

# Some analytical considerations in the evaluation of rock phosphates using citric acid

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## SUMMARY

The percent citric acid soluble phosphorus in a rock phosphate is dependent on the weight of phosphate and the volume of citric acid used in its determination. The amount of phosphate brought into solution can also be influenced by the size of the reaction flask, the time of shaking and the rate of shaking. These factors must be standardised for a proper comparison of results between different determinations.

## INTRODUCTION

The amount of phosphorus dissolved by a two percent solution of citric acid is used commonly for evaluating the suitability of rock phosphates as a source of phosphate fertilizer for direct application to crops. Such evaluation is very important in Sri Lanka for a correct assessment of the quality of its own phosphate deposit at Eppawela as well as for the determination of the quality of rock phosphates which are imported annually at a cost of several millions of rupees.

A wide range of values (0.1 to 5.2 %  $P_2O_5$ ) of citric acid soluble phosphorus for Eppawela rock phosphate has been reported by Kathirgamathaiyah *et al* (1973), Loganathan (1976), Silva (1976) and Sivasubramaniam *et al* (1976). Such a wide range of values can mean that the rock phosphate is highly variable as far as its citric acid solubility is concerned. On the other hand such divergent values may result from use of differing analytical procedures by the various investigators.

In the citric acid procedure the rock phosphate is shaken with citric acid, the solution filtered and the phosphorus in the filtrate determined colorimetrically after addition of vanadium molybdate.

When a sample of rock phosphate is to be analysed the analyst has to decide on the following four factors ; the weight of the substance, the volume of extractant, the time of shaking and the rate of shaking. In this study these factors are examined using the same stock of Eppawela rock phosphate except in one instance which is mentioned in the text.

## MATERIALS AND METHODS

The mixture of rock phosphate and 2 % citric acid solution was shaken on a platform-type electrically-operated mechanical shaker. Different shaking rates were obtained by adjustment of its clutch. The solution was filtered immediately after a given time of shaking. Phosphorus in the filtrate was determined by the standard vanadium molybdate method.

For purposes of comparison the various analyses were also carried out using concentrated super phosphate. Here water was used as the extracting solution.

The results given in this paper are the means of triplicate determinations.

## RESULTS AND DISCUSSION

The effect of altering the ratio of weight of phosphate to volume of extractant, time of shaking and rate of shaking on the per cent  $P_2O_5$  obtained are reported here.

*Ratio of weight of phosphate to volume of extractant*

Mixtures with different ratios of solid to extractant were obtained by using different weights of phosphate with 100 ml. extracting solution. The mixture was placed in a 500 ml. flask and shaken for half an hour at a shaking rate of 120 oscillations per minute. The percent  $P_2O_5$  calculated after measuring the P in solution is given in Table 1. The data show that as the weight of rock phosphate is increased the percent citric acid solubility is decreased several fold. Such a result is to be expected for a sparingly soluble substance. Consider tricalcium phosphate for example. This will dissociate in solution as follows.



The activity product  $(Ca^{++})^3 (PO_4^{---})^2$  is a constant being the solubility product of tricalcium phosphate. If equilibrium is reached between the solid phase and the solution phase the activity of phosphate will be independent of the amount of solid. In other words increasing the weight of rock phosphate four fold from say 1g to 4g will not result in a proportionate increase in the activity of phosphate ions in solution. Thus increase of the solid leads to a decrease in percent phosphate. This of course does not happen with concentrated super phosphate since at the levels used all of it is soluble in water. Thus it becomes mandatory for all investigators to use the same ratio of weight of rock phosphate to volume of extractant.

Once a certain ratio of solid to extractant is taken as standard, the question then arises what amounts of solid and extractant to use. The British method (1960) uses 5g phosphate and 500 ml. citric acid. An analyst might wish to have some flexibility in the amounts of material to use when there are limitations in the availability of glassware, shape and size of the flask carriers of

mechanical shakers, chemicals, etc., while sticking to the accepted standard ratio of solid to extractant. The effect of changing the amounts of solid and extractant at a constant ratio of solid to extractant on phosphorus solubility is shown in Table 2. The mixtures were shaken for half an hour at a shaking rate of 120 oscillations per minute. Even though the ratio of rock phosphate to citric acid was kept constant, using 4g rock phosphate and 400 ml citric acid gave only 64 % of the  $P_2O_5$  that was obtained from using 1g. and 100 ml. The corresponding variation in the concentrated super phosphate values is very small.

Using larger volumes of extractant led to lower dissolution of phosphate. The efficiency of the stirring action of the contents in a flask will depend both on the volume of the contents and the shape and size of the container. All the above mixtures were shaken in 500 ml. conical flasks simultaneously. When larger volumes of extractant are used they occupy a greater proportion of the volume of the container. Under such conditions the stirring action of the contents of the flask is less efficient than when 50 or 100 ml. extractant is used and therefore reaction between rock phosphate and citric acid comparatively less complete. This could be one of the reasons for the low per cent  $P_2O_5$  for the 3:300 and 4:400 mixtures.

The above hypothesis was tested out in a subsequent experiment (with a different stock of Eppawela rock phosphate) by shaking 1g. phosphate with 100 ml extracting solution in 125ml. and 500 ml. flasks for half an hour on a mechanical shaker at a rate of 120 oscillations per minute. The phosphate coming into solution was 23 % lower in the smaller flask (Table 3). Concentrated super phosphate solubility was unaffected by the size of the flask.

#### *Time of shaking*

The effect of time of shaking on the per cent  $P_2O_5$  obtained for rock phosphate and super phosphate is given in Table 4. 1 g phosphate and 100 ml. extractant were shaken at the rate of 120 oscillations per minute. Longer times of shaking increase the amount of phosphate coming into solution from rock phosphate whereas solubility of super phosphate is unaffected by the time of shaking.

#### *Rate of shaking*

Most mechanical shakers have the facility to alter the rate of shaking. Table 5 gives the results obtained by altering the shaking rates. The rates were classed according to the number of oscillations per minute of the reaction flask in the shaker. 1 g sample and 100 ml. extractant were shaken for half an hour. On reducing the shaking rate to 80 oscillations per minute a 20 % decrease in solubility occurred for rock phosphate. Analytical procedures

which stipulate the rate of shaking are very scarce. Above data indicate the need to pay heed to the rate of shaking when analyses by different laboratories are compared.

It was observed that increasing the time and rate of shaking increased the solubility of rock phosphate. This suggests that equilibrium has not been reached in the above reactions. There are practical difficulties in increasing times and rates of shaking in order to obtain equilibrium between solid and solution phases. Further, different rock phosphates may require different reacting conditions in order to attain equilibrium. Yet equilibrium values per se may not be a satisfactory index of relative availability of phosphorus to plants. Therefore, for laboratory evaluation it seems sufficient to specify the times and rates of shaking irrespective of the attainment of equilibrium. The above results further demonstrate that while a certain flexibility is permissible in the procedure for the analysis of water soluble fertilizers, the procedure for the analysis of sparingly soluble materials such as rock phosphates must be standardised with respect to all detail and adhered to.

Keeping in mind the need for a simple, inexpensive and quick method for routine laboratory analysis of rock phosphate, it is suggested that 1g rock phosphate is shaken with 100 ml. citric acid in a 500 ml. Erlenmeyer flask for half an hour at a rate of about 120 oscillations per minute.

The above considerations also apply to other chemical analyses where an extractant is used to extract only a portion of an element or a compound from a given substance. Some such examples in soil analyses are determination of exchangeable cations and available phosphorus.

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EVALUATION OF ROCK PHOSPHATES USING CITRIC ACID

TABLE 1—Effect of changing solid to extractant ratio on % P O<sub>5</sub>

Weight of phosphate	Volume of extractant	Eppawela rock phosphate		Concentrated super phosphate	
		%P <sub>2</sub> O <sub>5</sub>			
g	ml				
0.5	100	6.99 (100)*	..	38.4 (100)	..
1.0	100	3.32 ( 47)	..	38.1 ( 99)	..
2.0	100	1.15 ( 16)	..	35.8 ( 93)	..
3.0	100	0.59 ( 8)	..	36.9 ( 96)	..
4.0	100	0.42 ( 6)	..	35.3 ( 92)	..

\*Percent of maximum.

TABLE 2—Effect of varying the amount of solid and extractant at the same ratio of solid to extractant on % P O<sub>5</sub>

Weight of phosphate	Volume of extractant	Eppawela rock phosphate		Concentrated super phosphate	
		%P <sub>2</sub> O <sub>5</sub>			
g	ml				
0.5	50	3.39 ( 99)*	..	36.3 ( 94)	..
1.0	100	3.42 (100)	..	38.1 ( 99)	..
2.0	200	3.26 ( 95)	..	38.6 (100)	..
3.0	300	2.33 ( 68)	..	37.8 ( 98)	..
4.0	400	2.19 ( 64)	..	37.5 ( 97)	..

\*Percent of maximum.

TABLE 3—Effect of size of reaction flask on % P<sub>2</sub>O<sub>5</sub>

Volume of flask	Eppawela rock phosphate		Concentrated super phosphate	
	%P <sub>2</sub> O <sub>5</sub>			
ml				
125	..	2.90 ( 77)*	..	34.8 ( 99)
500	..	3.75 (100)	..	35.0 (100)

\*Percent of maximum.

TABLE 4—Effect of time of shaking on % P<sub>2</sub>O<sub>5</sub>

Time of shaking	Eppawela rock phosphate		Concentrated super phosphate	
	%P <sub>2</sub> O <sub>5</sub>			
hr				
½	..	3.42 ( 86)*	..	37.5 (100)
1	..	3.65 ( 92)	..	37.5 (100)
1½	..	3.88 ( 98)	..	37.5 (100)
2	..	3.96 (100)	..	37.5 (100)

\*Percent of maximum.

**TABLE 5—Effect of rate of shaking on % P<sub>2</sub>O<sub>5</sub>**

<i>Rate of shaking</i> <i>Oscillations/</i> <i>minute</i>	<i>Eppawela rock</i> <i>phosphate</i>		<i>Concentrated</i> <i>super phosphate</i>	
	%P <sub>2</sub> O <sub>5</sub>			
200	..	3.56 (100)*	..	38.8 ( 99)
160	..	3.56 (100)	..	39.0 (100)
120	..	3.46 ( 97)	..	38.0 ( 97)
80	..	2.85 ( 80)	..	38.1 ( 98)

\*Percent of maximum.