

Results:

	Electrometric method. Per cent.	U. S. P. method. Per cent.		Electrometric method. Per cent.	U. S. P. method. Per cent.		Electrometric method. Per cent.	U. S. P. method. Per cent.
Sample 1	0.29	0.26	Sample 2	0.14	0.12	Sample 3	0.21	0.17
	0.26	0.20		0.18	0.13		0.24	0.20
	0.30	0.24		0.15	0.14		0.18	0.20
	0.10	

Again the electrometric method gives on the average higher results, which theoretically should be more accurate since the use of methyl red or cochineal as an indicator in titrating the mydriatic alkaloids introduces a considerable negative error, while the mechanical losses of the shaking-out process are also avoided.

SUMMARY.

1. Evidence adduced by other workers is cited to emphasize the contention previously made by the authors for a more rational selection of indicators in alkaloidal titrations.
2. Electrometric assay processes are given for nux vomica and belladonna and the advantages of these in time and accuracy reiterated.

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THE TITRATION OF FERRIC CHLORIDE WITH SODIUM HYDROXIDE, USING THE OXYGEN ELECTRODE: A PROOF OF THE NON-EXIS- TENCE OF IRON OXYCHLORIDE.*

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The National Formulary refers to iron oxychloride, but chemical literature indicates that this is not a definite chemical compound. Solutions have been prepared containing as low as 1 atom of chlorine to 22¹ or 31² atoms of iron.

It appeared to be of interest to investigate the curve of the precipitation of ferric hydroxide with sodium hydroxide to determine if there was any indication of the existence of a basic salt.

The hydrogen electrode was first tried but, as had been foreseen, the electrode was poisoned by the ferric chloride and gave only the oxidation-reduction potential of the solution. The oxygen electrode is not objectionable in this respect and while it was realized that it would not measure true hydroxyl ion concentrations, yet the results obtained are so internally consistent that they have justified the use of this method.

A ferric chloride solution was made up from the C. P. salt and standardized by adding nitric acid to a measured volume, evaporating and igniting. The amount of this solution, 84.75 cc, which would be exactly equivalent to 50 cc of *M*/3 solution, was placed in a 250-cc beaker, which was connected by a saturated KCl bridge to a calomel half cell. Normal sodium hydroxide was added in small

* Scientific Section, A. Ph. A., Asheville meeting, 1923.

¹ Malfitano, *Zeitschrift für Physikalische Chemie*, 68, 232, 1909.

² Browne, *J. A. C. S.*, 45, 298, 1923.

increments and the voltage read after each addition. The sodium hydroxide used had a normality of 1.0347 and 1.0358 using methyl orange and phenolphthalein, respectively, as indicators. The mean of these two values, 1.0352, was used.

The following are the results of two titrations, all additions of caustic being calculated to a normal basis:

Run 1. 84.75 cc 0.1967 *M* FeCl₃ = 50 cc *M*/3.

Cc 1.0352 <i>N</i> NaOH.	Corrected to cc <i>N</i> NaOH.	Voltage.
0	0	— 0.6460
5	5.18	— 0.6400
10	10.35	— 0.6365
15	15.50	— 0.6350
20	20.70	— 0.6335
25	25.90	— 0.6322
30	31.12	— 0.6280
38	36.20	— 0.6235
40	41.40	— 0.6050
45	46.6	— 0.5200

Run 1. 84.75 cc 0.1967 *M* FeCl₃ = 50 cc *M*/3.

Cc 1.0352 <i>N</i> NaOH.	Corrected to cc <i>N</i> NaOH.	Voltage.
47.5	49.2	— 0.4050
50.0	51.7	— 0.1010
52.5	54.3	0.0000
55.0	56.8	+ 0.0300
60.0	62.1	0.0400
65	67.3	0.0520
75	77.5	0.0630
85	87.9	0.0673
95	98.3	0.0710
100	103.5	0.0720

Run 2. 84.75 cc 0.1967 *M* FeCl₃ = 50 cc *M*/3.

Cc 1.0352 NaOH.	Corrected to cc <i>N</i> NaOH.	Voltage.
0	0	— 0.6430
10	10.35	— 0.6365
20	20.70	— 0.6322
30	31.05	— 0.6235
40	41.40	— 0.6045
42.5	44.0	— 0.5910
45.0	46.6	— 0.5490
47.5	49.15	— 0.3350
49.0	50.75	— 0.2530
50.0	51.70	— 0.1770
52.5	54.3	— 0.0380

Run 2. 84.75 cc 0.1967 *M* FeCl₃ = 50 cc *M*/3.

Cc 1.0352 NaOH.	Corrected to cc <i>N</i> NaOH.	Voltage.
55	56.85	+ 0.0030
60	62.10	0.0250
75	77.5	0.0460
100	103.5	0.0565
110	113.85	0.0568
120	124.10	0.0570
130	134.70	0.0570
150	155.2	0.0595
175	181.1	0.0610
200	207.0	0.0610
250	259.0	0.0640

The curve obtained by plotting these results is the typical curve of the neutralization of a strong acid by a strong base. The addition of caustic in the second run was continued until 250 cc had been added but no break appeared in the flat upper portion of the curve.

Tangents to the flat parts of the curve were drawn and the exact neutral point was determined by finding the point on the curve midway between the tangents. By interpolation this was found to be equivalent to 50.16 cc and 50.01 cc of normal caustic in two different runs.

The curve contains no breaks, which would certainly be present if there were any formation of intermediate or basic salts. We are therefore forced to conclude that iron oxychloride as a definite chemical compound is nonexistent.

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