

POTASSIUM CHLORATE AS A STANDARDIZING SUBSTANCE
FOR SOLUTIONS OF ALKALI.¹

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Introduction.

Many substances have been proposed for the standardization of a solution of an alkali. Glaser² mentions, among others, oxalic acid, potassium tetroxalate, potassium hydrogen tartrate and potassium hydrogen iodate. Except oxalic acid these substances are not well suited for this purpose, since they cannot be prepared in a state of purity so that it is certain that their actual composition agrees with their theoretical composition. Potassium hydrogen tartrate contains impurities and does not give strictly accurate results. Potassium hydrogen iodate contains no water of crystallization, but it must be carefully examined qualitatively for chlorides, chlorates, free chlorine and hydrogen chloride before it can be used; also it is not a common salt. Phelps and Weed³ proposed the use of certain organic acids and anhydrides—benzoic, malonic, succinic and phthalic acids and succinic and phthalic anhydrides. An objection to the use of organic acids is that some of them are only slightly soluble, which necessitates the use of somewhat bulky solutions. Furthermore, the results obtained by Phelps and Weed were not concordant. For example, with succinic acid the mean of 10 determinations differs as much as 15% from the theoretical value, while with phthalic and benzoic acids there is a difference of 12% and 16%, respectively, between the experimental and theoretical values. All of these results were higher than the theoretical value.

The Method.

A method which would be free from the objections to the various substances heretofore proposed, and yet give accurate and dependable results, would be desirable. This paper deals with a method proposed by Prof. C. G. Carroll (now deceased) and the work was carried out under his direction. The method is the reduction of potassium chlorate with sulfur dioxide and the standardization of the alkali with the definite amount of sulfuric acid thus formed. The equation which expresses the reaction may be written, $3\text{SO}_2 + \text{KClO}_3 + 3\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + \text{KCl}$. It will be seen that the method is a very simple one and that there are many advantages in its favor. Potassium chlorate can be obtained sufficiently pure by recrystallization, it contains no water of crystallization, it can be easily freed from any moisture without altering its composition, and only

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² "Indicatoren der Acidimetrie und Alkalimetrie," 1909.

³ *Z. anorg. Chem.*, 59, 114 (1908).

a small amount is necessary for one titration—from 0.6 to 0.9 g. for a normal solution.

The potassium chlorate used was dried for 6 hours at 170° and kept in a desiccator over phosphorus pentoxide, but the results obtained (Table III) seem to indicate that not all of the moisture had been driven off, so that in further work the salt was heated for 4 to 6 hours at 240° and more uniform results were obtained (Table IV). Stas had used potassium chlorate in determining the $\text{KClO}_3:\text{KCl}$ ratio. He fused the chlorate in order to free it from moisture, assuming that at the fusion temperature (357°) the salt undergoes no decomposition. But Stähler¹ found that when small quantities of potassium chlorate are fused rapidly, slight decomposition takes place, one g. losing about 0.02 mg. of oxygen; and when larger quantities (10 to 12 g.) are fused the loss is more considerable, about 0.4 mg. of chloride being formed for each g. of chlorate. The conclusion of Stähler is confirmed by the author's work, as shown in Table V.

Description of the Process.

Portions of the chlorate which had been previously dried, were weighed out and placed in 375 cc. Erlenmeyer flasks, 200 cc. water added, the solution boiled for 10 minutes, and a rather vigorous stream of sulfur dioxide passed into the boiling solution until all the chlorate was reduced. The excess of sulfur dioxide was then boiled off and the solution titrated, either hot or cold, against the alkali which was to be standardized. Phenolphthalein was used as indicator.

The solution was first boiled to expel all absorbed air and kept boiling to protect it from the air and thus prevent oxidation of any escaping sulfur dioxide. Various devices were used to insure against loss while boiling and the most satisfactory scheme was to boil the solution in unstoppered Erlenmeyer flasks. It was found that with samples not greater than one g. of chlorate, 30 minutes was long enough to reduce all the chlorate; it was also found that in some cases 20 minutes was not sufficient time to do this, so the gas was always passed in for 30 minutes. From 5 to 10 minutes was sufficient time to boil off the excess of sulfur dioxide. The sulfur dioxide was prepared by allowing conc. sulfuric acid to drop on to sodium hydrogen sulfite. The gas was allowed to run 5 minutes before being passed into the solution so as to free the apparatus from air.

Experimental.

An approximately normal solution of hydrochloric acid was made up and its strength determined by titrating against sodium carbonate prepared from the oxalate by slow and careful heating. The heating was done in platinum crucibles which were placed in beakers for the titration. A slight excess of acid was run in, the solution boiled to expel

¹ *Z. anorg. Chem.*, 71, 368 (1911).

carbon dioxide, and the excess acid determined by titrating back with sodium hydroxide whose relative strength was known. Phenolphthalein was used as indicator. The results are shown in Table I.

TABLE I.
Standardization of HCl Against Na₂CO₃ (from Na₂C₂O₄).

	Oxalate. G.	Acid required. Cc.	Normality of acid.
1.....	1.4472	21.24	1.0165
2.....	1.8376	26.96	1.0169
3.....	2.1049	38.85	1.0165

Mean normality, 1.0163.

Mean difference, 0.03%

An approximately normal solution of sodium hydroxide was prepared according to the method recommended by Cowles¹ and the relative strength of this solution determined by titrating against the standard acid, the solution being protected from the air by soda-lime tubes. The results are given in Table II.

TABLE II.
Standardization of NaOH Against Standard HCl.

Series I.			Series II.		
Acid. Cc.	NaOH. Cc.	Acid equiv. to one cc. NaOH.	Acid. Cc.	NaOH. Cc.	Acid equiv. to one cc. NaOH.
20.145	19.275	1.0451	20.20	19.33	1.0450
30.14	28.835	1.0452	30.14	28.85	1.0449
35.39	33.865	1.0450	36.16	34.60	1.0451
40.81	39.045	1.0452	40.19	38.445	1.0453
			44.21	42.31	1.0452
			48.24	46.045	1.0455

Mean, 1.04515

Mean, 1.04537

Mean of two series, 1.04525

Normality of NaOH, 1.06263

The sodium hydroxide solution was then standardized against potassium chlorate with the results given in Table III.

TABLE III.
Standardization of NaOH Against KClO₃ (dried at 170°).

	Chlorate used. G.	NaOH required. Cc.	Normality of NaOH.
1.....	0.96895	44.58	1.06398
2.....	1.3159	60.62	1.0626
3.....	0.6918	31.86	1.0630
4.....	0.8109	37.31	1.06403

Mean normality of NaOH, 1.06340

Normality against acid, 1.06263

Difference, 0.08%

It will be seen that the results given in Table III are slightly higher than those obtained against the acid. It was thought that this was due to the chlorate not having been entirely freed from moisture. To test

¹ THIS JOURNAL, 30, 1192 (1908).

this, the sample of chlorate used was heated for 4 hours at 240°, cooled, weighed out, reduced and titrated against the alkali solution, with the results as given in Table IV.

TABLE IV.
Standardization of NaOH Against KClO₃ (dried at 240°).

	Chlorate used, G.	NaOH required, Cc.	Normality of NaOH.
1.....	0.8117	37.41	1.0625
2.....	0.8085	37.25	1.06225
3.....	0.6750	31.085	1.0630
4.....	0.5091	23.465	1.0624
5.....	0.8970	41.305	1.0628
6.....	0.7112	23.78	1.0624
	Mean normality of NaOH,	1.06255	
	Normality against acid,	1.06263	
	Difference,	0.008%	

To see what effect fusing the chlorate would have upon the results, about 5 g. of the dried salt was placed in a quartz crucible and quickly fused, the operation requiring about a minute. Portions of this salt were then used to determine the normality of the alkali solution.

TABLE V.
Standardization of NaOH Against KClO₃ (fused).

Chlorate used, G.	NaOH required, Cc.	Normality of NaOH.
0.6801	31.285	1.0642
0.7437	34.215	1.0641
	Mean normality of NaOH,	1.06415
	Normality against acid,	1.06263
	Difference,	0.16%

It will be seen that the results are over 0.1% higher than the normality obtained by titrating against acid or dried but not fused salt. This may be accounted for by the fact that a small quantity of chloride was formed during fusion, which would cause the normality to be higher. The fused salt gave a distinct opalescence with silver nitrate, considerably more than did the salt which had been heated for 4 hours at 240°. Thus Stähler's results are confirmed.

Summary.

1. Solutions of alkali can be standardized against potassium chlorate with uniform results which agree closely with those obtained by standardizing against standard acid.
2. Potassium chlorate of sufficient purity for standardization can be prepared from the ordinary c. p. salt by recrystallization.
3. The best results are obtained by (1) drying the chlorate for 4 to 6 hours at 240°, (2) boiling the solution in an open Erlenmeyer flask, and (3) passing sulfur dioxide into the boiling solution for 30 minutes.

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