

## SUMMARY

In 1913, experiments on the effect of fertilizers on the composition of hops were begun at Wheatland, California. Two fields, each one acre in area, were laid out into fifteen plots each. The J. R. field was not irrigated, whereas the No. 1 field was irrigated. Corresponding plots in each field received like amounts of fertilizer each year during 1914, 1915, and 1916.

Each year a sample of hops from each plot was analyzed for soft resins, hard resins, total resins, soluble ash, insoluble ash, and total ash.

The percentage of yield of resins in the J. R. field varied with the various plots but the variations were not constant from year to year, the yearly average of all the plots being approximately the same throughout the experiment.

The percentage of yield of resins in the No. 1 field varied, as in the J. R. field, but the yearly average of all the plots gradually decreased.

The available soft resins in pounds per acre varied in each plot in each field each year. No continuity was noted as the effect of any fertilizer applied. There is, however, an increase in the amount of soft resins available each year. This increase is greatest in the No. 1 field.

The increase in amount of resins available is not due to an increase in the percentage of resins due to fertilizers, but is due to an increased yield of cones which are less rich in resins as the vegetative yield increases. In other words, the fertilizer causes a great increase in vegetative yield which, due to forced succulent growth, causes a smaller percentage of resins to be formed.

The percentage of soluble ash in the hops from the J. R. field varied with the season. Some apparent regularities in certain plots are traceable throughout the time of the experiment. It is doubtful if these regular effects are due wholly to the effect of the fertilizer; and the supposition is advanced that the effect of other factors plays an important rôle in producing the results as found.

The percentage of insoluble ash in the hops from the J. R. field likewise varied with the season. The percentage of total ash was fairly constant in 1914 and in 1916, but decreased somewhat in 1915.

The percentage of soluble ash in the hops from the No. 1 field also varied with the season, but plot for plot it ran higher than in the corresponding plots in the J. R. field, except in the year 1915 when considerable variation occurred.

The percentage of insoluble ash in the hops from the No. 1 field likewise varied with the season, being always lower plot for plot than the corresponding plots in the J. R. field, except in the year 1915 when variation occurred, and with this exception, that the yearly average shows a gradual decrease in the amount of insoluble ash present.

The total ash of the two fields varied with the various plots but shows no apparent significant differences throughout the time of the experiment. The yearly average of the ash from all the plots is less

each year in the No. 1 field than it is in the J. R. field, and this yearly average likewise grows somewhat less from year to year.

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## THE SOLVENT ACTION OF DILUTE CITRIC AND NITRIC ACIDS ON ROCK PHOSPHATE

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This Station has recently undertaken a series of experiments, one of the objects of which is to ascertain under what conditions the process of sulfur oxidation, termed sulfofication, will bring about an increase in the availability of phosphorus in rock phosphate.

In connection with the experiments in progress, it was of course of prime importance to secure a method by which a reliable index of the changes in availability of the phosphorus compounds in rock phosphate and soil mixtures attributable to sulfofication could be obtained.

Although the monocalcium and dicalcium phosphates are the forms of phosphorus commonly regarded as available, the sulfofication process, being to a great extent the result of biological agencies, will very probably convert some of the phosphorus into organic forms which may be more available than the tricalcium phosphate in the phosphate rock itself.

Neutral ammonium citrate has for a number of years, although without really valid and conclusive reasons, been regarded as the reagent whereby these two groups of phosphorus compounds, the available and non-available, could be distinguished one from the other, because it has been generally considered that neutral ammonium citrate possesses the faculty of dissolving dicalcium as well as monocalcium phosphate, leaving tricalcium phosphate intact. This is not strictly true, however, as neutral ammonium citrate will also dissolve varying amounts of phosphorus from tricalcium phosphate, the amount taken into solution depending upon the conditions under which the extraction is made.

In so far as the adaptability of neutral ammonium citrate is concerned, one cannot refrain from being skeptical as to its value for the determination of the availability of phosphorus, especially when this procedure is applied to composts or mixtures including rock phosphate and soil.

It was found, for instance, in the investigations pertaining to the effect of sulfur oxidation on the availability of phosphorus, that the available phosphorus of the untreated Wooster soil was 30 parts per million of soil; this comparatively high figure is surely contradicted by the fact that this particular soil responds very readily to applications of fertilizers carrying phosphorus. In fact, crop yields in fertility experiments of this soil show that phosphorus is the limiting element.

When neutral ammonium citrate is used to measure changes in mixtures of soil and rock phosphate, the amount of organic matter extracted from the soil,

judged by the color of the solution, approaches that obtained when the soil is extracted with the usual strength of ammonium hydroxide used for humus determinations.

While it must follow from this that neutral ammonium citrate cannot serve as a means for determining the absolute amount of available phosphorus, there still remains the possibility that it may be used to obtain an indication of changes which have occurred as a result of treatment.

Before the precipitation of the phosphorus with ammonium molybdate solution, there must be a complete oxidation of the organic material extracted from the soil, in order to convert any organic phosphorus compounds present into the form of orthophosphate, and at the same time to destroy the citrate itself, the presence of which will prevent the complete precipitation of the phosphorus.

The oxidation of the organic matter with aqua regia or with fuming nitric acid is unsatisfactory on account of the large amount of reagents and time required as well as the close attention necessary.

Destruction of the organic matter by ignition with magnesium nitrate is undoubtedly the most convenient method, the only possible objection being that the high temperature necessary may cause a partial change of the phosphorus compounds into forms which are not soluble in either hydrochloric or nitric acid.

The questionable value of the neutral ammonium citrate procedure for determining the availability of phosphorus produced in various mixtures which include rock phosphate and soil, together with the difficulties involved in destruction of the organic matter extracted from the soil, and that contributed by the neutral ammonium citrate, led to tests being made to determine the possible value of dilute citric and nitric acid solutions as substitutes for neutral ammonium citrate solutions.

#### SOLUBILITY IN CITRIC ACID

Citric acid of various strengths has been recommended as a suitable solvent for the determination of available phosphorus, and has been used with reported satisfaction in soil investigations.

In experimental work in which a number of acids were employed as solvents for the phosphorus of the soil, Russell and Prescott<sup>1</sup> found that the amount of phosphorus dissolved varies greatly with the nature of the acid employed. They also found that some of the acids were themselves absorbed by the soil. As a rule they found that an acid which is absorbed by the soil to a considerable extent also possesses a high extraction power for phosphorus.

The acids investigated were absorbed in the following order:

Oxalic	} most
Citric	
Phosphoric	
Sulfuric	
Hydrochloric	} least
Nitric	

It should not be inferred from this that citric acid when present will entirely satisfy the soil's absorptive properties; the fact is that when both are present, citric acid takes the place of some of the phosphoric acid in the absorption complex. It must be remembered that the solubility of the phosphorus in the soil as determined by a solvent is the resultant of the difference between the phosphorus dissolved and that absorbed from the solution by the soil. From a soil with a great absorptive power there is always a smaller percentage of the phosphorus capable of being taken into solution by the solvent extracted than from a soil with a small absorption power, although the absolute amounts of such soluble phosphorus compounds may stand in the reverse order.

Citric acid, which shows a high extractive power due to the fact that this acid is itself absorbed when brought into contact with the soil, would therefore seem to be a very desirable acid for extracting the phosphorus of the soil for the purpose of discrimination between the available and the unavailable phosphorus compounds.

To determine the solvent action of dilute solutions of citric acid varying in concentration within comparatively narrow limits, from 0.1 per cent to 0.05 per cent, extractions were made under the following conditions:

3 g. portions of rock phosphate were extracted with 100 cc. of citric acid of the prescribed strength by shaking in shaking machine at ordinary room temperature for 30 min. The solutions were diluted to a volume of 500 cc. After filtering, 200 cc. portions were taken for the phosphorus determinations.

From the amounts of phosphorus extracted, as shown in Table I, it is evident that variations in the strength of citric acid, even when a very weak solution is employed, decidedly influence the solubility of the phosphorus of rock phosphate.

TABLE I—SOLUBILITY OF ROCK PHOSPHATE IN CITRIC ACID SOLUTIONS OF VARIOUS CONCENTRATIONS

Strength of Acid Per cent	Phosphorus Extracted Per cent
0.5	0.4287
0.4	0.3700
0.3	0.2569
0.2	0.1918
0.1	0.1113

The availability of the phosphorus in the particular rock phosphate used in this experimental work was 0.2 per cent when 3 g. of rock phosphate were treated with 100 cc. neutral citrate solution for 30 min. at 65° C.; the citrate solution was then diluted to 500 cc., filtered, and 200 cc. taken for determination of phosphorus.

From the results obtained with the different strengths of citric acid it appears that an extraction with 0.2 per cent citric acid under these conditions has given a value for the availability of phosphorus in rock phosphate which is about equal to that obtained by using neutral ammonium citrate.

The additional data presented in Table II show that varying the amount of rock phosphate treated with a given volume of citric acid has a decided bearing on the solvent power of this acid for the phosphorus in rock phosphate.

<sup>1</sup> "The Reaction between Dilute Acids and the Phosphorus Compounds of the Soil," *J. Agr. Science*, September 1916, pp. 65-110.

TABLE II—INFLUENCE OF QUANTITY OF ROCK PHOSPHATE EXTRACTED  
Weight of Rock Phosphate Treated      Total Phosphorus Extracted  
Grams      Per cent

0.1	4.289
0.5	1.334
1.0	0.747
3.0	0.1918

When 0.1 g. of rock phosphate instead of 3 g. was treated with 100 cc. citric acid, it was found that 4.289 per cent of the phosphorus was taken into solution, and a still higher figure would doubtless have been obtained if a smaller amount of rock phosphate had been treated with the same strength of acid, or a larger volume of acid of the same strength had been used.

The weights of rock phosphate indicated were extracted with 100 cc. of 0.2 per cent citric acid in 500 cc. flasks, shaking every 5 min. during a period of 30 min., after which the solutions were diluted to 500 cc. and filtered.

When 0.1 g. of rock phosphate was treated with 100 cc. of 0.2 per cent citric acid, with continuous agitation in a shaking machine for a period of 30 min., it was found that 5.390 per cent of phosphorus was dissolved as compared with 4.289 per cent obtained when the shaking was not continuous during the extraction period.

When the same weight, 0.1 g., of phosphate rock was mechanically shaken for 30 min. with 500 cc. of 0.2 per cent citric acid, it was found that not less than 6.410 per cent phosphorus was extracted.

## EFFECT OF BASICITY

As pointed out by Cousins and Hammond<sup>1</sup> citric acid cannot be used as a discriminating agent for available phosphorus if applied to calcareous soils unless the basicity due to carbonates, etc., is compensated for by the use of a corresponding extra amount of citric acid.

For the purpose of determining the amount of phosphorus extracted by citric acid from rock phosphate alone and from a mixture of rock phosphate and soil with and without additions of calcium carbonate, the experimental data in Table III were obtained.

TABLE III—EFFECT OF BASICITY

No.	Material Treated	Phosphorus Extracted Per cent
1	0.1 g. Rock Phosphate.....	6.410
2	0.2 g. Rock Phosphate.....	5.527
3	0.2 g. Rock Phosphate + 0.05 g. Calcium Carbonate.....	5.000
4	0.2 g. Rock Phosphate + 0.1 g. Calcium Carbonate.....	3.300
5	0.2 g. Rock Phosphate + 0.20 g. Soil.....	3.587
6	0.2 g. Rock Phosphate + 0.20 g. Soil + 0.05 g. Calcium Carbonate.....	2.497
7	0.2 g. Rock Phosphate + 0.20 g. Soil + 0.1 g. Calcium Carbonate.....	1.950
8	0.2 g. Rock Phosphate + 0.20 g. Soil + 0.2 g. Calcium Carbonate.....	1.222
9	0.2 g. Rock Phosphate + 0.20 g. Soil + 0.5 g. Calcium Carbonate.....	0.712

The extractions of phosphorus were made in the same way and under uniform conditions, so far as the temperature, the strength of citric acid, time and manner of extraction and filtration were concerned. The strength of the citric acid was adjusted to equal 0.2 per cent at the end of the extraction, care being taken to neutralize the basicity due to the slight basic properties of the rock phosphate, the calcium carbonate added, and the soil itself which was naturally cal-

<sup>1</sup> "The Determination of Available Phosphoric Acid and Potash in Calcareous Soils," *The Analyst*, 1903, p. 238.

careous. This was done by addition of the necessary extra amount of citric acid to the 0.2 per cent citric acid employed. That the strength of the solution was as desired was ascertained by titration of the filtered extract with standard alkali and phenolphthalein.

When 0.2 g. rock phosphate was treated with 500 cc. citric acid, 5.527 per cent phosphorus were extracted. The addition of 0.05 g. and 0.1 g. calcium carbonate to the same weight of rock phosphate reduced this figure to 5.000 and 3.300 per cent, respectively. As might be expected, similar results in regard to phosphorus extracted were obtained when soil was mixed with rock phosphate and different amounts of calcium carbonate added.

The results obtained pertaining to the influence of basicity do not lend support to the contention of Cousins and Hammond that citric acid can be employed as discriminating agent for available phosphorus in calcareous soils, even though provision is made to add enough extra citric acid to neutralize the soluble bases present in the soil and have the final acidity of the solution at the required strength.

## NITRIC ACID

Another solvent which has been considered to afford useful information with respect to the availability of the supply of phosphorus in the soil is fifth-normal nitric acid. As this strength of nitric acid dissolves practically all the phosphorus in rock phosphate, it was decided to determine whether a weaker strength of nitric acid would be more satisfactory. By shaking for 30 min. 2 g. of rock phosphate with 500 cc. nitric acid of various strengths the percentages of phosphorus shown in Table IV were extracted.

TABLE IV—SOLUBILITY OF PHOSPHORUS IN DIFFERENT STRENGTHS OF NITRIC ACID

Strength of Acid Per cent	Phosphorus Dissolved Per cent of Sample
0.06	11.918
0.045	11.488
0.030	10.811
0.015	8.131

The sample of rock phosphate used in this work contained 12.37 per cent total phosphorus. It is evident, from the amount of phosphorus dissolved by weak nitric acid solutions, that this acid is no more satisfactory than citric acid for differentiating that part of the phosphorus which is more easily dissolved and therefore might be regarded as available, especially when one bears in mind that the figure for the availability of the phosphorus of the same sample of rock phosphate as determined by neutral ammonium citrate under accepted standard conditions is only 0.2 per cent.

Contrary to the results obtained with citric acid, the depressing influence of basicity of the sample on the extraction power of nitric acid for phosphorus can be wholly overcome by adding exactly the amount of nitric acid corresponding to the bases present, in this case calcium carbonate. This is shown by the results in the following table. The extraction was made for 30 min. with 100 cc. nitric acid corresponding to 0.2 per cent citric acid plus sufficient extra nitric acid to neutralize the calcium carbonate.

TABLE V--BASICITY AND EXTRACTION POWER OF WEAK NITRIC ACID

Material Extracted	Phosphorus Extracted Per cent
0.1 g. Rock Phosphate.....	8.555
0.1 g. Rock Phosphate + 0.1 g. Calcium Carbonate.....	8.413
0.1 g. Rock Phosphate + 0.2 g. Calcium Carbonate.....	8.362

The percentages of phosphorus extracted would have been higher had a larger volume of the nitric acid been employed for the extraction. Table VI shows that with various larger volumes of solvent, practically identical percentages of the phosphorus were dissolved, in all cases approaching the total phosphorus content of the rock phosphate, 12.37 per cent. The strength of the acid used was 0.01 per cent. The time for extraction was 30 min. as before and the amount of rock phosphate treated, 0.2 g.

Volume of Acid Used Cc.	Phosphorus Extracted Per cent
500	11.094
1000	12.150
1500	12.124
2000	12.131

## SUMMARY

Summing up our results as to the solubility of the phosphorus of rock phosphate in very dilute citric and nitric acids with a view to obtaining an indication as to the available phosphorus in this particular

material, we find that both possess too high a solvent power.

An additional objection to the use of citric acid is that basicity has a decidedly depressing influence on the solvent power and this cannot be altogether overcome by the addition of an extra amount of citric acid equivalent to the basicity present.

While neutral ammonium citrate cannot serve as a means for measuring the absolute amount of available phosphorus, it probably gives as reliable an indication of the available phosphorus of rock phosphate and eventual changes in availability due to sulfonation and other processes as any solvent can be expected to furnish. It is necessary, however, that two determinations be made, one at the beginning and one at the end of the experiment, and absolutely uniform conditions maintained in both instances.

This latter point must be observed because many factors, including the amounts of the material taken and the volume of solvent, will appreciably affect the availability of phosphorus as measured by neutral ammonium citrate.

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## LABORATORY AND PLANT

### THE RECOVERY OF WASTE PARAFFINED PAPER BY EXTRACTION WITH VOLATILE SOLVENTS

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Some time ago the Forest Products Laboratory was requested to determine whether there was a suitable method for recovering the paraffin and paper stock from waste paraffined paper. This waste paraffined paper has only a very limited value and in the majority of cases it is burned under the boilers. Other forms of paper waste such as oiled paper, asphalt-impregnated papers used for wrapping and case lining, board made damp-tight by means of asphalt or tar for the manufacture of cartons and containers of washing powder, coffee, etc., have very little application either, and are usually burned. Occasionally a small amount of the waste containing asphalt, not to exceed 2 per cent, is worked up in the beater with fresh paper stock, but the difficulties experienced with the pitch on the wire and presses of the paper machine, and the consequent loss of production due to breaks and the necessity of frequent clean-ups, makes the desirability of the practice very questionable.

No accurate statistics are available on the production of paraffined paper, but from a number of sources it is estimated that the production is close to 2,400,000 lbs. per week. Assuming a 4 per cent waste, there would be available 48 tons per week. In the above estimate no account has been taken of the waste incident to the manufacture of paraffined drinking cups, food containers, wrappers for special foods such as breakfast foods, etc.

From a review of the literature and from the experience of the manufacturer who brought the problem to us, it was believed that an attempt to remove the paraffin by melting it with hot water would not be successful. Several runs were made in which the paraffined paper was shredded and then opened up in a beater, the contents of which could be heated by the direct introduction of live steam. By this treatment it was possible to remove part of the molten wax by skimming and part by means of a washer, but the disintegrated pulp apparently held on tenaciously to a portion of the wax.

The resulting pulp was run off in the form of paper on our experimental paper machine, and an analysis for the percentage of wax in the finished paper is given for Run 7 in Table I. While the pulp prepared by this hot water treatment could be run over our experimental machine into finished paper, we believe, in view of the high wax content of the pulp, that it could not run for any length of time on a commercial machine. It was found from our experiment that the treatment of paraffined stock with hot water, heated by means of live steam, caused a decrease in the paraffin content to 0.90 per cent. In this experiment, however, the steaming operation was continued for 2 days, the condensed water carrying with it the extracted paraffin, overflowing constantly from the tub in which the stock was heated. A treatment of this nature, requiring so much time and steam expenditure, would not be commercially feasible.

Our coöperator supplied us with several hundred pounds of waste paraffin paper, some of which had