

tion is essential to the production of a carefully prepared pyroxylin. This drying is best carried out on the form of drier used in drying wool. The plan of such a drier is given in Fig. I. The surface *a* is covered with wire cloth, having a half inch mesh, and should be galvanized.

Heater coils can be placed within the frame *b* and the hot air forced through the fiber by means of the rotary fan *c*.

If the fiber is found to need scouring to make it fit for the process of nitration, it is best scoured by those who make a business of this branch. Absorbent cotton is produced on such a large scale at the present time, that the manufacturers will sell it at a very low figure, in order to keep their plants in operation. The author obtained the fiber used by him for several years from this source.

[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, NO. 6; SENT BY H. W. WILEY].

THE PREDOMINANT ORGANIC ACID IN SORGHUM JUICE.¹

BY OMA CARR.

Received June 1, 1893.

I N the work of the Department of Agriculture during the past few years attention has often been called to peculiarly tenacious and difficultly soluble incrustations forming upon the tubes of the evaporating apparatus of the sorghum-sugar houses of Kansas. Owing to the formation of these incrustations and the difficulty of removal the processes of manufacture are greatly impeded. Dr. Wiley collected a large amount of this scale at Medicine Lodge and directed me to make a study of its composition and properties. The following paper gives the results of a brief study of the scale.

The scale examined was in pieces of varying sizes, retaining the contour of the tubes from which it had been removed. A quantity of fifteen pounds was taken from some three hundred pounds forwarded from the factory at Medicine Lodge. The scale as prepared for examination consisted of a powder sufficiently fine to pass an eighty mesh sieve.

The analyses of two samples of the scale, one designated

¹ Read before the Chemical Society of Washington, May 11, 1893.

“Special,” selected by Dr. Wiley for its size and cleanliness, and “Ordinary,” representing the whole quantity removed, gave the following results :

	“Special.”	“Ordinary.”
Moisture.....	13.31 per cent.	14.21 per cent.
Magnesium oxide.....	15.93 “ “	17.70 “ “
Calcium oxide	7.27 “ “	9.80 “ “
Carbon dioxide	0.29 “ “	2.76 “ “
Fe ₂ O ₃ , Al ₂ O ₃ , P ₂ O ₅	6.22 “ “	4.10 “ “
Silica.....	2.72 “ “	1.75 “ “
Organic.....	54.40 “ “	49.31 “ “
Undetermined		0.37 “ “
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	100.14 “ “	100.00 “ “
Carbon.....	23.67 “ “	22.29 “ “
“ per cent. of organic	43.51 “ “	45.20 “ “

These data call for no special comments, aside from noting that the common scale has lain long enough for the absorption of considerable carbon dioxide, and that the elimination of this constituent would secure a greater uniformity between the two samples.

Solubility.—The ground material, one gram in quantity, was boiled an hour and a half with fifty cc. of the solvent, filtered hot upon a weighed asbestos film in a Gooch crucible, washed with alcohol and ether, dried at 105° and weighed. For this determination the “Special” sample was used, and it may be assumed that the slightly different composition of the two samples would cause but slight variation in the results.

Solvent.	Per cent. soluble.	Per cent. Inorganic insoluble.	Per cent. Organic insoluble.
2 per cent. HCl	95.67	2.85	1.48
5 “ “ “	95.00	2.78	1.32
10 “ “ “	95.97	2.60	1.43
20 “ “ “	95.87	2.59	1.54
Mean.....	95.85	2.70	1.45
2 per cent. H ₂ SO ₄	94.48	3.67	1.85
5 “ “ “	95.81	2.56	1.63
10 “ “ “	95.85	2.74	1.41
*20 “ “ “	81.03	16.29	2.68
Mean.....	91.79	6.32	1.89
** “ (2nd)	95.38	2.99	1.63
2 per cent. NaOH	67.15	21.58	11.27
5 “ “ “	62.45	24.68	12.87
10 “ “ “	59.85	29.47	10.68
20 “ “ “	60.35	26.29	10.20
Mean.....	62.45	26.29	11.26

* Boiled only one hour.

** Omitting the twenty per cent. determination.

It is seen from these results that hydrochloric acid has the highest solvent power of the three tried. Subtracting the organic insoluble from the total insoluble, the difference corresponds almost exactly to the per cent. of silica, showing that, aside from the small percentage of organic matter, the hydrochloric acid dissolves every thing but the silica. It is notable that the solvent power of hydrochloric acid depends very little upon its concentration.

The sodium hydroxide dissolves less than either acid, its power decreasing with increase of concentration. The portion insoluble in sodium hydroxide contains no silica.

In cleaning incrustated tubes, the above results, as well as good practice, suggest a procedure in which the use of hydrochloric acid precedes that of the lye.

As the work on the scale was done principally with the view of isolating and distinguishing the chief organic acids present, the following plan was pursued :

Finely divided scale (passing eighty mesh) was added to boiling sulphuric acid in ten per cent. solution until solvent action ceased and filtered hot, the filtrate being perfectly clear and transparent. The filtrate was cooled and two volumes eighty per cent. alcohol added. The calcium and magnesium sulphates precipitated were removed by filtration. The alcohol was expelled from the filtrate and the latter considerably reduced in volume by evaporation. There was added now a very strong alcohol (five volumes) and the white precipitate allowed to settle. It was decanted and washed with alcohol. The precipitate was purified by dissolving in water and repeated reprecipitation by alcohol. Finally from the solution in water free of carbon dioxide it was precipitated with a carbon dioxide-free solution of acetate of lead. This product was purified by repeated decomposition with hydrogen sulphide and reprecipitated with lead acetate. The final precipitation yielded my salt (I), or "scale salt," the combustion of which gave:

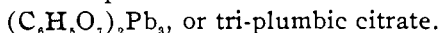
	Per cent.
Carbon	13.884
Hydrogen	1.210
Lead	58.420
Oxygen (difference)	26.486

100.000

The salt contained 2.46 per cent. moisture, eliminating which would give the following numbers :

	Per cent.
Carbon	14.23
Hydrogen	0.94
Lead	62.11
Oxygen	22.72
	<hr/>
	100.00

These figures correspond to the formula :



After digestion with sulphuric acid the insoluble residue, undried and unwashed, subjected to analysis, gave the following numbers :

	Per cent.
Moisture	6.83
Calcium oxide.....	13.92
Fe ₂ O ₃ and Al ₂ O ₃	1.70
Silica	4.26
SO ₃	62.43
Organic	10.47
Undetermined.....	0.39
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	100.00

The SO₃ present was combined, twenty per cent. with calcium (42.77 per cent. sulphate), and 1.98 per cent. with the Fe and Al (3.88 per cent. sulphates). The rest was free H₂SO₄. Eliminating the SO₃ we have :

	Per cent.
Moisture	18.18
Calcium oxide.....	37.05
Fe ₂ O ₃ and Al ₂ O ₃	4.52
Silica	11.34
Organic	27.87
Undetermined.....	1.04
	<hr/>
	100.00

Reducing to a water-free basis these data become :

	Per cent.
Calcium oxide.....	45.28
Fe ₂ O ₃ and Al ₂ O ₃	5.52
Silica	13.86
Organic	34.06
Undetermined.....	1.28
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	100.00

Reducing original scale to water-free substance and comparing its analysis with that of the residue after digestion we have :

	Original.	Residue.
Magnesium oxide	20.63 per cent.
Calcium oxide	11.41 "	45.28 per cent.
Carbon dioxide.....	3.22 "
Fe ₂ O ₃ and Al ₂ O ₃	4.78 "	5.52 "
Silica	2.04 "	13.86 "
Organic	57.48 "	34.06 "
Undetermined	0.43 "	1.28 "
	<hr style="width: 50px; margin-left: 0;"/> 100.00 "	<hr style="width: 50px; margin-left: 0;"/> 100.00 "

The silica having remained unaffected by the digestion, we may place the residue on the same plane as the original material by decreasing the percentages in the residue in the ratio of the respective percentages of silica. Analyses so corrected are as follows, calculated to water-free substance :

	Original.	Residue.
Magnesium oxide.	20.63 per cent.
Calcium oxide.....	11.41 "	6.66 per cent.
Carbon dioxide.....	3.22 "
Fe ₂ O ₃ and Al ₂ O ₃	4.78 "	0.81 "
Silica	2.04 "	2.04 "
Organic	57.48 "	5.01 "
Undetermined.....	0.43 "	0.13 "
Removed	85.35 "
	<hr style="width: 50px; margin-left: 0;"/> 100.00 "	<hr style="width: 50px; margin-left: 0;"/> 100.00 "

The organic matter has fallen from 57.48 per cent. to 5.01 per cent., 52.47 per cent. being removed, together with 20.63 per cent. MgO. Dividing the per cent. of the removed organic matter by the molecular weight of both aconitic and citric acid, we have :

$$\begin{aligned}
 52.47 \div 210 &= 0.25 = \text{citric} \\
 52.47 \div 174 &= 0.301 = \text{aconitic} \\
 20.63 \div 120 &= 0.172 = \text{MgO} \\
 20.63 \div 100 &= 0.206 = 2\frac{1}{2} \text{ MgO}
 \end{aligned}$$

As, however, the organic matter of the water-free original material contained 45.19 per cent. carbon, and as citric acid contains but 37.7 per cent., other organic matters are present containing the difference between 45.19 per cent. and 37.7 per cent., or 7.49 per cent. Correcting the decimal given for citric

acid (0.205) by the equation $45.19:37.7::0.205:x$, we find x to equal 0.171, or practically identical with the decimal for $3MgO$.

Aconitic acid contains 41.84 per cent. carbon, and correction of the decimal by substitution of 41.48 for 37.7 in above equation brings the decimal to 0.278.

ACETIC ACID DIGESTION.

As with sulphuric acid, in this digestion the scale was added to boiling acid, the solution being arrested before discoloration commenced. The lead salt was prepared in the manner described for sulphuric acid, due precautions being taken to prevent formation of lead carbonate. Combustion of this salt resulted as follows:

Salt II (acetic acid digestion).	
Carbon	13.03 per cent.
Hydrogen.....	1.74 “
Lead.....	57.69 “
Oxygen (diff.)	27.54 “
	<u>100.00</u> “

The salt contained 7.50 per cent. moisture, eliminating which we have:

	Salt II.	Theory tri-plumbic citrate.
Carbon	14.09 per cent.	14.42 per cent.
Hydrogen	0.89 “	1.00 “
Lead	62.37 “	62.15 “
Oxygen	22.65 “	22.43 “
	<u>100.00</u> “	<u>100.00</u> “

It would appear that this salt has slightly oxidized in drying. After digestion the insoluble residue contained:

	Moisture free.	
Moisture.....	11.84 per cent.
Magnesium oxide.....	16.63 “	18.98 per cent.
Calcium oxide	9.74 “	11.05 “
Fe ₂ O ₃ and Al ₂ O ₃	2.43 “	2.72 “
Silica	2.39 “	2.71 “
Organic.....	54.26 “	61.54 “
Undetermined	2.72 “	3.00 “
	<u>100.00</u> “	<u>100.00</u> “
Carbon	19.49 “	22.11 “
Carbon per cent. of organic matter	35.93 “

From an equal weight of material much less of the lead salt was secured from the acetic acid digestion than from the sulphuric acid preparation.

For the purpose of comparison a pure tri-plumbic citrate was prepared, the combustion resulting as follows:

	Salt III (tri-plumbic citrate).
Carbon	13.96 per cent.
Hydrogen	1.33 "
Lead.....	59.76 "
Oxygen (diff.)	24.95 "
	100.00 "

The salt contained 3.59 per cent. moisture, elimination of which produces the following numbers:

		Theory tri-plumbic citrate.
Carbon	14.42 per cent.	14.42 per cent.
Hydrogen	0.93 "	1.00 "
Lead.....	61.98 "	62.15 "
Oxygen	22.61 "	22.43 "
	100.00 "	100.00 "

The three lead salts, corrected for uncombined water, were grouped thus in the following table and compared with the theoretical salt:

- (I) From sulphuric acid digestion.
 (II) From acetic acid digestion.
 (III) Tri-metallic citrate of lead.
 (IV) Tri-metallic citrate of lead, theory.

	I. per cent.	II. per cent.	III. per cent.	IV. per cent.
Carbon	14.23	14.09	14.48	14.42
Hydrogen	0.94	0.89	0.93	1.00
Lead	62.11	62.37	61.98	62.15
Oxygen	22.72	22.65	22.61	22.43
	100.00	100.00	100.00	100.00

From the above it is apparent that the lead salts are unquestionably citrates.

For further proof the acid was freed of lead by hydrogen sulphide, excess of the precipitant removed, and in aqueous solution the following reactions were obtained:

(I) With bichromate of potash, *coffee brown color*.

(II) Boiled with strongly alkaline potassium permanganate gave *green color*.

(III) Heated at 100° C. for an hour with ten parts sulphuric acid, *lemon yellow color*.

(IV) Characteristic reaction of *precipitation when heated in aqueous solution*.

Parsons (*Am. Chem. J.*, 4, 39) gives the results of an examination of "scale from sorghum-sugar pans," and concludes that the "scale is a two-thirds metallic calcic aconitate (as this is a quotation we do not feel at liberty to change from Parsons' own words to "dicalcium aconitate") containing one molecule of combined water." Comparing Parsons' data with those obtained in these more recent researches it seems probable that the aconitic acid is a product formed in manufacture. The scale examined by Parsons was derived from pans in which the boiling was conducted under atmospheric pressure. The scale recently examined came from evaporators in which the boiling was done in vacuo. Inasmuch as citric acid when strongly heated loses one molecule of water and becomes aconitic according to the equation, $C_6H_8O_7 - H_2O = C_6H_6O_6$, it is probable that Parsons' scale formed under high temperature and prolonged heating may have suffered dehydration and become an impure calcium aconitate. It would appear also that the scale formed in the evaporating apparatus of sorghum-sugar houses contains little, if any, aconitate. At the same time it may be conjectured that the reported presence of aconitic acid in the refuse or final products of sugar cane houses, molasses, skimmings, etc., may be attributed to formation in the manufacturing processes and not to presence in the canes or juices.

A CRYSTALLINE CHROMIUM TUNGSTATE.

BY EDGAR F. SMITH AND HERMAN L. DIECK.

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POTASSIUM bichromate was brought together with an equivalent amount of pure tungstic oxide. Heat was applied to the mixture; fusion followed and the mass was held in this condition until the evolution of gas bubbles ceased. The temperature was never higher than necessary to maintain a liquid condition of the mixture. After cooling, the fused mass