

Sodium Carbonate as a Volumetric Standard*

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Sodium carbonate has frequently been proposed as a working standard for acidimetry, but objections have been made to its use on the grounds of alleged lack of purity and stability. In spite of this, sodium carbonate prepared by heating sodium sesquicarbonate is used by Imperial Chemical Industries Ltd. Recent experiments carried out on a thermobalance have confirmed that sodium carbonate prepared by heating sodium sesquicarbonate at 270° C is perfectly stable over long periods at this temperature.

Although the preparation of sodium carbonate and the method of referring it to pure silver used as the ultimate volumetric standard have been described, no account has ever been given of the work that first led to the adoption of sodium carbonate as a working standard for Imperial Chemical Industries Ltd. or of the preparation and assay of subsequent batches of the material. This work is now described and includes the assay of materials containing 100.023, 100.013 and 100.008 per cent. of sodium carbonate. It establishes beyond doubt the purity and stability, and hence the suitability as an acidimetric standard, of properly prepared sodium carbonate.

A recent spectrographic analysis of the ultimate standard silver, to which the sodium carbonate was referred, has given a value of rather better than 99.998 per cent. of silver.

SINCE early in the nineteenth century, sodium carbonate has been recommended as a volumetric standard and, in spite of alleged lack of purity and stability when prepared by different methods, it is still widely approved¹ for this purpose. The numerous papers published on the subject contain statements that appear to be contradictory, and these have been responsible for much of the uncertainty existing on the reliability of sodium carbonate as a reference standard in acidimetry.

Amongst the chief difficulties reported in the literature have been the removal of residual water,^{2,3} the apparent instability on heating,^{4,5} the high solubility in water, which defeats easy purification, and the hygroscopic nature of the anhydrous carbonate.^{6,7} It would seem that these objections may be associated with too severe or ill-defined experimental conditions, or both.

Sodium hydrogen carbonate of high purity has been largely adopted as the source of anhydrous carbonate, because it is simply converted at relatively low temperatures. This procedure was recommended by Gay-Lussac and also by Lunge,^{8,9,10} who showed that sodium carbonate obtained in this way was stable for long periods when heated in the region of 300° C, and his work is confirmed by the experimental work reported in this paper. There are, however, widely differing views in the literature, not only on the best temperature of conversion to the normal carbonate, but also on the composition of the final product, which is alleged to contain oxide or hydroxide.^{8,9,10,11,12,13,14} The temperature recommended for the conversion of sodium hydrogen carbonate to sodium carbonate varies over a wide range, namely from 102° to 450° C.¹⁴ At temperatures below 200° C some workers claim that the decomposition is incomplete, whereas at temperatures of 380° C or over it would appear that decomposition proceeds beyond the stage of normal carbonate, to carbon dioxide, water and sodium oxide or hydroxide. On these points there is some evidence to show that at lower temperatures complete conversion from the sesquicarbonate or hydrogen carbonate to the normal carbonate is not so much a function of the temperature as of the duration of the heating period; for instance, both salts are transformed to the normal carbonate by exposure in a boiling-water oven for a period of about 50 hours.

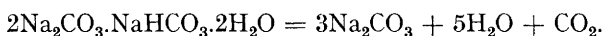
It would be difficult to reconcile all the conflicting views on this subject; however, the experimental work summarised below should help to dispel some of the many doubts that still exist in the minds of those who by tradition rely on sodium carbonate as a reference standard.

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THERMAL STABILITY AND HYGROSCOPICITY OF SODIUM CARBONATE DERIVED
FROM SODIUM SESQUICARBONATE

Sodium hydrogen carbonate is readily converted to sodium sesquicarbonate,^{1,15} which has obvious advantages as a starting material in preparing sodium carbonate. First, it is possible in this conversion to remove mechanical and other impurities and, secondly, the sodium sesquicarbonate so obtained is easier to handle than the finely divided sodium hydrogen carbonate from which it is derived.

The loss in weight of sodium sesquicarbonate on sustained heating is not a reliable criterion on which to judge purity, because of the ease with which the material dissociates at relatively low temperatures. The chief factor of concern in the present instance was the stability of the sodium carbonate derived as a residue on heating sodium sesquicarbonate under defined and controlled temperature conditions. The constancy in weight of the sodium carbonate was obviously one of the simplest means of measuring this stability. Simple experiments were carried out by heating the sodium sesquicarbonate in platinum or silver capsules in an electrically heated air-oven at 270° C. The decomposition is indicated by the equation—



The progressive change in weight and percentage loss in terms of time that sodium sesquicarbonate and sodium hydrogen carbonate undergo when heated to 270° C are given in Table I.

TABLE I

STABILITY OF SODIUM CARBONATE OBTAINED BY HEATING SODIUM SESQUICARBONATE
AND SODIUM HYDROGEN CARBONATE AT 270° C

Time of heating, hours	Sodium sesquicarbonate				Sodium hydrogen carbonate			
	Weight of residue in test 1, g	Loss in weight in test 1, %	Weight of residue in test 2, g	Loss in weight in test 2, %	Weight of residue in test 1, g	Loss in weight in test 1, %	Weight of residue in test 2, g	Loss in weight in test 2, %
2	10.5158	29.89	10.5151	29.90	9.4745	36.85	9.4729	36.86
6	10.5169	29.88	10.5143	29.91	9.4750	36.85	9.4736	36.86
10	10.5173	29.88	10.5149	29.90	9.4765	36.84	9.4752	36.84
14	10.5157	29.89	10.5145	29.90	9.4750	36.85	9.4741	36.85
30	10.5152	29.89	10.5147	29.90	9.4742	36.85	9.4737	36.85
46	10.5161	29.89	10.5133	29.91	9.4743	36.85	9.4732	36.86
Weight of sample	14.9983		15.0001	Theory 29.66	15.0035		15.0030	Theory 36.91

The losses in weight suffered by sodium hydrogen carbonate and sodium sesquicarbonate, respectively, remain constant during the heating time of from 2 to 46 hours. Although reasonable constancy in weight was found after 2 hours, small fluctuations that would appear to be of little practical importance persisted throughout the tests.

It seemed reasonable, however, to carry out tests of a more critical character with the aid of a thermal balance, so that a continuous instead of an intermittent record of the weight could be obtained. The results obtained with sodium sesquicarbonate are shown in Fig. 1, which shows that dissociation with loss of carbon dioxide and water was virtually complete at a temperature of 210° C and within 2 hours of the commencement of heating. Thereafter, the chart readings indicate no detectable change. This is shown in Figs. 2 and 3 of the continuous record, that is, after exposure at 270° C for 6 to 8 hours and for 19 hours. The operating temperature of the heating chamber was then increased to 340° C. In the intervening periods no appreciable change in weight was apparent.

The stability test was repeated with sodium sesquicarbonate that had already been converted to normal carbonate by exposure in an electrically heated air-oven at 270° C for 18 hours. By this means it was possible to increase the size of the sample under test from 2 to 5 g. The results obtained are shown in Fig. 4.

Figs. 4 and 5 represent 6 to 8 hours and 18 to 20 hours, respectively, of additional heating, and again they show no significant change in weight. The temperature of the heating chamber was finally raised to 340° C. At that temperature an increase of 1 mg in the weight was recorded; this is attributed to the change in buoyancy with increase of temperature. A

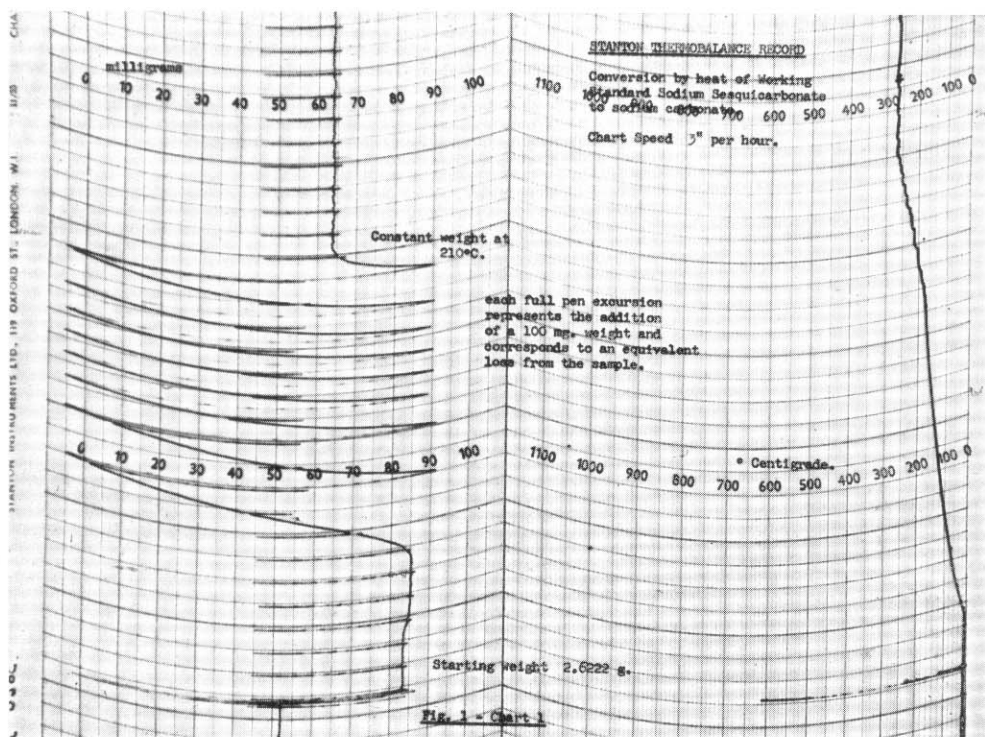


Fig. 1. Chart 1

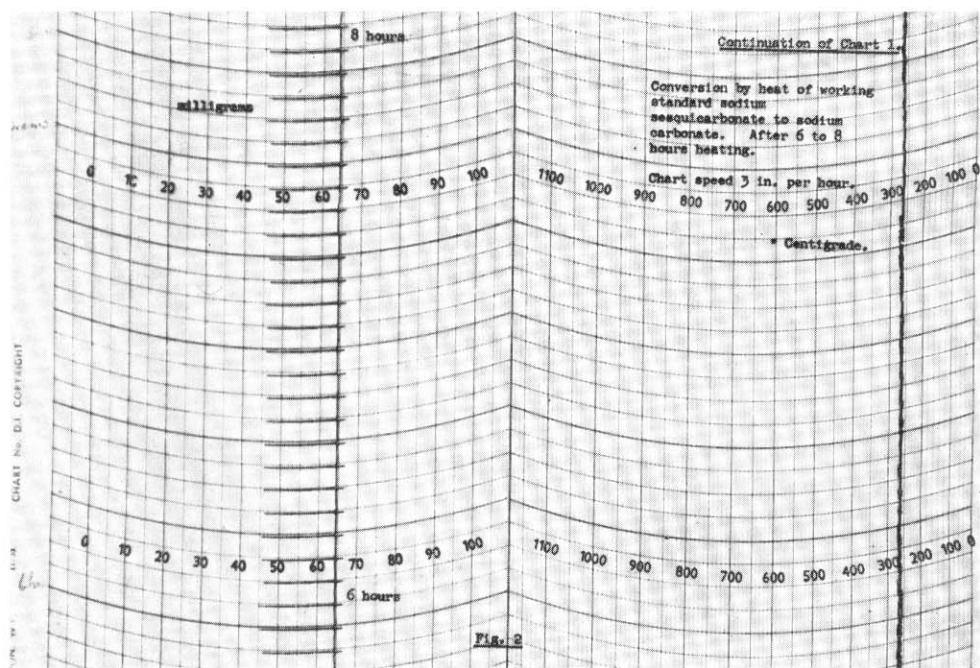


Fig. 2. Continuation of Chart 1

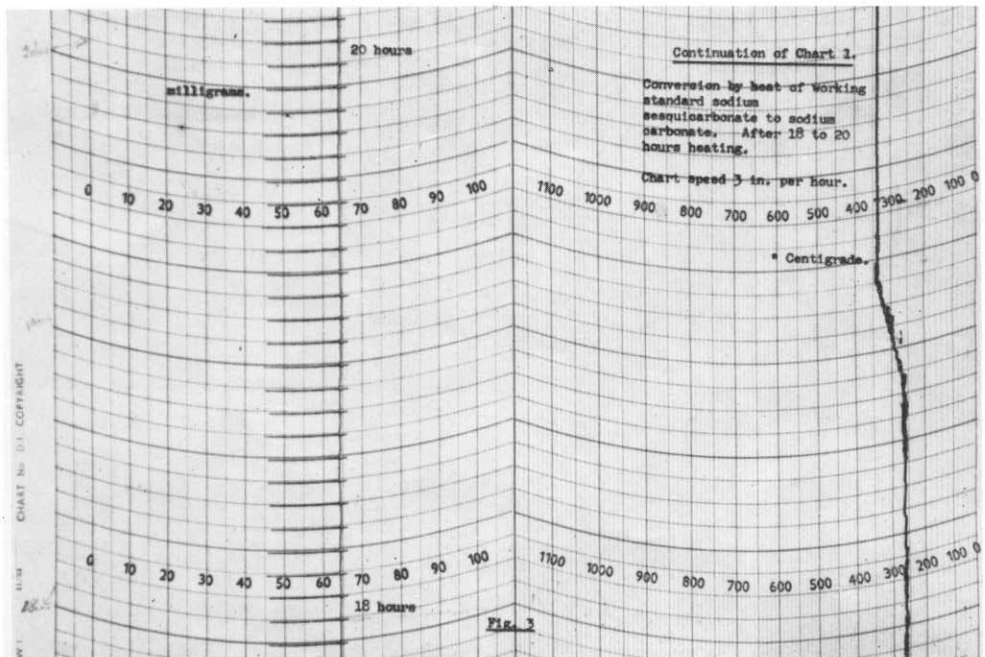


Fig. 3. Continuation of Chart 1

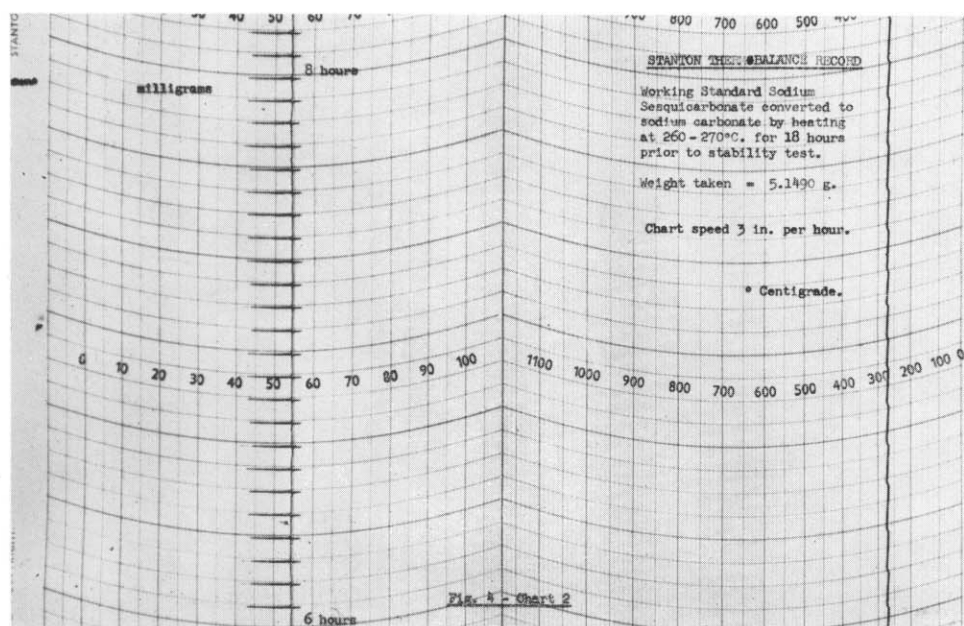


Fig. 4. Chart 2

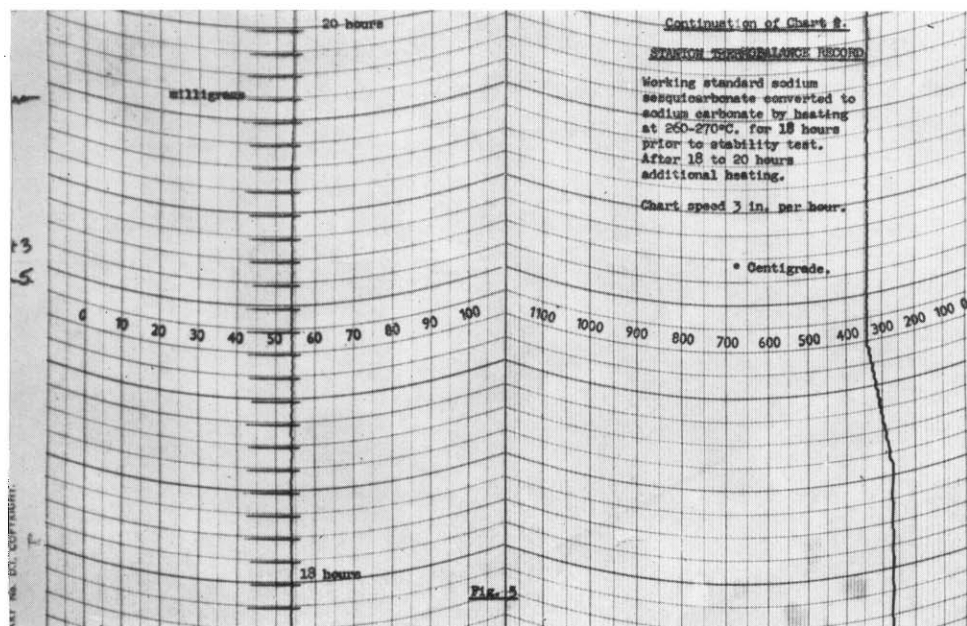


Fig. 5. Continuation of Chart 2

blank test made under the same conditions showed the same response. The maximum variation of the blank was estimated to be about ± 0.25 mg and is attributed chiefly to inherent variability of the instrument.

It is concluded from these tests that sodium carbonate obtained from sodium sesquicarbonate by heating under controlled conditions at 270°C for a period of 2 to 20 hours is completely stable at that temperature.

The sodium carbonate prepared in this way is very slightly hygroscopic at ordinary temperatures and under ordinary conditions. The magnitude of any error that might arise from this cause was examined in the following way—

Weigh the quantity of working standard into a silver or platinum crucible, and heat it to $270^{\circ} \pm 10^{\circ}\text{C}$ in an electrically heated oven until it is constant in weight. Transfer the crucible to a stoppered weighing bottle of suitable size, close the bottle and place it in a desiccator to cool thoroughly. Transfer the bottle to the balance case, momentarily release the stopper of the weighing bottle and, after an interval of 30 minutes, weigh it accurately. Empty the contents of the crucible into a dry 500-ml conical flask, placing the crucible well inside the neck of the flask in order to avoid loss. Replace the crucible immediately in the bottle, transfer the whole to the balance case and weigh it after an interval as before. When the weight of the weighing bottle with contents has been found to be constant, the time necessary to transfer the sodium carbonate to the conical flask was estimated at about 30 seconds. The increase in weight sustained by the weighing bottle with capsule and sodium carbonate was in the interval about $30\text{ }\mu\text{g}$, so that any uptake of moisture by the empty capsule and weighing bottle would be a fraction of this weight.

In an experiment 4.5 g of working-standard sodium sesquicarbonate were heated overnight in a silver capsule at 270°C . The capsule was then cooled in a weighing bottle as described above. The results are shown in Table II. For the first hour the increase in weight is fairly constant at about 0.00003 g per 30 seconds; after this the rate of increase falls off. The procedure adopted in weighing the sodium carbonate precludes any increase in weight that could significantly affect the analytical result.

TABLE II

HYGROSCOPICITY OF FRESHLY HEATED WORKING-STANDARD SODIUM CARBONATE
PREPARED BY HEATING SODIUM SESQUICARBONATE

Test No.	Details of test	Weight, g	Remarks
1	Weighing bottle with capsule and carbonate were weighed	54.96112	Weighing at 5-minute intervals
2		54.96118	
3		54.96117	
			Initial weighing after—
4	The stopper of the weighing bottle was removed and the weighings were continued	54.96117	$\frac{1}{2}$ minute
5		54.96120	1 minute
6		54.96123	$1\frac{1}{2}$ minutes
7		54.96128	2 minutes
8		54.96132	$2\frac{1}{2}$ minutes
9		54.96137	3 minutes
10		54.96166	10 minutes
11		54.96197	15 minutes
12		54.9643	1 hour
13		54.9657	2 hours
14		54.9658	3 hours
15		54.9664	$4\frac{1}{2}$ hours

SCHEME OF STANDARDISATION OF VOLUMETRIC SOLUTIONS

SODIUM CARBONATE AS A REFERENCE STANDARD IN ACIDIMETRY—

Unfortunately, there is insufficient systematic investigational work in the literature to justify reasonably the basis of a general scheme of standardisation with reference and ultimate standards, although such a scheme was recommended by Wagner at the Fifth International Congress in 1903. He suggested that reference and ultimate standards should be examined in two or more different ways, for example, acidimetrically and oxidimetrically. The success of such a plan would necessarily depend on the ultimate standard being of high

purity. This principle was in effect put into practice in 1912 by Dr. E. G. Beckett in the Research Laboratories of Nobel's Explosives Co. Ltd., when the initial part of the Imperial Chemical Industries Ltd. scheme of standardisation was first evolved. It was then decided that the substance that best fulfils the exacting and critical properties of an ultimate standard is silver. However, it is admitted that silver has certain disadvantages, namely it cannot be used directly for the standardisation of acids, except hydrochloric acid, and even in this instance the standardisation would only be correct if the acid were entirely free from its salts and from other acids. Further, it cannot be used directly for the standardisation of oxidising or reducing substances. To overcome these disadvantages, it was decided to employ "working standards" to be used for the standardisation of laboratory solutions direct.

As a working standard for acids and alkalis, pure sodium carbonate was selected and its strength was determined by titration with pure hydrochloric acid, the strength of which had been ascertained by comparison with the ultimate standard silver.

SELECTION OF SODIUM CARBONATE AS WORKING STANDARD—

At this stage it had been decided to use sodium sesquicarbonate as the source of anhydrous carbonate and two sources were available for its preparation, namely,

- (a) from pure sodium hydrogen carbonate ("sodium carbonate 1"),
- (b) from commercially pure anhydrous sodium carbonate ("sodium carbonate 2").

Preparation of sodium carbonate 1—The purest grade of sodium hydrogen carbonate available was added in small quantities to water at 86° C in a resistance-glass flask until no more would dissolve. The solution was then rapidly filtered and cooled thoroughly and the mother-liquor was poured off. The crystals of sodium sesquicarbonate were ground in a mortar and sucked dry in a Hirsch funnel. The moist powder was dried in a porcelain basin and heated on a water bath until the powder had a perfectly dry appearance. It was powdered again, well mixed and sealed in resistance-glass ampoules.

Preparation of sodium carbonate 2—An alternative method for the preparation of sodium carbonate from pure anhydrous carbonate was also examined. After recrystallisation, the salt was dissolved in water and purified carbon dioxide gas was passed into the solution at 0° C until no further gas was absorbed. The sodium hydrogen carbonate was isolated and it was then converted to the sodium sesquicarbonate by the method referred to above.

The purity of the two sodium sesquicarbonates and the hydrogen carbonate and anhydrous carbonate from which they were derived, after heating to 270° C, was determined by reference to ultimate standard silver. The true weights of sodium carbonate and silver were obtained by using a high-precision balance with a sensitivity of ± 0.01 mg. Weighings were made by the method of substitution with weights recently calibrated to class "A" accuracy on a mass basis at the National Physical Laboratory. The results are given in Table III.

TABLE III
PURITY OF SODIUM CARBONATES OBTAINED THROUGH SODIUM SESQUICARBONATE
FROM SODIUM HYDROGEN CARBONATE AND SODIUM CARBONATE BY
EVALUATION WITH ULTIMATE STANDARD SILVER

Description of sample	Purity of sodium carbonate after heating to 270° C until constant in weight, %
Sodium hydrogen carbonate used in the preparation of sodium sesquicarbonate	99.988
Sodium carbonate 1 derived from sodium sesquicarbonate	100.000
	100.003
Sodium carbonate (anhydrous) used in preparation of sodium sesquicarbonate	99.996
sodium carbonate 2—	
(a) derived from sodium sesquicarbonate	99.976
(b) derived from sodium sesquicarbonate after recrystallisation	99.974
(c) derived from sodium sesquicarbonate mother-liquor	99.972

The results in Table III show that—

- (a) sodium carbonate 1 (sesquicarbonate) and the sodium hydrogen carbonate from which it was derived gave carbonates of high purity, and

- (b) sodium carbonate 2 (sesquicarbonate) prepared from pure anhydrous sodium carbonate was slightly less pure than the original anhydrous carbonate from which it was derived. On account of this slight fall in purity, the sodium carbonate (sesquicarbonate) was recrystallised and both crystals and residue from the mother-liquor were tested as described above, but the results failed to show an improvement. This may be explained by small amounts of silica dissolved from the glass vessels used in recrystallisation.

The experiments, therefore, favoured the method in which high-grade sodium hydrogen carbonate was further purified and transformed to sodium sesquicarbonate before conversion to normal carbonate by heating to 270° C, and this method was finally adopted in the preparation of working-standard sodium carbonate.

During the preparation of a new lot of sodium sesquicarbonate the individual batches, the blended batches and the bottled material were exhaustively tested by weight titrations with *N* hydrochloric acid to ensure homogeneity.

In order to assess the purity of the sodium carbonate derived from the heat treatment of sodium sesquicarbonate at 270° C, pure silver was used as the ultimate standard. This procedure has been described in detail in the literature.¹ Briefly, it involves the weight titration of working-standard sodium carbonate with *N* hydrochloric acid previously standardised gravimetrically against the ultimate standard silver. This method has been employed for the evaluation of several lots of sodium carbonate prepared from different batches of sodium sesquicarbonate. The results of the evaluations are shown in Tables IV and V.

TABLE IV

PURITY OF WORKING-STANDARD SODIUM CARBONATE: SERIES I

- (a) *Determination of the ratio of silver to N hydrochloric acid by using ultimate standard silver and chemically pure silver, precipitants being 0.1 N—*

Expt. No.	True weight of silver required by <i>N</i> HCl, g	True weight of <i>N</i> HCl, g	Weight of silver equal to 100 g of <i>N</i> HCl, g	Silver used
5	9.80898	92.2569	10.6322	Ultimate standard
6	9.72351	91.4705	10.6302	Ultimate standard
7	8.10283	76.2103	10.6322	Chemically pure. Guaranteed minimum purity 99.99 per cent.
			Mean = 10.6315	

- (b) *Determination of the ratio of sodium carbonate to N hydrochloric acid and purity of sodium carbonate—*

Expt. No.	True weight of Na_2CO_3 , g	True weight of <i>N</i> HCl required by Na_2CO_3 , g	Weight of Na_2CO_3 equal to 100 g of <i>N</i> HCl, g	Mean weight of silver equal to 100 g of <i>N</i> HCl, g	Weight of Na_2CO_3 equivalent to 107.88 g of silver, g	Equivalent weight of Na_2CO_3 from International Atomic Weights (1925)	Purity of Na_2CO_3 , %
1	3.63071	69.5332	5.22154	10.6315	52.984(0)	52.997	100.025
2	3.68262	70.5230	5.22187	10.6315	52.987(4)	52.997	100.018
3	3.69363	70.7376	5.22159	10.6315	52.984(6)	52.997	100.024
4	3.64518	69.8081	5.22171	10.6315	52.985(8)	52.997	100.021
8	5.25565	100.6529	5.22155	10.6315	52.984(1)	52.997	100.024
9	5.24120	100.3753	5.22170	10.6315	52.985(7)	52.997	100.021
10	5.25910	100.7198	5.22152	10.6315	52.983(8)	52.997	100.025
Mean = 100.023							

From time to time during the interval covering the period of the experiments involving the determination of the actual sodium carbonate present, the standard hydrochloric acid was checked against the silver standard and the results given in the Tables show that no change occurred. The experiments described in Table IV were carried out with 0.1 *N* reagents, whereas those in Table V were obtained with reagents of normal strength. This was done in order to look for the possibility of adsorption of silver nitrate by silver chloride during the standardisation of the hydrochloric acid. The procedures recommended by

Richards and Wells¹⁶ for dilution, order of addition of precipitants and so on were followed throughout this work. Comparison of the results shown in Tables IV and V indicates that there is no evidence that the results were affected by adsorption of silver nitrate. Table V also shows that there is no evidence of difference in the strength of hydrochloric acid resulting from storage in wax-lined containers or resistance-glass bottles.

TABLE V

PURITY OF WORKING-STANDARD SODIUM CARBONATE: SERIES 2

- (a) *Determination of the ratio of silver to N hydrochloric acid by using chemically pure silver, precipitants being N—*

Expt. No.	True weight of silver required by N HCl, g	True weight of N HCl, g	Weight of silver equal to 100 g of N HCl, g
11	7.93567	73.52884	10.7926
12	8.07762	74.83967	10.7932
13	8.23127	76.26780	10.7926
14	8.28278	76.74637	10.7924

Mean = 10.7927

- (b) *Determination of the ratio of sodium carbonate to N hydrochloric acid and purity of sodium carbonate—*

Expt. No.	True weight of Na_2CO_3 , g	True weight of N HCl required by Na_2CO_3 , g	Weight of Na_2CO_3 equal to 100 g of N HCl, g	Mean weight of silver equal to 100 g of N HCl, g	Weight of Na_2CO_3 equivalent to 107.88 g of silver, g	Equivalent weight of Na_2CO_3 from International Atomic Weights (1925)	Purity of Na_2CO_3 , %
15	5.23072	98.67292	5.30107	10.7927	52.987(6)	52.997	100.018
16	5.23038	98.65911	5.30148	10.7927	52.991(7)	52.997	100.010
17	5.22948	98.64379	5.30138	10.7927	52.990(7)	52.997	100.012
18	5.22374	98.72326	5.30143	10.7927	52.991(2)	52.997	100.011

Mean = 100.013

In experiments No. 11, 12, 15 and 16 the acid was stored in wax-lined bottles.

In experiments No. 13, 14, 17 and 18 the acid was stored in resistance-glass bottles.

TABLE VI

PURITY OF WORKING-STANDARD SODIUM CARBONATE: SERIES 3

- (a) *Determination of the ratio of silver to N hydrochloric acid by using ultimate standard silver—*

Expt. No.	True weight of silver required by N HCl, g	True weight of N HCl, g	Weight of silver equal to 100 g of N HCl, g
19	9.85422	92.0528	10.7050
20	9.83063	91.8282	10.7055
21	9.94792	92.9289	10.7049

Mean = 10.7051

- (b) *Determination of the ratio of sodium carbonate to N hydrochloric acid and purity of sodium carbonate—*

Expt. No.	True weight of Na_2CO_3 , g	True weight of N HCl required by Na_2CO_3 , g	Weight of Na_2CO_3 equal to 100 g of N HCl, g	Mean weight of silver equal to 100 g of N HCl, g	Weight of Na_2CO_3 equivalent to 107.88 g of silver, g	Equivalent weight of Na_2CO_3 from International Atomic Weights (1925)	Purity of Na_2CO_3 , %
22	3.54248	67.3714	5.25814	10.7051	52.988(6)	52.997	100.016
23	3.49702	66.5003	5.25865	10.7051	52.993(7)	52.997	100.006
24	3.53805	67.2790	5.25879	10.7051	52.995(2)	52.997	100.004
25	3.56779	67.8450	5.25874	10.7051	52.994(6)	52.997	100.005

Mean = 100.008

The mean values of the purity of the sodium carbonate from Tables IV and V are 100.023 ± 0.003 and 100.013 ± 0.005 per cent., respectively. This leads to the conclusion that some oxide or hydroxide is formed during the decomposition¹⁷ of the sodium sesquicarbonate, but the amount is not sufficiently large to make any significant difference when the material is used as a standard. As Table I and the charts on thermal stability show that prolonged heating of sodium carbonate at 270° C does not result in any appreciable decomposition, it seems reasonable to conclude that the slight decomposition that occurs (accounting for the slightly high results, see Tables IV (a) and (b)) takes place during the decomposition of the sesquicarbonate (or hydrogen carbonate), oxide or hydroxide only being produced while moisture is being lost. The dry sodium carbonate is then completely stable to heat at 270° C.

The results of tests for the purity of a further lot of sodium carbonate are shown in Table VI.

For effective comparison, the results in Table VI have been calculated with the same atomic weights (1925) as those of the earlier figures. If the atomic weight of carbon, however, is taken as 12.01, *i.e.*, the 1954 value, the level of the purity of sodium carbonate would be raised by 0.009 per cent., and the magnitude of this increase is of the order of precision of the results, namely ± 0.007 per cent. if the three lots are treated as one population in the statistical sense. The results, in general, show that sodium carbonate obtained by heating sodium sesquicarbonate to 270° C is consistently of high purity.^{18,19}

Samples of sodium sesquicarbonate representing the material from Series 3 were submitted to three independent laboratories for examination. The detailed methods employed were the same in each instance. The results returned by each of the laboratories are given in Table VII.

TABLE VII

PURITY OF WORKING-STANDARD SODIUM CARBONATE DETERMINED BY THREE INDEPENDENT LABORATORIES: EVALUATION WITH ULTIMATE STANDARD SILVER

Expt. No.	Purity of sodium carbonate from sodium sesquicarbonate, %	Evaluation by laboratory
1	100.03	A
2	99.96	B
3	99.95	B
4	99.98	B
5	100.03	C
6	100.03	C
Mean = 100.00		

These results confirm the values in Table VI.

ULTIMATE STANDARD SILVER

The pure silver prepared by electrolytic deposition from chemically pure silver has a high degree of purity, probably 99.995 per cent.

It was assumed to have a purity of 100.00 per cent. in the evaluation of the various lots of sodium sesquicarbonate.

Four methods were used to check the purity, namely—

- direct gravimetric comparison with chemically pure silver of guaranteed minimum purity of 99.99 per cent. of silver, through *N* hydrochloric acid; the purity of ultimate standard silver was deduced to be 0.01 per cent. higher than that of the silver from which it was prepared,
- chemical examination for impurities before and after purification; this showed that the original silver contained 0.0007 per cent. of copper and some carbon, but these two impurities could not be detected in the purified silver,
- determination of the equivalent of working-standard iodine used for oxidimetry, which gave a value of 126.93 compared with the International Atomic Weight of 126.92, and
- recent spectrographic examination, which gave the total impurities as not more than 0.002 per cent.

The thermal balance was lent by the courtesy of Messrs. Stanton Instruments Limited.

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