used as the basis of calculating, as well as the calculated recovery of those series where the combinations of materials was used.

TABLE X.

	Series.	Nitrogen recovered. Per cent.	Calculated recovery. Per cent.	Nitrogen not recovered in the combinations of materials. Per cent.
Solid manure, fresh	3	19.78	....	....
Solid and liquid, fresh	4	38.61	....	....
Solid, leached	5	16.50	....	....
Solid and liquid, leached	6	26.94	....	....
Sodium nitrate	7	72.22	....	....
Sodium nitrate	8	75.03	....	....
Ammonium sulphate	17	65.84	....	....
Dried blood	18	54.83	....	....
7 and 3 in	9	27.89	28.94	1.24
8 and 3 in	10	35.66	35.07	....
7 and 4 in	11	48.14	44.14	....
8 and 4 in	12	51.62	48.84	....
7 and 5 in	13	26.90	25.60	....
8 and 5 in	14	31.07	32.87	5.48
7 and 6 in	15	38.95	34.25	....
8 and 6 in	16	43.80	40.27	....
17 and 5 in	19	27.02	30.11	10.26
18 and 5 in	20	26.48	26.92	1.63

The figures show that in six cases out of ten there was a gain on the combinations over the sum of the increase on the materials when they were used singly. Of the other four, 9 and 20 show but slight differences, and may be disregarded, and on 14 and 19 the losses were 5.48 and 10.25 per cent., respectively. It is evident from the results, that there was no denitrification, and this confirms the experience of last year.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 66.]

ON THE COMPOSITION OF THE FERROCYANIDES OF ZINC.

BY EDMUND H. MILLER AND J. L. DANZIGER.

Received June 7, 1902.

THIS work was undertaken to determine the ratios of iron, potassium and zinc in the potassium zinc ferrocyanides, when precipitated under certain definite conditions in view of the contradictory statements which have appeared regarding their composition. The precipitates were all formed in large beakers in the cold, using zinc sulphate and potassium ferrocyanide. When zinc was to be in excess 100 grams of zinc sulphate and 50 grams of potassium ferrocyanide were used, while for ferrocyanide in excess 100 grams potassium ferrocyanide to 50 grams of zinc sulphate were taken. They were lettered to correspond with those of cadmium described in this Journal, **24**, 226.

DESCRIPTION OF PRECIPITATES.

A. Neutral solution, zinc in excess; white gelatinous precipitate which became granular on washing.

B. Neutral solution, ferrocyanide in excess; white curdy precipitate settled by adding magnesium chloride.

C. Hydrochloric acid solution containing 10 cc. (sp. gr. 1.2 per liter) zinc in excess; bluish white curdy precipitate.

D. Hydrochloric acid solution, same with ferrocyanide in excess; pure white curdy precipitate.

E. Acetic acid solution containing 10 cc. (50 per cent. acetic acid per liter) zinc in excess; pure white flocculent precipitate, changing to a granular form after a few washings.

F. Acetic acid solution, same with ferrocyanide in excess; white precipitate which settles badly.

G. Ammoniacal solution, zinc in excess; formed by adding ferrocyanide to a solution of zinc hydroxide in ammonia, pure white and settled well.

H. Ammoniacal solution, ferrocyanide in excess; made in same way but settled very badly.

I. Zinc acetate and potassium ferrocyanide; no free acid was added but as the zinc acetate contained a trace of acetic acid the conditions were between *A* and *E*.

In general the precipitates were very difficult to wash when ferrocyanide was in excess, but the addition of magnesium chloride helped them to settle so that the most troublesome was clean when washed twenty-five times. They are all soluble in concentrated hydrochloric acid.

The method of analysis was in all cases the same, the object being to get the ratio between zinc and iron, but in some cases, especially when magnesium chloride was used to make the precipitates settle, the potassium was also determined to confirm the iron-zinc ratio.

Portions of the moist precipitate, judged to contain about 1 gram, were put in casseroles and about 50 cc. of hydrochloric acid (sp. gr. 1.2) added; then heated till completely dissolved. Twenty-five cc. of nitric acid were next added and the whole evaporated nearly to dryness, taken up with hydrochloric acid, and evaporated to 10 cc. After dilution the iron was separated from the zinc by one basic acetate precipitation and two precipitations with ammonia and ammonium chloride, ignited and weighed as ferric oxide. In the filtrate the zinc was precipitated as sulphide, dissolved in hydrochloric acid, precipitated as $ZnNH_4PO_4$ by $(NH_4)_2HPO_4$ and weighed as $Zn_2P_2O_7$. When potassium was also to be determined the iron and zinc were taken out as sulphide to avoid the accumulation of ammonium salts, and the potassium finally weighed as sulphate.

RESULTS OF ANALYSES OF PRECIPITATES.

All the analyses were made in duplicate and when a satisfactory agreement was not obtained the work was repeated. In order to save space only the final results are given in the following table:

Precipitate.	Remarks.	Ratio found, Fe : K : Zn.	Corresponding formula.	Theoretical ratio, Fe : K : Zn.
A.	Two weeks after precipitation ..	1 : ... : 1.51	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
A.	After standing ..	1 : 0.81 : 1.59	$K_4Zn_8(Fe(CN)_6)_5$	1 : 0.8 ; 1.60
B.	Fresh precipitate	1 : ... : 1.35	$K_4Zn_4(Fe(CN)_6)_3$	1 : 1.33 : 1.33
B.	After standing ..	1 : ... : 1.49	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
B.	After five days' heating	1 : 1.02 : 1.51	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 ; 1.50
C.	....	1 : ... : 1.50	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
D.	....	1 : ... : 1.40	$K_6Zn_7(Fe(CN)_6)_5$	1 : 1.2 : 1.40
E.	....	1 : ... : 1.51	$K_2Zn_3(Fe(CN)_8)_2$	1 : 1 : 1.50
F.	....	1 : ... : 1.43	$K_6Zn_7(Fe(CN)_6)_5$	1 : 1.2 : 1.40
G.	Washed with water	1 : 0 : 2.46	......	......
G.	Washed with ammonia	1 : 0 : 2.00	$Zn_2Fe(CN)_6$	1 : 0 : 2.00
H.	....	1 : 0 : 1.97	$Zn_2Fe(CN)_6$	1 : 0 : 2.00
I.	....	1 : ... : 1.51	$K_2Zn_3Fe(CN)_6$	1 : 1 : 1.50

We see from this table, (1) that from *A* and *B*, the composition changes on standing; (2) that the composition of the precipitates is entirely different from what Stone[1] and Van Ingen found under similar but not identical conditions; (3) that in hydrochloric acid

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[1] This Journal, 19, 544 (1897).

solution, with zinc in excess (*C*), the results agree with Wyrouboff,[1] De Koninck and Prost,[2] and Miller and Mathews;[3] with ferrocyanide in excess (*D*), the results agree with those of Miller and Mathews;[3] (4) that in an acetic acid solution, the composition is but slightly different from that formed in a hydrochloric acid solution; this explains why Galetti's[4] titration results do not agree with his theory; (5) that in an ammoniacal solution, the normal ferrocyanide is precipitated, whichever is in excess as given by Moldenauer,[5] but when zinc is in excess zinc hydroxide is carried down.

In order to show whether these ferrocyanides are mixtures of simple ferrocyanides or whether they are definite compounds, a method of separation must be employed. Two methods are available, one mechanical and the other chemical. It was noticed that in washing the precipitates one portion would always settle well, while another portion would invariably remain in suspension.

In the work on cadmium, it was shown in one case, that the composition of the precipitate that remained in suspension was $CdK_2Fe(CN)_6$. This fact was made the basis of an attempt at a mechanical separation. A large amount of precipitate was made, in a large bottle, using zinc acetate (*I*). It was washed without loss, by causing the entire precipitate to settle by the use of strontium nitrate. It was then analyzed and gave the ratio of zinc to iron of 1.51 : 1.00, corresponding to $Zn_3K_2(Fe(CN)_6)_2$.

After the strontium nitrate had been entirely washed out, the precipitate did not settle well, and the supernatant liquid had a milky appearance, due to suspended ferrocyanide. This supernatant liquid was siphoned into a second large bottle and allowed to stand over night. Fresh water was poured on the original precipitate, thoroughly stirred and allowed to stand. The supernatant liquid in the second bottle, which was still of a milky appearance, was siphoned into a third bottle, in which strontium nitrate was present. This caused the precipitate to settle completely, leaving a clear solution above, which was siphoned off and rejected.

The residue in the second bottle was washed by the supernatant liquid from the first bottle, and the process continued until a suffi-

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[1] *Ann. chim. phys.*, **5**, II, 485 (1876).
[2] *Chem. News*, **76**, 6 (1897).
[3] This Journal, **19**, 547 (1897).
[4] *Bull. Soc. Chim.*, II, p. 83 (1864).
[5] *Chem. Ztg.*, No. 14 (1891).

cient amount of precipitate had collected in the third bottle to be analyzed. The residue in the last bottle gave the ratio of zinc to iron 1.50:1.00, corresponding again to $Zn_3K_2(Fe(CN)_6)_2$. The residue in the first bottle gave the same ratio, showing that no separation was effected.

During the work on cadmium ferrocyanides, it was found that when a complex precipitate was treated several times with strong ammonia, and the residue analyzed, it gave a formula corresponding to the normal ferrocyanide, $Cd_2Fe(CN)_6$. This same treatment was applied to the zinc ferrocyanides.

First precipitate (*E*) was treated with strong ammonia seven times and the residue analyzed. It gave the ratio of zinc to iron of 2:1, corresponding to $Zn_2Fe(CN)_6$. Then precipitate *I* was treated in the same manner and both the residue and ammoniacal solution were analyzed.

The ammoniacal solution was of a strong yellow color and, on dilution with water, a white precipitate separated, and as the ammonia evaporated, more precipitate formed. The analysis of the residue gave the ratio of zinc to iron of 1.97:1.00, corresponding to $Zn_2Fe(CN)_6$. The analysis of the precipitate from the ammoniacal solution gave the ratio of zinc to iron of 1.97:1.00, the same as the residue. The latter was not what was expected, for, if the precipitates are mixtures of different proportions of $Zn_2Fe(CN)_6$ and $ZnK_2Fe(CN)_6$, and the residues gave $Zn_2Fe(CN)_6$, the ammoniacal solution should have given $ZnK_2Fe(CN)_6$.

The fact that the residue from treating either *E* or *I* with ammonia is $Zn_2Fe(CN)_6$ agrees with the results on cadmium, but we have not so far succeeded in obtaining $K_2ZnFe(CN)_6$ either as a precipitate or from the ammoniacal solution.

After finishing this article it seemed so important to obtain, if possible, the compound $K_2ZnFe(CN)_6$ that two more precipitations were made in neutral solutions, one with a very small excess of zinc, the other with a very small excess of ferrocyanide, thus duplicating as closely as possible the conditions under which Stone and Van Ingen state the compound to be formed,—as we thought we might have had too great an excess in our previous experiments. The precipitates were washed and analyzed as usual. The ratios were Fe:Zn::1.00:1.58 when zinc was in excess and 1.00:1.46 when the ferrocyanide was in excess. These results are in accord with those given on page 825 and are at variance with those of Stone and Van Ingen.

As the solution obtained by treating the zinc ferrocyanides with ammonia undergoes decomposition with the formation of blue precipitates and soluble ferricyanides, it is intended to continue the investigation of the action of ammonia on the potassium cadmium ferrocyanides instead of on the zinc salts.

QUANTITATIVE LABORATORY,
June 4, 1902.

ON STANDARD TARTAR EMETIC AND ITS STRUCTURAL FORMULA.

BY F. E. HALE.

Received May 23, 1902.

GRUENER[1] has already shown that tartar emetic solutions containing about 16 grams of tartar emetic, 20-30 grams of tartaric acid, and 1-10 cc. of concentrated hydrochloric acid to the liter, will keep from five to twelve months without any change in strength. There is no deposit of antimonious oxide under these conditions, no oxidation, and no signs of fungous growth. Gruener determined the strength of his tartar emetic solutions by titration with a decinormal iodine solution, standardized by decinormal arsenite. The mean of twenty-nine determinations showed 43.95 per cent. of antimonious oxide in tartar emetic. Theory required 43.37 per cent. ($Sb = 120$, $KSbOC_4H_4O_6.\frac{1}{2}H_2O = 332$). The cause of this discrepancy between arsenite and tartar emetic solutions made up as standards according to the accepted molecular formulas is a matter of considerable interest. One suggested explanation of this difference has been found in the supposition that the end reaction between starch and iodine is delayed when titrating tartar emetic by iodine until an excess of iodine is present. I have already shown in a previous paper[2] that a pure starch solution gives a sharp end reaction with both tartar emetic and arsenite solutions and that while with impure starch there is a loss of iodine accompanied by the production of reddish hues in titrating tartar emetic, as shown by the difference between the readings made in the presence of potassium iodide by the yellow color of

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[1] *Am. J. Sci.*, **46**, 206.

[2] *Ibid.*, May, 1902, pp. 379-399.