

# A New Method for the Determination of Sodium and Potassium in a Mixture of their Salts.

By

**Kichiro Okada.**

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For the determination of potassium in the presence of sodium, precipitation as potassium chloroplatinate is a most accurate and moreover very convenient method, but the high price of platinum is a disadvantage. Indirect analysis, depending on the difference of the atomic weights of these two elements is often employed, but from it in general great accuracy can not be expected. At the suggestion of Prof. Y. Osaka the writer has undertaken to work out a new analytical method for the determination of sodium and potassium, each in the presence of the other, utilizing the slight solubility of potassium hydrogen tartrate.

When a given quantity of a mixture of sodium and potassium salts is mixed with a given quantity of sodium hydrogen tartrate in solution, and the temperature and the total volume of the solution is kept constant, the concentration of the tartrates remaining in the solution is a function of the percentage of potassium in the sample. If this function be given in the form of a curve, a mixture of sodium and potassium salts may be analysed by determining the concentration of the tartrates remaining in the solution. Naturally any other quantity which is a function of the concentration of the tartrates may be taken instead in drawing such a curve. Such curves have been sought for mixtures of chlorides and of sulphates, as they are the most common cases.

## 1. *Sodium and Potassium Chlorides.*

The sodium and potassium chlorides used were the purest preparations of C. Merck and sodium hydrogen tartrate used was an ordinary salt recrystallised. A standard solution of sodium hydroxide was pre-

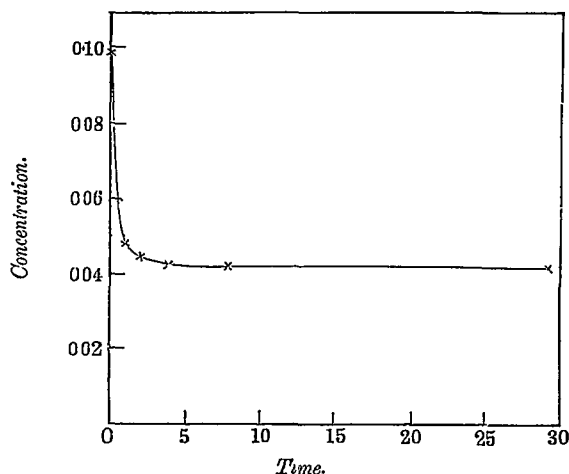
pared from metallic sodium and water free from carbonic acid and standardised by succinic acid.

To find the time necessary for the reaction in question to attain a state of equilibrium, 0.4980 grams of potassium chloride and 1.0456 grams sodium hydrogen tartrate were dissolved to an aqueous solution of 70 c.c. at 25.0° C. This was shaken constantly in a well stoppered flask in a thermostat of the same temperature; 10 c.c. of the solution were taken out at certain intervals of time; and the concentration of the tartrates determined by a method to be described later. The results were as follows:

TABLE I.

Time in hours.	Concentration of the tartrates in solution in mols per liter.
0	0.0993
1	0.0481
2	0.0447
3 $\frac{3}{4}$	0.0425
7 $\frac{3}{4}$	0.0422
29 $\frac{1}{4}$	0.0415

This is graphically represented in Fig. 1; and it may be concluded that equilibrium was attained practically in five hours.



#### *The Determination of the Standard Curve.*

1.000 gram of mixed chlorides of known composition and 2.400 grams of sodium hydrogen tartrate were dissolved in water and diluted

to 50 c.c. at 25.0°. It was shaken in a thermostat at the same temperature for at least five hours, and then allowed to stand in the same thermostat. When the precipitate subsided, 20 c.c. of the clear solution were taken out, evaporated to dryness; and the residue brought to red heat, when it partially fused. The alkalies thus produced were extracted with a given amount of a standard solution of hydrochloric acid, the excess of the acid being back-titrated with a standard solution of sodium hydroxide, using methyl orange as indicator. The results are given in the following table:—

TABLE II.

Molar percentages.		Mixed chlorides taken. Grams.		Normal hydrochloric acid used. c.c.		
KCl	NaCl	KCl	NaCl	I	II	Mean.
—	100	—	1.0000	5.62	5.59	6.15
2	98	0.0254	0.9742	5.60	5.58	5.60
5	95	0.0629	0.9371	5.54	5.56	5.55
10	90	0.1242	0.8758	5.20	5.23	5.22
20	80	0.2417	0.7582	4.55	4.57	4.56
30	70	0.3534	0.6466	4.02	4.01	4.02
40	60	0.4594	0.5405	3.54	3.54	3.54
50	50	0.5605	0.4395	3.05	3.02	3.04
60	40	0.6567	0.3433	2.56	2.56	2.56
70	30	0.7485	0.2515	2.19	2.17	2.18
80	20	0.8361	0.1639	1.79	1.79	1.79
90	10	0.9199	0.0801	1.47	1.45	1.46
100	—	1.0000	—	1.20	1.19	1.20

As the quantity of hydrochloric acid used is equivalent to that of the tartrates in the original solution it is a function of the amount of sodium and potassium in the sample taken, and is graphically represented in Fig. 2. The quantity of hydrochloric acid solution used is plotted along the axis of ordinate; and in curve I. the percentage by weight of sodium chloride and in curve II. its percentage by mols along the axis of abscissa. As may be seen from the curves, they can not be used for a mixture in which the potassium chloride is less than five percent with the same accuracy as in other cases.

## 2. Sodium and Potassium Sulphates.

The potassium sulphate used was the purest preparation of C. Merck, sodium sulphate was an ordinary salt recrystallised and dehydrated in an air bath at 120°C. The other reagents used were the same as in the case of the chlorides. The period of time required for the attainment of equilibrium was experimentally determined in this case also; and the result was quite the same as in the case of the chlorides.

Thus the data for the standard curves were obtained by experiments which were carried out quite similarly to those in the case of the chlorides, the only difference being that 2.000 grams of sodium hydrogen tartrate were used instead of 2.400 grams. The results were as follows:

TABLE III.

Mixed sulphates taken.				Normal hydrochloric acid used.		
Molar percentages.		Gram.		c c.		
K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	I	II	Mean
—	100	—	1.0000	4.86	4.85	4.86
10	90	0.1199	0.8801	4.44	4.46	4.45
20	80	0.2347	0.7653	3.97	3.99	3.98
30	70	0.3446	0.6554	3.54	3.54	3.54
40	60	0.4499	0.5501	3.11	3.11	3.11
50	50	0.5505	0.4491	2.70	2.70	2.70
60	40	0.6479	0.3521	2.32	2.29	2.31
70	30	0.7411	0.2589	1.94	1.93	1.94
80	20	0.8309	0.1693	1.65	1.66	1.66
90	10	0.9169	0.0831	1.39	1.38	1.39
100	—	1.0000	—	1.17	1.18	1.18

This is graphically represented in Fig. 3 and the curves have the same meaning as in Fig. 2.

## 3. Practical Applications.

To see how far this method of analysis might be relied upon in practice, the following experiments were conducted. 1.000 grams of mixed chlorides or sulphates of known proportions and 2.400 or 2.000 grams of sodium hydrogen tartrate respectively were taken, and treated

Fig. 2.

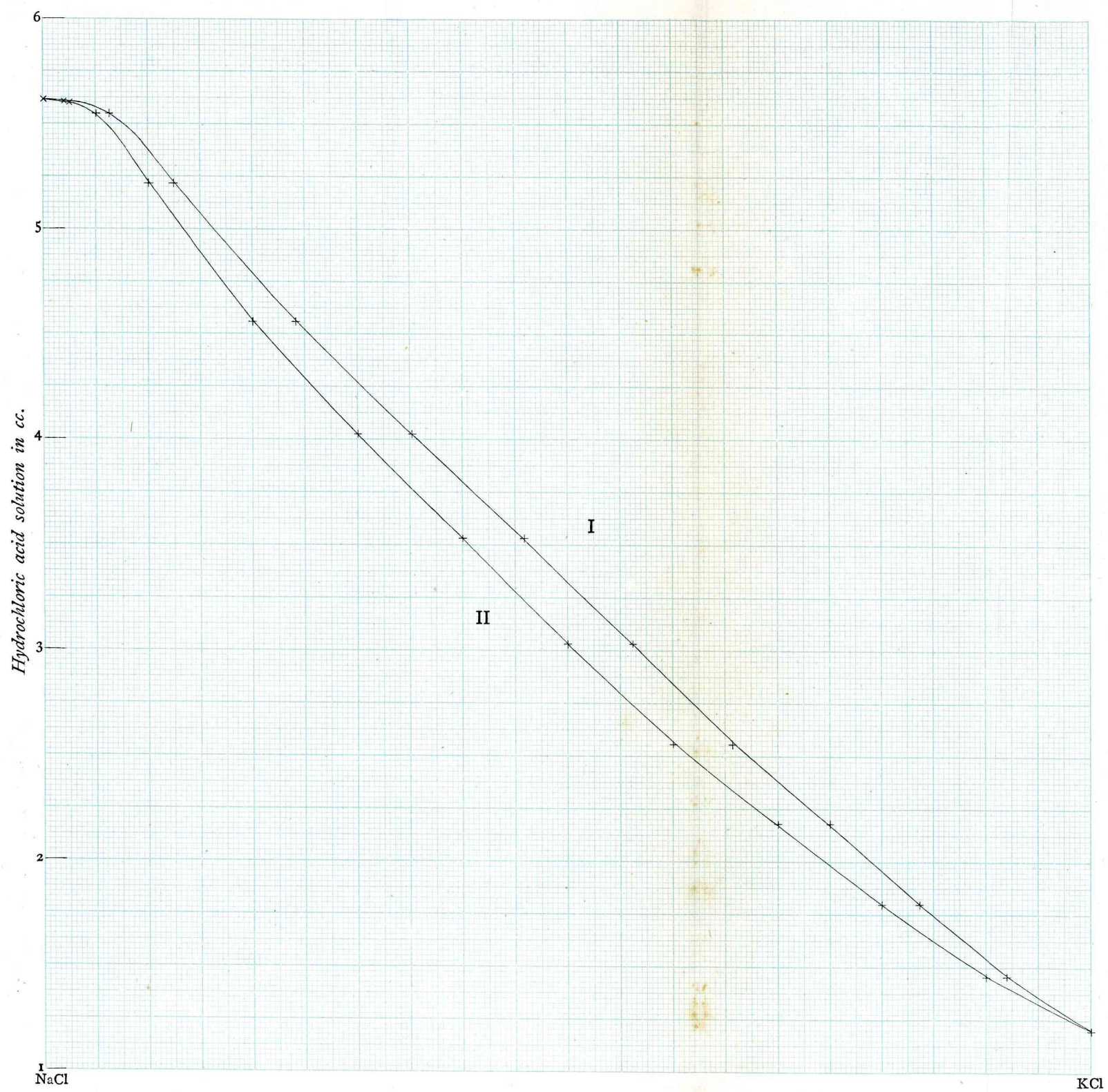
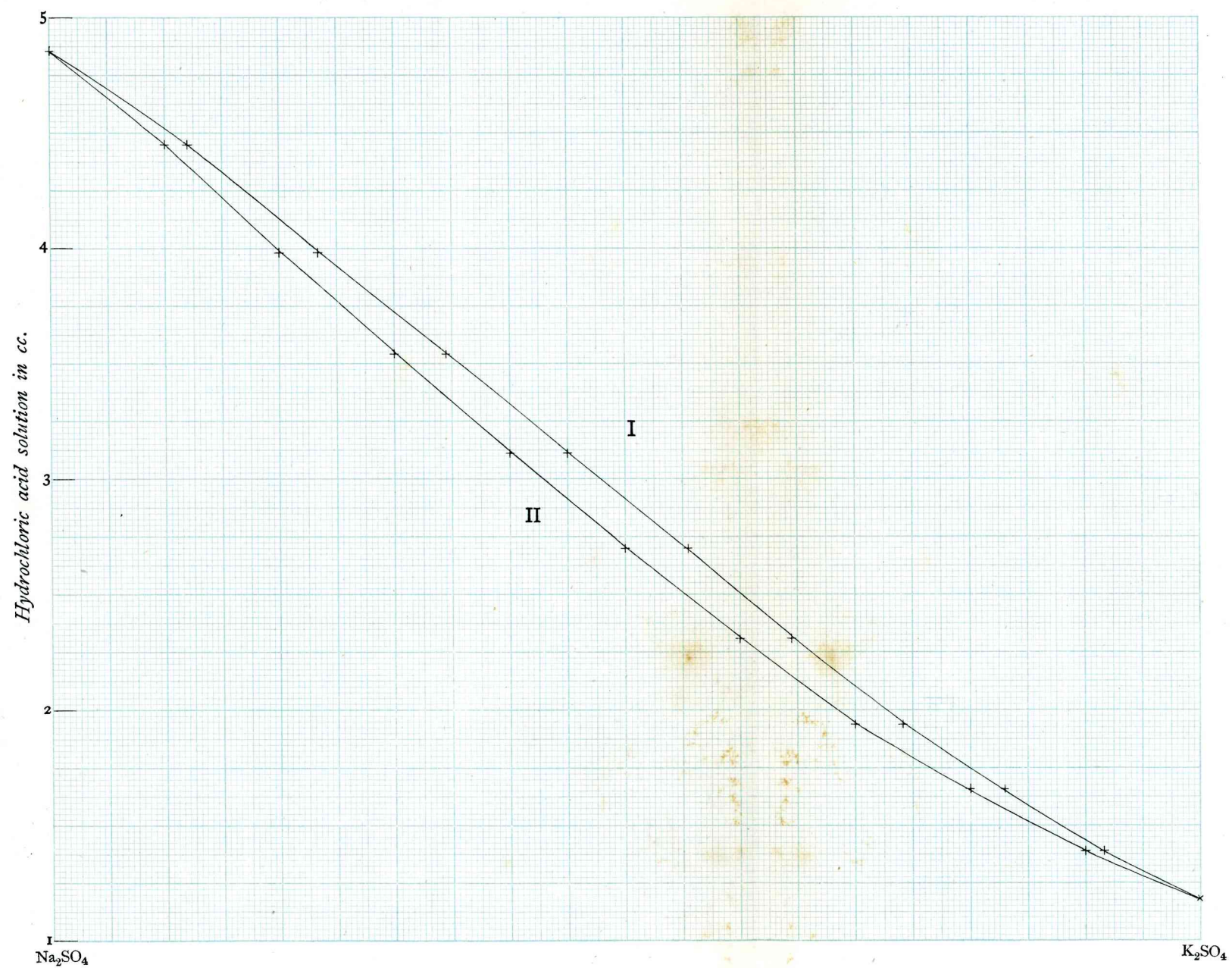




Fig. 3.



as when the data for the fundamental curves were sought. The results were as follows:—

TABLE IV.

Normal hydrochloric acid, required in c.c.	Potassium chloride in the mixture in molar percentage.		
	From the curve.	Taken.	Difference.
5.53	6.6	5.8	0.8
5.45.	8.3	8.0	0.3
4.14	33.0	33.2	0.2
3.85	39.5	40.5	1.0
3.22	52.3	52.3	0.0
3.21	52.3	52.4	0.1

TABLE V.

Normal hydrochloric acid, required in c.c.	Potassium sulphate in the mixture in molar percentage.		
	From the curve.	Taken.	Difference.
4.77	2.7	2.8	0.1
3.90	25.5	25.9	0.4
3.19	42.9	43.2	0.3
2.88	50.6	50.6	0.0
1.77	79.2	79.3	0.1
1.59	85.3	84.9	0.4
1.43	90.7	91.1	0.4

Thus this method of analysis may be taken as tolerably reliable for ordinary purposes.

In conclusion I wish to express my sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instruction during this work.

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