

table shows the percentages of deficient crops, D and DD, and of those injured by potash T.

The percentage of deficient crops decreases with the quantity of active potash in the soil. The percentage of injured crops increases with the quantity of active potash in the soil.

TABLE I.—RELATION OF ACTIVE POTASH TO NUMBER OF DEFICIENT CROPS.

Active potash in soil. Parts per million.	Percentage deficient. (DD and D).	Percentage injured. (T).
0-50	86.7	7
50-100	55.1	17
100-150	54.3	16
150-200	39.1	17
200-300	37.5	31
300-400	42.6	25
400-600	15.0	46
600-800	18.0	44

Relation to Weight of Crop.—The weight of the crop without potash divided by the weight with potash, expressed in percentages, shows the relative effect of the potash on the growth of the plant. The average figures for 403 crops are given in Table II.

TABLE II.—RELATIVE SIZE OF CROP WITHOUT AND WITH POTASH.

Active potash in soil in parts per million.	Percentage PN/PNK.
0-50	67
50-100	79
100-150	84
150-200	91
200-300	100
300-400	98
400-600	101
600-800	116

The effect of fertilizer potash on the weight of the crop decreases with the active potash in the soil. When the active potash exceeds 200 parts per million, the fertilizer potash effects no increase, on an average.

Relation to Potash Content of Crop.—The average potash content of (a) the corn crop and (b) the kaffir and sorghum crop, is given in Table III.

TABLE III.—RELATION OF ACTIVE POTASH OF SOIL TO POTASH CONTENT OF CROP.

Active potash in parts per million.	Percentage of potash.	
	Corn crop.	Kaffir and sorghum crop.
0-50	1.38	0.78
50-100	1.70	0.93
100-150	2.29	0.89
150-200	2.55	1.45
200-300	3.65	1.68
300-400	3.53	1.72
400-600	3.83	2.44
600-800	4.31	1.79

The potash content of the crops increases with the active potash content of the soil.

Relation of Active Potash to Total Potash Removed.—The average and maximum quantity of potash re-

TABLE IV.—RELATION OF QUANTITY OF POTASH REMOVED BY ALL CROPS TO ACTIVE POTASH OF SOILS.

Potash in soil. Parts per million.	Potash removed by crops in parts per million of soil.	
	Average.	Maximum.
0-50	29.3	53.4
50-100	37.2	143.3
100-150	51.0	176.2
150-200	80.9	249.6
200-300	120.1	434.6
300-400	156.9	354.8
400-600	119.4	295.8
600-800	206.9	380.8

moved by the crop which received no potash is given in Table IV.

The average quantity of potash removed by the crop increases with the active potash content of the soil.

SUMMARY AND CONCLUSIONS.

1. The average percentage of crops deficient in potash decreases with the active potash in the soil.
2. The average percentage of crops injured by potash increases with the active potash in the soil.
3. The effect of fertilizer potash on the weight of the crop decreases as the active potash content of the soil increases.
4. The percentage of potash in the crop increases as the active potash in the soil increases.
5. The total potash removed by the crop from the soil increases as the active potash content of the soil increases.

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THE DETECTION OF FORMIC ACID IN FRUIT PRODUCTS.

By F. L. SHANNON.

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In *Bull.* 195, of the Dairy and Food Department of the State of Michigan, the author called attention to the fact that formic acid was being used in this country as a preservative of fruit products.

It has been the general belief among chemists, for some time, that some preservatives other than the ones ordinarily found were being used in the preservation of fruit products, and investigations have been made in various laboratories throughout the country for the purpose of determining the identity of the substance used. Owing to its use in Germany, a number have suspected formic acid and have built up their investigations with that substance in mind, but because of the unsatisfactory and indirect methods of identification it has been difficult to reach a positive conclusion.

A search of the literature on the subject revealed the fact that the detection of formic acid did not depend upon its isolation and subsequent identification, but mainly upon the indirect method of its reducing power, principally upon silver nitrate and mercuric chloride solution. For example, the older literature states that formic acid is a constant constituent of many plant and animal products, a statement based on the fact that when they are subjected to steam distillation some substance is obtained in the distillate which reduces silver nitrate and mercuric chloride solution. However, in view of recent investigations along this line, it seems that this whole subject of the natural occurrence of formic acid needs further study, as it has been found possible to subject a host of substances which were known to contain no formic acid, to steam distillation and obtain a distillate which gave a pronounced reduction with both silver nitrate and mercuric chloride solution. From none of these substances, however, has it been possible to isolate and identify formic acid as such. Therefore, it is evident that we are not justified in designating as formic acid every substance obtained by steam dis-

tillation which reduces silver nitrate and mercuric chloride solution. It was found, for example, that when phosphoric acid was subjected to distillation, the distillate possessed the reducing properties generally ascribed to formic acid. Furthermore, in a number of methods in which the formic acid recovered by steam distillation is neutralized using phenolphthalein as indicator, the indicator itself was found to have a reducing action on mercuric chloride.

One of the most satisfactory indirect methods for the detection of formic acid is based on its reduction to formaldehyde by means of magnesium and dilute sulphuric acid. Fenton¹ has shown that carbonic acid may be reduced in the same way, but Bacon² has called attention to the fact that this is of theoretical importance only, there being no danger of confusing the two in practice. However, every step in this method must be carried out with absolute precision, or erroneous conclusions may be drawn.

The qualitative method as applied to the products used in this investigation is as follows: To about 200-500 cc. of the syrup or crushed fruit in a two-liter, long-necked round bottom flask provided with a Reitmeier bulb, add about 50-100 cc. of water. Subject to steam distillation, collecting the distillate (usually about 2500 cc.) until it ceases to give an acid reaction with litmus. Exactly neutralize the distillate with $N/1$ NaOH, using litmus as an indicator. Evaporate on a steam or water bath to about 50 cc., transferring from the large evaporating dish to smaller ones as the volume decreases. Transfer to an Erlenmeyer flask, provided with a glass tube about three feet long as an air condenser, add a few pieces of pure magnesium ribbon or wire and a slight excess of dilute sulphuric acid and set in a cool place for one hour, adding dilute sulphuric acid through the tube from time to time as the reaction ceases. Transfer the liquid to a suitable distilling flask and collect the first ten cc. of the distillate, which will contain most of the formaldehyde, if the original syrup contained formic acid.

There are a number of methods published for the detection of formaldehyde and nearly every analyst has his favorite test. However, the methods which proved the most satisfactory in this work were, Leach's Method,³ Phloroglucinol Method,³ Rimini's Method,³ and the Rescorcin Method of the United States Pharmacopoeia. A positive reaction with *these four tests* was considered conclusive evidence of the presence of formaldehyde.

CRYSTALLOGRAPHIC IDENTIFICATION.

Inasmuch as practically all methods for the detection of formic acid previously reported are indirect methods depending upon the decomposition of the formic acid or upon its reducing powers, it seemed desirable to attempt the isolation of formic acid in the form of an insoluble salt.

The usual procedure in determining the identity of an organic acid in plants is to prepare some readily crystallizable salt, sparingly soluble in water. Of the

various formates the lead salt crystallizes readily without water of crystallization, is very stable and requires 63 parts of water for solution. The formation and identification of lead formate would therefore constitute a direct and positive proof of the presence of formic acid. After numerous attempts the following procedure was adopted:

Steam distil about 1000-1200 cc. of the syrup as in the first operation, collecting the distillate (2500-3000 cc.) in a receiving flask to which about 5 cc. of lead cream has been added. (This is made as follows: Precipitate a solution of lead nitrate with potassium or sodium hydrate in the presence of phenolphthalein until a faint pink color appears. Wash by decantation 8-10 times.) Shake the flask occasionally and as the lead hydrate is dissolved add a few cc. more, until all of the formic acid is combined. Concentrate the liquid in a large dish on a steam or water bath to about 50 cc. Filter and transfer to a suitable crystallizing dish and set aside in a desiccator. If formic acid was present in the original material, needle-like crystals of lead formate will form. Wash the crystals with absolute alcohol, to remove any lead acetate which may be present, spread on filter paper and dry. To the dry crystals apply the following tests:

(a) Aqueous solution will reduce $AgNO_3$ upon warming.

(b) Aqueous solution will reduce mercuric chloride solution upon warming.

(c) Aqueous solution will reduce platinum chloride upon warming.

(d) To a portion of the crystals in a dry test tube add sulphuric acid and warm. Carbon monoxide is generated which will burn in the tube with a blue flame when ignited. Further note that the lead formate is not discolored.

(e) Transfer some of the crystals to a small distilling flask, treat with concentrated phosphoric acid and distil. The distillate, which is formic acid, will react as follows:

1. Acid to litmus and acid taste.
2. Reduces silver nitrate on warming.
3. Reduces mercuric chloride on warming.
4. Reduces platinum chloride on warming.
5. Is reduced to formaldehyde by magnesium and dilute sulphuric acid.

As previously mentioned it was found that when phosphoric acid and water alone were distilled, the distillate would reduce silver nitrate and mercuric chloride solution. Therefore, before test (e) was carried out the phosphoric acid was subjected to distillation until it no longer gave a distillate that would reduce silver nitrate or mercuric chloride. The crystals of the lead compound were then added and the distillation continued.

Although the chemical evidence that the volatile acid obtained from the fruit products used in this investigation is conclusive, it was thought desirable to submit the crystals to Dr. Edward H. Kraus, Professor of Geology and Mineralogy, University of Michigan and he reports as follows:

¹ *J. Chem. Soc. London*, 1907, 91, 687.

² *Circ.* 74, U. S. Dept. Agric., Bur. of Chem.

³ *Bull.* 107, 185, U. S. Dept. Agric., Bur. of Chem.

"The crystals, which were examined crystallographically, were obtained by slow crystallization from an aqueous solution of the material furnished by Fern L. Shannon, State Analyst, Lansing, Michigan. They are prismatic in habit and about 2-3 mm. in length and of slightly yellowish color. All crystals were clear and transparent. Although the crystals were in general doubly terminated, readings were made only upon the faces of the prism zone, the end faces being extremely small and, hence, difficult of adjustment. The images obtained were very good, considering the size of the crystals.

"The measured angles, compared with the values given by Plathan,¹ for lead formate are as follows:

	Kraus.	Plathan.
$m : m$ (110) : (110)	$73^{\circ} 26'$	$73^{\circ} 28'$
$m : m$ (110) : (110)	$53^{\circ} 17\frac{1}{2}'$	$53^{\circ} 16'$

"This comparison shows that the agreement in the values for this material and those given by Plathan for lead formate are exceedingly close.

"Parallel extinction was observed upon all the faces examined. The indices of refraction are higher than that of methylene iodide, as determined by the Becke and the Schroeder van der Kolk methods.

"The above crystallographic-optical properties, together with the fact that a distinct reaction for lead is easily obtained upon the plaster tablet with the blowpipe, indicates conclusively that the substance examined is lead formate."

To further substantiate the proof a number of fruit syrups that were known to contain no added formic acid were subjected to steam distillation, and an attempt made to separate a lead compound. In some instances a few crystals were obtained, but at no time would the crystals give the characteristic tests for lead formate.

It would seem then that the formation of formaldehyde coupled with the formation of lead formate and their subsequent identification would furnish a conclusive and positive proof of the presence of formic acid.

The author desires to take this opportunity to thank Dr. Edward H. Kraus for his cooperation in this work.

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THE DETECTION OF PRUSSIAN BLUE IN TEA.

By FRED WEST.

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In this test advantage is taken of the well known blue color reaction between Prussian blue and a solution of oxalic acid.

Grind about 15 grams of the tea to be examined, in a mortar, and pass through a 20-mesh sieve, neglecting the few stems which resist comminution.

Procure five squares of plate glass 15 × 15 cm. each; upon each plate place an 11 cm. circular filter, as thin as procurable and having a smooth surface.

Saturate each filter with test solution oxalic acid, U. S. P., removing any air spaces under filter.

The well wetted filters are now to be sprinkled with the ground tea. This is best performed by sifting the tea from the sieve, holding it about 30 cm. above the plates, which should lie flat. Sprinkle filters well but avoid overlapping the particles of tea.

Allow the filters to dry on the plates in the air. When thoroughly dry remove filters from plates and brush off tea with a stiff brush.

The presence of Prussian blue is indicated by bright blue spots, best seen with the aid of a hand glass, and where large particles of the Prussian blue have rested, the color radiates and spreads through the filter fiber.

If smooth filters are not procurable, rough ones may be used, but a second glass plate should be clamped over the filter to press the particles of tea against the fiber. This necessitates the use of gentle heat to dry the plate.

Comparison of the amount of color in different samples may be observed by noting the total number of spots to each sample, using five plates to each one. Difficulty in counting spots on the filters can be overcome by using a Wolffhuegel counting plate and a large hand lens.

As the natural coloring matter in tea does not stain the filters in the presence of the oxalic acid, this gives a clear white field upon which any blue spots will show very clearly. The blue spots on the filters are fairly permanent and the filters may be attached to the report sheets for reference.

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LABORATORY AND PLANT

FACTORS DETERMINING THE CAPACITY OF A FILTER PRESS.

By C. ALMY, JR., AND W. K. LEWIS.

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Very little information can be found in the literature regarding the flow of a liquid through a filter cake. Hitherto the popular assumption has been that the rate of flow is, up to a certain point, directly proportional to the pressure and inversely proportional to the thickness of the cake. The object of this investigation has been to establish more accurately the relationships existing between the rate of flow, pressure, and thickness of cake: relationships which, as will

be shown, can for any particular sludge be expressed by a simple mathematical equation.

For this purpose we used a chromium hydrate sludge made by reducing dichromate with glucose and precipitating with sodium carbonate. The filter press was a six inch corner-feed laboratory press. It was of course impracticable to measure the thickness of the cake during the progress of a run, but as the volume of filtrate at any time is obviously proportional to the thickness and is an equally significant value in filtration, this figure has been substituted throughout this work in both plots and equations.

Six runs were made, at 100 lbs., 75 lbs., 50 lbs., 25 lbs., 10 lbs. and 5 lbs. pressure per square inch re-

¹ Groth, *Chemische Krystallographie*, 1910, 3, 16.