg. Chem.*, 66, 157 (1910).

prepared. The formula of basic ferric acetate is commonly given as $Fe(OH)_2C_2H_3O_2$. But the basic acetate precipitated in the usual manner was found to correspond to the formula $\left[\begin{matrix}C_2H_2O_2\\ Fe_3(OH)_2\\ O_3\end{matrix}\right]$, or, if the three iron atoms do not remain together, it may be written $Fe_2O_3.Fe(OH)_2C_2H_3O_2$ or



Ludwig[1] and also Scheuer-Kestner[2] claim to have prepared ferric triformate by allowing formic acid to act upon moist ferric hydroxide, the acid being present in large excess, crystals of the salt appearing after gradual evaporation. It was, however, found to be impossible to obtain the triformate by this or any of the other processes tried.

Ferric hydroxide was prepared by neutralizing ferric chloride with ammonium hydroxide, the precipitation being carried out at great dilution and both hot and cold. When precipitated in the cold ferric hydroxide dissolves readily in excess of cold formic acid; precipitated hot, it dissolves very slowly, but may be made to dissolve completely by continued agitation. When ferric hydroxide is boiled with excess of formic acid, complete solution does not take place. For the following experiments a paste of well washed ferric hydroxide and water was prepared, which contained about 1 mol. per liter. The formic acid used was a Kahlbaum preparation and had a specific gravity of 1.22.

A certain volume of the ferric hydroxide paste was treated with an equal volume of the formic acid, and the mixture shaken until complete solution took place. Whether evaporated in the air or under a desiccator, crystals were deposited upon the sides of the containing vessel. These were collected and kept in a desiccator over soda-lime for several days to remove the last traces of acid and then were transferred to one containing sulphuric acid, where they remained until analyzed. The mother liquor from these also deposited a good crop of fine crystals on the bottom of the containing vessels, which were dried in the manner just described. Formic acid was determined by treating a weighed quantity of the crystals with excess of 0.5 *N* sodium hydroxide, heating carefully for 15 minutes, letting cool, and transferring to a graduated cylinder. After the ferric hydroxide had completely subsided, an aliquot portion of the supernatant liquid was drawn off and titrated with 0.2 *N* hydrochloric acid. The method was rapid, although not very accurate, but sufficiently so for the present purpose. Iron was determined by filtering off the ferric hydroxide remaining in the cylinder, washing with

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[1] *Arch. Pharm.*, [2] 107, 1 (1861).

[2] *Compt. rend.*, 56, 1092 (1863).

hot water free from alkali, and weighing the residue in a platinum crucible. The accompanying table gives the results of the analysis of crystals obtained in all the ways mentioned above. It will be observed that they were of uniform composition, and that this composition does not correspond to the formula of the triformate but to that of a basic salt of a triferric base of the same composition as the acetate precipitated under similar conditions except for the molecule of water of crystallization. Various modifications of the process outlined above were tried but no normal ferric formate could be obtained.

Fe. Per cent.	CHO_2. Per cent.
31.2	60.6
31.5	61.5
34.0	60.5
32.4	60.2
33.2	59.6

Required for $Fe(CHO_2)_3$, Fe 29.3 per cent., CHO_2 70.7 per cent.

Required for $Fe_3\genfrac{}{}{0pt}{}{(CHO_2)_7}{(OH)_2}$, Fe 32.4 per cent., CHO_2 61.0 per cent.

The formate obtained dissolves very slowly in cold water, more rapidly in warm. The salt cannot be obtained again from the solution, as a more basic salt described below was the only one deposited. It also dissolves slowly in formic acid. Neither the acid nor the aqueous solution gives a precipitate with chloroplatinic acid, and no evidence has yet been obtained to show that one, and only one, of the CHO_2 radicals is ionized as was found by Weinland and Gussmann to be the case with the corresponding acetate.

When ammonium formate in excess is added to ferric chloride solution the liquid becomes dark red and on warming deposits a brown flocculent precipitate. This precipitate was filtered out, washed, dried and analyzed in the manner just described. The results of the analysis are shown in the accompanying table. The composition of the precipitate is evidently that of the second formula and is therefore analogous in composition to the basic acetate thrown down under similar conditions.

Fe. Per cent.	CHO_2. Per cent.
57.0	15.1
56.4	14.8
57.1	14.8

Required for $Fe(OH)_2CHO_2$, Fe 41.4 per cent., CHO_2 33.4 per cent.

Required for $\left[\begin{array}{c} CHO_2 \\ Fe_3(OH)_2 \\ O_3 \end{array}\right]$, Fe 56.5 per cent., CHO_2 15.3 per cent.

Whether ammonium chloride is present or not during the precipitation makes no difference in the composition of the precipitate. When a mixture of ferric chloride and ammonium formate in excess stands at ordinary temperature for several days an amorphous precipitate is deposited whose composition in the samples investigated does not correspond to that of the basic salt just described, as can be seen from the following table. The substance is richer in formate than the one precipitated hot. It corresponds somewhat closely in composition to the formula of a basic diformate, but I incline to the belief that it is a mixture of the basic monoformate with a small quantity of some formate richer in formic acid.

Fe. Per cent.	CHO_2 Per cent.
53.0	17.2
51.6	18.5
50.7	19.3

Required for $\left[\begin{matrix}(CHO_2)_2\\ Fe_3\ OH\\ O_3\end{matrix}\right]$, Fe 51.9 per cent., CHO_2 27.9 per cent.

Summary.

1. The iron group may be precipitated as basic formates, which filter somewhat more readily than the basic acetates.
2. The presence of iron is necessary for the precipitation of chromium.
3. It was found impossible by any of the methods heretofore described to prepare normal ferric formate. In its place was always obtained a good crystalline precipitate corresponding to the formula $Fe_3{(CHO_2)_7 \atop (OH)_2}$.
4. The basic formate precipitated under the usual conditions possesses a composition expressed by the formula $\left[\begin{matrix}Fe_3{CHO_2 \atop (OH)_2}\\ O_3\end{matrix}\right]$

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A RAPID AND ACCURATE METHOD FOR THE DETERMINATION OF TITANIUM.

BY O. L. BARNEBEY AND R. M. ISHAM.

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Having a number of determinations of titanium in rutile and iron ores to make and failing to obtain consistent results by use of the common methods the authors proceeded to investigate for a shorter yet accurate process for this determination. Low's method[1] adapted from Blair gives good results, but requires too much time for the ordinary analysis. This method was used in checking three series of analyses. Gooch's method was not tried as it seemed to have the same disadvantage as the other methods—requiring too much time to obtain a pure product of weighable titanium oxide.

Methods depending on the precipitation of titanic acid in boiling solutions containing sulphurous and sulphuric acids gave low results. Those requiring SO_2 or H_2S reduction of the iron and precipitation of the titanium with ammonia or by boiling with sodium or ammonium acetate and acetic acid were found to give high results when a large excess of iron was present, and required repeated treatments to completely remove the latter element.

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[1] Low's "Technical Analysis of Ores," p. 189.