lows : 0.4351 gram of material gave 0.1222 gram of tungsten or 28.08 per cent.

A third preparation was made. On subjecting 0.1775 gram of it to analysis these results were obtained :

0.0496 gram tungsten or 27.94 per cent.

0.1266 gram bromine or 71.32 per cent.

Tabulating the series, we have :

		Found.		Mean	Required for hexabromide.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Tungsten.....	27.43	28.08	27.94	27.81	27.72
Bromine.....	73.53	71.32	....	72.33	72.28

These figures give evidence that the body analyzed is tungsten hexabromide.

In analyzing the third portion of the blue-black needles the bromine was determined by placing the material in a small Erlenmeyer bulb, covering it with nitric acid and then distilling. The liberated bromine was passed into a silver nitrate solution.

The tungsten hexabromide prepared by us consists, as already observed, of blue-black needles. Moderately elevated temperatures decompose the compound. It gives off fumes when brought in contact with the air. Water decomposes it with the formation of a royal-blue colored oxide. Ammonia water dissolves it, the solution remaining colorless. A vapor density determination resulted negatively, as decomposition was apparent early in the experiment.

NOTES ON THE FERROCYANIDES OF ZINC AND MANGANESE.

By Edmund H. Miller.

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THE composition of the ferrocyanides of zinc and manganese, formed when salts of these metals are precipitated by potassium ferrocyanide, is given by Prescott and Johnson[1] as $Zn_2Fe(CN)_6$ and $Mn_2Fe(CN)_6$, while the books on volumetric analysis, such as Sutton's and Beringer's, ignore the composition of this precipitate.

[1] Qualitative Analysis, pages 67 and 57.

The prevailing idea is that in the titration of zinc by potassium ferrocyanide, a normal zinc ferrocyanide is formed. This I believe to be incorrect, for if the reaction is

$$K_4Fe(CN)_6 + 2ZnCl_2 = Zn_2Fe(CN)_6 + 4KCl,$$

a solution of potassium ferrocyanide, one cc. of which is equivalent to ten milligrams of zinc, would contain 32.32 grams of $K_4Fe(CN)_6.3H_2O$ to the liter, not 43.2[1] to 45[2] grams, as has been found by experiment. Using forty-four grams per liter as a basis for calculation, the reaction becomes

$$2K_4Fe(CN)_6 + 3ZnCl_2 = Zn_3K_2(Fe(CN)_6)_2 + 6KCl.$$

This reaction is not merely one that may possibly be true, but according to Wyrouboff,[3] the precipitate formed by the action of potassium ferrocyanide on a zinc salt, whichever is in excess, is $3Zn_2Fe(CN)_6.K_4F_3(CN)_6.12H_2O$, white, while the normal salt, $Zn_2Fe(CN)_6.4H_2O$, is formed only by the action of hydroferrocyanic acid on a zinc salt.

This statement agrees both with the preceding reaction and with the results obtained in standardizing potassium ferrocyanide solution.

The manganese precipitate with potassium ferrocyanide, as obtained in titration, is given by Stone[4] as $Mn_3Fe_2(CN)_{12}$. This is a ferri-, not a ferrocyanide, thus making necessary a change of quantivalence. Mr. Stone also states that an amount of potassium ferrocyanide which will precipitate four atoms of zinc will only precipitate three of manganese, thus basing his calculation on the formation of a normal zinc ferrocyanide.

Wyrouboff[3] gives the precipitate obtained from potassium ferrocyanide and a manganese salt, whichever is in excess, as

$$5Mn_2Fe(CN)_6.4K_4Fe(CN)_6.4H_2O, \text{ rose white;}$$

while the normal salt $Mn_2Fe(CN)_6.7H_2O$, cream, is formed as in the case of zinc by hydroferrocyanic acid.

The solution used by Mr. Stone had the following strength:

[1] Sutton: Volumetric Analysis, p. 329; Beringer: Assaying, p. 219.
[2] Furman: Assaying, p. 205.
[3] *Ann. chim. phys.*, [5], 8. 485.
[4] *J. Am. Chem. Soc.*, 17, 473.

One cc. = 0.00606 gram zinc.
One cc. = 0.00384 gram manganese.

If the ratio were exactly four zinc to three manganese, using the most recent atomic weights, the strength of this solution against manganese would be one cc. = 0.00382 gram, while, according to Wyrouboff, $10Mn = 9K_4Fe(CN)_6$ and $6Zn = 4K_4Fe(CN)_6$, or $10Mn = 13.5\ Zn$, or $1Mn = 1.35\ Zn$, and the strength against manganese would be 1 cc. = 0.003774 gram.

These figures show but little difference between the two ratios and while Mr. Stone's experimental results are undoubtedly accurate, this theory based on the formation of $Zn_2Fe(CN)_6$ and $Mn_3Fe_2(CN)_{12}$ is not satisfactorily proved.

This article is only a preliminary note regarding the composition of the ferrocyanides as they are being investigated in this laboratory.

In connection with the ferrocyanide of zinc I have found a very strong solution of hydrochloroplatinic acid, H_2PtCl_6, acidified with hydrochloric acid, a most satisfactory indicator for the titration of zinc by potassium ferrocyanide, when performed in a hot solution. This indicator is used in the same way as uranium acetate and is less affected by a varying amount of hydrochloric acid. The end reaction is a bright emerald green, which takes a few seconds to develop. It will not work with a cold solution.

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A MODIFICATION OF THE GUNNING METHOD FOR NITRATES.

BY JOHN FIELDS.

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THE full text of the official Gunning[2] method is as follows: "In a digestion flask, holding from 250 to 500 cc., place from seven-tenths to three and five-tenths grams of the substance to be analyzed, according to the amount of nitrogen present. Add thirty to thirty-five cc. of salicylic acid mixture; namely, thirty cc. sulphuric acid to one gram of salicylic acid, shake until thoroughly mixed and allow to stand five to ten

[1] *Ann. chim. phys.*, [5], 8, 474.
[2] Bulletin 46, U. S. Dept. of Agr., p. 18.