25 ml of absorbent solution are measured into a 250 ml Erlenmeyer flask and the latter is connected with the condenser, as shown in the accompanying cut, and the assembled apparatus is evacuated.

25 ml 1:1 HCl are carefully added to the evolution flask, followed by 25 ml trichlorbenzol and some aqueous methyl orange indicator. Heat is then applied, and boiling begins promptly and will slow down gradually as CO_2 distils over. Heating should be continued for 30 minutes, then the source of heat removed and the evolution flask filled with boiled distilled water at about 50°C. With caution the water may be added until it reaches the upper bulb, but the operator should be ready to close off the rubber tube leading to the receiver in case any sudden ebullition takes place in the evolution flask. The rubber connection to the receiver is now closed with a pinch cock, disconnected from the condenser and the receiver is filled with air free from CO_2 by connecting it to a wash bottle containing strong alkali. It is then closed with a rubber stopper and set aside until wanted for titration.

Titrations are made drop-wise with N/4 HCl and phenolphthalein indicator. A blank test is run exactly the same as above, using the same quantities of reagents and 400 ml unboiled distilled water. The difference between the two titrations is equivalent to CO_2 in terms of N/4 HCl. 1 ml N/4 HCl is equivalent to 0.0055 CO_2.

A comparison of the direct titration of 25 ml absorbent solution with the titration of the blank test will show the quantity of CO_2 in the reagents + 400 ml unboiled water. The absorbent solution is prepared by mixing equal volumes of normal NaOH and normal barium chloride solutions and standing over night. The resultant clear solution will be very nearly half normal in alkaline strength. It is a very efficient absorbent for CO_2.

This method is capable of giving very precise results which are very slightly higher than theoretical when it is employed on chemically pure sodium carbonate. When tested in Committee work on special samples of synthetic detergents, the results were equal in accuracy to those obtained by the gravimetric train method.

Report of the Soap Analysis Committee—1940

M. L. SHEELY, Chairman

Tetra Sodium Pyrophosphate in Soap—In view of the extensive use of tetra sodium pyrophosphate in certain types of soap, the Committee undertook cooperative studies on its determination in soap products. The program included the following determinations on a sample of soap powder containing tetra sodium pyrophosphate as well as other builders including sodium silicate.

1. Determination of tera sodium pyrophosphate by zinc acetate gravimetric method.
2. Determination of tetra sodium pyrophosphate by conversion to orthophosphate by acid treatment and determination of total P_2O_5 by official A.O.C.S. method.
3. Moisture determination on the soap sample at time of analysis to permit calculation of results to a definite moisture basis.

Procedure No. 2 (above) was intended only as a check determination on Procedure No. 1, since the sample under study contained no added orthophosphate. Obviously this method could not be considered specific for tetra sodium pyrophosphate if both forms of phosphate were present.

Fourteen laboratories participated in these studies and the reported results are shown in Tables I and II. As a matter of record, the procedure followed by the Committee was as follows:—

Determination of Tetra Sodium Pyrophosphate ($Na_4P_2O_7$) in Soap Products

Reagents Required

1. Neutral Ethyl Alcohol (94% or higher). Denatured alcohol, formula No. 30, or 3-A may be used.
2. Acetic acid, glacial. C. P. grade.
3. Bromphenol Blue, 0.04% solution. Dissolve 0.4 grams Bromphenol Blue in distilled water and make up to 1 liter.
4. Zinc acetate, 3.7% solution. Dissolve 44 grams of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in water. Add glacial acetic acid to make the final solution to a pH of 3.3 (about 200 ml of glacial acetic acid), and make the volume to 1000 mls with distilled water. (pH may be determined by using Bromphenol Blue as an indicator with a series of color standards ranging from a pH of 3.0 to 4.0, or by the electrometric method.)
5. Acetic acid, dilute solution, pH 3.4. Make up this solution by adding a few drops of acetic acid to distilled water, to a pH of 3.4.

Procedure

Digest hot, a 5 gram (±0.01) sample with 200 ml of freshly boiled neutral alcohol. Filter through a filter paper or a Gooch crucible with suction, washing with hot alcohol until free from soap. Wash the alcohol insoluble portion remaining on the filter paper with hot water until washings are neutral to phenolphthalein. Combine filtrate and washings and transfer to a 250 ml volumetric, cool to room temperature and make up to mark with distilled water.

Transfer an aliquot containing an equivalent of approximately 0.1 gram of tetra sodium pyrophosphate to a 250 ml beaker, and adjust the pH using Bromphenol Blue as an inside indicator to between 3.3 and 3.5 by adding glacial acetic acid. pH adjustment can also be accomplished at this point by using a glass electrode. Adjust the final volume to approximately 75-100 ml with distilled water and add an excess of 3.7% solution of zinc acetate, dropwise, with constant stirring. Filter off the precipitated zinc pyrophosphate using an ashless filter paper or a tared Gooch crucible and wash the precipitate thoroughly with dilute acetic acid (pH 3.4).

Dry the zinc pyrophosphate carefully over a low flame and ignite to constant weight at a dull red heat and calculate to tetra sodium pyrophosphate.

Calculation:

$$\frac{\text{Wt. of } Zn_2P_2O_7 \times 0.8728 \times 100}{\text{Wt. of Sample}} = \%\ Na_4P_2O_7$$

Conclusions

A meeting of the Committee was held on October 1, 1940 at the Stevens Hotel, Chicago. It was the opinion of the Committee, after due consideration of the data, that the results by the proposed zinc acetate, gravimetric

1940 A.O.C.S. SOAP COMMITTEE COOPERATIVE RESULTS

TABLE I.

TETRA SODIUM PYROPHOSPHATE DETERMINATION

		% $Na_4P_2O_7$ Zinc Acetate Gravimetric Method		% $Na_4P_2O_7$ Total P_2O_5 by Official A.O.C.S. Method		% $Na_4P_2O_7$ by Special Methods Submitted by Members	
	Moisture	Actual	5% Moisture Basis	Actual	5% Moisture Basis	Actual	5% Moisture Basis
Armour & Company 31st St. Aux.	3.41%	11.84%	11.65%	12.36%	12.16%	....	....
	3.41	11.91	11.72	12.47	12.27	....	....
Average	3.41%	11.88%	11.69%	12.41%	12.22%	....	....
Colgate-Palmolive-Peet Company	3.39%	11.61%	11.41%	12.01%	11.81%	(a) 11.69%	11.49%
	3.41	11.49	11.29	11.91	11.71	11.73	11.53
Average	3.40%	11.55%	11.35%	11.96%	11.76%	11.71%	11.51%
Davies Young Soap Company	4.50%	11.53%	11.47%	13.19%	13.12%	....	....
	....	11.32	11.26	13.25	13.18	....	....
	....	11.41	11.35	12.97	12.91%	....	....
Average	4.50%	11.42%	11.36%	13.14%	13.07%	....	....
Foster D. Snell, Inc.	3.45%	10.40%	10.25%	11.24%	11.06%	....	....
Hooker Electro-chemical Company	3.58%	11.5%	11.33%	12.2%	12.02%	(b) 12.3%	12.11%
	....	11.3	11.13	12.1	11.92	....	....
	....	11.4	11.23	....	....	....	....
Average	3.58%	11.4%	11.23%	12.15%	11.97%	12.3%	12.11%
Lever Bros.	4.2%	11.74%	11.64%	11.82%	11.72%	(c) 11.98%	11.88%
	....	11.51	11.41	11.93	11.83	12.00	11.90
	....	11.57	11.47	....	....	....	....
	....	11.94	11.84	....	....	....	....
	....	11.84	11.74	....	....	....	....
	....	12.05	11.95	....	....	....	....
	....	11.54	11.44	....	....	....	....
	....	11.44	11.34	....	....	....	....
Average	4.2%	11.70%	11.60%	11.88%	11.78%	11.99%	11.89%
Los Angeles Soap Company	3.78%	11.04%	10.90%	11.73%	11.58%	(c) 12.12%	11.97%
	....	10.68	10.54	11.76	11.61	12.11	11.96
	....	12.09	11.94	11.93	11.78	12.10	11.95
	....	....	....	11.95	11.80	12.37	12.21
	....	....	....	....	....	12.39	12.23
Average	3.78%	11.27%	11.13%	11.84%	11.69%	12.22%	12.06%
New York Produce Exchange	3.83%	11.84%	11.69%	11.98%	11.83%	....	....
Proctor and Gamble Company	3.30%	12.83%	12.60%	11.95%	11.73%	(a) 12.02%	11.80%
Southern Cotton Oil Company	5.50%	10.40%	10.45%	11.83%	11.89%	....	....
Stillwell-Gladding	5.10%	12.22%	12.23%	12.87%	12.88%	(d) 12.61%	12.62%
	....	12.36	12.37	12.96	12.97	12.57	12.58
	....	12.79	12.80	13.13	13.14	13.00	13.01
	....	12.59	12.60	....	....	....	....
Average	5.10%	12.49%	12.50%	12.99%	13.00%	12.73%	12.74%
Swift & Company	3.33%	11.85%	11.65%	12.45%	12.23%	(a) 11.76%	11.56%
	....	11.95	11.74	....	....	11.76	11.56
	....	11.61	11.41	....	....	11.93	11.73
	....	11.96	11.75	....	....	11.83	11.63
	....	....	....	....	....	11.90	11.70
Average	3.33%	11.84%	11.64%	12.45%	12.23%	11.84%	11.64%
U. S. Dept. of Commerce, Nat'l Bureau of Stds.	3.91%	11.35%	11.23%	15.77%	15.60%	....	....
	3.94	11.28	11.16	15.70	15.53	....	....
Average	3.93%	11.32%	11.20%	15.74%	15.57%	....	....
Allen B. Wrisley Company	....	11.00%	10.83%	11.53%	11.36%	....	....

(a) Method consisted essentially of titration either with a glass electrode or an indicator of the sulphuric acid liberated when zinc sulphate was added to the tetra sodium pyrophosphate sample in solution at a pH of 3.3 to 3.5.

(b) Total P_2O_5 determined on an ashed sample using official A.O.C.S. method, and P_2O_5 calculated to tetra sodium pyrophosphate.

(c) Volumetric method depending on the titration of precipitated phosphomolybdate, tetra sodium pryophosphate being converted to the ortho form by boiling with nitric acid.

(d) Zinc Acetate gravimetric method, except using zinc acetate wash solution and 50% alcohol.

method were too much at variance to warrant even tentative adoption of the method. It was agreed that further studies should be made using the same sample and a volumetric procedure which briefly is as follow:—The aqueous solution of the alcohol insoluble is adjusted to a pH of 3.8, preferably by means of a glass electrode. A solution of zinc sulfate is then added and the H_2SO_4 liberated is titrated with standard alkali. Many laboratories are now using this method and report satisfactory results.

Carbon Dioxide (combined) in Soap—The Committee has made further studies on the proposed Evolution-Volumetric Method[1] for the determination of carbonates as CO_2 in soaps. The original authors have done some further work on this method and have suggested several modifications to the procedure previously published. Accordingly, a subcommittee was appointed to study the revised method on the following samples:

1) A washing powder with a high carbonate content, marked sample "A".

2) A powdered soap with a relatively low carbonate content marked sample "B".

3) C. P. sodium carbonate.

4) C. P. sodium carbonate with the addition of coconut fatty acids to the reaction flask. This pro-

---

[1] Hitchcock & Divine. Oil & Soap, January 1938, issue No. 1, Vol. XV, pages 8, 9, 10.

cedure was included to determine the effect of volatile acids on the amount of CO_2 recovered,

The following determinations were requested on these samples:

1. The revised Evolution-Volumetric Method.
2. A.O.C.S. procedure as outlined in the present standard official methods — Carbon Dioxide Absorption.
3. By the usual method of determining by difference from the titration of the alcohol insoluble, that is, correcting for any small amount of sodium silicate that may be present.

Conclusions

The results, in general, were in reasonably good agreement, although in the case of the C.P. sodium carbonate, the reported figures were about ½ to 1% on the high side. Notwithstanding this, the Committee decided to recommend adoption of the method as a tentative procedure, subject to a few minor changes, which will be included in the published data. The proposed method is intended as an alternate to the present official procedure, which will be retained until the further experience of the Committee indicates that the latter may be deleted in favor of the new method. The cooperative results of six collaborators are published as a part of this report in Tables III and IV.

The recommended procedure and diagram of apparatus (Sketch No. 1) are as follows:—

Evolution-Volumetric Method for Determination of Carbonates as CO_2 in Soaps and Other Detergents

Reagents Required

1. N/2 HC1.
2. Alkaline absorbent solution. — This is prepared by mixing equal volumes of 1-normal caustic soda (carbonate-free) and 1-normal barium chloride and filtering after settling over night.
3. Dilute hydrochloric acid made by mixing 1 part of concentrated C.P. HC1 (Sp. Gr. 1.183) and 2 parts of distilled water.
4. Trichlorbenzol (1-2-4 isomer) reagent grade; boiling point about 213°C; specific gravity about 1.47.
5. 20% magnesium chloride solution.
6. Phenolphthalein indicator, 1% solution.
7. Methyl Orange Indicator, 0.1% solution.

TABLE II.

(Summary of Table I, Tetra Sodium Pyrophosphate Determination)

	% $Na_4P_2O_7$ Zinc Acetate Gravimetric Method 5% Moisture Basis	% $Na_4P_2O_7$ Total P_2O_5 Official A.O.C.S. Method 5% Moisture Basis	% $Na_4P_2O_7$ by Special Methods Submitted by Members 5% Moisture Basis
Armour & Company 31st St. Aux.	11.69%	12.22%	....
Colgate-Palmolive-Peet Company	11.35	11.76	11.51%
Davies Young Soap Company	11.36	13.07	....
Foster D. Snell, Inc.	10.25	11.06	....
Hooker Electrochemical Company	11.23	11.97	12.11
Lever Bros.	11.60	11.78	11.89
Los Angeles Soap Company	11.13	11.69	12.06
New York Produce Exchange	11.69	11.83	....
Proctor & Gamble Company	12.60	11.73	11.80
Southern Cotton Oil Company	10.45	11.89	....
Stillwell-Gladding	12.50	13.00	12.74
Swift & Company	11.64	12.23	11.64
U. S. Dept. of Commerce Nat'l Bureau of Standards	11.20	15.57*	....
Allen B. Wrisley Distributing Company	10.83	11.36	....
Average	11.39%	11.97%	11.96%
High	12.60	13.07	12.74
Low	10.25	11.06	11.51

* Not included in average.

TABLE III.

SODIUM CARBONATE DETERMINATION

		% Na_2CO_3 Evolution-Volumetric Method	% Na_2CO_3 A.O.C.S. Absorption Method	% Na_2CO_3 Titration Method
Armour & Company 31st St. Aux.	Sample A	62.02%	62.03%	61.46%
		62.91	61.56	61.38
	Average	62.46%	61.79%	61.42%
	Sample B	1.86%	1.89%	1.46%
		1.86	1.83	1.67
	Average	1.86%	1.86%	1.56%
	C.P. Sodium Carbonate	101.17%	99.39%	....
		100.69	99.69	....
	Average	100.93%	99.54%	....
	C.P. Sodium Carbonate plus Coco Fatty Acids	101.61%	....	....
		100.11	....	....
	Average	100.86%	....	....
Davies Young Soap Company	Sample A	61.45%	....	....
		61.50	....	....
	Average	61.48%	....	....
	Sample B	1.93%	....	....
		1.91	....	....
	Average	1.92%	....	....
	C.P. Sodium Carbonate	99.40%	....	....
		99.43	....	....
	Average	99.42%	....	....
Hooker Electrochemical Company	Sample A	62.28%	....	....
		62.28	....	....
		62.41	....	....
		62.28	....	....
	Average	62.31%	....	....
	Sample B	1.92%	....	....
		1.91	....	....
		1.91	....	....
	Average	1.91%	....	....
	C.P. Sodium Carbonate	100.96%	....	....
		100.96	....	....
		100.96	....	....
	Average	100.96%	....	....
	C.P. Sodium Carbonate plus Coco Fatty Acids	101.23%	....	....
		101.23	....	....
		101.23	....	....
	Average	101.23%	....	....
Proctor & Gamble Company	Sample A	61.48%	60.7%	60.13%
		60.84	60.5	60.86
		....	....	59.84
		....	....	59.84
	Average	61.16%	60.6%	60.17%
	Sample B	1.59%	1.7%	1.54%
		1.64	1.7	1.52
	Average	1.62%	1.7%	1.53%
	C.P. Sodium Carbonate	101.33%	99.2%	99.99%
		101.02	101.08	99.84
		100.22	99.68	100.17
		100.76	....	100.17
	Average	100.83%	99.99%	100.04%
	C.P. Sodium Carbonate plus Coco Fatty Acids	100.22%	....	....
		99.43	....	....
		100.22	....	....
	Average	99.96%	....	....
Swift & Company	Sample A—Average	61.70%	61.00%	61.12%
	Sample B—Average	1.94%	1.86%	1.83%
	C.P. Sodium Carbonate	102.00%	100.00%	....
		101.00	99.10	....
	Average	101.50%	99.55%	....
	C.P. Sodium Carbonate plus Coco Fatty Acids	101.60%	99.9%	....
Allen B. Brisley Distributing Company	Sample A	62.7%	62.5%	61.8%
	Sample B	1.90%	1.90%	1.89%
	C.P. Sodium Carbonate	100.5%	99.60%	....
	C.P. Sodium Carbonate plus Coco Fatty Acids	100.5%	....	....

TABLE IV.

(Summary of Table III, Sodium Carbonate Determination)

	% Na_2CO_3 Evolution-Volumetric Method	% Na_2CO_3 A.O.C.S. Absorption Method	% Na_2CO_3 Titration Method
SAMPLE A			
Armour & Co., 31st St. Aux.	62.46%	61.79%	61.42%
Davies Young Soap Co.	61.48	....	....
Hooker Electrochemical Co.	62.31	....	....
Procter & Gamble Co.	61.16	60.6	60.17
Swift & Co.	61.70	61.0	61.12
Allen B. Wrisley Distributing Co.	62.7	62.5	61.8
Average	61.97%	61.47%	61.13%
SAMPLE B			
Armour & Co., 31st St. Aux.	1.86%	1.86%	1.56%
Davies Young Soap Co.	1.92	....	....
Hooker Electrochemical Co.	1.91	....	....
Procter & Gamble Co.	1.62	1.7	1.53
Swift & Co.	1.94	1.86	1.83
Allen B. Wrisley Distributing Co.	1.90	1.90	1.89
Average	1.86%	1.83%	1.70%
C.P. SODIUM CARBONATE			
Armour & Co., 31st St. Aux.	100.93%	99.54%	....
Davies Young Soap Co.	99.42	....	....
Hooker Electrochemical Co.	100.96	....	....
Procter & Gamble Co.	100.83	99.99	100.04%
Swift & Co.	101.50	99.55	....
Allen B. Wrisley Distributing Co.	100.5	99.6	....
Average	100.69%	99.67%	100.04%
C.P. SODIUM CARBONATE PLUS COCO FATTY ACIDS			
Armour & Co., 31st St. Aux.	100.86%	....	....
Hooker Electrochemical Co.	101.23	....	....
Procter & Gamble Co.	99.96	....	....
Swift & Co.	101.64	99.90%	....
Allen B. Wrisley Distributing Co.	100.5	....	....
Average	100.84%	99.90%	....

Apparatus

See Sketch No. 1.

Procedure

Weigh up sample containing an equivalent of approximately 0.2 g. of CO_2 into flask "A". Introduce about 400 ml of unboiled, distilled water to which has been added 2 ml of the absorbent solution to prevent loss of CO_2; heat the flask over a steam bath until the soap is dissolved. Cool the dissolved sample until slightly warm to the hand. Add 30 ml of the 20% magnesium chloride solution to the thoroughly cooled dissolved sample. A few glass beads may be added to the flask to prevent bumping when the solution is boiled. Place 25 ml of absorbent solution in flask "C," connect apparatus as shown in Sketch No. 1 including cooling water for condenser "D". Evacuate the air through "B" with a suitable aspirator pump, reducing the pressure to 65 to 80 mm., as indicated on manometer "G". Care should be taken to maintain a proper reduced pressure throughout the test.

Add dilute HCl (1:2) containing a few drops of methyl orange indicator through dropping funnel "B" until an acid reaction is obtained in solution in flask "A," avoiding a large excess of acid.

Introduce trichlorbenzol through "B," approximately 1 ml being used for every 2 g. of material being tested. Precautions should be taken to prevent air entering the system at any time during the tests. Place a burner with a *small flame* immediately in contact with bottom of evolution flask "A" and heat continuously for 30 minutes. Remove flame and fill flask "A" and condenser "D" with CO_2-free water at approximately 50°C to just below the side-arm on the condenser. Flask "C" should be agitated at intervals from the time the dilute hydrochloric acid is added until the evolution flask and condenser have been filled with water. Disconnect flask "C," guarding against access of air. Titrate absorbent solution in flask "C" dropwise with N/2 HCl until neutral to phenolphthalein indicator.

Run a blank determination without the detergent, using the same quantities of water and reagents. Some CO_2 will show its presence. The blank establishes the values of the absorbent solution in terms of N/2 HCl, and any CO_2 in the reagents is in this way corrected for.

Calculations:

$$\frac{(\text{Blank Titr.} - \text{Sample Titr.}) \times 0.022 \times N \times 100}{\text{Wt. of Sample}} = \%\ CO_2$$

Free Alkali in Potash Soaps—The attention of the Committee has frequently been called to the fact that the present official method gives erroneous results in the case of potash soaps containing small amounts of K_2CO_3. A suggestion has been proposed in which isopropyl alcohol is substituted for ethyl alcohol in the standard method, the theory being that K_2CO_3 is less soluble in isopropyl alcohol.

The Committee agreed to test two samples of potash soaps using isopropyl alcohol as a solvent vs. ethyl alcohol (or specially denatured alcohol Formula 30 or 3-A) now prescribed in the official methods. One sample is to be prepared with as little potassium carbonate as possible and the other to contain about 1 to 2% commonly found in commercial soaps of this type.

McNicoll Method for Rosin—The Committee was of the opinion that our experience has been sufficient to warrant recommending official adoption of the McNicoll Method and deletion of the Wolff Method as an official method of the Society.

Summary

Recommendations of the Committee are as follows:—

1) Pyrophosphate in soap — No recommendations for official action. Further studies to be undertaken.

2) Combined CO_2 in soap—Recommend tentative adoption of Evolution--Volumetric method. Retain present official absorption method (A.O.C.S.) as alternate.

3) Free alkali in potash soaps—Studies to be undertaken using isopropyl alcohol as solvent instead of ethyl alcohol.

4) McNicoll method for rosin in soap—Recommend official adoption of this method and deletion of present Wolff method.

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