The average content of sugar found by Buignet, *viz.*, 13.9 per cent. as invert sugar is not materially different from the amount found in these investigations.

## THE EFFECT OF MOISTURE ON THE AVAILABILITY OF DEHYDRATED PHOSPHATE OF ALUMINA.

BY FRED. W. MORSE.

Received January 3, 1903.

THE author has from time to time encountered samples of phosphatic material, which have borne the name of concentrated phosphate, and which really are dehydrated phosphate of alumina and iron.

Such materials usually contain approximately 45 per cent of phosphoric anhydride, of which more than 0.5, and sometimes as much as 0.8, will dissolve in a neutral solution of ammonium citrate.

The phosphatic mineral from which this fertilizer is made, is obtained principally from the islands of Redonda and Grand Connetable in the West Indies, and is a hydrated phosphate of alumina and iron.

The author has made several analyses of the mineral from the former island, and a number of analyses have been published by Shepard,[1] Tate,[2] and Hitchcock,[3] while only one analysis made by Andouard,[4] is yet known to him of the latter phosphate. The composition of the two phosphates is very similar. The phosphoric anhydride ranges from 35 per cent. to 39 per cent. in cargoes and as high as 43 per cent. in the richest specimens.

The water contained in the mineral is nearly proportional to the phosphoric anhydride, the ratio averaging $2P_2O_5$ to $9H_2O$. Two analyses including Andouard's give $10H_2O$, while two analyses have been as low as $8H_2O$. The proportion of $Al_2O_3$ to $Fe_2O_3$ is irregular; usually the former exceeds the latter, especially in the richer specimens.

The process of preparing the mineral for use as a fertilizer, was patented by the late Stephen L. Goodale,[5] who described the prin-

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[1] *Am. J. Sci.*, **47**, 428.

[2] *J. Soc. Chem. Ind.*, **5**, 570.

[3] *Bull. Geol. Soc. Am.*, **2**, 6-9.

[4] *Ann. Agronom.*, **21**, 171.

[5] "Conversion of Hydrous Phosphates of Alumina and Iron." Monograph, 1893.

ciples of his method in a pamphlet from which the following is quoted.

"The sample properly prepared by reduction to fineness and removal of dust, is gradually heated in a properly equipped receptacle. Elevation of temperature proceeds regularly to about 100° C., at which point a halt ensues, usually attended by a fall of several degrees. During this halt, heat is apparently absorbed; when the halt ceases, elevation of temperature again proceeds regularly to a point near 150°, when another notable halt occurs; when this ceases, elevation proceeds without interruption to full dehydration and beyond, if permitted. This point may be determined by seasonably exposing a cold surface to the orifice where escaping vapor may be deposited as dew. Application of the test should begin at least as soon as 250° or 260° is reached; the point of complete dehydration varies in samples of differing composition, sometimes as low as 275°, rarely beyond 330°, usually near 325° C."

In speaking of the results of the process, Goodale further says: "To attain these fully, the heat must reach the definite, critical point of complete dehydration. If only one-fourth, one-half or three-fourths be expelled, corresponding enhancement in value does not accompany such expulsion. Moreover, if elevation of temperature goes beyond the critical point, change also goes on toward non-solubility, so that most skilful watchfulness is indispensable to avoid loss."

Although this dehydration results in a high percentage of available phosphoric acid as measured by its solubility in ammonium citrate, the use of the calcined phosphate in experiments with plants, has not shown itself to possess any such degree of availability when applied to the soil.

This fact has been especially demonstrated by several series of pot experiments made at the Main Experiment Station,[1] with twelve different kinds of plants; and by three successive years of field experiments at the Rhode Island Experiment Station[2] with a rotation of corn, oats and grass.

It was further noted in the Maine experiments, for which the dehydrated Redonda phosphate was prepared in the Station laboratory, that the availability of the substance in ammonium citrate

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[1] Maine Agr. Expt. Sta. Reports (1893), pp. 10-20; (1895), pp. 10-20; (1898), pp. 64-74.

[2] R. I. Agr. Expt. Sta. Reports (1894), pp. 122-128; (1896), pp. 327-343.

decreased on standing, and that it was necessary to prepare a fresh quantity of phosphate for each series of comparisons, which suggested that the dehydrated phosphate reverts to the hydrated condition in the soil. Goodale mentions in his pamphlet that, under certain conditions, the phosphate retrogrades; but does not give any particulars beyond intimating that it is due to overheating.

In order to get more knowledge of the nature of the dehydrated phosphate, and of its availability, a series of experiments was carried out in the spring of 1900, to determine the amount of dehydration at different temperatures, with the resultant solubility in ammonium citrate of the phosphate, and to see if the dehydrated mineral would revert in the presence of moisture.

In this series of experiments, the author was assisted by Mr. R. H. Shaw, now of the Kansas Experiment Station. For material there was used ground Redonda phosphate obtained in 1891 from Mr. Goodale for field experiments.

The mineral was analyzed with the following results: Water at low red heat, 21.33 per cent.; phosphoric anhydride, 35.92 per cent.

The temperatures selected for dehydration were those mentioned by Goodale, *viz.*, 100°, 150°, 250° and 325° C., and in addition 560° and 830° C., or the fusing points of borax and sodium carbonate respectively.

The estimation of water at 100° was made by heating the mineral in wide weighing bottles, in an air-bath, at a temperature of 100° to 105° C. The material was weighed at intervals of two hours, and the weight at the end of the fourth hour was practically the same as that at the end of the sixth.

At the approximate temperature of 830° the determination was conducted by heating in a platinum crucible over a Bunsen flame, and ascertaining the loss in weight, as in the foregoing experiment. The temperature was reached by adjusting the lamp flame so that anhydrous sodium carbonate was brought to a quiet fusion in a platinum crucible. Then, without disturbing the lamp, the sodium carbonate crucible was removed and another platinum crucible of the same size containing the phosphate was placed in the triangle.

At the intermediate temperatures, the water was not only determined by the loss in weight of the material, but also by the gain in weight of a calcium chloride tube into which the vapor was passed.

The apparatus was arranged similarly to that for a combustion in a current of air or oxygen, and consisted of a combustion tube connected at one end with a drying tower and at the other end with a weighed U-tube containing calcium chloride.

The charge of phosphate was placed in a porcelain boat, inserted in the combustion tube, and pushed to the middle. For the temperatures of 150°, 250°, and 325°, a tube oven was used instead of a combustion furnace. For that at 560° a special furnace was constructed of a piece of magnesium-asbestos steam-pipe covering, a little shorter than the combustion tube. A rectangular opening was cut in the middle of the lower half-section long enough to admit the tops of three Bunsen burners placed in a line. The tube was supported above the burners by a strip of asbestos board, and when the upper half section was in place, the flames played around the tube as in a combustion furnace. In order to determine the degree of heat sustained by the mineral, a porcelain boat containing anhydrous borax was inserted in the combustion tube along with the boat containing the phosphate, the latter being next to the calcium chloride tube. The borax was maintained at the stage of fusion, which could be observed by removing the upper half section of the improvised furnace.

Determinations of the loss in weight at the temperature of fusing borax were also made by heating in a platinum crucible in exactly the way used with sodium carbonate.

In the tube oven, the temperatures of 150° and 250° were determined by thermometers as in heating sealed tubes; but since in this operation, a current of air was slowly drawn through the tube, the temperature of the mineral would be somewhat below that registered by the thermometers, which were therefore allowed to run about 10° above the stated temperatures before readjusting the lamps.

For the approximate temperature of 325°, the thermometer registered 350°; but powdered potassium nitrate contained in a boat placed in the tube reached only the stage of incipient fusion.

The three salts used for determining temperatures were of Kahlbaum's sealed brand of C. P. chemicals, and showed no impurities excepting with the spectroscope.

Richards[1] gives them the following melting-points: Potassium nitrate, 339° C.: sodium biborate, 561° C.; sodium carbonate, 830° C.

In the tube method, at the temperatures of 325° and 560° the water was expelled from the mineral quickly and condensed around the end of the combustion tube next the calcium chloride tube, requiring several hours for its removal by the current of air drawn through the apparatus, since it was necessary to pass the air slowly in order to insure complete absorption.

For the absorption method, it was found necessary to use smaller charges than for the methods depending solely on loss of weight. The effectiveness of the drying-tower was demonstrated by blank determinations, and that of the U-tube by connecting a second calcium chloride tube and weighing it separately. The results are given in the following table.

PERCENTAGES OF WATER EXPELLED AT DIFFERENT TEMPERATURES.

| Temperature. °C. | Per cent. by loss. | Per cent. by absorption. |
|---|---|---|
| 100 | 18.14 | .... |
| 150 | 19.72 | 19.93 |
| 250 | 20.32 | 20.26 |
| 325 | 20.71 | 20.78 |
| 560 | 21.34 | 20.98 |
| 560 | 21.32 | after heating 15 min. in crucible. |
| 830 | 21.57 | " " 5 " " " |
| 830 | 21.54 | " " 15 " " " |
| 830 | 21.63 | " " 30 " " " |
| 830 | 21.45 | " " 60 " " " |

The results corroborate the statements of Goodale regarding the expulsion of water at 100° and 150° but do not show complete dehydration at 325°.

The slightly lower results obtained by absorption at 560° were probably due to incomplete removal of water from the combustion tube; but might also be due to the destruction of organic matter which can hardly fail to be present, owing to the fact that the porous phosphate is more or less penetrated by the roots of grasses and cacti, and Andouard in his analysis of Grand Connetable phosphate reports traces of carbon dioxide.

In determining the availability of the phosphate, the official neutral solution of ammonium citrate[2] was used; but the citrate-

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[1] *Am. Chem. J.*, **20**, 704.

[2] "Methods of Analysis, Association of Official Agricultural Chemists," Bull. 46, Bur. of Chem., U. S. Dept. Agr., p. 11.

soluble phosphoric acid was determined directly, instead of indirectly as in the official method. This was done because in all previous work with this particular phosphate, it was found impossible to prevent the finest particles of mineral running through any paper filter that would permit a ready passage of the citrate solution. Ross' method[1] was therefore selected, which is based on digesting the filtrate of citrate-soluble phosphoric acid with sulphuric acid and oxidizing agents, as in the Kjeldahl method for nitrogen, after which the molybdate solution is used as usual. Of course, this method gives somewhat lower results than the indirect method; but this is not due to incomplete recovery of the phosphoric acid, which was repeatedly verified. The method of procedure then, was to digest 1 gram of the mineral in 100 cc. of neutral ammonium citrate, filter through an asbestos felt with the aid of a pump, digest aliquot parts of the filtered solution after Ross' method, and determine the phosphoric acid as usual. By the use of an asbestos felt, it was possible to get a clear filtrate and to remove the citrate solution quickly from the mineral. The availability of the phosphate at the different stages of dehydration was found to be as follows:

| | |
|---|---|
| Undehydrated | 2.08 per cent. $P_2O_5$ |
| Heated to 100° | 19.64 " " " |
| " " 150° | 27.25 " " " |
| " " 250° | 32.76 " " " |
| " " 325° | 31.53 " " " |
| " " 560° | 32.65 " " " |
| " " 830° 15′ | 11.35 " " " |
| " " 830° 90′ | 2.53 " " " |

These results show, that to get the highest degree of availability, it is necessary to remove practically all of the water; but they do not confirm the statement that a continuation of the heat beyond 325° lowers the solubility, since at 560° the mineral underwent the heating for from six to eight hours while the water was being aspirated from the tube. The high temperature required to fuse sodium carbonate produces, however, a marked decrease in solubility, and this is intensified by prolonging the heating.

The effect of exposure to a moist atmosphere was determined by placing the dehydrated phosphate under a bell-jar, in an atmosphere saturated with moisture from an open dish containing water. The phosphate was weighed in a porcelain boat placed

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[1] Bull. 38, Bur. of Chem., U. S. Dept. Agr., p. 16.

inside a weighing-tube, and the boat was exposed under the bell-jar, until it had reached equilibrium with respect to moisture, before the dehydrated mineral was weighed into it. The charges used were small, in order to expose as much surface as possible to the action of the moist atmosphere.

The different degrees of dehydration, which were compared, were those obtained by heating to 250°, 325°, 560°, and 830° respectively. The results obtained were unlooked for and of much interest.

Phosphate dehydrated at 250°; charge, 0.2965 gram.

Water absorbed in 24 hours, 0.0565 gram.
" " " 72 " 0.0690 "
" " " 120 " 0.0705 "
Total water absorbed, 23.78 per cent. of charge taken

Phosphate dehydrated at 325°; charge, 0.2200 gram.

Water absorbed in 24 hours, 0.0425 gram.
" " " 72 " 0.0485 "
" " " 120 " 0.0495 "
Total water absorbed, 22.50 per cent. of charge taken.

Phosphate dehydrated at 560°; charge, 0.6495 gram.

Water absorbed in 24 hours, 0.0415 gram.
" " " 48 " 0.0585 "
" " " 96 " 0.0605 "
Total water absorbed, 9.32 per cent. of charge taken.

Phosphate dehydrated by heating fifteen minutes at 830°; charge, 0.4730 gram.

Water absorbed in 24 hours, 0.0065 gram.
" " " 48 " . 0.0095 "
Total water absorbed, 2.00 per cent. of charge taken.

The moistened phosphate was next transferred to an ammonium citrate solution and its availability determined by the same method that was employed after dehydration. As the charges of phosphate of the temperatures 250° and 325° were so small, they were combined for the determination of available acid. The quantity of citrate solution was reduced to 50 cc. in all these cases, since the charges were approximately only 0.5 gram each.

The availability of the four grades of phosphate was now found to be as follows:

250° and 325°, 19.30 per cent. $P_2O_5$ in dehydrated phosphate.
560° 29.76 " " " " " "
830° 7.09 " " " " " "

ative is a crystalline substance, and analysis seems to indicate that it is a ketone.

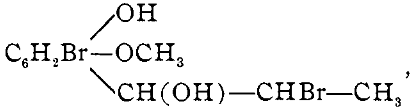
Five grams of α-oxy-β-brom-dihydro-bromisoapiol (m. p. 85° to 86°) were dissolved in 25 cc. of ethyl alcohol, treated with a concentrated solution of 2 grams of potassium hydroxide in alcohol, and boiled in a reflux apparatus for about two hours; at the expiration of this time the separation of potassium bromide was complete and 100 cc. of water were added. Five cc. of hydrochloric acid were then introduced, and the whole boiled for about half an hour. After standing for about twelve hours, a solid substance separated; this was filtered, dried, and crystallized from alcohol. It melts at 128° to 129°.

Another preparation of this substance was made by boiling 23 grams of the α-oxy-compound with a solution of 7 grams of potassium hydroxide in 100 cc. of alcohol, and subsequently treating with water and acid as above-mentioned. The solid product crystallized from alcohol in beautiful, small crystals, which melt at 128° to 129° and are rather sparingly soluble in alcohol.

Analysis gave the following results: Calculated for $C_{12}H_{13}O_5Br$, C, 45.42; H, 4.10. Found, C, 45.36, 45.67; H, 4.45, 4.31.

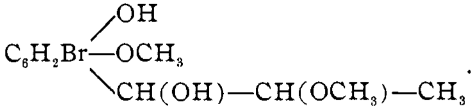
The analysis, therefore, indicates the formula given above. That this compound is a ketone, however, has not been absolutely proved, since our investigation was interrupted at this point; we expect to continue it during the current year. It is exceedingly probable that the substance will prove to be the ketone.

According to Auwers and Müller,[1] α-oxy-β-brom-monobrom-dihydro-isoeugenol,



$$C_6H_2Br\begin{array}{l}\diagup OH\\ -OCH_3\\ \diagdown CH(OH)-CHBr-CH_3\end{array},$$

obtained by the action of aqueous acetone upon monobromisoeugenol dibromide, reacts with sodium methylate, yielding α-oxy-β-methoxy-monobrom-dihydro-isoeugenol,



$$C_6H_2Br\begin{array}{l}\diagup OH\\ -OCH_3\\ \diagdown CH(OH)-CH(OCH_3)-CH_3\end{array}.$$

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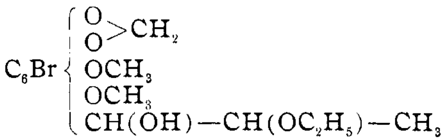
[1] Auwers and Müller : *Ber. d. chem. Ges.*, 35, 121.

If a similar reaction had taken place in the treatment of $\alpha$-$\beta$-oxy-brom-dihydro-brom-isoapiol with ethyl alcoholic potash, a compound having the following composition would have resulted:



$$C_6Br\left\{\begin{array}{l}\begin{matrix}O\\O\end{matrix}>CH_2\\OCH_3\\OCH_3\\CH(OH)-CH(OC_2H_5)-CH_3\end{array}\right.$$

This substance contains 46.28 per cent. of carbon and 5.23 per cent. of hydrogen, which are quite different from the figures obtained by analysis. For the present, therefore, we prefer to retain the ketone formula above-mentioned. This line of investigation will be continued and extended to some other substances of a similar constitution.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE NO. 47.—SENT BY H. W. WILEY.]

# THE COMPOSITION OF FRESH AND CANNED PINEAPPLES.

BY L. S. MUNSON AND L. M. TOLMAN.

Received January 2, 1903.

THE work undertaken in connection with the investigation of the composition of fresh and canned pineapples consists of the analysis of (1) fresh pineapples from various sources, (2) canned pineapples that were put up under supervision of the Consuls General of the United States at Singapore and Nassau, and (3) commercial samples of canned pineapples.

## DESCRIPTION OF SAMPLES.

Of the thirty-eight samples of fresh pineapples examined, twenty-one were from Florida, ten from Cuba, four from Porto Rico, two from the Bahamas and one from Jamaica. The Florida pineapples were largely obtained from representative growers; the Cuban pineapples were nearly all purchased on the market at Havana; the Porto Rican pineapples were obtained from F. D. Gardner, Director of Porto Rican Experiment Station; the Bahama samples were obtained on the market in New York; and the sample from Jamaica was obtained in the Washington market. So far as possible, the samples obtained were the well-ripened fruit, but in some cases they were shipped so far that it was not practicable to use the thoroughly ripened fruit but such as would stand shipment. Samples 804 to 808 and 818 were secured early in the season and were very green. Their composition shows them to be of inferior quality and therefore they have been excluded from the averages for total solids and for sugars. The first sample of fresh pineapples was received March 4, 1902, and the last sample September 26, 1902, and samples were secured at varying intervals between these dates.

Sixteen samples of canned pineapples were obtained from the Consul-General at Singapore. Of this number, ten were put up in the normal pressed juice of the pineapple without addition of cane-sugar and six were put up in the pressed juice to which cane-sugar had been added. Two samples were obtained from the Consul-General at Nassau, preserved without addition of cane-sugar.

The forty-two samples of commercial canned pineapples came from Singapore, the Straits Settlements and from the Bahamas.

### METHODS OF ANALYSIS.

The methods of analysis employed in this work were essentially those given under "Fruits and Fruit Products, Provisional Methods for the Analysis of Foods," Bulletin 65, Bureau of Chemistry. The total solids were determined by drying in a water-oven with asbestos for twenty hours. Solids in the syrup were calculated from the specific gravity, using the table of H. Ellion. Reducing sugars were determined by Meissl's method for invert sugar, and cane-sugar was determined both by the increase in reduction after inversion with hydrochloric acid, and by double polarization. The polarimetric method used was that of the German Official Chemists, and cane-sugar was calculated by the Herzfelt formula,

$$S = \frac{100(A - B)}{141.89 + 0.05B - \frac{T}{2}}.$$

Results by the two methods agreed very closely, especially where the amount of cane-sugar was small. With samples of high content of cane-sugar, the results by the reduction method were less reliable, owing to the influence of the cane-sugar upon the reduction.

While the acids of pineapples are largely citric they are expressed in this paper as $H_2SO_4$ for the reason set forth in a previous contribution from this laboratory.[1]

## ANALYTICAL DATA.

Table I contains the results of analyses of the fresh pineapples. As will be seen by reference to this table, there is no material difference in composition due to the source of the pineapples; neither does the variety seem to have any influence on the composition. Insoluble solids, ash, acids, and proteïn do not show a wide variation, while on the other hand the samples show a wide difference in the content of sugars. As is well known, the sugars develop very rapidly with the ripening of the fruit. On the other hand the other constituents appear to be present in equally large amounts in the green fruit. Of particular interest is the relative amounts of reducing- and cane-sugars in the fresh fruit. In nearly all cases the cane-sugar is largely in excess of the reducing sugar. The average amount of reducing sugar in all the samples of fresh fruit is 3.91 per cent. while the average amount of cane-sugar is 7.59 per cent.—nearly double the amount of reducing sugar.

Table II contains the results of the analyses of the pineapples canned under direction of the Consuls General at Singapore and Nassau. The samples put up without addition of cane-sugar were preserved in expressed pineapple juice, the amount of juice added being about 30 per cent. of the entire contents of the can. So far as content of total sugars are concerned, therefore, the composition of these canned pineapples should not be materially different from the composition of the normal fresh fruits. Other constituents, especially insoluble solids, will be lowered by the addition of the juice as comparison of Tables I and II shows. While the amount of total sugar is practically the same as in the fresh fruit, the relative proportions of reducing- and cane-sugars are entirely different, due to the inverting action of the organic acids during the processes of canning. In many cases the amount of the cane-sugar remaining is quite small, the average for all the samples being 3.41 per cent. of cane-sugar and 7.99 per cent. of reducing sugars—just the reverse of the condition in the fresh fruit. This condition also holds in the samples put up with addition of cane-sugar, and with the commercial samples.

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[1] This Journal, **23**, 347 (1901).

### TABLE I.—COMPOSITION OF FRESH PINEAPPLES.

| | | Solids. | | Ash. | | | | Sugars. | | | Polarizations. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Serial Number. | Variety. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Alkalinity as $K_2CO_3$. Per cent. | Acids as $H_2SO_4$. Per cent. | Protein ($N \times 6.25$). Per cent. | Reducing. Per cent. | Cane. Per cent. | Total as Invert. Per cent. | Direct. °V. | Invert. °V. | Temperature. °C. |
| FLORIDA: | | | | | | | | | | | | | |
| 571 | Spanish red...... | 11.93 | 1.60 | 0.438 | 0.321 | 0.847 | 0.406 | 1.94 | 5.98 | 8.24 | 4.75 | —3.08 | 22.0 |
| 807 | | 8.06[1] | 1.55 | 0.326 | 0.390 | 0.366 | 0.494 | 1.74[1] | 2.96[1] | 4.86[1] | 1.85 | —2.20 | 23.4 |
| 808 | | 10.19[1] | 1.59 | 0.434 | 0.497 | 0.825 | 0.419 | 1.44[1] | 5.37[1] | 7.09[1] | 4.35 | —2.30 | 28.4 |
| 1054 | Spanish red...... | 16.53 | 1.48 | 0.505 | 0.377 | 0.509 | 0.418 | 5.89 | 8.71 | 15.06 | 6.70 | —4.45 | 28.0 |
| 1055 | Porto Rico....... | 12.27 | 1.48 | 0.408 | 0.345 | 0.307 | 0.262 | 4.06 | 6.49 | 10.89 | 5.00 | —3.30 | 28.0 |
| 1056 | Egyptian queen.. | 18.86 | 1.47 | 0.548 | 0.377 | 0.483 | 0.381 | 5.20 | 8.48 | 14.13 | 6.85 | —4.01 | 28.0 |
| 1059 | Sugar loaf....... | 15.06 | 1.51 | 0.356 | 0.337 | .... | 0.275 | 3.64 | 9.12 | 13.24 | 8.00 | —3.85 | 30.0 |
| 1060 | Spanish red...... | 13.30 | 1.55 | 0.361 | 0.243 | .... | 0.474 | 4.40 | 6.48 | 11.22 | 5.00 | —3.30 | 30.0 |
| 1061 | Abakka.......... | 10.78 | 1.45 | 0.385 | 0.292 | .... | 0.331 | 3.95 | 4.68 | 8.88 | 3.90 | —2.20 | 30.0 |
| 1062 | Blood............ | 11.82 | 1.29 | 0.446 | 0.317 | .... | 0.406 | 3.02 | 6.13 | 9.48 | 5.15 | —2.75 | 30.0 |
| 1063 | Spanish red...... | 17.52 | 1.68 | 0.428 | 0.374 | .... | 0.418 | 4.54 | 10.20 | 15.28 | 8.55 | —4.62 | 30.0 |
| 1064 | Smooth cayenne. | 12.93 | 1.27 | 0.378 | 0.355 | 0.444 | 0.400 | 3.17 | 7.51 | 11.08 | 6.20 | —3.30 | 27.8 |
| 1066 | Smooth cayenne. | 14.85 | 1.03 | 0.373 | 0.322 | 0.445 | 0.393 | 9.75 | 2.98 | 12.89 | 0.20 | —3.63 | 27.8 |
| 1067 | Abakka.......... | 13.70 | 1.31 | 0.349 | 0.278 | 0.465 | 0.419 | 5.28 | 6.35 | 11.97 | 4.70 | —3.52 | 27.8 |
| 1068 | Porto Rico....... | 12.20 | 1.84 | 0.526 | 0.478 | 0.545 | 0.569 | 3.98 | 6.03 | 10.33 | 4.60 | —3.08 | 27.8 |
| 1069 | Abakka.......... | 12.73 | 1.27 | 0.466 | 0.418 | 0.620 | 0.306 | 4.38 | 6.22 | 10.93 | 4.80 | —3.30 | 27.8 |
| 1070 | Spanish red...... | 13.10 | 1.49 | 0.464 | 0.596 | 0.300 | 0.475 | 4.52 | 6.53 | 11.40 | 5.20 | —3.19 | 27.8 |
| 1071 | Pernambuco ..... | 15.60 | 1.68 | 0.487 | 0.403 | 0.560 | 0.406 | 4.33 | 8.27 | 13.03 | 6.50 | —4.23 | 27.8 |
| 1092 | Egyptian queen.. | 13.62 | ... | 0.479 | 0.459 | 0.565 | 0.469 | 3.62 | 7.44 | 11.45 | 6.40 | —3.08 | 30.0 |
| 1093 | Abakka.......... | 11.02 | 1.02 | 0.395 | 0.276 | 0.400 | 0.338 | 4.08 | 4.91 | 9.45 | 3.40 | —3.02 | 25.8 |
| 1125 | Spanish red...... | 15.25 | ... | 0.401 | 0.316 | 0.560 | 0.494 | 4.53 | 8.22 | 13.19 | 6.70 | —4.20 | 21.0 |
| | Average...... | 13.85 | 1.45 | 0.421 | 0.370 | 0.515 | 0.407 | 4.44 | 6.88 | 11.69 | | | |
| CUBAN: | | | | | | | | | | | | | |
| 572 | Spanish red...... | 12.63 | 1.35 | 0.272 | 0.272 | 0.561 | 0.406 | 2.19 | 6.81 | 9.36 | 6.70 | —2.36 | 21.0 |
| 646 | Sugar loaf....... | 11.45 | 1.70 | 0.324 | 0.355 | 0.646 | 0.206 | 1.76 | 6.12 | 8.20 | 4.80 | —3.19 | 23.0 |

[1] Not included in averages.

TABLE I (continued).—COMPOSITION OF FRESH PINEAPPLES.

| Serial Number. | Variety. | Solids. Total. Per cent. | Solids. Insoluble. Per cent. | Ash. Total. Per cent. | Ash. Alkalinity as $K_2CO_3$. Per cent. | Acids as $H_2SO_4$. Per cent. | Protein ($N \times 6.25$). Per cent. | Sugars. Reducing. Per cent. | Sugars. Cane. Per cent. | Sugars. Total as invert. Per cent. | Polarizations. Direct. °V. | Polarizations. Invert. °V. | Polarizations. Temperature. °C. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CUBAN : | | | | | | | | | | | | | |
| 647 | Spanish red | 14.12 | 1.64 | 0.319 | 0.328 | 0.602 | 0.381 | 3.00 | 8.76 | 12.23 | 7.10 | −4.33 | 23.0 |
| 802 | Spanish red | 13.45 | 1.63 | 0.457 | 0.461 | 0.670 | 0.475 | 2.31 | 8.23 | 10.97 | 7.20 | −3.57 | 27.6 |
| 803 | Sugar loaf | 12.67 | 1.80 | 0.277 | 0.223 | 0.502 | 0.513 | 2.76 | 6.77 | 9.89 | 5.90 | −3.09 | 27.6 |
| 804 | | 9.13[1] | 1.49 | 0.313 | 0.353 | 0.673 | 0.512 | 1.34[1] | 4.60[1] | 6.18[1] | 3.50 | −2.53 | 23.4 |
| 823 | Spanish red | 17.53 | 1.54 | 0.425 | 0.401 | 0.511 | 0.387 | 3.76 | 10.48 | 14.79 | 9.20 | −4.18 | 28.6 |
| 855 | Sugar loaf | 16.53 | 1.33 | 0.342 | 0.360 | 0.457 | 0.363 | 4.55 | 9.43 | 14.48 | 8.10 | 4.29 | 22.6 |
| 860 | Spanish red | 15.38 | 1.81 | 0.444 | 0.476 | 0.624 | 0.375 | 2.84 | 9.65 | 12.00 | 8.35 | −4.07 | 25.8 |
| 1053 | Sugar loaf | 16.99 | 1.64 | 0.296 | 0.327 | 0.359 | 0.357 | 4.65 | 9.73 | 14.89 | 8.50 | −3.90 | 26.0 |
| | Average | 14.52 | 1.59 | 0.347 | 0.356 | 0.561 | 0.397 | 3.09 | 8.44 | 11.87 | | | |
| BAHAMA : | | | | | | | | | | | | | |
| 809 | | 14.97 | 1.52 | 0.387 | 0.410 | 0.798 | 0.500 | 2.56 | 9.18 | 12.23 | 8.10 | −4.07 | 28.4 |
| 868 | Spanish red | 14.65 | 1.59 | 0.408 | 0.409 | 0.747 | 0.462 | 2.75 | 8.98 | 12.21 | 7.85 | −3.74 | 25.8 |
| | Average | 14.81 | 1.56 | 0.398 | 0.410 | 0.772 | 0.481 | 2.65 | 9.08 | 12.22 | | | |
| PORTO RICAN : | | | | | | | | | | | | | |
| 805 | | 8.69[1] | 1.64 | 0.416 | 0.399 | 0.697 | 0.431 | 1.35[1] | 3.67[1] | 5.22[1] | 2.30 | −2.36 | 23.4 |
| 818 | Cabezona | 8.48[1] | 1.63 | 0.332 | 0.304 | 0.807 | 0.519 | 2.74[1] | 3.30[1] | 6.22[1] | 2.30 | −1.92 | 28.6 |
| 819 | Pan de Azucar | 14.14 | 1.69 | 0.404 | 0.437 | 0.524 | 0.444 | 2.97 | 8.22 | 11.62 | 7.15 | −3.41 | 28.6 |
| 820 | Caraquena | 17.69 | 1.83 | 0.333 | 0.370 | 0.838 | 0.531 | 4.59 | 9.97 | 15.09 | 8.20 | −4.62 | 28.6 |
| | Average | 15.91 | 1.70 | 0.371 | 0.378 | 0.716 | 0.481 | 3.78 | 9.09 | 13.36 | | | |
| JAMAICA : | | | | | | | | | | | | | |
| 806 | | 9.23[1] | 1.48 | 0.410 | 0.410 | 0.646 | 0.475 | 1.28[1] | 4.67[1] | 6.19[1] | 3.55 | −2.58 | 23.4 |
| | Av'ge of all samples | 14.17 | 1.52 | 0.396 | 0.370 | 0.603 | 0.420 | 3.91 | 7.59 | 11.90 | | | |
| | Maximum | 18.86 | 1.83 | 0.548 | 0.596 | 0.847 | 0.569 | 9.75 | 10.48 | 15.28 | | | |
| | Minimum | 10.78 | 1.02 | 0.272 | 0.223 | 0.300 | 0.206 | 1.76 | 2.98 | 8.20 | | | |

[1] Not included in averages.

TABLE II.—COMPOSITION OF CANNED PINEAPPLES PUT UP UNDER DIRECTION OF CONSULS GENERAL AT SINGAPORE AND NASSAU.

| | Solids. | | Ash. | | | | Sugars. | | | Polarizations. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Serial Number. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Alkalinity as $K_2CO_3$. Per cent. | Acids as $H_2SO_4$. Per cent. | Protein $(N \times 6.25)$. Per cent. | Reducing. Per cent. | Cane. Per cent. | Total as invert. Per cent. | Direct. °V. | Invert. °V. | Temperature. °C. |
| *Preserved in natural juice without addition of cane-sugar.* | | | | | | | | | | | | |
| SINGAPORE: | | | | | | | | | | | | |
| 1103 | 14.34 | 1.18 | 0.447 | 0.312 | 0.450 | 0.566 | 8.92 | 3.28 | 12.38 | 0.90 | — 3.30 | 23.0 |
| 1104 | 14.26 | 1.31 | 0.357 | 0.295 | 0.466 | 0.562 | 9.54 | 3.34 | 13.06 | 0.90 | — 3.52 | 23.0 |
| 1105 | 14.41 | 1.20 | 0.474 | 0.338 | 0.472 | 0.438 | 10.96 | 1.85 | 12.91 | — 1.10 | — 3.52 | 23.0 |
| 1106 | 13.48 | 1.15 | 0.476 | 0.329 | 0.490 | 0.481 | 9.56 | 2.44 | 12.13 | 0.00 | — 3.20 | 23.0 |
| 1107 | 17.44 | 1.44 | 0.434 | 0.352 | 0.436 | 0.488 | 10.56 | 4.11 | 14.89 | 1.60 | — 3.80 | 24.4 |
| 1108 | 13.10 | 1.34 | 0.309 | 0.257 | 0.450 | 0.506 | 7.44 | 4.20 | 11.86 | 2.30 | — 3.20 | 24.4 |
| 1109 | 10.96 | 1.16 | 0.242 | 0.214 | 0.250 | 0.500 | 5.84 | 3.85 | 9.90 | 2.30 | — 2.65 | 24.4 |
| 1111 | 11.70 | 1.62 | 0.333 | 0.301 | 0.333 | 0.412 | 7.53 | 2.08 | 9.72 | 0.30 | — 2.50 | 24.4 |
| 1112 | 11.28 | 0.87 | 0.330 | 0.253 | 0.294 | 0.444 | 6.59 | 3.00 | 9.83 | 1.40 | — 2.60 | 24.4 |
| 1113 | 12.95 | 1.83 | 0.391 | 0.308 | 0.299 | 0.356 | 7.30 | 3.17 | 10.64 | 1.60 | — 2.70 | 24.4 |
| Average.. | 13.39 | 1.31 | 0.379 | 0.300 | 0.389 | 0.475 | 8.42 | 3.13 | 11.73 | | | |
| NASSAU: | | | | | | | | | | | | |
| 1013 | 10.00 | 1.07 | 0.257 | 0.300 | 0.443 | 0.250 | 5.44 | 2.96 | 8.55 | 1.65 | — 2.09 | 26.0 |
| 1014 | 16.35 | 2.18 | 0.563 | 0.663 | 0.711 | 0.456 | 6.20 | 6.61 | 13.16 | 4.65 | — 3.68 | 26.0 |
| Average.. | 13.18 | 1.63 | 0.410 | 0.482 | 0.577 | 0.403 | 5.82 | 4.79 | 10.86 | | | |
| *Preserved in natural juice with addition of cane-sugar.* | | | | | | | | | | | | |
| SINGAPORE: | | | | | | | | | | | | |
| 1114 | 18.07 | 1.02 | 0.370 | 0.286 | 0.378 | 0.412 | 11.93 | 4.63 | 16.70 | 1.50 | — 4.50 | 24.4 |
| 1115 | 18.48 | 1.38 | 0.267 | 0.164 | 0.202 | 0.350 | 12.68 | 4.88 | 17.82 | 1.55 | — 4.75 | 24.4 |
| 1116 | 18.15 | 1.60 | 0.460 | 0.329 | 0.260 | 0.400 | 7.51 | 8.82 | 16.80 | 7.00 | — 4.30 | 24.4 |
| 1117 | 18.61 | 2.06 | 0.505 | 0.336 | 0.284 | 0.456 | 9.02 | 7.83 | 17.26 | 6.50 | — 4.60 | 24.4 |
| 1118 | 19.11 | 1.25 | 0.450 | 0.328 | 0.417 | 0.450 | 15.39 | 2.41 | 17.93 | 1.65 | — 4.80 | 24.4 |
| 1119 | 16.61 | 1.33 | 0.334 | 0.234 | 0.378 | 0.375 | 13.28 | 2.28 | 17.93 | 0.20 | — 4.25 | 24.4 |
| Average.. | 18.17 | 1.44 | 0.398 | 0.280 | 0.320 | 0.407 | 11.63 | 5.14 | 17.41 | | | |

TABLE III.—COMPOSITION OF CANNED PINEAPPLES—COMMERCIAL SAMPLES.

|  |  |  | Solids. |  | Ash. |  |  |  | Sugars. |  |  | Polarizations. |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Specific gravity of syrup. | Solids in syrup. Per cent. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Alkalinity as $K_2CO_3$. Per cent. | Acids as $H_2SO_4$. Per cent. | Protein ($N \times 6.25$). Per cent. | Reducing. Per cent. | Cane. Per cent. | Total as invert. Per cent. | Direct. °V. | Invert. °V. |
| SINGAPORE—(Twenty-one samples) : |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Average... | 1.0869 | 20.15 | 21.03 | 1.17 | 0.284 | 0.225 | 0.269 | 0.461 | 9.61 | 7.88 | 17.86 | 5.01 | -5.22 |
| Maximum. | 1.1112 | 25.30 | 26.84 | 1.67 | 0.363 | 0.282 | 0.433 | 0.569 | 13.73 | 16.48 | 25.10 | 15.00 | -6.60 |
| Minimum. | 1.0744 | 18.18 | 18.45 | 0.92 | 0.208 | 0.164 | 0.156 | 0.388 | 7.05 | 4.34 | 14.87 | 0.00 | -4.40 |
| STRAITS SETTLEMENTS—(Ten samples) : |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Average... | 1.0868 | 20.08 | 21.04 | 1.08 | 0.259 | 0.225 | 0.259 | 0.466 | 10.51 | 7.54 | 18.45 | 4.53 | -5.37 |
| Maximum. | 1.0998 | 22.86 | 24.28 | 1.27 | 0.322 | 0.324 | 0.323 | 0.569 | 15.18 | 10.65 | 21.94 | 7.70 | -6.27 |
| Minimum. | 1.0717 | 16.79 | 17.32 | 0.91 | 0.224 | 0.138 | 0.171 | 0.394 | 7.70 | 4.70 | 14.55 | 0.00 | -4.20 |
| BAHAMAS—(Eleven samples) : |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Average... | .... | .... | 14.13 | 1.39 | 0.381 | 0.304 | 0.558 | 0.335 | 7.96 | 2.78 | 9.98 | 0.56 | -3.31 |
| Maximum. | .... | .... | 26.78 | 2.51 | 0.497 | 0.388 | 1.176 | 0.456 | 12.84 | 9.05 | 22.37 | 4.70 | 7.15 |
| Minimum. | .... | .... | 8.54 | 0.88 | 0.222 | 0.199 | 0.220 | 0.200 | 5.55 | 0.53 | 6.33 | 2.40 | 1.32 |

Table III contains the results of analyses of forty-two samples of canned pineapples from Singapore, the Straits Settlements and the Bahamas. It is apparent from the high content of sugars that practically all of the canned pineapples from Singapore and the Straits Settlements are preserved with addition of cane-sugar. On the other hand, the analyses indicate that but few of the samples from the Bahamas have had any addition of cane-sugar.

A study of the data contained in the foregoing tables fails to bear out the common supposition that the pineapples grown upon or near the equator contain more sugar than those grown at some distance farther north, and in fact, the normal content of sugar in pineapples grown in Florida differs so little from that of pineapples grown at Singapore that the difference is practically negligible.

It may not be out of place to state at this point, that these investigations were undertaken in the Bureau of Chemistry at the request of the Secretary of the Treasury for the purpose of establishing a basis of classification for imported pineapples for the guidance of the appraisers. Since the classification of these bodies for dutiable purposes depends upon the answer to the question of whether or not sugar has been added during the process of preserving, it was necessary, first to establish the normal content of sugar in the pineapples. It is evident, from inspection of the analyses, that since the normal pineapples contain a large quantity of cane-sugar, the mere presence of this substance would be no evidence whatever of its artificial addition. It is further evident, that if a syrup containing practically the same quantity of sugar as the natural syrup of the pineapple were added, it would be quite impossible, by a mere determination of the sugar present, to detect the addition. The only guide in this case would be to determine the relation of the sugar present to the total insoluble matters of the pineapple.

If, on the other hand, a syrup rich in sugar were added in preserving, it would be easily detected by the increase in the percentage of sugar in the contents of the can.

In looking over the literature accessible to us relating to the analysis of pineapples, at the commencement of these investigations, we were surprised to find that no paper has been published on this subject except one by Buignet in "Les Sucres," published by Maquenne (Paris, 1900).

The average content of sugar found by Buignet, *viz.*. 13.9 per cent. as invert sugar is not materially different from the amount found in these investigations.

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# THE EFFECT OF MOISTURE ON THE AVAILABILITY OF DEHYDRATED PHOSPHATE OF ALUMINA.

BY FRED. W. MORSE.

Received January 3, 1903.

THE author has from time to time encountered samples of phosphatic material, which have borne the name of concentrated phosphate, and which really are dehydrated phosphate of alumina and iron.

Such materials usually contain approximately 45 per cent of phosphoric anhydride, of which more than 0.5, and sometimes as much as 0.8, will dissolve in a neutral solution of ammonium citrate.

The phosphatic mineral from which this fertilizer is made, is obtained principally from the islands of Redonda and Grand Connetable in the West Indies, and is a hydrated phosphate of alumina and iron.

The author has made several analyses of the mineral from the former island, and a number of analyses have been published by Shepard,[1] Tate,[2] and Hitchcock,[3] while only one analysis made by Andouard,[4] is yet known to him of the latter phosphate. The composition of the two phosphates is very similar. The phosphoric anhydride ranges from 35 per cent. to 39 per cent. in cargoes and as high as 43 per cent. in the richest specimens.

The water contained in the mineral is nearly proportional to the phosphoric anhydride, the ratio averaging $2P_2O_5$ to $9H_2O$. Two analyses including Andouard's give $10H_2O$, while two analyses have been as low as $8H_2O$. The proportion of $Al_2O_3$ to $Fe_2O_3$ is irregular; usually the former exceeds the latter, especially in the richer specimens.

The process of preparing the mineral for use as a fertilizer, was patented by the late Stephen L. Goodale,[5] who described the prin-

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[1] *Am. J. Sci.*, **47**, 428.

[2] *J. Soc. Chem. Ind.*, **5**, 570.

[3] *Bull. Geol. Soc. Am.*, **2**, 6-9.

[4] *Ann. Agronom.*, **21**, 171.

[5] "Conversion of Hydrous Phosphates of Alumina and Iron." Monograph, 1893.

ciples of his method in a pamphlet from which the following is quoted.

"The sample properly prepared by reduction to fineness and removal of dust, is gradually heated in a properly equipped receptacle. Elevation of temperature proceeds regularly to about 100° C., at which point a halt ensues, usually attended by a fall of several degrees. During this halt, heat is apparently absorbed; when the halt ceases, elevation of temperature again proceeds regularly to a point near 150°, when another notable halt occurs; when this ceases, elevation proceeds without interruption to full dehydration and beyond, if permitted. This point may be determined by seasonably exposing a cold surface to the orifice where escaping vapor may be deposited as dew. Application of the test should begin at least as soon as 250° or 260° is reached; the point of complete dehydration varies in samples of differing composition, sometimes as low as 275°, rarely beyond 330°, usually near 325° C."

In speaking of the results of the process, Goodale further says: "To attain these fully, the heat must reach the definite, critical point of complete dehydration. If only one-fourth, one-half or three-fourths be expelled, corresponding enhancement in value does not accompany such expulsion. Moreover, if elevation of temperature goes beyond the critical point, change also goes on toward non-solubility, so that most skilful watchfulness is indispensable to avoid loss."

Although this dehydration results in a high percentage of available phosphoric acid as measured by its solubility in ammonium citrate, the use of the calcined phosphate in experiments with plants, has not shown itself to possess any such degree of availability when applied to the soil.

This fact has been especially demonstrated by several series of pot experiments made at the Main Experiment Station,[1] with twelve different kinds of plants; and by three successive years of field experiments at the Rhode Island Experiment Station[2] with a rotation of corn, oats and grass.

It was further noted in the Maine experiments, for which the dehydrated Redonda phosphate was prepared in the Station laboratory, that the availability of the substance in ammonium citrate

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[1] Maine Agr. Expt. Sta. Reports (1893), pp. 10-20; (1895), pp. 10-20; (1898), pp. 64-74.

[2] R. I. Agr. Expt. Sta. Reports (1894), pp. 122-128; (1896), pp. 327-343.

decreased on standing, and that it was necessary to prepare a fresh quantity of phosphate for each series of comparisons, which suggested that the dehydrated phosphate reverts to the hydrated condition in the soil. Goodale mentions in his pamphlet that, under certain conditions, the phosphate retrogrades: but does not give any particulars beyond intimating that it is due to overheating.

In order to get more knowledge of the nature of the dehydrated phosphate, and of its availability, a series of experiments was carried out in the spring of 1900, to determine the amount of dehydration at different temperatures, with the resultant solubility in ammonium citrate of the phosphate, and to see if the dehydrated mineral would revert in the presence of moisture.

In this series of experiments, the author was assisted by Mr. R. H. Shaw, now of the Kansas Experiment Station. For material there was used ground Redonda phosphate obtained in 1891 from Mr. Goodale for field experiments.

The mineral was analyzed with the following results: Water at low red heat, 21.33 per cent.; phosphoric anhydride, 35.92 per cent.

The temperatures selected for dehydration were those mentioned by Goodale, *viz.*, 100°, 150°, 250° and 325° C., and in addition 560° and 830° C., or the fusing points of borax and sodium carbonate respectively.

The estimation of water at 100° was made by heating the mineral in wide weighing bottles, in an air-bath, at a temperature of 100° to 105° C. The material was weighed at intervals of two hours, and the weight at the end of the fourth hour was practically the same as that at the end of the sixth.

At the approximate temperature of 830° the determination was conducted by heating in a platinum crucible over a Bunsen flame, and ascertaining the loss in weight, as in the foregoing experiment. The temperature was reached by adjusting the lamp flame so that anhydrous sodium carbonate was brought to a quiet fusion in a platinum crucible. Then, without disturbing the lamp, the sodium carbonate crucible was removed and another platinum crucible of the same size containing the phosphate was placed in the triangle.

At the intermediate temperatures, the water was not only determined by the loss in weight of the material, but also by the gain in weight of a calcium chloride tube into which the vapor was passed.

The apparatus was arranged similarly to that for a combustion in a current of air or oxygen, and consisted of a combustion tube connected at one end with a drying tower and at the other end with a weighed U-tube containing calcium chloride.

The charge of phosphate was placed in a porcelain boat, inserted in the combustion tube, and pushed to the middle. For the temperatures of 150°, 250°, and 325°, a tube oven was used instead of a combustion furnace. For that at 560° a special furnace was constructed of a piece of magnesium-asbestos steam-pipe covering, a little shorter than the combustion tube. A rectangular opening was cut in the middle of the lower half-section long enough to admit the tops of three Bunsen burners placed in a line. The tube was supported above the burners by a strip of asbestos board, and when the upper half section was in place, the flames played around the tube as in a combustion furnace. In order to determine the degree of heat sustained by the mineral, a porcelain boat containing anhydrous borax was inserted in the combustion tube along with the boat containing the phosphate, the latter being next to the calcium chloride tube. The borax was maintained at the stage of fusion, which could be observed by removing the upper half section of the improvised furnace.

Determinations of the loss in weight at the temperature of fusing borax were also made by heating in a platinum crucible in exactly the way used with sodium carbonate.

In the tube oven, the temperatures of 150° and 250° were determined by thermometers as in heating sealed tubes; but since in this operation, a current of air was slowly drawn through the tube, the temperature of the mineral would be somewhat below that registered by the thermometers, which were therefore allowed to run about 10° above the stated temperatures before readjusting the lamps.

For the approximate temperature of 325°, the thermometer registered 350°; but powdered potassium nitrate contained in a boat placed in the tube reached only the stage of incipient fusion.

The three salts used for determining temperatures were of Kahlbaum's sealed brand of C. P. chemicals, and showed no impurities excepting with the spectroscope.

Richards[1] gives them the following melting-points: Potassium nitrate, 339° C.: sodium biborate, 561° C.; sodium carbonate, 830° C.

In the tube method, at the temperatures of 325° and 560° the water was expelled from the mineral quickly and condensed around the end of the combustion tube next the calcium chloride tube, requiring several hours for its removal by the current of air drawn through the apparatus, since it was necessary to pass the air slowly in order to insure complete absorption.

For the absorption method, it was found necessary to use smaller charges than for the methods depending solely on loss of weight. The effectiveness of the drying-tower was demonstrated by blank determinations, and that of the U-tube by connecting a second calcium chloride tube and weighing it separately. The results are given in the following table.

PERCENTAGES OF WATER EXPELLED AT DIFFERENT TEMPERATURES.

| Temperature. °C. | Per cent. by loss. | Per cent. by absorption. |
|---|---|---|
| 100 | 18.14 | .... |
| 150 | 19.72 | 19.93 |
| 250 | 20.32 | 20.26 |
| 325 | 20.71 | 20.78 |
| 560 | 21.34 | 20.98 |
| 560 | 21.32 | after heating 15 min. in crucible. |
| 830 | 21.57 | " " 5 " " " |
| 830 | 21.54 | " " 15 " " " |
| 830 | 21.63 | " " 30 " " " |
| 830 | 21.45 | " " 60 " " " |

The results corroborate the statements of Goodale regarding the expulsion of water at 100° and 150° but do not show complete dehydration at 325°.

The slightly lower results obtained by absorption at 560° were probably due to incomplete removal of water from the combustion tube; but might also be due to the destruction of organic matter which can hardly fail to be present, owing to the fact that the porous phosphate is more or less penetrated by the roots of grasses and cacti, and Andouard in his analysis of Grand Connetable phosphate reports traces of carbon dioxide.

In determining the availability of the phosphate, the official neutral solution of ammonium citrate[2] was used; but the citrate-

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[1] *Am. Chem. J.*, **20**, 704.

[2] "Methods of Analysis, Association of Official Agricultural Chemists," Bull. 46, Bur. of Chem., U. S. Dept. Agr., p. 11.

soluble phosphoric acid was determined directly, instead of indirectly as in the official method. This was done because in all previous work with this particular phosphate, it was found impossible to prevent the finest particles of mineral running through any paper filter that would permit a ready passage of the citrate solution. Ross' method[1] was therefore selected, which is based on digesting the filtrate of citrate-soluble phosphoric acid with sulphuric acid and oxidizing agents, as in the Kjeldahl method for nitrogen, after which the molybdate solution is used as usual. Of course, this method gives somewhat lower results than the indirect method; but this is not due to incomplete recovery of the phosphoric acid, which was repeatedly verified. The method of procedure then, was to digest 1 gram of the mineral in 100 cc. of neutral ammonium citrate, filter through an asbestos felt with the aid of a pump, digest aliquot parts of the filtered solution after Ross' method, and determine the phosphoric acid as usual. By the use of an asbestos felt, it was possible to get a clear filtrate and to remove the citrate solution quickly from the mineral. The availability of the phosphate at the different stages of dehydration was found to be as follows:

| | |
|---|---|
| Undehydrated | 2.08 per cent. $P_2O_5$ |
| Heated to 100° | 19.64 " " " |
| " " 150° | 27.25 " " " |
| " " 250° | 32.76 " " " |
| " " 325° | 31.53 " " " |
| " " 560° | 32.65 " " " |
| " " 830° 15′ | 11.35 " " " |
| " " 830° 90′ | 2.53 " " " |

These results show, that to get the highest degree of availability, it is necessary to remove practically all of the water; but they do not confirm the statement that a continuation of the heat beyond 325° lowers the solubility, since at 560° the mineral underwent the heating for from six to eight hours while the water was being aspirated from the tube. The high temperature required to fuse sodium carbonate produces, however, a marked decrease in solubility, and this is intensified by prolonging the heating.

The effect of exposure to a moist atmosphere was determined by placing the dehydrated phosphate under a bell-jar, in an atmosphere saturated with moisture from an open dish containing water. The phosphate was weighed in a porcelain boat placed

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[1] Bull. 38, Bur. of Chem., U. S. Dept. Agr., p. 16.

inside a weighing-tube, and the boat was exposed under the bell-jar, until it had reached equilibrium with respect to moisture, before the dehydrated mineral was weighed into it. The charges used were small, in order to expose as much surface as possible to the action of the moist atmosphere.

The different degrees of dehydration, which were compared, were those obtained by heating to 250°, 325°, 560°, and 830° respectively. The results obtained were unlooked for and of much interest.

Phosphate dehydrated at 250° ; charge, 0.2965 gram.

Water absorbed in 24 hours, 0.0565 gram.
" " " 72 " 0.0690 "
" " " 120 " 0.0705 "
Total water absorbed, 23.78 per cent. of charge taken

Phosphate dehydrated at 325° ; charge, 0.2200 gram.

Water absorbed in 24 hours, 0.0425 gram.
" " " 72 " 0.0485 "
" " " 120 " 0.0495 "
Total water absorbed, 22.50 per cent. of charge taken.

Phosphate dehydrated at 560° ; charge, 0.6495 gram.

Water absorbed in 24 hours, 0.0415 gram.
" " " 48 " 0.0585 "
" " " 96 " 0.0605 "
Total water absorbed, 9.32 per cent. of charge taken.

Phosphate dehydrated by heating fifteen minutes at 830° ; charge, 0.4730 gram.

Water absorbed in 24 hours, 0.0065 gram.
" " " 48 " 0.0095 "
Total water absorbed, 2.00 per cent. of charge taken.

The moistened phosphate was next transferred to an ammonium citrate solution and its availability determined by the same method that was employed after dehydration. As the charges of phosphate of the temperatures 250° and 325° were so small, they were combined for the determination of available acid. The quantity of citrate solution was reduced to 50 cc. in all these cases, since the charges were approximately only 0.5 gram each.

The availability of the four grades of phosphate was now found to be as follows:

250° and 325°, 19.30 per cent. $P_2O_5$ in dehydrated phosphate.
560° 29.76 " " " " " "
830° 7.09 " " " " " "

The experiment was repeated with the phosphates dehydrated at 325° and 560°.

Phosphate dehydrated at 325°; charges (*a*), 0.4160 gram; (*b*), 0.5330 gram.

Water absorbed in 75 hours, (*a*) 0.0900 gram ; (*b*) 0.1140 gram.
" " " 96 " " 0.0950 " " 0.1200 "
" " " 240 " " 0.1090 " " 0.1460 "

Total water absorbed, (*a*), 26.20 per cent.; (*b*), 27.39 per cent. of charge taken.

Phosphate dehydrated at 560°; charges (*a*), 0.4450 gram; (*b*), 0.6820.

Water absorbed in 24 hours, (*a*), 0.0370 gram; (*b*), 0.0540 gram.
" " " 48 " " 0.0480 " " 0.0660 "
" " " 120 " " 0.0580 " " 0.0800 "
" " " 240 " " 0.0710 " " weight lost.

Total water absorbed in 120 hours, (*a*), 13.04 per cent.; (*b*), 11.72 per cent.
Absorbed in 240 hours, (*a*), 15.95 per cent.

For the estimation of available phosphoric acid the duplicate charges of each grade were combined, making an approximate charge of 1 gram for each grade, and 100 cc. of citrate solution were used. The availability in this trial was respectively:

325° 11.54 per cent. $P_2O_5$ in dehydrated phosphate.
560° 27.70 " " " " " "

Having on hand about 200 pounds of the dehydrated phosphate obtained in 1891, which had been stored, since then, in the basement of the laboratory exposed in an open barrel, it was tested for availability in ammonium citrate in order to determine its keeping qualities. In 1891 this lot contained 46.85 per cent. total and 21.91 per cent. available phosphoric acid, and but a trace of moisture. In 1900 a new analysis yielded 10.98 per cent. water; 41.95 per cent. total phosphoric acid and 14.60 per cent. available. The decrease in total phosphoric acid is proportional to the absorption of water, while the drop in available is far in excess of such hydration.

Some of the material was next exposed to a moist atmosphere for eight days, in which time it gained 9.42 per cent. of its weight, and on determining the available phosphoric acid, it was found to have fallen to 11.31 per cent. of the original charge.

The phosphates dehydrated at 325° and 560°, respectively, were next subjected to the action of water saturated with carbon dioxide, and its effect was also tried on the undehydrated mineral. One gram of material was taken in each instance and placed in a flask with 200 cc. of water. Carbon dioxide was passed into the water in each flask, during thirty to sixty minutes, twice a day for six days, and the flask was shaken two or three times during its passage. The gas was prepared from sodium bicarbonate and sulphuric acid, to avoid any acid vapors, and was washed before it entered the flask. At the end of the period, an aliquot part of clear liquid was taken from each flask and tested for phosphoric acid. The amount appeared so slight in each case, that no attempt was made to determine the proportion for each grade of material: but the filtrates from the three were combined and then concentrated by evaporation, after which the phosphoric acid was determined as the average for the lot, and found to be 0.31 per cent. of the charges taken.

Each residue was next digested with the ammonium citrate solution and the amount of available phosphoric acid estimated, which was as follows:

| | | |
|---|---|---|
| Undehydrated | 0.69 | per cent. of charge taken. |
| Dehydrated at 325° | 6.67 | “ “ “ “ “ |
| “ “ 560° | 24.95 | “ “ “ “ “ |

By these different series of experiments, the rapid deterioration of the dehydrated phosphate with respect to its available phosphoric acid, is clearly shown in the case of the material prepared according to Goodale's process, and the claim is contradicted that heating beyond 325° is injurious. The results show without exception that the temperature at which borax fuses is not too high for good results, and that the phosphate, after being heated to that point, is more permanently soluble, and less apt to again become hydrated. Whether it would be more available to plants than those lots subjected to lower temperatures, cannot be told without vegetation tests.

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