

It would appear, that as far as salivary digestion is concerned, there is no danger of excessive dilution with any water of fair quality.

On the other hand it seems probable that a dilution as great as that of the optimum for salivary digestion is not reached under ordinary conditions. For this reason the ingestion of large amounts of water would increase the efficiency of salivary amylase through the production of a satisfactory dilution of the digestion mixture.

These results are in accord with work carried out in this laboratory showing a better utilization of carbohydrates during periods of high water ingestion.¹

Conclusions.

On the basis of experiments made *in vitro* it is apparent that the digestive efficiency of normal human saliva is *increased* when such saliva is *diluted*. The *optimum dilution* is dependent upon the nature of the diluent, being *four volumes* for sodium chloride solution (0.3%) and *seven volumes for water*, either distilled or tap water.

Softened water exerts an *inhibitory* influence, due principally to the presence of *magnesium hydroxide*.

The fact that salivary amylase acts more efficiently when the saliva is diluted is an added argument in favor of *water drinking with meals*.

The influence of dilution, as above set forth, aids in explaining the better digestion of ingested carbohydrates when accompanied by a copious water ingestion.

[CONTRIBUTION OF THE KANSAS AGRICULTURAL EXPERIMENT STATION.]

ACIDITY IN SILAGE: METHOD OF DETERMINATION.

BY C. O. SWANSON, J. W. CALVIN AND EDWIN HUNGERFORD.

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As far as ascertained by the writers, acidity in silage is determined by extracting either with water or with alcohol and titrating with a standard alkali solution, using phenolphthalein as indicator. Esten,² Hart and Willaman,³ Dox and Neidig,⁴ use water as the solvent. With certain kinds of silage, water gives an extract difficult to filter. Alcohol as a solvent appears not to have been so thoroughly tried by experiment station chemists. To compare water and alcohol as extractive reagents in determining the acidity in silage, was the object of the following experiments.

The work of Dox and Neidig, and of Hart and Willaman has shown that the principal volatil acids in silage are: acetic, propionic, butyric and valeric, acetic constituting 75% or more of the total. Lactic is as-

¹ Mattill and Hawk, THIS JOURNAL, 33, 2019 (1911).

² Conn. Storrs Expt. Sta., Bull. 70.

³ THIS JOURNAL, 34, 1619.

⁴ Research Bull. No. 7, Iowa Expt. Sta.; THIS JOURNAL, 35, 93.

sumed to be the principal non-volatile acid. To make the results comparable, all percentages in the following experiments are calculated as acetic acid. As data accumulate it will probably be better to calculate the acidity on the basis of a mean of all the acids present, but this is not practicable at present.

Partly because these experiments were a part of a larger investigation, the work was done on several kinds of silage and on different samples of the same silage. For this reason the percentage of acidity obtained in one experiment is not always comparable with that obtained in another. The comparisons are confined to each separate trial. In all cases, however, the ratio between the silage and the solvent was 1 to 10 by weight.

Fineness of Grinding.—The first trial was to compare the percentage of acidity obtained by extracting the silage with water for the same periods, in the condition in which it came from the silo, with the percentage of acidity obtained after it had been finely ground in a large power sausage mill. The following results were obtained and they show that fine grinding is an absolute necessity:

Sample 1.	Extracted without grinding.....	0.60% acidity
Sample 1.	Extracted after grinding.....	0.75% acidity
Sample 2.	Extracted without grinding.....	0.84% acidity
Sample 2.	Extracted after grinding.....	1.22% acidity

Influence of Carbon Dioxide.—Extracts from silage contain carbon dioxide in varying amounts. To determine what influence carbon dioxide has on the percentage of acidity, the water extract from finely ground silage was boiled under a reflux condenser for 20 minutes, the acidity determined and compared with that obtained from the unboiled extract.

Sample 3.	Water extract, not boiled.....	1.22% acidity
Sample 3.	Water extract, boiled.....	1.16% acidity
Sample 4.	Water extract, not boiled.....	1.33% acidity
Sample 4.	Water extract, boiled.....	1.30% acidity

There is evidently a small amount of acidity due to the presence of carbon dioxide. But by using recently boiled distilled water this error is reduced to a minimum and is neglected for the present in this investigation.

The Acidity in the Water and Alcohol Extracts Compared.—The following determinations were made under the same conditions of temperature, volume and time of extraction. The only difference was the solvent used on the different samples.

Sample 5.	Extracted with water.....	1.17% acidity
Sample 5.	Extracted with 95% alcohol.....	1.78% acidity
Sample 6.	Extracted with water.....	1.56% acidity
Sample 6.	Extracted with 95% alcohol.....	1.98% acidity
Sample 7.	Extracted with water.....	1.57% acidity
Sample 7.	Extracted with 95% alcohol.....	2.10% acidity
Sample 7.	Extracted with 50% alcohol.....	2.04% acidity

The increase in acidity was 0.61, 0.42 and 0.53% and shows conclusively that alcohol is the more efficient solvent. The trial with 50% alcohol indicates that the weaker alcohol may be as effective as the stronger. To ascertain this more fully was the object of the next experiment.

THE ACIDITY IN THE EXTRACTS FROM 50% AND 95% ALCOHOL.

Sample 8. Extracted with 50% alcohol.....	2.07% acidity
Sample 8. Extracted with 95% alcohol.....	2.13% acidity
Sample 9. Extracted with 50% alcohol.....	1.98% acidity
Sample 9. Extracted with 95% alcohol.....	2.07% acidity

The stronger alcohol extracted from 0.06 to 0.09% more acidity. This slight amount is not sufficient to offset the advantage of the weaker alcohol in a long series of determinations where the comparisons have a greater importance than the absolute quantity. The weaker alcohol, aside from being more economical, gives an extract which is easier to filter and titrate, the end point being more distinct, which doubtless accounts to some extent for the slightly lower results.

Completeness of Extraction; Shaking by Hand.—In all the above determinations the shaking was done by hand. To determine to what extent the extraction was complete was the object of the next experiment. A weighed amount of silage was put into a large flask and a definite volume of alcohol added. The average volume occupied by this silage was previously determined and corrections made for it. The flask was then shaken several times during half an hour after which an exact portion was filtered off. This was then replaced with an equal portion of fresh alcohol and the shaking and filtering repeated. This operation was performed a third time. The acidity in the several extracts was determined. Correction in each case was made for the volume occupied by the silage. The details of the method of calculation will be shown more fully in connection with the next trial. In this trial the following results were obtained. All are calculated on the basis of 100 grams of silage:

Sample 10.		Sample 11.		Sample 12.	
1st extract	2.40 g. acid	1st extract	2.27 g. acid	1st extract	1.66 g. acid
2nd extract	0.09 g. acid	2nd extract	0.02 g. acid	2nd extract	0.11 g. acid
3rd extract	0.03 g. acid	3rd extract	0.09 g. acid	3rd extract	0.04 g. acid
	—	4th extract	0.02 g. acid		—
Sum,	2.52 g. acid	Sum,	2.40 g. acid	Sum,	1.81 g. acid

This shows that the first extraction is not as complete as desirable. To secure better extraction was the object of the next trial.

Completeness of Extraction; Shaking by Machine.—100 grams of silage were placed in a 500 cc. flask and made up to volume with 50% alcohol. The average volume occupied by the dry matter in 100 grams of silage was found in a number of separate trials to be 30 cc. The contents of

the 500 cc. flask were then transferred to a 2-liter flask and the flask was rinsed with 50% alcohol, using exactly 500 cc. The large flask was then placed on the machine and shaken for 30 minutes. This machine gives a horizontal motion through a space of 2", 90 times a minute. Exactly 500 cc. were filtered off and replaced with 500 cc. of fresh alcohol and the whole operation performed a second and a third time. 100 cc. of the separate filtrates were titrated with 0.2 *N* sodium hydroxide. These exhaustive extractions were performed on three separate samples with the results given below. The data are given complete so as to show the method of calculating the results. They are all based on 970 cc. volume of the liquid, 30 cc. being occupied by the dry matter of the silage. This would leave 470 cc. of the extract in the flask after each filtration.

Extract No.		Cc. 0.2 <i>N</i> NaOH neutralized by 100 cc. extract.	Cc. 0.2 <i>N</i> NaOH equivalent to extract filtered off.	Cc. 0.2 <i>N</i> NaOH equivalent to extract left in flask.	Cc. 0.2 <i>N</i> NaOH equivalent to total extract.	Cc. 0.2 <i>N</i> NaOH neutralized above amount calculated.	Grams of acid from 100 g. silage.
Sample 13	1	16.0	80.0	75.2	155.2	0.0	1.860
	2	8.0	40.0	37.6	77.6	2.4	0.030
	3	4.5	22.5	21.1	43.6	6.0	0.073
						Sum,	1.963
Sample 14	1	15.5	77.5	72.8	150.3	0.0	1.804
	2	7.25	36.25	34.0	70.3	—2.5	—0.030
	3	4.0	20.0	18.8	38.8	8.8	0.057
						Sum,	1.831
Sample 15	1	18.2	91.0	85.5	176.5	0.0	2.118
	2	10.3	50.5	49.5	100.0	14.5	0.173
	3	5.1	25.5	24.0	49.5	0.0	0.000
						Sum,	2.291

The figures in column 1 are the figures obtained by titration; the figures in columns 2, 3 and 4 are calculated on the basis of the results expressed in column 1, using in each case 500 cc. for the amount of extract filtered off, 470 cc. for the amount left in the flask, and the sum of the two for the total amount. From the cc. of 0.2 *N* NaOH equivalent to the 970 cc. extract is calculated the quantity of acid obtained from 100 grams silage in the first extraction. The difference between the cc. 0.2 *N* NaOH equivalent to the extract left in the flask after the first extraction and the cc. 0.2 *N* NaOH equivalent to the total extract obtained in the next extraction would be the equivalent amount of acid extracted the second time. This and its repetition give the figures in the column 5 from which the additional amounts of acid given in column 6 are calculated.

While these results are somewhat better than when the shaking was done by hand, they are not as uniform as would be desirable. The ex-

tract is very highly colored and the end point in titration is not distinct. The analytical error is about 0.4 cc. of 0.2 *N* sodium hydroxide and the tendency is to make that error count on the plus side. It is hoped that as the work goes on the exact conditions may be more accurately ascertained. An error of 0.4 cc. on 100 cc. extract would be equivalent to nearly 4 cc. on 100 grams of silage or almost 0.05%. As this error may be introduced in the separate titrations it accounts in part for the acidity obtained in the second and third extractions. In addition the presence of carbon dioxide involves some error.

Uniformity of Results from Different Charges of the Same Sample.—One large sample of the silage from the surface of the cane silo was divided into three portions and each portion extracted twice. The following results were obtained calculated as above:

	G. acid from 100 g. silage.
Sample 16, Portion I, 1st extract	1.46
Sample 16, Portion I, 2nd extract	0.05
	—
Sum,	1.51
Sample 16, Portion II, 1st extract	1.47
Sample 16, Portion II, 2nd extract	0.07
	—
Sum,	1.54
Sample 16, Portion III, 1st extract	1.49
Sample 16, Portion III, 2nd extract	0.06
	—
Sum,	1.55

Two other samples were taken from a corn silo and each divided into two portions.

	G. acid from 100 g. silage.
Sample 17, Portion I, 1st extract	1.77
Sample 17, Portion I, 2nd extract	0.05
	—
Sum,	1.82
Sample 17, Portion II, 1st extract	1.79
Sample 17, Portion II, 2nd extract	0.04
	—
Sum,	1.83
Sample 18, Portion I, 1st extract	1.80
Sample 18, Portion I, 2nd extract	0.07
	—
Sum,	1.87

	G. acid from 100 g. silage.
Sample 18, Portion II, 1st extract.....	1.86
Sample 18, Portion II, 2nd extract.....	0.03
	Sum, 1.89

With water the repeated extractions on one sample resulted as follows:

Sample 19, 1st extract, 1.80 g. acid from 100 g. silage
Sample 19, 2nd extract, 0.00 g. acid from 100 g. silage

This shows the uniformity of results possible from the same sample. Whether one or two extractions shall be used depends on conditions. Where the total amount of acid is of first importance, two or three extractions appear to be necessary; but where comparative results are desired such as the development of acidity in the silage or the comparison of different kinds of silage, one extraction is sufficient.

However, two or more extractions add to the error of titration. Using phenolphthalein as an indicator, the red color does not appear till the solution is alkaline to litmus. This was found true in both the alcohol and the water extract. The end point is taken to be when the first faint red color appears. As the solution is colored, the exact end point is not easy to determine.

Length of Extraction Necessary.—One sample of silage was divided into three portions and each portion extracted with alcohol for 15, 30 and 60 minutes with the following results:

Sample 20	{	15 minutes, 2.04% acid
		30 minutes, 2.05% acid
		60 minutes, 2.04% acid

With water the results were as follows:

Sample 21	{	30 minutes, 1.804% acid
		60 minutes, 1.804% acid
		120 minutes, 1.804% acid

This shows that nothing is gained by the longer extraction either with alcohol or with water.

Amount of Acid Extracted by Water and 50% Alcohol in Different Kinds of Silage.—The foregoing shows that equally uniform results may be obtained either with the water or with the 50% alcohol extraction, and that more acid is obtained by the latter. To compare these two solvents on different kinds of silage was the object of the next experiment. For this purpose samples of corn, kafir and cane silage were obtained. The corn and kafir samples were divided into four portions each and the cane into three portions. The treatments and results are given in the following table:

	Grams of acid from 100 g. silage.	Average.	Excess ex- tracted by alcohol.
Sample 22, Corn, Portion I, Water extraction, 1st extract	1.58		
Sample 22, Corn, Portion I, Water extraction, 2nd extract	0.01		
Sum,	1.59		
Sample 22, Corn, Portion II, Water extraction, 1st extract	1.58		
Sample 22, Corn, Portion II, Water extraction, 2nd extract	0.01		
Sum,	1.59	1.59	
Sample 22, Corn, Portion III, Alcohol extraction, 1st extract . . .	2.04		
Sample 22, Corn, Portion III, Alcohol extraction, 2nd extract . . .	0.04		
Sum,	2.08		
Sample 22, Corn, Portion IV, Alcohol extraction, 1st extract	1.96		
Sample 22, Corn, Portion IV, Alcohol extraction, 2nd extract	0.09		
Sum,	2.05	2.07	0.48
Sample 23, Kafir, Portion I, Water extraction, 1st extract	0.89		
Sample 23, Kafir, Portion I, Water extraction, 2nd extract	—0.05		
Sample 23, Kafir, Portion II, Water extraction, 1st extract	0.900		
Sample 23, Kafir, Portion II, Water extraction, 2nd extract	—0.006	0.89	
Sample 23, Kafir, Portion III, Alcohol extraction, 1st extract . . .	1.24		
Sample 23, Kafir, Portion III, Alcohol extraction, 2nd extract . . .	0.06		
Sum,	1.30		
Sample 23, Kafir, Portion IV, Alcohol extraction, 1st extract	1.20		
Sample 23, Kafir, Portion IV, Alcohol extraction, 2nd extract	0.04		
Sum,	1.24	1.27	0.38
Sample 24, Cane, Portion I, Water extraction, 1st extract	1.25		
Sample 24, Cane, Portion I, Water extraction, 2nd extract	0.00		
Sum,	1.25	1.25	
Sample 24, Cane, Portion II, Alcohol extraction, 1st extract	1.39		
Sample 24, Cane, Portion II, Alcohol extraction, 2nd extract	0.05		
Sum,	1.44		
Sample 24, Cane, Portion III, Alcohol extraction, 1st extract	1.42		
Sample 24, Cane, Portion III, Alcohol extraction, 2nd extract	0.05		
Sum,	1.47	1.45	0.20

Since equally uniform results are possible with either the water or the alcohol extraction and since the alcohol extracts contain a high percentage of acidity in every case, it must follow that some of the acids in silage which are soluble in alcohol are insoluble in water. The amounts of these insoluble in water are different in the various kinds of silage, corn silage having the largest relative amount.

Since preparing the above paper we have learned that Dr. C. A. Browne several years ago obtained similar results when determining the free acid in rice bran and other cattle feeds and found that the increase in acid in the alcoholic extract occurred only in old feeds. Dr. Browne suggests that the liberation of free fatty acids from the oil of the feed was due to the action of lipase and that this might also occur in silage, the fats and oils of the fresh cut material undergoing hydrolysis in the silo.

ON THE DISTRIBUTION OF ANTE-MORTEM ADMINISTERED ARSENIC IN THE HUMAN CADAVER.

BY JOHN B. EKELEY.

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Some years ago the writer made a very complete chemico-legal examination of the organs of G. R., who had died from the effects of arsenic, criminally administered. The results of the analyses appeared at the time in a publication of local circulation. The writer is not aware of any other investigation carried out to such an extent upon the body of a person *known to have died from arsenic poisoning*. It is therefore desirable that the results of this investigation find their way into the literature of arsenical poisoning.

The stomach, liver, kidneys, and heart had been removed from the body previous to burial by the physicians who had attended the case, in the belief that the cause of death was arsenical poisoning. An analysis of a very small portion of the stomach contents showing arsenic, it was deemed advisable that the body should be exhumed in order to obtain further material for analysis. The body was found to be in an advanced state of moist decomposition. The casket, being of very thin material, had been soaked through by the moisture percolating through the gravel soil in which it had been buried for six weeks of very wet weather. Samples of earth from both sides of the casket were taken and analyzed for arsenic. It is interesting to note that soil which had been very near to the casket showed marked traces of arsenic, while that a little removed was almost arsenic free. The intestines, brain, spinal cord, a section of the thigh, and the right foot were taken for examination. The intestines were practically empty. The brain was in a liquid condition, about the consistency of thin gravy. The stomach walls, having been removed before burial, were in good condition. They showed about forty square