periods served to effect a constant weight. Slight differences are undoubtedly produced by the size, weight and thickness of the crucible.

TABLE V—TIME REQUIRED IN HEATING ALUMINA TO CONSTANT WEIGHT

Time Min.	No. 1	No. 2	No. 3	No. 4	HEATED IN 20-MIN. PERIODS		
					20 min.	40 min.	60 min.
10	36.9620	29.6670	21.0587	29.6647	29.6538	29.6530	29.6527
20	36.9615	29.6653	21.0570	29.6638	33.7635	33.7627	33.7625
30	36.9605	29.6643	21.0569	29.6638	33.7760	33.7760	
40	36.9605	29.6643			36.9621	36.9602	36.9602
					29.6730	29.6730	29.6730

One precipitate was given a special series of blastings to determine whether or not the alumina was hygroscopic after the blasting. The results (Table VI) indicate that this change in weight was very largely

TABLE VI—SHOWING HYGROSCOPIC PROPERTY OF ALUMINA

	Weights
Constant weight obtained (cruc. + ppt.)	21.0598
Left 6 days in the desiccator	21.0636
Blasted 10 min.	21.0611
After 24 hrs. blasted 20 min.	21.0605
After 24 hrs. blasted 20 min.	21.0604
After 24 hrs. blasted 20 min.	21.0602
Blasted a second 20 min.	21.0598
Left covered in the balance case 24 hrs.	21.0624

due to the precipitate, since a platinum crucible treated in much the same way did not change appreciably in weight.

CONCLUSIONS

I—Boiling for 1 min. completely precipitates all aluminum present, and longer boiling may lead to a re-resolution of part of it.

II—Aluminum hydroxide need not be washed free from ammonium chloride before ignition.

III—The excess of ammonia present when precipitation is made should be as small as possible and never more than 1 or 2 cc. in 250 cc. of solution.

IV—Aluminum hydroxide freshly precipitated is soluble to a slight extent in water and to about the same extent in dilute ammonium nitrate solution.

V—The precipitated hydroxide, when large, must be blasted 40 min. to insure its being reduced to a constant weight.

VI—The ignited alumina is strongly hygroscopic.

NOTE—Since this paper was written a paper has been published by W. H. Daudt, *THIS JOURNAL*, 7 (1915), 847, confirming what we have found to be true regarding the presence of ammonium chloride at the time of ignition.

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THE ANALYSIS OF SOAP POWDERS

By LOUIS ROSENBERG AND VICTOR LENHER

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During recent years great progress has been made in those industries which supply cleansing materials. The advent of the modern washing powder has brought into the household a convenient, economical cleanser. The powders which to-day are in common use divide themselves into three general classes:

I—So-called Washing Powders, composed of tri-sodium phosphate, borax, or a mixture of various proportions of sodium carbonate and bicarbonate: it is obvious from the composition of these powders that their main efficiency lies in their ability to soften the water used.

II—Soap Powders proper, a mixture consisting of various proportions of sodium carbonate and soap: the soaps used are commonly prepared from cottonseed soap stock and have as a filler sodium carbonate, which itself is a water softener of great value.

III—Scouring Powders, which contain an abrasive and soap either with or without the addition of sodium carbonate.

In this article are described various experiments which have been conducted on the soap powders proper. The basic scheme used is that given by Leffmann in Allen's "Commercial Organic Analysis." During our studies, Dr. Leeds published a scheme for the analysis of soap, which is quite similar to the one used by us for the analysis of soap powders. Additions and modifications to the older schemes were made as the work progressed, and it is to aid the soap analyst that important details are described.

Our purpose in presenting this paper is to offer our experience to those interested in the analysis of soap powders, and we do so because the particular problems we have found are not discussed in the form that is desirable for those who have similar problems to solve.

MOISTURE

The ordinary methods for determining water in soap are not satisfactory when applied to washing powders. Experiments have repeatedly demonstrated that heating a 10-g. sample at 105° C. until the weight becomes constant is worthless, for the odor of decomposing soap is usually observed before this temperature is reached. When heated for 1 hr. to 105°, most of the soap powders give off a strong odor of decomposed soap, hence the determination is of little value. Further, the soap powder upon heating to 105° frequently forms lumps which prevent complete drying: even if a weighed glass rod is used to break up the lumps, it is difficult to keep the sample from caking. In powders which contain as high as 30-40 per cent water, spattering frequently occurs. Leffmann's suggestion for soap—that the drying be done on a sand bath—is useless with many powders, inasmuch as even with the greatest care decomposition takes place. The methods in use for the determination of moisture in a high-grade stearic acid soap are unsatisfactory, as they frequently fail entirely when applied to soap powders containing cottonseed soap stock or low-grade tallow soap.

The method of Fahrion, in which the sample is heated with three times its weight of oleic acid until a clear solution is obtained, indicating the removal of the water, was found to be inapplicable, as difficulty was experienced in determining when the solution became clear. The recommendation of Fahrion, to heat the sample (to which has been added oleic acid) in a platinum dish over a free flame, was also tried with the soap powders, but even with the greatest care decomposition of the soap took place. On a sand bath the powder soon decomposed. Sample 1, containing actually 37.8 per cent of water, was used in experimenting with oleic acid in order to test this method for moisture. Six samples of 2 g. each were

mixed with 6 g. of anhydrous oleic acid. On heating, the odor of decomposing soap was noticed from all. The two samples showing the clearest solution and the least odor indicated 56.5 per cent and 60.3 per cent water, respectively, or an error of 50 to 60 per cent more water than they actually contained.

The method recommended is one in which the heating can be done at low temperature. A vacuum drying oven is admirably suited for this purpose. The various powders examined in our studies were heated between 60 and 65° at a pressure of 60 mm. until the weight became constant. In the 2-g. samples used, constant weight was attained only after 10 hrs.' heating, and in some cases 20 hrs. of heating were required. No odor was observed and the samples did not cake. The results (percentages) were as follows:

No. 1, 37.85 and 37.82; No. 2, 23.75 and 23.99.

The recommendations commonly given to heat for 12 hrs. are insufficient. No. 3, for example, required 20 hrs.' heating in the vacuum oven before constant weight was attained.

PETROLEUM ETHER EXTRACTION

The usual procedure of extraction with petroleum ether, with a Soxhlet extractor, was used in order to determine the unsaponified fat, unsaponifiable matter from the fat and free fatty acids. A 10-g. sample of the soap powders frequently required as much as 15 hrs. of extraction with petroleum ether. The solvent was subsequently evaporated and the residue weighed. All of the powders examined were found to contain less than 1 per cent of unsaponified matter.

FATTY ACID DETERMINATION

The determination of the fatty acids in the soap powders is, of course, of the greatest importance, inasmuch as it means the soap content of the powder. Of the various methods which have been suggested for the determination of the fatty acid content in soaps, the most important are: (1) Direct weighing; (2) petroleum ether extraction; (3) potassium soap; (4) volumetric. Fendler and Frank¹ have shown the inaccuracies of all of these methods.

In the direct weighing method, a piece of weighed paraffin or stearic acid is added to the liberated fatty acids, and the cooled solidified mass is subsequently weighed. The results are frequently very high. Extraction of the fatty acids with petroleum ether and evaporation of the solvent commonly gives low results. The variation in the results depends largely on length of drying of the fatty acids obtained. In one instance the percentage of fatty acids was reduced nearly 60 per cent by long drying. Fendler and Frank preferred for accuracy the potassium soap method, but inasmuch as the potassium soap must be dried for 20 to 28 hrs. on a water bath, the method is rather too time-consuming for ordinary commercial analysis. Volumetric methods can be said to give only fair results.

The cake method is a simple, rapid method; but unless due precautions are taken, discordant results

are obtained. The inaccuracies of the cake method, according to Noerdlinger, are attributed to the stearic acid used to collect the fatty acid. If the stearic acid is previously heated to 160° the inaccuracies are avoided. In our experiments the cake method was adopted as the most satisfactory procedure, and was carried out as follows:

A 2-g. sample of the powder is placed in a tall, narrow, 200-cc. beaker 4 in. high, and the sample dissolved in hot water. An excess of $N/2$ nitric acid is then added to separate the fatty acids. The solution, stirred continuously, is heated for $1/2$ hr. in boiling water, and a weighed portion of 4 g. of stearic acid, previously heated to 160°, added. The solution is stirred repeatedly and warmed for another $1/2$ hr., after which the beaker and contents are allowed to cool. The stirring rod, which should be about 1 in. longer than the beaker, is allowed to remain in the beaker. The fatty acid and the stearic acid on cooling solidify, and can be easily lifted out of the beaker by means of the stirring rod. The liquid in the beaker can be filtered in order to collect any solidified fat which has not adhered to the cake, but usually this amount is small. The circle left by the cake around the beaker can be readily scraped off and added to the cake. The cake is then wiped with filter paper and placed upon a weighed cover glass, allowed to dry for several hours, after which it is weighed. The weighed cake less the weight of the stearic acid added gives the amount of fatty acid in the sample.

If the melted fat is allowed to cool rather slowly, a more uniform cake is formed, and the cake can be more easily removed from the beaker; whereas if the cake be cooled quickly, the rapid solidification causes moisture to be enclosed in the cake. If cavities are formed, these are likely to enclose the solution. A 200 cc. beaker of the tall, narrow type is a convenient size, inasmuch as a cake suitably fitted to the balance pan is formed. Furthermore, the addition of mineral acid to a washing powder commonly causes much effervescence, due to large percentages of sodium carbonate: the use of a tall beaker lessens the danger of overflow during this sudden effervescence.

TOTAL ALKALI DETERMINATION

Should the percentage of total alkali be required, the excess of standard acid required to liberate the fatty acid can be titrated back with $N/2$ alkali. In washing powders, the total alkali reported does not have the significance that it does in soap. The presence of sodium carbonate marks the amount of alkali combined as soap. A total alkali determination cannot be used as a means for determining the relative merits of different powders, since the powder with the highest per cent of sodium oxide may be the one which contains the lowest per cent of soap. A total alkali determination is unnecessary, unless it is desirable to check the individual alkali determinations.

SODIUM CHLORIDE DETERMINATION

In our hands the gravimetric method is preferable over the volumetric method for the determination of chlorides in soap powders.

¹ *Z. angew. Chem.*, **22** (1909), 252-61.

ALCOHOL EXTRACTION

In order to separate the soap content of the powders from such fillers as sodium carbonate, sodium silicate, borax, etc., it is necessary to make an extraction with alcohol. Due to the fact that soap powders contain a high percentage of water, it is preferable to use absolute alcohol. If, however, the analysis is to be made on a sample which has been dried in the vacuum oven, 95 per cent alcohol is satisfactory.

A 2-g. sample of the powder can be extracted in a 250-cc. beaker with 100 cc. of alcohol for $1\frac{1}{2}$ hr. The alcohol becomes yellow colored and a white residue of the inorganic salts, such as sodium carbonate, sodium silicate, and borax, separates out and can be filtered off and washed with alcohol. In this extract, phenolphthalein will show the presence of caustic alkali. No free alkali was found in any of the powders examined. On the other hand, all of the soap powders showed a trace of free fatty acid. The alkali combined as soap is found by adding a large excess of water to the alcoholic solution and boiling off the alcohol, decomposing the soap with an excess of $N/2$ nitric acid and titrating back with $N/2$ alkali. The alkali found is reported as Na_2O . No distinction need or-

DETERMINATION OF SODIUM CARBONATE AND SILICATE

The residue from the extraction with alcohol is dissolved in water and diluted to exactly 250 cc. in a volumetric flask. The residue from all of the samples analyzed was completely soluble in hot water. In one or two powders a slight residue remained upon the filter paper, but the amount was too small to warrant further examination. Aliquot portions of 50 cc. are taken for the silica determination. The solution is acidulated with hydrochloric acid and evaporated to dryness, as in the ordinary method for the determination of silica. The acidification and evaporation are repeated. The soluble matter is extracted with hot water and the residue when dried and ignited is weighed as SiO_2 . The percentage of silica was calculated to sodium silicate ($Na_2Si_4O_9$). In the soap powders analyzed the amount of silica found was so small that it was probably present as an impurity rather than as a real constituent of the powder. Borax was not found to be present in any of the powders analyzed. In the absence of borates and with less than 1 per cent of sodium silicate, a fair determination of the sodium carbonate can be made by direct titration with $N/2$ hydrochloric acid, using methyl orange as the indicator.

TABLE I—SCHEME OF ANALYSIS

Weigh out a 2-gram sample. Dry in vacuum oven at 65° C.		Loss in weight = Moisture. Extract with petroleum ether.	
EXTRACT	RESIDUE consists of Soap and Mineral Constituents.	Extract with 95 per cent alcohol.	
Contains Uncombined Fat.	EXTRACT consists of Soap and free Alkali.	RESIDUE consists of Na_2CO_3 , $NaCl$, $Na_2Si_4O_9$, Na_2SO_4 , $Na_2B_4O_7$, Starch and Insoluble Matter. Dissolve in hot water, dilute to 250 cc. and filter: divide the filtrate into five equal parts.	
Evaporate the ether, dry at 110° C. and weigh.	(1) Add 2 or 3 drops of phenolphthalein, and titrate with $N/10$ acid; the amount used corresponds to free caustic alkali: calculate as Na_2O .	1— Na_2CO_3 : Titrate with $N/2$ HCl.	RESIDUE
	(2) Next add a large excess of water, boil off the alcohol, decompose with excess of $N HNO_3$ and boil: add 4 g. stearic acid, boil again, and cool.	2— $NaCl$: Precipitate with $AgNO_3$ and weigh as $AgCl$.	Consists of Starch and Insoluble Matter.
	SOLUTION contains Soda CAKE contains Fatty combined as Soap. Ti- Acid. Remove cake, trate excess of acid back dry and weigh.	3— $Na_2Si_4O_9$: Add HCl and evaporate to dryness; repeat. Add water, filter, dry, ignite and weigh as SiO_2 . Calculate to $Na_2Si_4O_9$.	
		4— Na_2SO_4 : Precipitate with $BaCl_2$ and weigh as $BaSO_4$. Calculate to Na_2SO_4 .	
		5—Borates: If present, determine by glycerol or mannitol method.	

dinarily be made between the sodium and the potassium in soap powders. The alcoholic extract should be diluted to at least 250 cc. before titrating in order to get a satisfactory end-point.

A rapid method for analysis of soap powders is based on the alcoholic extraction procedure: A 2-g. sample is extracted with absolute alcohol, the solution filtered and the filtrate tested with phenolphthalein for free alkali. If the solution contains free alkali it is titrated with $N/2$ nitric acid: the alcohol is then evaporated off, leaving a residue of dry soap, which, if it has not been necessary to add nitric acid, can be weighed and reported as percentage of total soap. To determine the alkali combined as soap, the dry residue of soap is dissolved in water and the solution titrated with $N/2$ nitric acid, using methyl orange as the indicator. The residue from the alcoholic extraction, which consists of sodium carbonate, sodium silicate, borax, etc., can be tested by the methods given below. The percentage of total soap plus sodium carbonate, etc., deducted from 100 per cent will give the approximate amount of water, or, an accurate water determination can be made in the vacuum drying oven.

Should sodium bicarbonate be present in the powder, the treatment of the residue insoluble in petroleum ether and in alcohol, would necessarily need to be materially modified.

SCHEME OF ANALYSIS

The condensed scheme of analysis outlined in Table I is suggested for soap powders. It is based on the solubility of soap in alcohol and the insolubility of the inorganic constituents. It possesses the advantage that but one sample need be taken for analysis, and the soap itself is separated at once from the other constituents of the powder. In the simple scheme, as given, such substances as fluorides, rosins, glycerin, sugar, and sodium bicarbonate are not provided for. Our experience with the powders examined showed them to be of simple composition.

DISCUSSION OF RESULTS

The analyses of a number of representative soap powders are given in Table II. Their composition in a number of cases differs materially from that given for the same powder by Bragg¹. This difference is doubtless due to the introduction of the continuous

¹ *Chemical Engineer*, 18 (1913), 73.

drying apparatus which has changed the formula used by a number of the larger manufacturers. The continuous drying apparatus allowed the manufacturer to

TABLE II—TABULATION OF RESULTS (PERCENTAGES)

Sam- ple No.	Mois- ture	Fatty Anhy- dride	Na ₂ O as Soap	Total Soap	Na ₂ CO ₃	Na ₂ SiO ₃	NaCl	Unsa- ponified Matter	Total Per cent
1	37.82	18.39	2.63	21.02	39.37	0.45	0.55	0.69	99.90
2	22.06	19.44	3.58	23.02	53.53	0.99	0.75	0.24	100.59
3	23.75	21.63	2.71	24.34	50.35	0.72	0.35	0.85	100.36
4	20.86	18.93	2.65	21.58	55.38	0.90	0.86	0.45	100.03
5	18.52	20.34	2.68	23.02	56.45	0.36	1.32	0.74	100.41
6	43.38	16.74	2.23	18.97	36.30	0.72	0.34	0.87	100.58
7	30.40	21.46	2.86	24.32	40.00	0.99	0.72	0.79	97.22

increase the water content of the product and to lessen the amount of soap. Previously this addition of water resulted in an inferior caked powder.

The determinations made show that the soap powders consist essentially of sodium carbonate and soap. This should be the case from the method of manufacture employed, *i. e.*, the soap stock, caustic alkali and soda are incorporated and the product prepared similar to that of soap. After hardening it is ground into the powder form in which it appears on the market.

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THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL BY ELECTROMETRIC TITRATION

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The method to be described includes the solution of the steel in acid, the oxidation of the elements in question under suitable conditions, and the titration of the solution with ferrous sulfate using the electrometric method of determining the end-point. This method of titrating chromates has been described recently by Hildebrand¹ and by Forbes and Bartlett,² and has been applied by the authors to the determination of vanadium.³ The apparatus is in all respects identical with that described elsewhere for the determination of vanadium and therefore will not be dealt with here.

DETERMINATION OF CHROMIUM IN STEEL

It was hoped that by the application of the electrometric method to the determination of chromium, an accurate and rapid method could be devised for the determination of this element. To this end the oxidation of chromium salts to chromates was undertaken after the methods suggested by Walters,⁴ Rich⁵ and Tusker.⁶ These methods were selected because of their simplicity and because they involve no filtering. In these methods ammonium persulfate is used to oxidize chromium and manganese to chromate and permanganate, sometimes with the addition of silver nitrate. Hydrochloric acid, added in small amounts to the hot solution, serves to reduce the permanganic acid, but is without action on the chromates. On trying the different modifications of this method which have been published, extremely variable and unsatisfactory results were obtained. This experience

led us to undertake a more careful study of the conditions necessary to make the method work with certainty.

It seemed possible to us that the following errors might interfere with the successful working of the method: (a) Incomplete decomposition of ammonium persulfate, (b) incomplete oxidation of chromium, (c) reduction of part of the chromate by hydrochloric acid during the breaking up of permanganic acid, and (d) incomplete reduction by the hydrochloric acid of manganese in the higher states of oxidation. (a) and (d) would tend to make the results too high, while (b) and (c) would have the opposite effect; thus it might be possible for some of the errors to exist undetected because of counterbalancing. We therefore planned to test each point separately.

DECOMPOSITION OF AMMONIUM PERSULFATE

Eight solutions of 300 cc. volume, each containing 0.0102 g. of chromium as chromate and 65 cc. of sulfuric acid (sp. gr. 1.20), were heated to boiling and 5 g. of ammonium persulfate added. The solutions were then boiled in groups of two for 5, 10, 15 and 30 min., after which they were cooled and titrated with ferrous sulfate, using the electrometric end-point. The potassium dichromate solution had been standardized against ferrous sulfate electrometrically and this in turn had been compared with standardized potassium permanganate solution.

From the experiments shown in Table I, it is evident that 5 min. boiling of such a solution does not

TABLE I—THE DECOMPOSITION OF AMMONIUM PERSULFATE 0.0102 G. Chromium Present in Each Case

Time of Boiling (min.)	5	10	15	30
Chromium Found (g.)	{ 0.0159 0.0196	{ 0.0101 0.0117	{ 0.0095 0.0094	{ 0.0096 0.0082

completely remove the ammonium persulfate and the oxidizing agents into which it decomposes. Even 10 min. is insufficient in some instances. Boiling for a much longer time has the apparent effect of reducing some of the chromate, for the values are uniformly lower than the expected values. It is not improbable that this reduction goes on from the first, but its effect upon the titration is masked by the fact that other oxidizing agents have not been removed. This may be explained as due to the breaking down of the ammonium persulfate in acid solution to give Caro's acid and hydrogen peroxide, both of which reduce chromium. We believe that any method depending upon ammonium persulfate alone for its oxidizing action can give correct results only by a balancing of errors. This opinion is supported by other experiments in which the sulfuric acid mentioned above was changed to higher and lower concentrations, and in which it was partly and completely replaced by nitric acid.

DECOMPOSITION OF AMMONIUM PERSULFATE IN THE PRESENCE OF SILVER NITRATE

Marshall¹ suggested the use of ammonium persulfate and silver nitrate in dilute nitric acid as an oxidizing agent for manganese. Experiments parallel

¹ *J. Am. Chem. Soc.*, **35** (1913), 869.

² *Ibid.*, **35** (1913), 1527.

³ *Ibid.*, **38** (1916), 341.

⁴ *Mel. Chem. Eng.*, **12** (1914), 310.

⁵ *Ibid.*, **13** (1915), 239.

⁶ *Chem.-Zig.*, **39** (1915), 122.

¹ *Chem. News*, **83**, 16.