

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION  
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

## CIDER VINEGAR AND SUGGESTED STANDARDS OF PURITY.

BY ALBERT E. LEACH AND HERMANN C. LYTHGOE.

Received February 10, 1904.

THERE is no food product in which competition and cheap methods of manufacture have resulted so disastrously to the quality of the substance as in the case of cider vinegar. Where formerly the farmer by the slow fermentation process and from pure cider produced all the vinegar consumed and obtained a good price for it, now the price of so-called cider vinegar is so low that the self-respecting farmer can hardly afford to enter the race. Much skill has been shown of late in the manufacture of spurious "cider" vinegar with a view to deceiving the analyst, so that it is incumbent on him to know very thoroughly the composition of cider vinegar and especially of the various qualities or characteristics which serve to distinguish it from the factitious variety.

More or less complete analyses of vinegar, of interest in comparison with the results that follow, have been made by Smith,<sup>1</sup> by Doolittle and Hess,<sup>2</sup> by Frear,<sup>3</sup> by Brown,<sup>4</sup> and, previously, by the writers.<sup>5</sup> During the past year, from a large number of vinegars examined by the writers in the routine of food inspection, twenty-two samples of cider vinegar of known purity have been analyzed in full with a view to suggesting helpful standards in addition to those which for twenty years have prevailed in Massachusetts for acidity and total solids.

The list comprises (1) samples made in the laboratory, (2) samples made by farmers, and (3) samples from reputable manufacturers made both by the slow and by the generator processes, all those obtained from outside the laboratory being furnished for the purpose of analysis with a guarantee that nothing but apple juice was used in their manufacture.

Determinations were made of acetic acid, solids, ash, alkalinity of the ash, soluble and insoluble phosphates, reducing sugars both

<sup>1</sup> This Journal, 20, 3.

<sup>2</sup> *Ibid.*, 22, 218.

<sup>3</sup> Penn. Dept. Agriculture, Annual Report, 1898-145.

<sup>4</sup> Penn. Dept. Agriculture, Bull. 58.

<sup>5</sup> Mass. State Board of Health, Annual Reports, 1900-661, 1901-467, 1902-483.

Number.	Acetic acid, Per cent.	Total solids, Per cent.	Ash, Per cent.	Alkalinity of ash of 100 grams of vine- gar, N/10 acid.	Soluble P <sub>2</sub> O <sub>5</sub> in ash of 100 grams of vinegar, mg.	Insoluble P <sub>2</sub> O <sub>5</sub> in ash of 100 grams of vinegar, mg.	Reducing sugars (dextrose) before inversion, Per cent.	Reducing sugars (dextrose) after inversion, Per cent.	Polarization, de- grees Verdet, 200 mm.	Lead acetate test for malic acid, Ppt.	Calcium chloride test for malic acid, Ppt.	Malic acid, Per cent.	Percent ash in total solids.	Per cent. reducing sugars in total solids.	Ratio of soluble P <sub>2</sub> O <sub>5</sub> to total P <sub>2</sub> O <sub>5</sub> .	Alkalinity of 1 gram of ash, cc. N/10 acid.
1	5.86	2.00	0.20	22.2	25.0	22.7	0.23	0.23	-0.9	..	..	..	10.0	11.5	51.7	111.0
2	5.78	2.86	0.29	26.2	31.7	31.5	0.34	0.34	-3.6	..	..	..	10.0	11.9	50.1	90.0
3	5.68	2.80	0.38	34.6	19.5	14.0	0.24	0.24	-1.3	..	..	0.07	13.6	8.6	57.6	94.0
4	5.63	2.04	0.36	31.1	20.0	14.0	0.15	0.15	-1.1	..	..	..	17.6	7.4	60.6	85.0
5	5.48	2.35	0.29	26.6	12.1	12.1	0.23	0.24	-2.1	..	..	..	12.3	10.2	50.0	92.0
6	5.44	2.75	0.40	36.1	16.2	6.5	0.23	0.23	-1.1	..	..	0.09	14.5	8.4	71.4	90.0
7	5.21	2.70	0.42	30.2	16.2	8.4	0.24	0.24	-1.1	..	..	0.09	15.6	8.9	61.8	72.0
8	5.12	2.04	0.21	26.7	14.0	12.1	0.22	0.22	-1.6	..	..	..	10.3	10.8	53.2	122.0
9	4.84	3.20	0.32	31.0	14.0	12.6	0.51	0.53	-1.1	..	..	0.08	10.0	16.6	52.6	97.0
10	4.81	3.00	0.34	30.1	19.0	17.3	0.32	0.32	-1.8	..	..	..	11.3	10.7	52.3	89.0
11	4.81	2.45	0.38	28.2	24.7	17.6	0.34	0.34	-0.9	..	..	..	15.5	13.9	57.0	74.0
12	4.80	2.55	0.37	30.3	15.8	7.8	0.21	0.23	-1.1	..	..	0.09	14.5	9.0	66.9	82.0
13	4.55	2.19	0.37	31.1	18.6	18.1	0.26	0.26	-1.2	..	..	0.14	16.9	12.4	50.4	84.0
14	4.52	3.14	0.41	28.2	21.7	19.0	0.28	0.28	-0.7	..	..	0.10	13.0	8.9	68.4	69.0
15	4.52	2.69	0.42	29.0	24.9	21.7	0.23	0.23	-0.6	..	..	..	15.6	8.6	53.5	69.0
16	4.51	2.15	0.41	33.9	16.7	16.3	0.16	0.16	-0.4	..	..	0.15	19.0	7.5	50.3	80.0
17	4.50	2.20	0.39	35.1	18.9	11.6	0.16	0.16	-0.3	..	..	0.16	17.7	7.3	56.9	90.0
18	4.28	1.95	0.26	32.4	17.2	12.1	0.18	0.18	-0.7	..	..	..	13.3	9.2	58.6	125.0
19	4.27	2.23	0.40	30.8	17.2	15.3	0.18	0.18	-0.5	..	..	..	17.9	8.1	52.9	77.0
20	4.02	2.98	0.32	29.8	16.2	13.5	0.29	0.29	-0.9	..	..	..	10.7	9.7	53.9	93.0
21	3.94	2.74	0.37	32.4	17.1	12.0	0.25	0.26	-1.8	..	..	0.16	13.5	9.5	58.8	85.0
22	3.92	1.84	0.25	26.4	16.8	16.7	0.25	0.25	-2.7	..	..	0.08	13.6	13.6	50.1	105.0
Highest,	5.86	3.20	0.42	36.1	31.7	31.5	0.51	0.53	-3.6	..	..	0.16	19.0	16.6	66.9	125.0
Lowest,	3.92	1.84	0.20	22.2	12.1	6.5	0.15	0.15	-0.3	..	..	0.08	10.0	7.3	50.0	69.0
Average,	4.84	2.49	0.34	29.7	19.2	15.6	0.25	0.25	-1.3	..	..	0.11	13.8	10.7	56.3	90.0

before and after inversion, polarization, and malic acid. Percentage of ash in solids, percentage of reducing sugars in solids, ratio of soluble to total phosphates, and alkalinity of one gram of ash have been calculated.

#### METHODS.

The methods used in making the above analyses are as follows:

*Acetic Acid.*—Three cc. of vinegar were diluted with about 300 cc. of water and titrated with tenth-normal sodium hydroxide, using phenolphthalein as an indicator. The number of cubic centimeters of alkali used, multiplied by 0.2, gives the percentage of acetic acid.

*Solids.*—Five grams of vinegar were weighed into a tared, flat-bottomed platinum dish, subjected for an hour to direct contact with the live steam, of a boiling water-bath, and the residue weighed.

*Ash.*—The residue from the solids was carefully ignited in a muffle and the resulting ash weighed.

*Alkalinity of the Ash.*—One hundred grams of vinegar were evaporated to dryness in a platinum dish and the residue reduced to an ash in a muffle. The resulting ash was boiled with water, the solution filtered and the precipitate washed with boiling water till free from alkali. The filtrate was then treated with an excess of tenth-normal hydrochloric acid carefully measured, the solution boiled to expel carbon dioxide and the excess of acid titrated with tenth-normal sodium hydroxide, using phenolphthalein as an indicator. The number of cubic centimeters of tenth-normal acid required for neutralization expresses the alkalinity of the ash.

*Soluble Phosphoric Acid.*—The solution of the ash, after titration, was made acid with hydrochloric acid and evaporated to dryness, after which 50 cc. of boiling water were added and the phosphoric acid determined by titration with uranium acetate in the usual way.<sup>1</sup>

*Insoluble Phosphoric Acid.*—The residue from the ash soluble in water was dissolved in hydrochloric acid and the acid solution evaporated to dryness. The residue was then dissolved in about ten drops of dilute hydrochloric acid, 50 cc. of boiling water were added, then about 1 gram of sodium acetate, and the solution

<sup>1</sup> Sutton's "Volumetric Analysis," 8th Edition, p. 313.

titrated with uranium acetate, as in the case of the soluble phosphoric acid.

*Reducing Sugars.*—Two portions of 25 cc. each were measured with 100 cc. flasks. One portion was diluted with 20 cc. of water, 5 cc. of concentrated hydrochloric acid were added and the solution subjected to inversion by heating to 70° for ten minutes and cooling. Both portions were neutralized with sodium hydroxide and made up to the mark. The reducing sugars were determined in each portion by Defren's modification of O'Sullivan's method<sup>1</sup> and calculated as dextrose.

*Polarization.*—Two and one-half cc. of lead acetate (10 per cent. solution) were placed in a beaker, 25 cc. of vinegar run in from a pipette, the mixture stirred, and, after standing a few minutes it was filtered and the filtrate polarized in a 200-mm. tube in a Schmidt & Haensch polariscope. Ten per cent. was added to the reading for the dilution due to the clarifier, the polarization being expressed directly in degrees Ventzke for 200 mm. of vinegar.

#### MALIC ACID.

Malic acid is a constituent of many fruits but is especially characteristic of the apple. If a sample of alleged cider vinegar is found to contain no malic acid, this fact alone is absolute evidence of its spurious nature, but on the other hand the presence of malic acid does not necessarily stamp a sample of vinegar as being the product of pure cider.

*The Lead Acetate Test.*—The application of the common lead acetate test to vinegar was apparently first made by Davenport<sup>2</sup> and, while useful, serves chiefly as a negative test in showing the possible absence of malic acid, since phosphates present to the extent found in malt vinegar, and other substances, such as molasses, give a precipitate which is liable to be confounded with malic acid by one not skilled in carrying out the test. If the vinegar under treatment with lead acetate does not give a precipitate settling in a few minutes and leaving a clear supernatant liquid, it is not cider vinegar.

*The Calcium Chloride Test.*—The following test for malic acid as proposed by the writers for its positive identification has been

<sup>1</sup> This Journal, 18, 749.

<sup>2</sup> Mass. State Board of Health, Annual Report, 1886, p. 159.

successfully used in the laboratory of Food and Drug Inspection of the Massachusetts State Board of Health for the past two years.

Five cc. of vinegar are treated with about 1 cc. of 10 per cent. calcium chloride solution and made alkaline with ammonium hydroxide. A precipitate nearly always occurs at this point, which may consist of calcium phosphate, ferric hydroxide, etc. Filter, and to the filtrate add about three volumes of 95 per cent. alcohol and heat to boiling. In the presence of malic acid, a flocculent precipitate of calcium malate separates. A precipitate of dextrine would occur at this point, if the sample contained glucose or malt, and, if sulphates were present, a precipitate of calcium sulphate would be formed. The presence of dextrine would be indicated by a right-handed polarization. If, therefore, the sample is found to polarize normally to the left and to be free from sulphates, a flocculent precipitate on heating the alcoholic solution as above may ordinarily be assumed to indicate malates.

To positively confirm the presence of malates, filter off the precipitate, dry out the alcohol therefrom (to prevent subsequent explosion of ethyl nitrite,) dissolve in dilute nitric acid and evaporate to dryness over the boiling water-bath. This treatment transforms the calcium malate to calcium oxalate. Boil with sodium carbonate solution for a few minutes to decompose the salt, filter from the precipitated calcium carbonate, make the filtrate acid with acetic acid and add a solution of calcium sulphate. A precipitate of calcium oxalate at this stage confirms the presence of malic acid in the vinegar. Calcium sulphate solution is used so that, if sulphates were present, a precipitate of calcium sulphate would not occur and thus vitiate the test.

*Importance of Making Both Tests.*—A sample of vinegar made from partly exhausted apple pomace will sometimes give a test for malic acid with the calcium chloride method, where only a turbidity would occur with the lead acetate. This is due to the fact that the apple pomace used has still retained some of the malic acid, and that the lead acetate test is less delicate than the calcium chloride test because lead malate is slightly soluble in acetic acid. In a pure cider vinegar there should always be sufficient malic acid present to give a distinct precipitate with lead acetate, and such a

vinegar should respond in a perfectly normal manner to both tests. If either test fails, the sample should be condemned.

*Determination of Malic Acid. (a) Calcium Chloride Method.*—This was the method employed in making the above analyses. One hundred grams of vinegar were treated with 10 cc. of 10 per cent. calcium chloride and made alkaline with ammonium hydroxide. After standing for one hour, the solution was filtered and the precipitate washed with water. The filtrate was evaporated to about 25 cc. and 3 volumes of 95 per cent. alcohol were added, the solution heated to boiling and filtered on an ashless filter-paper. The separated calcium malate was washed with hot 75 per cent. alcohol and burned in a platinum crucible. The ash was dissolved in 35 cc. of tenth-normal hydrochloric acid by boiling, and the excess of acid determined by titrating with tenth-normal sodium hydroxide, using phenolphthalein as an indicator. The number of cubic centimeters of tenth-normal acid used up, multiplied by 0.0067 gives the percentage of malic acid in the sample.

*(b) Modification with Lead Acetate.*—One hundred grams of vinegar are neutralized with sodium hydroxide, an excess of lead acetate added and the resulting lead malate filtered and washed. The precipitate is suspended in water, which is heated to boiling and saturated with hydrogen sulphide to set free the acid. After filtering from the lead sulphide and washing the precipitate with hot water, the filtrate is evaporated to a volume of about 75 cc. cooled, 10 cc. of 10 per cent. calcium chloride solution are added and ammonium hydroxide to alkalinity. A precipitate occurs at this point, indicating the presence of an acid other than malic. Filter, wash, and treat the filtrate as in the calcium chloride method. A sample analyzed in duplicate by both methods gave the following results in percentage of malic acid.

	(1)	(2)
Method (a) .....	0.092	0.098
“ (b) .....	0.093	0.091

#### NOTES ON THE RESULTS.

*Acid and Solids.*—But few of the samples fall below the Massachusetts standard of 4.50 per cent. acid and 2.00 per cent. solids, and these standards do not appear to be excessively high for thoroughly fermented cider vinegar.

*Ash.*—The quantity of the ash should be about 10 per cent. of the solids, although some samples are a little lower. Less than 8 per cent. of ash in the solids of pure cider vinegar rarely occurs. The quality of the ash is much more important than the quantity.

*Alkalinity of the Ash.*—The apple contains a large percentage of organic potassium salts, consequently the ash of cider vinegar is very alkaline. One gram of cider vinegar ash will require about 90 cc. of tenth-normal acid for neutralization, consequently the reading in cubic centimeters of the acid used to neutralize the ash of 100 grams of vinegar will approximately equal the percentage of ash multiplied by 100. If the alkalinity falls below 65 per cent. of this figure (per cent. ash x 100), the sample should be viewed with suspicion.

Watering with hard water, or admixture of other fruit juices will tend to reduce the ratio.

*Ratio of Soluble to Total Phosphates.*—On account of the large amount of alkali, at least one-half of the total phosphates of cider vinegar ash are soluble in water. Hard water will naturally decrease the soluble phosphates.

*Reducing Sugars.*—These should be the same in amount after as before inversion. Any increase after inversion is due to cane-sugar (as in molasses vinegar) or to dextrine from glucose added to increase the solids.

*Percentage of Reducing Sugars in the Solids.*—The highest percentage of reducing sugars in the solids of the above vinegars is 16.6 per cent., and any sample having more than 20 or at most 25 per cent. of reducing sugars in the residue would be viewed with suspicion.

*Polarization.*—Pure cider vinegar *always* polarizes to the left; indeed the polarization of apple juice in all the stages of its career whether in the form of cider or vinegar is left handed, and any deviation from this rule is sufficient to condemn the sample. Excessive laevo-rotation in vinegar indicates either the addition of invert sugar, or the incomplete acetification of the vinegar. Dextro-rotation before and laevo-rotation after inversion indicates added sucrose, while right-handed rotation both before and after inversion indicates glucose.

*Suggested Standards.*—Pure cider vinegar should contain at least 4.50 per cent. of acetic acid, and at least 2 per cent. of cider

vinegar solids. The ash should constitute at least 6 per cent. of the solids. The alkalinity of 1 gram of ash should be equivalent to at least 65 cc. of tenth-normal acid. At least 50 per cent. of the phosphates in the ash should be soluble in water. The reducing sugars should be the same in amount after as before inversion, and should not exceed 25 per cent. of the solids. The polarization, expressed in terms of 200 mm. of undiluted vinegar, should lie between  $-0.1^{\circ}$  and  $-4.0^{\circ}$  Ventzke. Malic acid should be indicated by both the calcium chloride and lead acetate test.

A standard for malic acid is desirable, but before suggesting such, a larger number of determinations should be made than those hitherto recorded. The writers hope to cover this point more completely in the near future.

*Routine Examination of Vinegar for Adulteration.*—In determining whether or not an alleged vinegar is spurious, it is rarely necessary for the public analyst to make a complete analysis. Aside from the determination of acidity and total solids, by far the most important tests consist in the polarization and in the calcium chloride and lead acetate tests for malic acid. It is rare that spurious vinegar will fail of detection by at least one of these tests. Only in doubtful cases is it necessary to go farther. It is well, however, to be able in some cases to confirm one's judgment by added proof, and where litigation is involved a complete analysis may be helpful.

---

## A PORTABLE OUTFIT FOR THE DETERMINATION OF CARBONIC ACID, DISSOLVED OXYGEN AND ALKALINITY IN DRINKING-WATER.

BY FRED B. FORBES.

Received February 17, 1904.

VARIOUS forms of portable apparatus for different analytical purposes have been described and have proved their usefulness in practice. Having occasion to make many determinations of carbon dioxide, dissolved oxygen and alkalinity in the field, a portable outfit has been devised which has resulted in a considerable economy of time and labor. The following description is published as a suggestion to any one who may have similar determinations to make at present or in the future.