

ANALYSIS OF FERROCYANIDES.

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Two years ago I read a paper before the Society on the Commercial Analysis of Ferrocyanides (ANALYST, 1908, **33**, 261), in which I stated that the Feld method of estimation gave very reliable results. Recently, however, F. W. Skirrow (*J. Soc. Chem. Ind.*, 1910, **29**, 319) has published a series of determinations which seem to throw doubts on the accuracy of the method, his experiments, starting from known quantities of ferrocyanide and of cyanide, giving results from 3 to 4 per cent. low. Skirrow's experience is entirely contrary to mine, and as I have largely employed the Feld method during the past few years, both for the analysis of commercial products and of the pure salts, it seems advisable to publish a representative set of the actual figures obtained.

The Feld method is, briefly, as follows: A quantity of ferrocyanide amounting to from 0.3 to 0.5 grm. of potassium ferrocyanide or its equivalent is dissolved in water, heated to boiling with 10 c.c. of $\frac{N}{1}$ caustic soda, 15 c.c. of 3N magnesium chloride solution added, and the boiling continued for five minutes. (If free cyanide is also present, the hydrocyanic acid in this form then distils over, and may be condensed and collected for analysis, the boiling being in that case continued for a longer period.) One hundred c.c. of boiling $\frac{N}{10}$ mercuric chloride are then added, and the boiling continued for a further ten minutes, all ferrocyanide being thus converted into mercuric cyanide. The hydrocyanic acid in the latter is recovered by distilling for twenty to thirty minutes with 30 c.c. of 3N sulphuric acid, the condensed distillate being collected in 25 c.c. of $\frac{N}{1}$ caustic soda, and, after addition of a crystal of potassium iodide, titrated with $\frac{N}{10}$ silver nitrate until a permanent yellow precipitate of silver iodide makes its appearance.

From the results of his tests Skirrow concludes that there are two sources of error in the method: (1) That on boiling the ferrocyanide solution with magnesium chloride solution and magnesium hydroxide some hydrocyanic acid is evolved, and (2) that loss of hydrocyanic acid occurs either in conversion of the ferrocyanide into mercuric cyanide or in the distillation with acid.

ACTION OF MAGNESIUM CHLORIDE SOLUTION.

With regard to the first point, the two following tests made with pure potassium and sodium ferrocyanides may be given, in which the boiling with magnesium chloride was prolonged to twenty-five minutes.

Weight of Salt taken.	$\frac{N}{10}$ Silver Nitrate Solution used.			
	25 Min. with $MgCl_2$.	After $HgCl_2$, etc.	Total.	Theory.
0.3350 $K_4Fe(CN)_6 \cdot 3H_2O$	0.15 c.c.	23.65 c.c.	23.8 c.c.	23.79 c.c.
0.4140 $Na_4Fe(CN)_6 \cdot 10H_2O$	0.15 c.c.	25.45 c.c.	25.6 c.c.	25.66 c.c.

THE ANALYST.

These and other tests of a similar character are so far in agreement with Skirrow that they show a loss of hydrocyanic acid on long-continued boiling with the magnesium chloride solution, although the extent of the loss (0.6 per cent.) is much smaller than he found; and it will also be seen that there is no absolute loss of cyanide, the total yield of hydrocyanic acid being practically in accord with theory.

Where, on the other hand, the boiling with magnesium chloride is continued only for the specified five minutes, I have found in a large number of tests that no appreciable evolution of hydrocyanic acid occurs, a single drop of $\frac{N}{10}$ silver nitrate solution always producing a decided yellow cloudiness in the alkaline distillate. The two following tests may be given as an example :

Weight of Salt taken.	$\frac{N}{10}$ Silver Nitrate Solution used.			
	5 Min. with MgCl ₂ .	After HgCl ₂ , etc.	Total.	Theory.
0.3240 K ₄ Fe(CN) ₆ ·3H ₂ O	nil	23.05 c.c.	23.05 c.c.	23.01 c.c.
0.3675 Na ₄ Fe(CN) ₆ ·10H ₂ O	nil	22.75 c.c.	22.75 c.c.	22.78 c.c.

In testing for ferrocyanide in absence of cyanide, correct results are therefore obtained if the boiling with magnesium chloride is not continued longer than the specified five minutes. When, on the other hand, a mixture of cyanide and ferrocyanide is being analysed, and the boiling must be continued for longer than five minutes to drive off all hydrocyanic acid present as cyanide, the tendency from this source of error will be to give rather too high results for cyanide, and correspondingly low figures for ferrocyanide. It is found however that, with the quantities of cyanide present in such analyses, ten minutes' fairly quick distillation is sufficient to remove the hydrocyanic acid present as cyanide, without also driving off material quantities of the hydrocyanic acid present as ferrocyanide, as shown by the following tests :

1. 0.3006 gram. K₄Fe(CN)₆·3H₂O (= 21.35 c.c. $\frac{N}{10}$ AgNO₃) was dissolved in water, mixed with 10 c.c. of pure sodium cyanide solution (= 12.15 c.c. $\frac{N}{10}$ AgNO₃), and analysed by Feld's method.

	Found.	Theory.
After ten minutes' boiling with MgCl ₂ ...	12.15 c.c.	12.15 c.c.
After HgCl ₂ and distillation with H ₂ SO ₄ ...	21.30 c.c.	21.35 c.c.

2. 0.4094 gram. Na₄Fe(CN)₆·10H₂O (= 25.37 c.c. $\frac{N}{10}$ AgNO₃) and 10 c.c. sodium cyanide solution (= 12.15 c.c. $\frac{N}{10}$ AgNO₃) treated in the same manner.

	Found.	Theory.
After ten minutes' boiling with MgCl ₂ ...	12.10 c.c.	12.15 c.c.
After HgCl ₂ and distillation with H ₂ SO ₄ ...	25.50 c.c.	25.37 c.c.

EXPERIMENTS STARTING FROM SODIUM CYANIDE SOLUTION.

Skirrow found, further, that, starting with cyanide solution, and converting this into ferrocyanide by the action of ferrous sulphate solution and caustic alkali, the yield of hydrocyanic acid in subsequent analysis by the Feld method was from 3 to 4 per cent. less than that found by the direct titration of the original cyanide solution

with $\frac{N}{10}$ silver nitrate. A set of experiments was therefore made with a solution of pure sodium cyanide prepared by distilling hydrocyanic acid into a solution of pure caustic soda. Twenty-five c.c. of this solution required 30.4 c.c. of $\frac{N}{10}$ silver nitrate on direct titration.

Successive quantities of 25 c.c. of this solution were converted into ferrocyanide by addition of 25 c.c. of $\frac{N}{1}$ caustic soda and a solution of 0.5 grm. of ferrous sulphate crystals, the mixture being allowed to stand for an hour, with occasional shaking. The whole was then analysed by Feld's method, with the following results :

Sodium Cyanide Solution taken.		$\frac{N}{10}$ Silver Nitrate used.				
		After $MgCl_2$ 5 Min.	After $HgCl_2$.	Total.	Theory.	Loss.
	C.C.		C.C.	C.C.	C.C.	Per Cent.
1.	25	nil	30.20	30.20	30.4	0.66
2.	25	nil	30.25	30.25	30.4	0.50
3.	25	nil	30.35	30.35	30.4	0.16
4.	25	nil	30.30	30.30	30.4	0.33
5.	25	nil	30.25	30.25	30.4	0.50
Average, 0.43						

Here, again, whilst a small loss was always found, averaging about 0.5 per cent., this is much less than the 3 to 4 per cent. observed by Skirrow. It was further noticed that the residual liquid in the flask after the distillation, which is normally a yellow solution coloured by ferric sulphate and containing a precipitate of mercurous chloride, had in all cases a greenish tinge, indicating the presence of undecomposed iron ferrocyanides. It seemed most probable that the formation of such insoluble ferrocyanides would be due to the presence of ferrous hydroxide in the liquid analysed, owing to an excess of ferrous sulphate having been used for conversion of the cyanide into ferrocyanide, as the presence of ferrous hydroxide might be expected to result in the formation of some ferrous ferrocyanides, which are known to be more stable towards alkalis than the ferric ferrocyanides. To avoid this formation, attempts were made to remove the excess of ferrous hydroxide from the solution before analysis ; but these were unsuccessful, as it was found impracticable to wash the precipitate free from ferrocyanide. A further test was therefore made in which, previous to analysing the solution, the ferrous hydroxide was oxidised to ferric hydroxide by addition of a few drops of ammonium persulphate solution. The result then obtained was as follows :

		$\frac{N}{10}$ Silver Nitrate used.				
		After $MgCl_2$.	5 Min. after $HgCl_2$.	Total.	Theory.	Loss.
(6)	25 c.c. ...	0.6 c.c.	29.8 c.c.	30.4 c.c.	30.4 c.c.	Nil.

In this case it will be seen that the total hydrocyanic acid obtained was in accordance with theory, although, owing to the action of the slight excess of persulphate used, a small amount of ferrocyanide was converted into cyanide, this quantity being evolved on boiling with magnesium chloride. The residual solution in this case did not show the slightest green tinge.

THE ANALYST

To ascertain further the effect of ferrous hydroxide, a mixture of pure potassium ferrocyanide with ferrous sulphate solution and caustic soda was made and analysed, with the following result :

0.3272 grm. $K_4Fe(CN)_6 \cdot 3H_2O$ ($= 23.25$ c.c. $N/10$ $AgNO_3$) was mixed with 0.5 grm. $FeSO_4 \cdot 7H_2O$ and 25 c.c. $N_1^F.NaOH$, and the mixture analysed by Feld's method.

N/10 $AgNO_3$ used.				
After $MgCl_2$.	5 Min. after $HgCl_2$, etc.	Total.	Theory.	Loss.
Nil.	22.8 c.c.	22.8 c.c.	23.25 c.c.	1.9 per cent.

The residual solution in this case had a decided green colour.

The loss observed by Skirrow in this and many of his other experiments appears, therefore, to be due largely to the fact that an excess of ferrous hydroxide was present in the solutions tested, which is not the case when the test is carried out under normal conditions. The reason that Skirrow also obtains a much greater loss during the boiling with magnesium chloride solution is, however, unaccounted for, and the only suggestion that occurs to me is that it may have been due to some impurity present in the magnesium chloride used. In the tests given above, pure crystalline magnesium chloride was employed throughout.

Generally, therefore, these tests seem to show that the Feld method, when carried out under the conditions specified in the former paper, gives results which are substantially accurate.

ANALYSIS OF PURE SALTS.

As indirect evidence of the accuracy of the method, the following complete analyses of various ferrocyanides which had been prepared in as high a state of purity as possible may be quoted. In these analyses the basic metals and the iron were determined in the usual manner, the cyanogen by Feld's method, and the water by heating the salt in a current of air, and collecting the moisture evolved in a calcium chloride tube. Determination of the water by loss of weight on heating gives unsatisfactory results.

Potassium Ferrocyanide.

						Calculated for K ₄ Fe(CN) ₆ ·3H ₂ O.
K	...	0.5395 grm.	gave 0.4424 grm.	K ₂ SO ₄	...	K = 36.80 37.02
Fe	...	0.6035	„ took 14.3 c.c. $\frac{N}{10}$	K ₂ Cr ₂ O ₇	...	Fe = 13.24 13.23
CN	...	0.3028	„ took 21.45 c.c. $\frac{N}{10}$	AgNO ₃	...	CN = 36.84 36.96
H ₂ O	...	0.8874	„ gave 0.1118 grm.	H ₂ O	...	H ₂ O = 12.60 12.79
						99.48 100.00

Sodium Ferrocyanide.

						Calculated for Na ₄ Fe(CN) ₆ .10H ₂ O.
Na	...	0.8315 grm.	gave 0.4847 grm.	Na ₂ SO ₄ ...	Na = 18.86	19.00
Fe	...	0.7518	„ took 15.5 c.c. $\frac{N}{10}$	K ₂ Cr ₂ O ₇ ...	Fe = 11.53	11.55
Cy	...	0.3253	„ took 20.15 c.c. $\frac{N}{10}$	AgNO ₃ ...	CN = 32.20	32.23
H ₂ O	...	0.6418	„ gave 0.2382 grm.	H ₂ O ...	H ₂ O = 37.12	37.22
						99.71
						100.00

THE ANALYST.

299

Calcium Ferrocyanide.

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							Calculated for $\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 11\frac{1}{2}\text{H}_2\text{O}$.	
Ca	...	0.6912	gram.	gave 0.1568	gram. CaO	...	Ca = 16.21	16.06
Fe	...	0.6912	"	took 13.95	c.c. $\frac{N}{10}$ $\text{K}_2\text{Cr}_2\text{O}_7$...	Fe = 11.28	11.20
CN	...	0.4688	"	took 28.35	c.c. $\frac{N}{10}$ AgNO_3	...	CN = 31.46	31.26
H ₂ O	...	0.4120	"	gave 0.1696	gram. H ₂ O	...	H ₂ O = 41.18	41.48
							100.13	100.00

Strontium Ferrocyanide.

							Calculated for Sr ₂ Fe(CN) ₆ ·14H ₂ O.		
Sr	...	0.6224	gram.	gave 0.3598	gram.	SrSO ₄	...	Sr = 27.53	27.40
Fe	...	0.6224	"	took 9.75	c.c.	$\frac{N}{10}$ K ₂ Cr ₂ O ₇	...	Fe = 8.76	8.74
CN	...	0.3464	"	took 16.3	c.c.	$\frac{N}{10}$ AgNO ₃	...	CN = 24.47	24.40
H ₂ O	...	0.4166	"	gave 0.1650	H ₂ O	H ₂ O = 39.61	39.46
								<hr/> 100.37	<hr/> 100.00

Magnesium Ferrocyanide.

							Calculated for Mg ₂ Fe(CN) ₆ · 12H ₂ O.	
Mg	...	0.5054	gram.	gave 0.2384	gram.	Mg ₂ P ₂ O ₇ ...	Mg = 10.31	10.21
Fe	...	0.4832	"	took 10.15	c.c. $\frac{N}{10}$	K ₂ Cr ₂ O ₇ ...	Fe = 11.74	11.73
CN	...	0.3419	"	took 21.45	c.c. $\frac{N}{10}$	AgNO ₃ ...	CN = 32.62	32.73
H ₂ O	...	0.3402	"	gave 0.1544	gram.	H ₂ O ...	H ₂ O = 45.37	45.33
							100.04	100.00

It will be seen that the figures are generally satisfactory, which would not be possible if the Feld method gave results from 3 to 4 per cent. too low, as found by Skirrow. This is particularly the case with the percentages of iron and cyanogen, for, whatever the exact degree of purity of the salts may have been in other respects, it is reasonably certain that all the iron and cyanogen were present in each case solely as the radical $\text{Fe}(\text{CN})_6$, the theoretical ratio Fe : CN in this radical being 1 : 2.792. The actual ratio found in the analysis of the above five salts was as follows :

					Error.
K salt	Fe : CN =	1 : 2.783	- 0.4 per cent.
Na salt	"	= 1 : 2.793	Nil.
Ca salt	"	= 1 : 2.789	- 0.1 "
Sr salt	"	= 1 : 2.793	Nil.
Mg salt	"	= 1 : 2.778	- 0.5 "
Average					1 : 2.787
					- 0.18 per cent.

It may be remarked that the number of molecules of water of crystallisation found in some of the above salts does not agree with the statements found in the literature. Potassium ferrocyanide has long been known to crystallise with $3\text{H}_2\text{O}$, and sodium ferrocyanide, though still stated in many textbooks to crystallise with $12\text{H}_2\text{O}$, has for many years been recognised as only containing $10\text{H}_2\text{O}$. Calcium ferrocyanide is usually stated to crystallise with $12\text{H}_2\text{O}$, and this is probably correct ; but the crystals are very efflorescent, and the author has never succeeded in getting

THE ANALYST.

figures corresponding with that formula in different preparations, giving results varying between those required for 11 and $12\text{H}_2\text{O}$. Strontium ferrocyanide is described by Bette (*Annalen*, 1836, **22**, 148) and Wyruboff (*Ann. Chim. Phys.*, 1868 (4) **16**, 287; 1870, (4) **21**, 271) as crystallising with $15\text{H}_2\text{O}$; whereas, with several different preparations, the author finds only $14\text{H}_2\text{O}$. These crystals lose $7\text{H}_2\text{O}$ on standing in the air, and a further $6\text{H}_2\text{O}$ over sulphuric acid *in vacuo*. Apparently only one analysis of magnesium ferrocyanide has been published (Bette, *Annalen*, 1836, **23**, 115), leading to the formula $\text{Mg}_2\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, against $12\text{H}_2\text{O}$ found by the author; but Bette's figures are too incomplete and approximate to justify his formula. The magnesium ferrocyanide crystals lose $5\text{H}_2\text{O}$ on standing in the air.

DISCUSSION.

Dr. LESSING said that he commenced to use the Feld method shortly after it was introduced, five or six years ago, and at the beginning experienced some difficulty with it. He had then just completed some experiments relating to the decomposition of ferrocyanides by acids, and had found that the complex nature of the ferrocyanogen ion by no means prevented its decomposition by ordinary mineral acids. He had even found it possible to decompose some of the alkaline ferrocyanides with sulphur dioxide, liberating free hydrocyanic acid. That, of course, had made him particularly careful to see that no ferrocyanide was decomposed during the boiling with magnesium chloride, and he had never found any appreciable decomposition to occur, provided that Feld's original instructions were followed. Long-continued boiling was quite unnecessary, the only object of the boiling being to convert any free alkali into magnesium hydroxide. With regard to the green coloration observed by the author, he (Dr. Lessing) had frequently obtained this coloration at first, and the results were very discordant in consequence, since the ferrocyanide was not completely decomposed, a certain quantity of cyanogen remaining in the flask in the form of some compound of ferrocyanogen and iron. This difficulty was overcome by so adjusting the reagents that they were always present in approximately equivalent quantities—*i.e.*, starting with a certain quantity of caustic soda for the purpose of decomposing the original substance, an equivalent quantity of magnesium chloride was used, and the caustic soda and magnesium chloride were both adjusted in relation to the excess of iron present. Under these conditions the green coloration was never obtained, and the results for total cyanogen were always satisfactory. With regard to the question of water of crystallisation, he had found that, to make pure potassium or sodium ferrocyanide with a constant proportion of water, it was necessary to dry the recrystallised salt over a quantity of the same salt which itself had been previously freed from water of crystallisation. Possibly this difficulty in obtaining as a basis for analysis a salt of constant composition might furnish a clue to the lowness of some of Skirrow's results.

Mr. J. L. FOUCAR said that he also was able to corroborate the author's observations. He had not at first been able quite to understand Skirrow's results, but Dr. Colman had explained the main differences, especially with regard

to the question of excess of ferrous hydroxide. The following results might be of interest :

Sodium cyanide : by direct titration, 125·2 per cent. HCN ; by Feld's method 125·38 ; by precipitation as silver cyanide, 125·13. Here, if anything, Feld's method seemed to give rather higher results than the others.

A cyanogen liquor ; 4·14 pounds of Prussian blue per gallon by Feld's method, 4·11 pounds by titration with zinc.

He had recently followed very closely some work the object of which was the investigation of this question, and he could state with certainty that under standard conditions the Feld method for the determination of ferrocyanide was at least as accurate as any other.

