

saturated with a few drops of the platinic chloride solution. Too much of the solution causes blurring and too little of it or too dilute a solution results in dim numbers. After the numbers are dry the crucibles are gently heated until the platinum is reduced and the gelatin burned off. This is most conveniently accomplished in a muffle. Finally, the numbers are heated for one-half minute in the flame of the blast lamp—*i. e.*, for one-half minute from the time it attains the temperature of the flame.

If the wares are cleaned and fired as directed, the markings adhere well. The figures become more prominent if burnished by use of a china painter's burnishing stone, if available, or of seashore sand, or less advantageously of a silica soap. The deposit is resistant to single acids, but not to alkalis. In some experiments library paste was substituted with good results for the gelatin sizing. Gold and mixtures of gold and platinum solutions may be applied similarly, but there is more danger of volatilizing the gold chloride before reduction takes place, and thereby causing a spreading of the deposit. The resulting figures also are less conspicuous than when platinum is used. This method of getting the deposit of platinum or gold may possibly find use also in decorating chinaware. If the solution is applied with a brush, a quill, or a glass stylus, it may be more dilute. The same method applied to silica wares also gives very satisfactory results.

#### APPLICATION OF CHINA COLORS BY USE OF RUBBER STAMPS.

Paints mixed in oil are not satisfactory for use with rubber stamps because the type leaves on the porcelain a rim of thickened paint while the main surface of contact is relatively bare. The method finally adopted is to stamp the wares to be marked with a sizing or varnish similar to that which painters use for applying gold leaf. "Fat oil"—*i. e.*, partly oxidized linseed oil, supplied by paint dealers—proved very satisfactory for this purpose. While this sizing is still sticky, the dry pigment is dusted on with a camel's-hair brush. After the varnish has set, the excess of pigment is wiped off and the crucible is fired at a strong red heat, preferably in a muffle. The "fat oil" dries slowly. This is an advantage because then some time may be allowed between its application and the dusting on of the pigment, for the irregular layer on the porcelain to draw out by surface tension into a smoother one. Standing over night at room temperature, or for one hour in a drying oven at 100° C., suffices for the varnish to set. The pad used for "inking" the type may consist of several thicknesses of linen cloth and is nearly saturated with this varnish. Too much varnish on the pad must be avoided, as it results in figures with ragged outlines. This varnish may readily be cleaned from the rubber type, before it has set, by use of a 10 per cent. alcoholic solution of caustic potash applied with a small bristle brush.

#### COLOR TESTS.

Seeking a prominent color and one resistant to both

acids and alkalis, a series of tests was made with samples of overglaze blues, blacks, and reds supplied by a dealer and one blue prepared by the writer. These were stamped onto porcelain crucibles as above described. The heat used in firing was a red heat slightly lower than that at which the colored figures on the white background disappeared (the radiation plus reflection from a colored surface equaling that from a white surface). In one test they were brought from a dull red to the above temperature during the course of one hour and then cooled. This sufficed to make the blacks and the reds resistant to nitric acid (35 per cent.) and to sodium hydroxide solution (10 per cent.), but the blues were appreciably soluble in the acid. To make the blues resistant, they had to be fired to a higher temperature or held at the above maximum temperature for about an hour. To test the permanence of the markings, the acid and the alkali were each applied five minutes cold, followed by five minutes at a boiling temperature. Of the seven blacks tried, two—*viz.*, a lettering black and a blue black—gave especially good effects in that they yielded a very strong black. Of the same samples when applied to silica dishes and fired as indicated, both the blacks and the reds were again resistant to both nitric acid and alkali, but the blues, even when fired more strongly, came off very readily in nitric acid.

In these tests an electric muffle was used. In heating porcelain crucibles to a high temperature in gas muffles in which the muffle chambers were not thoroughly sealed off from the gas chambers, and occasionally also in the electric muffle, a brown stain developed on the porcelain. This could readily be removed by heating the crucible half a minute in the blast flame, most conveniently in a suitable chimney.

In applying the rubber stamp to the crucibles it is difficult to avoid a sliding motion that blurs the imprint. This may be prevented by using a suitable guide or a steadying support. The writer found it convenient to rest both the inverted crucible and the type holder on a smooth surface while making the impression. In numbering crucibles, etc., it is often advantageous to have the number on three sides so as to make it visible, no matter which way the crucible is turned.

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#### ON THE QUANTITATIVE ESTIMATION OF SODIUM HYDROXIDE IN "BLACK LIQUOR."

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In the manufacture of cellulose by the soda process wood is digested under pressure with a solution of sodium hydroxide. The liquid separated from the resulting pulp is called "black liquor," and contains the sodium hydroxide unconsumed in the reaction, together with the sodium salts of acids formed by the decomposition of the wood. A precise evaluation of this residual sodium hydroxide would give valuable information on the exact consumption of caustic soda

by wood, and perhaps help to explain the chemistry of the digestion process.

#### PRESENT METHOD.

The method now employed is simply one of titration with acid, using a solution of phenolphthalein as an outside indicator.<sup>1</sup> In detail: 25 cc. of black liquor are diluted with 300 cc. of water; 10 cc. of a concentrated  $\text{BaCl}_2$  solution (400 grams to liter) are added to precipitate carbonates and the organic acid radicles which yield insoluble barium salts, and the solution is titrated with N acid ( $\text{HCl}$ ,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ). The end point is determined by removing drops of the solution at intervals during the titration and allowing them to fall gently from a stirring rod into a solution of phenolphthalein in water just covering the bottom of a beaker. When a drop fails to develop a red color in the indicator solution immediately surrounding it, the end point is considered to be reached. This method is approximate only, but checks within 5 per cent. can generally be obtained; *e. g.*, three successive titrations required respectively 5.00, 4.90, 5.11 cc. N acid.

The difficulties in arriving at the end point are: first, the distinguishing of the red color of the indicator from the brown of the drop; and, second, the slow development of the red color around the drop. The real trouble, however—dependent, perhaps, on the two just mentioned—is that the end point recorded varies with the working conditions. Thus if the titration is carried out at dilutions other than the one given above, widely differing values are obtained, as is shown in the following table which gives the results of titrating 25 cc. of black liquor at different dilutions:

Total vol. of diluted black liquor.	Individual titrations. N acid.	Average.
39 cc.	3.50 cc. } 3.42 cc. }	3.46 cc.
88 cc.	3.67 cc. } 3.60 cc. }	3.63 cc.
185 cc.	3.56 cc. } 3.70 cc. } 3.60 cc. }	3.62 cc.
435 cc.	4.13 cc. } 4.62 cc. } 4.30 cc. } 4.74 cc. }	4.45 cc.
835 cc.	5.00 cc. } 4.90 cc. } 5.11 cc. }	5.00 cc.
1635 cc.	4.92 cc. } 5.15 cc. }	5.03 cc.

Again, if there is added to a black liquor (which has been analyzed by the present method) a known amount of  $\text{NaOH}$  and this "fortified" black liquor is then titrated, the increase of acid used in titration is smaller than the amount equivalent to the  $\text{NaOH}$  added. For instance: to a black liquor titrating 6.39 cc. acid,  $\text{NaOH}$  was added equivalent to 8.28 cc. acid, and duplicate titrations of this "fortified" black liquor showed readings of 13.54 and 13.64 cc., an average of 13.59 cc., while the calculated result is 14.67 cc.

One possible explanation of these inconsistencies is that the  $\text{OH}$  ions are adsorbed by the colloids present.

<sup>1</sup> For the basic idea involved in this method we are indebted to Mr. Chas. N. Waite, of Wilmington, Del.

Another theory supposes the presence of an organic complex which combines with  $\text{OH}$  ions, the resulting molecule having but a small dissociation constant. On increasing the concentration of  $\text{OH}$  ions (as in a "fortified" black liquor) the dissociation is checked, whereas a decrease in the concentration of  $\text{OH}$  ions (as in dilution) increases the dissociation and hence the total amount of  $\text{OH}$  ions present.

#### ATTEMPTS TO IMPROVE PRESENT METHOD.

The following is a description of numerous attempts to improve our original method, and is published in the hope of bringing forth some more successful method, or of starting a discussion and stimulating further work along this line.

*Preliminary Experiments.*—Small test tubes, partly filled with a solution of phenolphthalein in water, were tried for the examination of the individual test drops, but no satisfactory end point was obtainable. The idea of using phenolphthalein directly in the solution to be titrated, after the addition of a white substance such as  $\text{BaSO}_4$  or China clay to lighten the color, proved a failure as the color change was gradual and indefinite.

*Elimination of Precipitate.*—We next sought to eliminate the voluminous precipitate produced on addition of  $\text{BaCl}_2$ , in order to obtain a clear liquid for titration. Ordinary settling, filtration, and centrifugal filtration proved unsatisfactory, but in a Babcock centrifuge a clear orange colored solution was secured by adding clay to the regular titration mixture and centrifuging for 7 or 8 minutes. This clear liquid when poured off and titrated with phenolphthalein directly did not give very close duplicates, *e. g.*, 13.76 and 14.64 cc. N/10  $\text{HCl}$ .

*Indicators Tried.*—As we were unable to decolorize the clear centrifuged solution with charcoal, we directed our attention to procuring a better indicator. Litmus, Congo red, and lacmoid, with blue-red or red-blue color change were unavailable as the orange color of the solution interfered with the end point. A mixture of dyes, the color of which was practically complementary to the orange shade, was added in an attempt to produce a gray—so that an indicator could be used to better advantage—but the dyes changed color, owing to the action of the alkaline solution, and satisfactory results were not obtained. A mixture of phenolphthalein and malachite green showed some promise but was finally discarded as the malachite green when used in sufficient amount to cover the orange color tended both to precipitate in neutral solution and to mask the last traces of the red of the phenolphthalein. We found, however, that by using an excess of phenolphthalein alone we arrived at a satisfactory and definite end point. Our method was to add a few drops of indicator, titrate to disappearance of red; add a large excess of indicator, and again titrate to the disappearance of red, repeating this operation till no red color developed on addition of more indicator.

*Determination of Ratio.*—Up to this point we were titrating a portion of the clear liquid obtained by precipitating the black liquor with  $\text{BaCl}_2$  and centri-

fuging. It now became necessary to determine the ratio of the NaOH in the portion used to that in the entire volume of clear liquor and precipitate.

The first method attempted was to find the total amount of NaOH present in the entire mixture (20 cc. BaCl<sub>2</sub>, 50 cc. black liquor, 20 grams clay, and 175 cc. of water) by titrating the entire quantity of centrifuged liquor in the usual way and then repeatedly extracting the sludge with water, and centrifuging till the final extraction gave no test with phenolphthalein. As the total volume of the solution was too large to work with conveniently, one-fifth was taken. This idea worked well until the third extraction with water when the clay did not drag down the sludge, but left it in suspension making titration impossible. Addition of more clay was of no avail, and consequently as the sludge still reacted strongly alkaline, the method was abandoned.

The problem was next attacked on the theory that if a known amount of NaOH were added to a black liquor and the mixture centrifuged as usual the same percentage of the added NaOH as of that originally present would be found in the clear liquor. Having determined what percentage of the added NaOH was present in the centrifuged liquor titrated we could then calculate the total amount of NaOH present in the original sample of black liquor.

With this basic idea, we made up the following two mixtures: 25 cc. of black liquor, 10 grams of clay, and 50 cc. of BaCl<sub>2</sub>; and 25 cc. of black liquor, 10 grams of clay, 45 cc. of BaCl<sub>2</sub>, and 5 cc. NaOH (= 48.80 cc. N/5 HCl). These were centrifuged under the same conditions and 10 cc. of each of the centrifuged liquors titrated. The first titration (2.12 cc. N/5 HCl) represented the amount of NaOH present from the black liquor; the second (8.80 cc. N/5 HCl) the amount of NaOH present from the black liquor plus added NaOH. Thus the added NaOH present in the 10 cc. of centrifuged liquor = 8.80—2.12 = 6.68 cc. N/5 HCl. The percentage of the total added NaOH present in the 10 cc. of centrifuged liquor =  $\frac{6.68}{48.80} = 13.7$  per cent.

According to the above theory only 13.7 per cent. of the NaOH present in the original black liquor is to be found in 10 cc. of the clear centrifuged liquor and as this 13.7 per cent. is represented by 2.12 cc. N/5 acid the total amount of NaOH present would be equivalent to 15.48 cc. N/5 or 3.09 cc. N acid. A series of similar tests were made of which the following is a summary: two determinations of pure black liquor, carried out in the manner outlined above, gave as titrations for 10 cc. of the centrifuged liquor 2.14, 2.10, and 2.19, 2.14, 2.12 cc. N/5 acid; average, 2.14 cc. N/5 HCl. The table below gives the results of four tests on "fortified" black liquors, *i. e.*, black liquors to which NaOH has been added. All figures given, except the last column, indicate N/5 acid used.

The average of the four values found below is 3.14 cc. N HCl for the titer of 25 cc. of black liquor. The peculiar part, however, for which we can assign no reason is: that by titrating according to our original method we get a value of from 6—7 cc. N acid for the

	Titration 10 cc. centrifuged fortified black liquor.	Value of NaOH present from black liquor.	Value of NaOH present from added NaOH (I-II)	Value of total NaOH added.	Per cent. total added NaOH present in 10 cc. centrifuged liquor (III)	Calculated value of NaOH in original black liquor (IV) $\left( \frac{100}{V} \right)$	NaOH value of original black liquor in terms of N acid.
1.....	8.82 8.79	2.14	6.66	48.80	13.65	15.68	3.14
2.....	8.71 8.67	2.14	6.55	48.80	13.42	15.94	3.19
3.....	15.45 15.45	2.14	13.31	97.60	13.63	15.70	3.14
4.....	22.55 22.54	2.14	20.40	146.40	13.92	15.37	3.07

Average = 3.14 cc. N acid

titer of the same volume of black liquor. Until we can explain why this discrepancy occurs, we cannot proceed further with this method.

In the above series of determinations we centrifuged the mixtures 12 minutes, poured off equal quantities of clear liquor, and centrifuged again for 3 minutes, which left a perfectly clear liquid for titration.

*Electrometric Method.*—A problem very similar to the one at hand, *i. e.*, the determination of the acidity of tan liquors, has reached a successful solution by the employment of the electrometric method of titration, as reported by Sand and Law<sup>1</sup> and by Sand, Law and Wood.<sup>2</sup> They measure the voltage of a cell, one arm of which is a normal calomel electrode, and the other a hydrogen electrode dipping into the tan liquor to be titrated. Acid is added to the tan liquor until a potential of 0.69 volt is registered, which indicates neutrality.

Through the kindness of Dr. Geo. S. Forbes, of Harvard University, one of the writers was permitted to use apparatus and space in his laboratory to test out this method. We are also indebted to Dr. Forbes for much valuable advice and assistance. The work reported below was carried out very roughly, the object being merely to test the applicability of the method for our use. Our apparatus consisted of a cell similar to that employed in the tan liquor determination, the potential of which was measured by the compensation method using a potentiometer box. We employed a D'Arsonval galvanometer and although this tended to polarize the hydrogen electrode, for approximate work it proved more convenient than an electrometer.

As we were uncertain as to the magnitude of a possible reducing action of black liquor on the hydrogen electrode, we could not assume that the potential corresponding to a given concentration of a pure NaOH solution would necessarily indicate the same concentration of NaOH in the black liquor solution. To test this point we titrated a black liquor according to our original method to get the approximate concentration of NaOH; then we made up a pure NaOH solution of similar concentration (0.026 N), and read off the potentials of the two solutions in the cell.

<sup>1</sup> *J. Soc. Chem. Ind.*, **30**, 1, 3.

<sup>2</sup> *Ibid.*, **30**, 14, 872.

Calculated potential	{ 1.00 volt
Black liquor	{ 0.97-0.98 volt
Alkali	{ 0.99 volt

The above potential in the alkali, and especially in the case of the black liquor, was not reached for several minutes.

Another determination of a solution one-tenth as strong, 0.0026 *N*, gave a voltage of 0.91 in the black liquor. The calculated voltage is 0.94.

Both the above determinations indicated that the reducing action of the black liquor did not greatly affect the hydrogen electrode in alkaline solution so we next tried the direct titration of the black liquor.

For this purpose we took 25 cc. black liquor, 10 cc. BaCl<sub>2</sub> (400 grams to liter), and 200 cc. water. A similar mixture by our old method titrated 13.1 cc. *N*/2 acid. The first titration registered no sudden fall of potential but rather a steady diminution of voltage up to 28.6 cc. acid (as much as was added) and a second trial resulted similarly. When, however, about 10 cc. concentrated HCl was added, the colloids coagulated and the voltage dropped to 0.33.

To make certain that the H electrode had not been affected by its immersion in the black liquor, immediately after the above titration it was placed in a neutral KCl solution and the voltage found to be above 0.6 volt. In contrast with the black liquor titration above, at the neutral point in the titration of an NaOH solution, as indicated by phenolphthalein, the addition of an extra quarter cc. of *N*/2 acid causes a very sharp diminution of the potential of the cell. From the determinations given above we concluded that the electrometric method was, as applied, inapplicable in our case.

#### SUMMARY.

The present method for the determination of NaOH content of black liquors is one of titration with acid, using phenolphthalein as an outside indicator.

In the attempt to improve this method, the more important ideas worked upon were:

1. The elimination by centrifugal action of the precipitate formed by BaCl<sub>2</sub> and the subsequent titration of the clear liquor.
2. The use of various indicators, and the successful method of employing phenolphthalein.
3. The determination of a ratio between the centrifuged liquor and the sample of black liquor taken.
4. Electrometric method.

None of the methods or modifications thus far tested has proved entirely satisfactory, and the original method, although it gives only approximate results, is the best one at present available.

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### THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

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#### VIII. The Examination of Anaesthetic Chloroform.

##### 10. THE DETERMINATION OF THE ACIDITY OF CHLOROFORM.

Chloroform of all grades should always be examined

for the presence of acids.<sup>1</sup> In this way it may be ascertained whether the chloroform under examination has been purified by a method serving to eliminate any acids resulting during manufacture or used during purification; if in a tin container, whether the proper care has been exercised in capping; and, since the water extract is usually tested, the extent of any oxidation, either of alcohol or chloroform, may be determined.

The *Codex Medicamentarius Hamburgensis* of 1847 required that anaesthetic chloroform (density 1.48) should not afford a water extract possessing an acid reaction towards litmus. This test has met with general favor, and is essentially the one usually recommended.<sup>2</sup>

It has been proposed, however, that the chloroform be allowed to evaporate spontaneously after the addition of a drop of neutral litmus solution;<sup>3</sup> and that pieces of pith steeped in Congo red solution be used for the detection of acids in chloroform.<sup>4</sup>

Vulpius<sup>5</sup> found that several chloroform samples which satisfied the conditions of the silver nitrate<sup>6</sup> and litmus paper tests showed an acid reaction when treated as follows: To 1 cc. of water, 1 drop of phenolphthalein solution and 1 drop of centinormal potassium

<sup>1</sup> The possible contaminants of this class are: hydrochloric, hypochlorous, sulphuric, acetic and formic acids; of these, however, only hydrochloric and acetic acids are probable now. There are cases on record which indicate that samples of chloroform may sometimes contain free hydrochloric acid; in all such instances, all of which are extreme in the case of anaesthetic chloroform, either the chloroform originally contained no preservative or had been very carelessly stored for protracted periods of time.

<sup>2</sup> Acids, free chlorine and chlorides are all extracted from chloroform by water, so that when the sample is shaken with, say, twice its volume of water for about 5 minutes, free acids may be detected, when present in appreciable amounts, by blue litmus paper. The detection of the products of the oxidation of pure chloroform will be referred to specifically in the next section.

Brown (*Pharm. J.*, [3] 25, 865) stated that a water extract of the chloroform under examination should be neutral to litmus; Gay (*Loc. cit.*) recommended that when 6 cc. are shaken with 3 cc. of water, the water extract should not redden litmus paper; Regnault (*Mon. Sci.*, [3] 5, 417) also recommended that chloroform should be neutral to litmus; White (*Pharm. J.*, [4] 25, 540) directed that 5 mils be agitated with 10 mils of water, and that the water layer stand the test with litmus; and Krauch (*Testing of Chemical Reagents*, 1902, 77) gives a test wherein 2 parts of chloroform are shaken with 3 parts of water, the latter being then tested with blue litmus paper. See also Linke, *Apoth.-Ztg.*, 25, 285.

The pharmacopoeias of Spain and France require that chloroform shall be completely neutral to litmus solution; the pharmacopoeias of Switzerland and Austria direct that the chloroform be agitated with an equal volume of water, and that the latter should then not redden litmus or be rendered turbid by silver nitrate solution, while the Danish pharmacopoeia directs that the test be made on the aqueous extract obtained by agitating 10 cc. of chloroform with 5 cc. of water. Practically the same test recommended in the *Codex Medicamentarius Hamburgensis* of 1847 is in the *Deutsches Arzneibuch* of 1910. The *Pharmacopoeia of Japan* of 1907 requires that the sample be shaken with one-half its volume of water, and that the aqueous extract should not redden blue litmus paper. It was specified in the sixth revision of the *Pharmacopoeia of the United States* (1882) that if 5 cc. of purified chloroform be thoroughly agitated with 10 cc. of distilled water, the latter, when separated, should not affect litmus paper (blue).

<sup>3</sup> It was required in the fifth revision of the *Pharmacopoeia of the United States* (1873, p. 78) that when 1 fluidrachm of chloroform was evaporated spontaneously with 1 drop of a neutral water solution of litmus, the color of the indicator must not be reddened; it was stated that the result of the test is the same if the chloroform, contained in a white glass bottle, had been previously exposed to direct sunlight for 10 hours. A similar test is given in the *National Dispensatory* of 1887 (p. 439) for incipient decomposition.

<sup>4</sup> A change to "blue" results in the presence of acids. Concerning this test, see *Lancet*, 1907, I, 1033.

<sup>5</sup> *Arch. Pharm.*, [3] 25, 998.

<sup>6</sup> This test will be discussed in the next section.