

phthalic anhydride titer of an exactly $N/10$ NaOH solution is 0.0074.

It will be found that the cotton plugs can be used again and again provided they be washed carefully with neutralized water after each run. Occasional titrations must be made on the cotton blanks to be sure of their uniformity and their acid equivalent. New cotton must be thoroughly boiled with $N/10$ caustic soda and washed well with neutral water.

Where there are a number of determinations to be run daily it will be found that this method using the detachable tube considerably simplifies the method as described by Boswell and in addition the weight of the unsublimable residue is obtained. This is an important feature in connection with plant control.

It is important to note that when a crude phthalic is obtained containing sulfuric and sulfurous acids it must be washed free of these compounds before testing. The presence of sulfuric acid in the crude is generally indicated by a charring of the cotton and, if this happens, the test must be repeated.

This method has been thoroughly checked by analyses of pure phthalic anhydride.

A further proof that this method is correct, when applied to crude phthalic acid, is that the actual sublimation in the plant, where there are small known losses, has given, at the lowest, 95 per cent of the analytical figure for phthalic anhydride as determined by the above method.

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AN IMPROVED DISTILLATION METHOD FOR THE DETERMINATION OF WATER IN SOAP

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Received May 20, 1918

Water in soap is usually calculated after determining all the other ingredients. In many instances, however, it is found directly by drying the soap to constant weight in an oven at 105°C . This procedure, of course, takes considerable time and the result indicates not only water but also any other volatile constituents that may be present. A quicker method is to heat the sample over a free flame until a watch glass held over it for a moment shows no condensation of vapor, or until the odor of acrolein is just noted. This method, evidently, depends a good deal upon the personal equation.

A method occasionally employed and originally suggested by Marcusson¹ is to distill with xylene. The distillate containing the water is received in a special flask having a graduated leg in which the water settles, and the reading of the lower layer is taken as the water content of the sample. In the case of soaps containing alcohol or ammonia, these are found partly in the water layer; corrections are made by taking the specific gravity in the case of alcohol, or by titrating with standard acid in the case of ammonia.

The distillation method has been employed quite

successfully for the determination of moisture in such materials as foods, oils, tars,¹ creosoted wood,² etc. A comparison of this method with that of drying to constant weight is given in the following table taken from S. S. Sadtler:³

Analyses	Distillation Tests Per cent		Oven Tests at 100°C . Per cent	
	I	II	I	II
Egg Albumen.....	15.90	15.35	15.70	...
Cheese.....	29.75	29.90	29.25	29.51
Butter.....	11.48	11.88	12.25	13.22
Linseed Meal A.....	5.90	5.90	5.83	5.72
Linseed Meal B.....	12.00	11.80	9.85	...
Sawdust.....	17.20	...	16.50	...

In the case of soaps, however, the distillation method gives considerable trouble on account of excessive foaming during the heating. The operation becomes tedious and slow, and considerable care is necessary to prevent the foam from entering the condenser tube. Another objection to this method is the very viscous condition of the xylene-soap solution towards the end of the distillation, thereby hindering the free escape of the vapor. The solution at the end of the distillation usually gelatinizes on cooling.

These obstacles, the writer found, are very satisfactorily overcome by the addition of red oil or oleic acid before distilling. The foaming is entirely eliminated and the solution remains very fluid even at low temperatures. The addition of red oil presents another advantage in that the xylene-red oil mixture is a much better solvent for soap than xylene alone; under like conditions it takes considerably less time to dissolve a sample of soap in the mixture than in pure xylene.

The quantity of red oil required is about the same as the weight of the soap taken for analysis. In that case, the soap is quickly and completely dissolved by the xylene, and the foaming is entirely eliminated, allowing the distillation to be carried out at any desired rate. The results compare favorably with the oven method for soap as recommended by the U. S. Bureau of Standards.⁴ The two methods are compared in the following table:

	Distillation Test with Red Oil Per cent	Oven Test at 105°C . Per cent
Soft Soap.....	42.5	42.7
Degumming Soap.....	69.5	70.6
Fuiling Soap.....	16.2	17.1
3 cc. 0.5 N NaOH.....	96.4	98.0(a)

(a) Theoretical.

Michel⁵ finds it necessary in the determination of water in foods to apply a correction of 0.125 cc. to the water reading to allow for the shape of the meniscus. This correction is not necessary in soap analysis as the meniscus is very nearly flat, probably due to traces of soap mechanically carried over; for it was noticed that the meniscus between fresh water and xylene became flat on adding a few drops of a liquid soap. However, a correction of 0.05 cc. may be allowed for moisture left in the condenser, since the results in the table are uniformly lower than by the oven test.

¹ J. Am. Chem. Soc., 25 (1903), 814.

² U. S. Dept. Agr., Forest Service, Circ. 134 (1908).

³ THIS JOURNAL, 2 (1910), 66.

⁴ Circular 62 (1916), 21.

⁵ J. Soc. Chem. Ind., 32 (1913), 445.

In this connection, it may be of interest to note that on shaking the water and xylene layers in the receiver after the distillation, the water formed a permanent emulsion with some of the xylene, but on adding sufficient red oil, the emulsion was destroyed and the layers separated completely in a short time. No emulsion, however, was formed on shaking pure water with fresh xylene. This emulsion is probably also due to traces of soap. Those familiar with the manufacture of soluble mineral oils, which consist mostly of mineral oil, red oil, and soap, or other emulsifiers, are probably aware with what care the red oil must be incorporated; only a slight excess of the latter to the compounded oil is sufficient to destroy its property of emulsifying in water.

The method, as carried out in our laboratory, is to weigh into a 500 cc. Erlenmeyer flask enough of the soap to yield about 3 cc. of water. An equal quantity of red oil and 150 cc. of water-saturated xylene are added and the contents distilled at the rate of 1 to 2 drops per second. The receiver at the start is filled with 5 cc. of the water-saturated xylene and the distillation is stopped when about 85 cc. are collected. The inside of the condenser tube is finally rinsed out with the xylene and the washings added to the distillate; this rinsing is best accomplished by distilling rather vigorously 15 cc. more of xylene. The receiver¹ consists of a cylinder holding about 120 cc. and is constricted at the bottom to a tube which is about 4 cm. long, graduated in tenths of a cc., and holds about 4 cc. of water.

The reading may be taken at room temperature or brought to any desired temperature in a water bath. Any drops of water adhering to the glass of the vessel may be dislodged by means of a very thin wire twisted at one end into a circle. The xylene layer is usually somewhat emulsified. On standing over night, however, the layers get clear, but the reading is practically no different than if taken a half hour after distillation.

The addition of oleic acid or red oil to the xylene in the distillation method for the determination of moisture in soap, as recommended, increases the accuracy by keeping the soap-xylene liquid more fluid and shortens the time of the distillation by hastening the solution of the soap in the xylene, and by eliminating foaming.

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THE USE OF SODIUM SULFATE IN THE KJELDAHL-GUNNING METHOD

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Received February 2, 1918

W. G. Latshaw gave in THIS JOURNAL, 8 (1916), 586, the results of some analyses which showed very conclusively that sodium sulfate could be substituted for potassium sulfate in nitrogen determinations by the Gunning modifications of the Kjeldahl method. One of the writers found on coming to this laboratory

that sodium sulfate had been substituted for potassium sulfate since the appearance of Latshaw's article, but instead of using 7 to 8 g. of the anhydrous salt as was done by Latshaw, 10 g. of the hydrated salt were being used. This is equivalent to 4.4 g. of the anhydrous salt. It was thought that it should be determined whether or not the addition of water (as the water of crystallization of the sodium sulfate) would affect the result and the time required for the completion of the digestion following the Kjeldahl-Gunning method.

TABLE I

MATERIAL USED	Clear after Hours	PER CENT NITROGEN	
		9.25 g. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	4.076 g. Na_2SO_4
Cottonseed feed.....	1 1/4	3.032	3.054
Cottonseed meal.....	1 1/4	5.896	5.896
Standard wheat shorts...	1 1/2	3.020	3.001
Wheat white shorts.....	1 1/4	2.606	2.603
Molasses feed.....	1 1/2	1.707	1.702
Standard wheat shorts...	1 1/2	2.918	2.918
Standard wheat shorts...	1 1/2	2.841	2.824

Table I shows the results of analyses made to decide this point. There was little or no difference in the time required for digestion, about 10 min. longer time being required where the hydrated salt was used. It should be noted that 4.07 g. of the anhydrous salt were used and not 4.4 g. This was because we wished to compare the results obtained when 5 g. of potassium sulfate were used with the results when its molecular equivalent of sodium sulfate was used. Table II shows the results of analyses made for this comparison.

TABLE II

MATERIAL USED	Clear after Hours	Number of Analyses	PER CENT NITROGEN	
			K_2SO_4 5 g.	Na_2SO_4 4.076 g.
Poultry mash.....	..	2	3.163	3.230
Mill run bran.....	..	2	2.760	2.760
Rice bran.....	..	2	1.891	1.986
Standard wheat shorts	..	2	2.858	2.851
Mill run bran.....	1 1/4	2	2.491	2.485
Mill run bran.....	1 1/4	2	2.690	2.715
Mill run bran.....	1 1/4	2	2.595	2.616

The sulfuric acid cleared up in about the same time using the above salts.

The time of digestion was independent of the salt used.

It should be noted that in our comparisons we used 5 g. of potassium sulfate instead of 10 g. as called for in the official method.

It might be said that this would give wrong results and that the time of digestion would be different from that obtained and the time required when 10 g. are used. Table III shows the results of four analyses made to answer this question.

TABLE III

MATERIAL USED	Number of Analyses	PER CENT NITROGEN	
		K_2SO_4 5 g.	K_2SO_4 10 g.
Oat feed.....	2	0.787	0.792
Cottonseed meal.....	2	6.072	5.909
Dried blood.....	2	14.032	13.880
Mill run bran.....	2	2.943	2.896

The time required to clear was the same, about 60 min., in each analysis. It should be pointed out that a slightly higher per cent of nitrogen was obtained in each analysis where 5 g. of potassium sulfate were used instead of 10. This might be due to a slight oxidation of the ammonia by the great amount of

¹ Graefe's Oil Cylinder, Eimer & Amend Catalogue for 1913, No. 4784.