acid will have been carried over, along with some hydrochloric acid, if chlorides are present in the material being analyzed. Also, any formic acid or higher homologs of acetic acid present will be distilled over along with the acetic acid. Do not carry the distillation further than the point indicated, as some phosphoric acid may at this point begin to be carried over with the last traces of the xylene. The distillate usually separates into two liquid layers. The upper layer consists of xylene, with some acetic acid dissolved in it, and the lower layer consists of a water solution of acetic acid. Titrate for total acidity in the distillate with 0.33 *N* carbonate-free sodium hydroxide, using phenolphthalein as an indicator, and taking care to neutralize all acid dissolved in the xylene layer. After correction of the burette readings for calibration and temperature variation,

$$\frac{\text{Cc. of alkali} \times \text{normality factor} \times 6.0}{\text{Weight of sample}} =$$

A = Total acidity as acetic acid.

If chlorides were present, make a correction for the hydrochloric acid which was distilled over, as follows: Add potassium chromate indicator to the distillate after the above alkali titration, and titrate with 0.1 *N* silver nitrate. Then,

$$\frac{\text{Cc. silver nitrate} \times \text{normality factor} \times 6.0}{\text{Weight of sample}} =$$

B = Acetic acid equivalent of the hydrochloric acid present.

A — B = Organic acids as acetic acid.

Typical results by the new method are given in Table I. These were obtained by high school students trained in our laboratory and by graduate chemists. Large amounts of chlorides were present in the samples analyzed. These, however, did not in any way prevent accurate results from being obtained for the acetic acid values.

TABLE I—DETERMINATIONS OF ACETIC ACID VALUES BY NEW METHOD

No.	DESCRIPTION	Total Acidity as CH ₃ COOH Per cent	HCl as CH ₃ COOH Per cent	Actual CH ₃ COOH Per cent	Difference between Checks
3,610	Residue	61.14	56.23	4.91	
		59.30	54.39	4.91	0.00
3,616	Residue	59.79	54.17	5.62	
		61.61	56.02	5.59	0.03
3,637	Residue	61.44	58.85	4.59	
		48.53	43.90	4.63	0.04
3,946	Sodium Acetate	69.28	19.60	49.68	
		68.49	18.81	49.68	0.00
3,974	Residue	61.26	52.74	8.52	
		61.50	53.00	8.50	0.02
4,394	Sodium Acetate	75.80	14.55	61.25	
		76.29	14.84	61.45	0.20
4,491	Sodium Acetate	56.68	21.01	35.67	
		57.47	21.85	35.62	0.05
4,501	Sodium Acetate	59.43	21.73	37.70	
		60.24	22.72	37.52	0.18
4,541	Sodium Acetate	67.58	18.63	48.95	
		68.57	19.50	49.07	0.12
4,851	Sodium Acetate	68.85	19.93	48.92	
		68.82	19.91	48.91	0.01
9,944	Calcium Acetate	55.78	14.02	41.76	
		55.88	14.11	41.77	0.01
10,066	Calcium Acetate	57.15	12.70	44.45	
		56.82	12.58	44.24	0.21
10,232	Calcium Acetate	56.64	14.26	42.38	
		55.98	13.51	42.47	0.09
10,271	Calcium Acetate	45.38	5.61	39.77	
		43.22	3.60	39.62	0.15

In order to check the xylene distillation method against pure materials of known strength, tests were made upon pure acetic acid and upon chemically pure sodium acetate. A dilute solution of acetic acid was analyzed by direct titration against standard 0.33 *N*

sodium hydroxide solution and also by the xylene method as described above. A sample of pure sodium acetate was also analyzed by this method. This material was tested for purity and strength by determining the sodium content by smoking off with sulfuric acid, according to the usual method of determining metals in organic salts. From the amount of sodium sulfate formed, the percentage of CH₃COONa·3H₂O was calculated. The results are shown in Table II.

TABLE II—CHECK ANALYSES ON PURE MATERIALS (PER CENT)

SAMPLE No.	ACETIC ACID		SODIUM ACETATE	
	CH ₃ COOH by Xylene Distillation and Titration	CH ₃ COOH by Direct Titration	CH ₃ COONa·3H ₂ O by Xylene Distillation and Titration	CH ₃ COONa·3H ₂ O by Conversion to Na ₂ SO ₄
1	19.62	19.58	100.00	100.00
2	19.50	19.58	100.03	100.07
3	19.63	19.59	99.92	99.80
4	19.65	19.68		99.80
AVERAGE	19.60	19.61	99.98	99.92

The new method has been used continuously in our laboratory for more than a year, and has been found to be very satisfactory, both as to time required for an analysis and as to the ease with which considerable accuracy is attained. It has been adopted in the analysis of sodium acetate, commercial calcium acetate, and sodium acetate residues carrying from 0 to 10 per cent of acetic acid. With all of these materials the method gives accurate results. It has also been used successfully for the determination of propionic and butyric acids in their salts. As to the time required to make a complete analysis, it has been found that 45 min. are usually sufficient.

SUMMARY

A method has been developed whereby acetic acid in its salts can be determined.

The former difficulty of obtaining accurate results has been eliminated by using xylene, instead of water, as a carrier for the acetic acid in the distillation of the acetate with phosphoric acid.

The usual time required for an analysis has been greatly reduced.

The method has been used for factory control over a considerable period, and can be recommended for use in technical laboratories.

INDICATORS USED FOR DETERMINING FREE ACID IN PICKLING SOLUTIONS

By C. L. Boyle

THE STUDEBAKER CORPORATION, DETROIT, MICHIGAN

Received December 10, 1919

The usual method for determining the amount of free acid in pickling solutions consists in titrating 10 cc. quantities of the pickling solution with standard alkali, using either phenolphthalein or methyl orange as the indicator. The presence of a large amount of ferrous sulfate renders the end-point with either methyl orange or phenolphthalein very hard to see. Of the two, methyl orange is to be preferred. Either sodium or potassium thiocyanate, however, can be used, enabling the analyst to recognize the end-point more easily.

The use of either sodium or potassium thiocyanate is based on the facts that iron is always present in a

pickling solution, and that ferric thiocyanate is deep red in acid solution, but loses this color the minute the solution becomes alkaline.

The following procedure is recommended for use of this indicator:

To a 10-cc. sample of the pickle liquor at a temperature of about 70° F. add several drops of a concentrated solution of either sodium or potassium thiocyanate. Without diluting, titrate the solution with standard alkali until the red color of the ferric thiocyanate entirely fades, leaving the solution a greenish yellow.

In connection with this titration, it may be pointed out that the coloration is more intense when the solution is used undiluted and that if the color does not develop at first, the addition of the alkali soon brings it out.

The selection of the standard alkali depends upon whether the results of the titration are to be expressed as percentage acidity by weight, percentage acidity by volume, or pounds of anhydrous sulfuric acid per cubic foot of pickling solution. A standard normal solution of sodium hydroxide will be found convenient for expressing the percentage by volume or by weight. In this case each cc. of normal alkali represents approximately one per cent of free acid by volume. A 0.816 *N* solution of sodium hydroxide will be found convenient for expressing the results of the titration in pounds of sulfuric acid per cubic foot. Here the number of cc. of standard alkali used to titrate 10 cc. of pickling solution multiplied by 4 will represent the number of pounds of anhydrous sulfuric acid present in each cubic foot of the pickling solution.

In making the standard alkali solution it must be borne in mind that this indicator, though of constant accuracy, gives an end-point slightly on the alkaline side and it is therefore necessary to use this indicator when making up the standard solution. The addition of some iron salt like ferrous sulfate to the acid solution which is used to titrate against the alkali solution in standardizing the latter gives the necessary iron content to the solution and is without influence on the titration. By this means a condition parallel to the actual titration of the pickling solution is obtained.

SOY-BEAN OIL

By Wilson H. Low

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Received December 18, 1919

A sample of filtered soy-bean oil was examined for total fatty acids, unsaponifiable matter, and glycerol, by calculation.

Fifty grams of the oil were saponified by boiling for 1.5 hrs. under a reflux condenser with about 600 cc. of approximately 0.5 *N* alcoholic potash solution.

UNSAPOINIFIABLE MATTER—The solution was transferred to a separatory funnel, diluted with water to a volume of 2400 cc., and extracted with 750 cc. of ethyl ether, followed by five more extractions of 250 cc. each. The ether residue (unfortunately not examined for free fatty acids) amounted to 1.16 per cent, recorded as unsaponifiable matter. This is probably higher

than would be found had a correction been made for free fatty acids with the residue.

FATTY ACIDS—The solution, presumably free from unsaponifiable matter, was evaporated to dryness in a large porcelain dish, treated with water, again evaporated to pastiness, and finally dissolved in water, and the fatty acids set free with dilute hydrochloric acid. The mixture was transferred to a separatory funnel and washed free from mineral acid, as indicated by methyl orange. The washings were combined and subsequently extracted with ether.

The melted fatty acids were allowed to stand warm in the separatory funnel and from time to time the water which had collected upon rotating the funnel was drawn off, until finally very little was in evidence. The clear melted fatty acids were then drawn into a filtering tube illustrated by the accompanying figure.

Shredded, or, better, rasped filter paper, if well dried, will absorb considerable moisture and be without action on the fatty acids. By maintaining the arrangement at a low temperature, yet sufficiently high to keep the contents well melted, the fatty acids percolated through into the dish. Filtration was allowed to go on over night.

The aqueous washings were extracted with more ether, the separatory funnel washed out with ether, and all the extracts combined and the fatty acids recovered.

FATTY ACIDS	GRAMS	PER CENT
Recovered directly.....	39.7080	
Recovered in ether extracts, etc.....	7.7752	
TOTAL (Free from unsaponifiable matter).....	47.4832	94.966
Unsaponifiable matter.....	1.160	
TOTAL (Ordinary fatty acids).....		96.126

In weighing the fatty acids a constant slight gain was noted. This was probably due to oxidation, as the dish and fatty acids had remained in the balance case a long time before weighing. If oxidation was the cause, it must also have been going on during the time of filtering, and our result would be slightly high.

GLYCEROL—Ten grams of the original oil (refined and practically free from free fatty acids) were saponified with standard alcoholic potash solution. The alkali consumed was equivalent to 33.80 cc. of *N* solution, or $(33.8 \times 0.02168 = 0.732784 \text{ g.})$ 7.33 per cent of glycerol anhydride or 10.37 per cent of glycerol.

It may be said in passing that this method of determining glycerol, if properly and carefully followed, is as accurate as any other known method. If there are any free fatty acids present in the oil they must be allowed for, using the true combining weight of the