The form of discharger above described leaves the terminals free and exposes the slit to spattering. This difficulty is removed by simply covering the slit with a glass microscope slip of suitable size. We use a slip three inches long by two wide and about one-sixteenth of an inch in thickness, and hold it in place by two rubber bands. If the glass becomes spattered, it can easily be wiped clean or replaced by a clean slip.

The upper terminal, which is not shown in the figure, consists of an insulated platinum wire or a graphite cone, around which the wire is wrapped.

CORNELL UNIVERSITY,
October, 1897.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. NO. 30.]

VINEGAR ANALYSIS AND SOME CHARACTERISTICS OF PURE CIDER VINEGAR.

BY ALBERT W. SMITH.

Received November 17, 1897.

THE laws of Ohio, copying the food laws of several older states, require, among other things, that apple or cider vinegar to be sold in the state shall contain at least two per cent. of cider vinegar solids. As to the chemical composition of what constitute the solids of pure cider vinegar, very little has been published. The *Analyst* for May, 1891, contains some analyses of pure malt vinegar and the prosecution, in 1893, of several cases in the courts of England, by the food inspectors against dealers in distilled and wood-acid vinegar, attracted considerable attention in that country to the subject of the chemical composition of vinegar and methods of distinguishing from each other the several kinds of vinegar upon the English market. Some valuable data were published by Allen and Moore,[1] especially concerning the character of vinegar made from grain. From the discussion of the question by the Society of Public Analysts[2] it appears that the English vinegar market is largely supplied by products made from distilled alcohol and from malted or unmalted grain. In this country the principal sources of vinegar are from apple cider and from distilled alcohol, the

[1] *Analyst*, 18, 240; and 19, 214.

[2] *Analyst*, 18, 180 and 240; 19, 8 and 33.

latter being usually made from maize and malt. Almost all of this distilled or spirit vinegar, which is originally nearly colorless, is colored by caramel in imitation of the color of cider and malt vinegar.

The chemical distinction between cider and spirit vinegar, when pure, offers little difficulty. The cider vinegar, except that made from early summer apples, is of a dark brown color, contains from two and a half to four per cent. solids and 0.30 to 0.50 per cent. ash, and when old has a pleasant, fragrant odor and characteristic taste. The distilled vinegar contains little solid matter and almost no ash, with little taste or odor besides that imparted by its acetic acid contents. The caramel used in this coloring is usually made by burning or caramelizing glucose or from an aqueous extract of charred grain. Although many manufacturers stoutly contend its use to be to impart flavor and " body" to the vinegar, the palpable and sole object of the coloring process is to enable the unscrupulous dealer to sell the product for "pure cider vinegar" or "pure malt vinegar," which, to my personal knowledge, was the all too common practice in Ohio until the statutes against food adulteration were vigorously and honestly enforced.

The chemical distinction of the source of a sample of vinegar must depend largely upon the quantity and composition of its solid constituents. The organic portion of these solids would seem to offer an excellent opportunity for differentiation, in its maleïc and succinic acids, glycerol and sugar contents, and the accurate determination of these would undoubtedly furnish the most valuable basis for judgment. At present, however, the methods in use for the determination of each of these are so tedious and, in the end, so unsatisfactory, that the mineral contents of the ash afford a more advantageous and practical method for the public analyst.

The ash of cider vinegar differs from that of most other kinds in a number of characteristics, only a few of which have heretofore been pointed out.[1]

The first peculiarity to be noticed is that the ash from cider vinegar commences to volatilize and is fusible at a comparatively

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[1] Allen : Commercial Organic Analysis, 1, 389; Cox : *Analyst*, **19**, 89.

low temperature. If the ash fuses before all the carbon is burned, particles of this are apt to become enclosed and then to resist further oxidation. To prevent this it is best to evaporate and burn small quantities at a time (not to exceed ten cc.), and to keep the temperature as low as is consistent with complete oxidation. A low red heat must not be exceeded, else loss by volatilization occurs.

A second qualitative difference is the fact that the ash from pure cider furnishes a potassium flame unobscured by sodium light, which is usually not the case with a vinegar containing much added natural water, as imitations usually do.

The ash of cider vinegar differs quantitatively from others so far examined in being quite low in chlorides and sulphates, and high in alkaline carbonates and phosphates. A determination of each of these is quickly and easily made by volumetric methods and the results afford data from which reliable conclusions as to the genuineness of the sample may be drawn. About two-thirds of the phosphates of pure cider vinegar ash are soluble in water. In the ash of other vinegars upon the market a much lower proportion of the total phosphates is soluble in water, and the addition of natural water containing lime or magnesia, to pure cider vinegar, reduces this proportion of soluble phosphates, by converting potassium into alkaline earth phosphates.

The complete analysis may be conveniently carried out as follows: For solids, five to ten grams are evaporated in a flat-bottomed dish and dried to constant weight in a water oven. For total acidity five grams, diluted to about fifty cc., are titrated with standard alkali, using phenol-phthalein as indicator. The result is usually reported as acetic acid, without attempting to separate this from the small amounts of other organic acids present.

For ash, ten grams are dried and burned in a crucible, using the before-mentioned precaution of a low temperature. This is weighed and dissolved, and the solution tested qualitatively for color of flame and presence of sulphates and chloride. Unless these are excessive, as compared with a sample of known purity, they need not be determined quantitatively.

For alkalinity of ash and proportion of phosphates, twenty-five grams are dried and burned, the ash extracted repeatedly with hot water, and the aqueous solution titrated with standard acid, using methyl orange as indicator. The undissolved residue of ash is then treated with nitric acid, the solution partially neutralized, and the phosphorus in each solution separately precipitated by molybdate solution, the yellow precipitate dissolved in ammonia, reduced with zinc and sulphuric acid, and titrated with standard permanganate solution.

All colored samples should be tested for coloring-matter, which, in imitation vinegars, is most commonly caramel. To test for this, mix five to ten cc. of the sample with about twenty-five cc. paraldehyde, and add alcohol until the three liquids become soluble. After standing twelve to twenty-four hours, the caramel will separate as a sticky, dark-brown precipitate, which, after washing with a little absolute alcohol, has the characteristic bitter taste of caramel, and reduces Fehling's solution freely.

TWENTY-TWO SAMPLES PURE CIDER VINEGAR.

Number.	Acetic acid. (1)	Total solids. (2)	Ash. (3)	No. cc. tenth-normal acid required to neutralize ash from 100 grams vinegar. (4)	Millig'ms P_2O_5 in water solntion of ash from 100 grns. (5)	Millig'ms P_2O_5 in ash not soluble in water. (6)	Total P_2O_5 in ash from 100 grams vinegar. (7)	Original solids $\times$ =Solids $+ 1\frac{1}{2}$ acetic acid. (8)	Ash per 100 parts original solids. (9)	P_2O_5 millig'ms per 100 grams original solids. (10)
1	5.46	2.27	0.44	43.9	22.7^1	16.3	39.0^1	10.46	4.21	373
2	3.29	2.69	0.36	31.2	17.3	8.7	26.0	7.63^2	4.72	341
3	4.22	3.21	0.36	36.0	18.5	9.2	27.7	9.54	3.77	290
4	3.58	2.91	0.31^2	28.4^2	15.6	4.2^2	19.8^2	8.28	3.74	239
5	3.74	2.14	0.31	36.0	17.5	7.8	25.3	7.75	4.00	326
6	4.74	2.80	0.35	34.4	18.3	6.8	25.1	9.91	3.53	253
7	4.59	2.86	0.32	32.8	19.5	13.8	33.3	11.74	2.73^2	284
8	4.19	3.00	0.33	36.8	20.5	8.5	29.0	9.28	3.55	312
9	4.92	4.45^1	0.38	30.8	17.8	9.5	27.3	11.83	3.21	231
10	4.63	3.30	0.40	47.2	21.3	9.8	31.1	10.24	3.90	303
11	3.24^2	3.89	0.44	45.2	20.5	10.8	31.3	8.78	5.01	348
12	3.89	3.00	0.33	30.4	22.5	10.5	33.0	8.88	3.72	372
13	4.97	2.40	0.37	44.0	15.5	11.0	26.5	9.85	3.76	269
14	6.55	2.76	0.49	44.8	17.0	4.6	21.6	12.58	3.89	172^2
15	4.11	2.43	0.36	28.8	21.2	5.6	26.8	8.60	4.19	312
16	7.61^1	2.97	0.43	55.2^1	21.0	11.0	32.0	14.38^1	2.99	223
17	4.00	2.53	0.34	35.2	19.4	11.3	30.7	8.53	3.98	360
18	4.08	2.82	0.33	36.0	13.6^2	19.4^1	33.0	8.94	3.69	369
19	4.00	2.75	0.51^1	45.6	17.5	15.5	33.0	8.75	5.83	377^1
20	3.80	2.50	0.50	48.8	19.9	9.0	28.0	8.20	6.09^1	352
21	4.20	2.00^2	0.39	44.0	19.9	9.0	28.9	8.29	4.70	348
22	4.30	2.50	0.46	40.0	22.5	10.0	22.5	8.95	5.14	365
Aver.	4.46	2.83	0.39	38.8	19.1	10.1	28.6	9.65	4.11	310

[1] Maximum.

[2] Minimum.

TWENTY-SEVEN SAMPLES CIDER VINEGAR CONTAINING ADDED WATER OR ADDED SPIRIT VINEGAR SOLD IN OHIO MARKETS.

Number.	Acetic acid. (1)	Total solids. (2)	Ash. (3)	No. cc. tenth-normal acid required to neutralize ash from 100 grams vinegar. (4)	Millig'ms P_2O_5 in water solution of ash from 100 gms. (5)	Millig'ms P_2O_5 in ash not soluble in water. (6)	Total P_2O_5 in ash from 100 gms. vinegar. (7)	Original solids =Solids + 1½ × acetic acid. (8)	Ash per 100 parts original solids. (9)	P_2O_5 millig'ms per 100 grams original solids. (10)
1	4.10	2.64	0.53	24.4	none	8.4	8.4	8.79	6.03	95
2	4.21	2.94	0.47	10.8	15.2	8.1	23.3	9.25	5.08	252
3	4.11	2.50	0.28	24.4	4.4	4.0	8.4	8.66	3.23	97
4	3.84	2.35	0.30	9.8	4.4	20.2	24.6	8.11	3.70	303
5	4.31	2.10	0.27	24.0	12.8	8.5	21.3	8.56	3.15	249
6	4.26	2.41	0.27	26.8	15.0	5.0	20.0	8.80	3.07	227
7	4.15	2.35	0.27	29.6	...	...	...	8.58	3.15	...
8	4.07	2.14	0.27	27.6	...	...	...	8.24	3.27	...
9	4.01	2.09	0.26	23.0	12.0	5.0	17.0	8.10	3.21	210
10	3.84	2.06	0.26	26.4	...	...	...	7.82	3.33	...
11	3.43	1.69	0.25	18.8	12.0	12.0	24.0	6.83	3.66	351
12	4.46	2.99	0.25	16.6	6.0	3.0	9.0	9.68	2.58	94
13	3.73	1.21	0.25	1.4	none	7.5	7.5	6.81	3.67	110
14	3.97	1.91	0.24	22.8	5.3	8.8	14.1	6.86	3.50	205
15	4.83	2.20	0.24	21.6	11.4	15.8	27.2	9.44	2.54	288
16	3.68	2.45	0.23	15.6	8.6	6.6	15.2	7.97	2.88	191
17	4.00	1.74	0.22	25.2	5.8	8.4	14.2	7.74	2.84	183
18	3.65	1.42	0.20	17.6	...	...	...	6.89	2.90	...
19	4.70	2.14	0.20	13.4	10.0	10.5	20.5	9.19	2.18	223
20	3.01	3.41	0.20	20.8	...	...	...	7.92	2.53	...
21	3.84	1.90	0.20	27.6	5.2	15.2	20.4	7.66	2.61	266
22	4.10	1.20	0.18	14.4	5.0	3.0	8.0	7.35	2.45	109
23	3.88	1.57	0.18	13.0	...	...	...	7.39	2.43	...
24	3.74	1.41	0.17	9.6	...	...	...	7.02	2.42	...
25	4.62	2.02	0.17	11.2	5.8	3.0	8.0	8.95	1.90	89
26	3.44	1.19	0.14	14.0	...	...	...	6.35	2.20	...
27	4.03	1.64	0.14	7.4	trace	4.5	4.5	7.68	1.83	59

SAMPLE MADE FROM DRIED APPLES AND GLUCOSE.

	4.29	3.89	0.25	21.0	..	..	5.5	10.33	2.42	53

SAMPLE MADE FROM APPLE CIDER AND GRAPE JUICE.

	4.54	2.77	0.30	34.0	..	..	4.0	9.58	3.13	42

FOUR SAMPLES MALT VINEGAR.

Eng.	5.90	2.21	0.28	6.0	..	..	12.5	11.06	2.53	113
Am.	5.16	2.67	0.26	6.0	..	..	9.0	10.41	2.50	86
"	4.40	2.04	0.23	5.6	..	..	9.2	8.64	2.66	106
"	4.01	1.75	0.20	4.4	..	..	9.5	7.76	2.58	122

SIXTY-FIVE SAMPLES SPIRIT VINEGAR.

Av..	3.84	0.38	0.06	1.1	none	trace
Max.	5.99	0.78	0.15	5.6	"	"
Min.	2.87	0.14	0.01	0.0	"	"

In columns 1, 3, 5, and 8 of the accompanying tables, results are stated as grams per 100 grams of the sample. In column 4 are given the number of cubic centimeters of decinormal acid required to neutralize the filtered water solution of the ash derived from 100 grams of the vinegar. In columns 5 and 6 are the number of milligrams of phosphorus pentoxide (P_2O_5) respectively in the water solution and the water insoluble portion of the ash derived from 100 grams of the sample. Column 7 contains the sum of these two quantities, or the total phosphorus pentoxide. In column 8, what Hehner[1] calls "original solids" are given. These numbers are obtained by multiplying the acetic acid quantities by 1.5 and adding to this the total solids. It is assumed by Hehner that three parts of sugar by alcoholic and acetic fermentation yield two parts of acetic acid, this being approximately the theoretical quantitative relations:

$$\underset{180}{C_6H_{12}O_6} \rightarrow 2C_2H_5OH \rightarrow \underset{120}{2HC_2H_3O_2}.$$

Hence, by increasing the acetic acid in the ratio of two to three, we get approximately the theoretical quantity of sugar from which it was produced. By adding to this the amount of solids still remaining in the vinegar, the quantity of solids present in the unfermented liquid is assumed to be obtained. Of course such an assumption is extremely far from the truth, because, from various losses during fermentation, by volatilization of alcohol and acetic acid, only one-half to three-quarters of the theoretical yield of acid is obtained, and this loss varies greatly in the different processes, and in the same process depends largely upon individual care during each of its steps. Further, during the fermenting and settling periods albuminoid and other constituents settle in considerable quantities, so that such calculations possess little real worth, and, when spirit vinegar is used as an adulterant of cider or malt vinegar, they may become decidedly misleading. The figures in columns 8, 9, and 10 are given principally for the sake of comparison with previous analyses which have been reported in this way. In column 9 the percentages of ash to "original solids," found in column 8, have been given, obtained by dividing 100 times the

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[1] *Analyst*, 16, 82.

per cent. of ash as given in column 3 by the per cent. of "original solids." In the same way the milligrams of total phosphorus pentoxide per 100 grams of original solids are reported in column 10.

Of these results, the quantity of ash, the alkalinity of the ash, and amount of soluble phosphates are of considerable uniformity in pure cider vinegar, and these, when considered with the other characteristics above enumerated, serve to differentiate this kind quite sharply from all other commercial varieties and to afford a basis for the approximate estimation of the quantity of spirit vinegar or of water, with which pure cider vinegar may have been adulterated.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY, OHIO STATE UNIVERSITY.]

ROOT TUBERCLES IN WATER CULTURE.[1]

BY H. A. WEBER.

Received November 22, 1897.

SINCE the discovery by Hellriegel of the connection between root tubercles and the fixation of atmospheric nitrogen by leguminous plants, the literature on this interesting and important question is being constantly enriched by painstaking experiments on the part of scientific investigators all over the world. The subject has thus far been studied only in connection with sterilized soil or sand. It occurred to the writer that it might be possible to produce root tubercles in water culture and thus be able to observe the process better than when the roots of the plants were buried in soil or sand. The work of conducting the experiments about to be described was entrusted to Mr. J. C. Britton, one of the writer's advanced students. The results more than met my expectations, and this preliminary notice is made public for the benefit of those who may feel inclined to employ the method in their investigations.

For the past four or five years the writer has employed in water-culture experiments an apparatus designed by himself, which presents certain advantages over the methods heretofore described. As this apparatus was employed in the experiments

[1] Read before the Columbus Section of the American Chemical Society, Nov. 10, 1897.