

THE LIMITATIONS OF CITRIC SOLUBILITY AS A MEASURE OF AVAILABILITY OF ROCK PHOSPHATE

(Met opsomming in Afrikaans)

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Abstract

Rock phosphate is only partially soluble in two per cent citric acid according to the Wagner procedure. It is shown that the residue is soluble in a fresh solution of citric acid and available to plants. Rock phosphates of sedimentary origin are almost completely soluble in four successive extraction with 2 per cent citric acid compared with approximately 25 per cent for igneous apatites. Pot experiments are described which illustrate that citric solubility cannot be correlated with availability. Any solubility for a rock phosphate in citric acid can be obtained by varying the weight taken for the test.

Introduction

The use of citric acid as a criterion of availability was introduced by Professor Paul Wagner (1899) of Darmstadt and used by him to detect adulteration in basic slag. As the result of an extensive series of pot experiments he came to the conclusion that the availability of basic slag was directly correlated with its solubility in a two per cent citric acid solution.

The correlation was contested by Soxhlet but the results of subsequent pot experiments conducted by several German experimental stations were considered by the advocates of the method in Great Britain to justify Wagner's conclusions. Robertson & Dickinson (1923) criticized this finding on the grounds that the diminution in yields was not proportional to the decrease in solubility and the method exaggerated the inferiority of slags of low solubility.

Robertson (1914) pointed out that the solubility of rock phosphate in citric acid cannot be interpreted in terms of availability. From the results of a series of pot experiments he showed that equal weights of phosphorus applied in the form of Tunisian rock phosphate (40 per cent citric solubility) and a basic slag (95 per cent citric solubility) gave almost identical yields. He concluded that citric acid is worthless as a means of judging the relative value of phosphatic manures to the plant.

Robertson's work was continued by other workers in Great Britain. Vanstone (1926) demonstrated by means of an extensive series of pot experiments that the citric solubility test has no significance in the case of mineral phosphates. Cooke (1963) of the Rothamsted Experimental Station pointed out that no good solubility test exists for rock phosphates. It is more useful to know the origin of the material and its behaviour in pot and field experiments than to have solubility data.

Wagner's method was adopted in the United Kingdom

in 1906 but appears to have been discarded later on as the Fertilizers and Feeding Stuffs Act of 1926 recognizes only water solubility and total phosphorus. Many in Great Britain regard water-soluble phosphorus as the available phosphorus in a fertilizer but this is not specifically stated as such in the Act. For rock phosphate it is only necessary to have a statement of the total phosphorus content and the fineness on a prescribed sieve.

Hamence & Taylor (1950) have suggested that the citric acid method may be revived for basic slag. They point out that a slag which dissolves readily in two per cent citric acid under standard conditions is more likely to become available as a plant food in the soil than a slag which is so resistant and inert that it is only slightly soluble in citric acid under the same conditions.

In the Republic the Fertilizers and Feeding Stuffs Act of 1910 (Juritz, 1911) extended the use of the Wagner method to all phosphatic fertilizers, including rock phosphate. The regulation has not been changed and the original Wagner method is, therefore, the official method for rock phosphate in the Republic of South Africa to-day.

The method is as follows

Five grams of the slag shaken with 495 ml of two per cent citric acid for half-an-hour in an end-over-end shaker at 30 revolutions per minute. It is identical with Wagner's original formulation.

Methods, procedures and results

The solution of rock phosphate in citric acid

General

It is not the purpose of this paper to discuss the physical chemistry of the solution of rock phosphate in citric acid. In general it is an example of heterogeneous equilibria of a complex nature. Kalpagé (1954) after an extensive study of Gafsa rock confirmed that when an excess of rock phosphate remains undissolved in citric acid the resulting solution approaches a state of equilibrium with the residue of fluorapatite and fluorspar. The equilibrium state for Gafsa rock is characterized by the relationship

$$2\text{pH} - \frac{3}{2}\text{pCa} - \text{pH}_2\text{PO}_4 = 1.8$$

where pCa and pH_2PO_4 are the negative logarithms of the activities of the calcium ions and dihydrogen phosphate ions respectively.

It can be shown experimentally that equilibrium is reached when an excess of approximately 70 per cent of the phosphoric oxide in Langebaan rock phosphate remains undissolved in citric acid.

Five grams of finely ground Langebaan rock (21 per cent P₂O₅) were shaken with 495 ml of two per cent citric acid for 30 minutes in accordance with the Wagner method. The filtrate was found to be 1.8 per cent with respect to citric acid. Five grams of the residue were shaken with fresh solution of 1.8 per cent citric acid in accordance with the Wagner procedure. The results obtained are shown in Table 1 and illustrate that

- (1) A state of equilibrium was reached when 68.2 per cent remained undissolved.
- (2) 32.8 per cent of the residue was soluble in 1.8 per cent citric acid.

TABLE 1. Solubility of Langebaan rock in citric acid

Sample	Weight taken (g)	Total P ₂ O ₅ %	Citric acid strength %	Citric soluble P ₂ O ₅ %	Citric solubility %
Original	5.0	21.4	2.0	6.80	31.8
Residue	5.0	18.0	1.8	5.90	32.8

Note: Citric solubility = Citric soluble P₂O₅ to total P₂O₅ ratio expressed as a percentage.

When a rock phosphate is shaken with citric acid according to the Wagner procedure only a percentage of the phosphoric oxide dissolves. Thirty two per cent dissolves in the case of Langebaan rock (21 per cent P₂O₅) and creates the impression that the remaining 68 per cent is insoluble and, therefore, unavailable to plants. (See Pot Experiments below).

Successive extractions

Robertson (1914) found that field experiments on rock phosphates were more successful than their solubility in two per cent citric acid suggested. He showed that all the phosphoric oxide was removed by four to five successive extractions with two per cent citric acid which explained the anomaly.

Four successive two per cent citric acid extractions were made in our laboratory of eleven different mineral phosphates including several well-known foreign varieties. After each extraction the solution was filtered and the residue again extracted with a fresh 495 ml of two per cent citric acid.

To make the results comparable, the extractions were carried out within the same screening range. The fraction -200+350 mesh was chosen as several of the samples obtained from foreign sources were very finely ground when received.

The results are illustrated graphically in Figure 1.

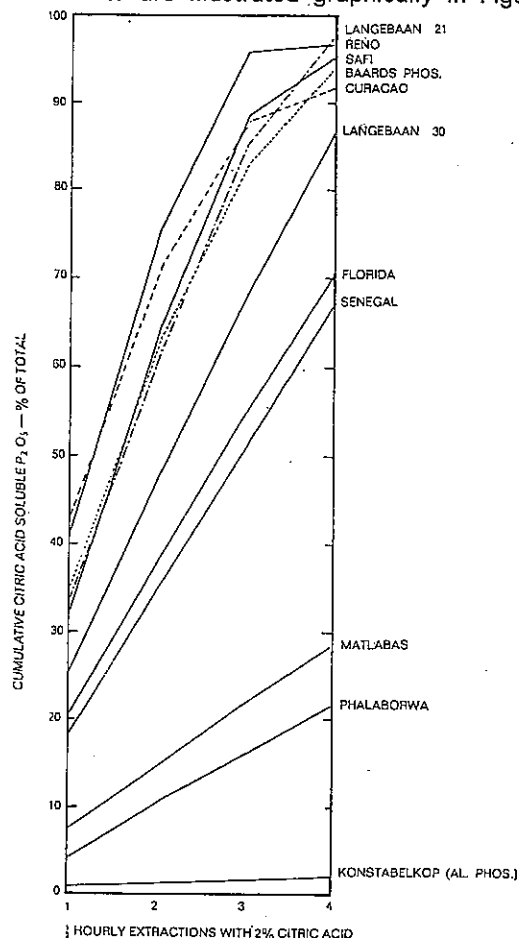


Figure 1 — Phosphoric oxide removed by four successive extractions

It is interesting to note that Phalaborwa, Matlabas (crystalline apatites) and Konstabelkop phosphates (aluminium phosphate) exhibited very different properties from the remaining eight samples which are fluorapatites of sedimentary origin. Four successive extractions removed only 28.9 per cent, 21.8 per cent and 2.3 per cent of total P₂O₅ in the case of Phalaborwa, Matlabas and Konstabelkop ores respectively compared with 88 per cent for Langebaan rock (30 per cent P₂O₅).

Hoffman & Breen (1964) carried out similar studies in the United States of America on 14 mineral phosphates representing well known varieties or sources of phosphate rock, including Phalaborwa, Virginia and Kola apatites and an aluminium phosphate from the

TABLE 2. Phosphoric oxide removed by four successive extractions

Variety or Source of Rock	Total P ₂ O ₅	% Progressive citric solubility							
		1st Extract		2nd Extract		3rd Extract		4th Extract	
		CS	%	CS	%	CS	%	CS	%
Curacao	31.6	13.3	42.1	9.3	71.5	5.3	88.3	1.0	91.5
Reno (Gafsa)	30.0	12.3	41.0	10.5	76.0	6.2	96.6	0.8	97.4
Safi (Egyptian)	33.0	10.6	32.2	10.6	64.4	8.1	88.9	2.3	95.9
Langebaan Concentrate	30.1	7.6	25.3	6.8	47.9	6.2	68.5	5.6	87.1
Florida Pebble Concentrate	35.3	7.3	20.6	6.4	38.7	5.8	55.2	5.5	70.8
Senegal	37.4	6.8	18.2	6.5	35.6	6.1	51.9	5.8	67.4
Langfos 21%	20.2	6.6	32.7	5.9	61.9	4.8	85.7	2.5	98.1
Baards Quarry (Langebaanweg)	16.7	5.8	34.7	4.8	63.4	3.3	83.2	2.0	95.2
Matlabas (Transvaal)	36.0	2.8	7.8	2.6	15.0	2.6	22.2	2.4	28.9
Phalaborwa Concentrate	39.2	1.6	4.1	2.5	10.5	2.3	16.4	2.1	21.8
Konstabelkop (Aluminium phosphate)	34.4	0.3	0.9	0.1	1.2	0.2	1.8	0.2	2.3

Connetable Islands. Their results confirm our findings. They conclude that successive extractions group rocks according to their solubility more effectively than data based on a single extraction.

Weight of material taken

Many workers have shown that the percentage of phosphoric oxide extracted by the Wagner method from rock phosphate is in inverse ratio to the weight taken. They demonstrated that if the weights taken were small enough, one extraction removed almost 100 per cent. The effect is shown in Table 3 for Langebaan Rock.

Vanstone (1925) pointed out that basic slags for which the Wagner method was developed differ greatly in this respect. In basic slags, solubility is usually independent of the weight taken and the ratio soluble phosphate to total phosphate is approximately constant. Figures for a sample of basic slags are included in the table and show this relationship.

TABLE 3. Citric solubility as a function of weight taken

Weight taken (g)		Citric solubility (%)	
Langebaan rock (21% P ₂ O ₅)	Basic slag	Langebaan rock (21% P ₂ O ₅)	Basic slag
1.00	1.00	77.4	95.7
3.00	3.00	46.0	89.1
5.00	5.00	31.8	87.4
6.00	6.00	27.9	87.0
8.00		21.8	
10.00		18.0	

It appears that the choice of five grams is fortuitous and that any desired result can be obtained for rock phosphate by simply varying the weight taken.

Depression of solubility by lime (calcium carbonate)

Rock phosphate deposits often occur in limestone regions and it is obvious that the commercial product will contain varying amounts of free calcium carbonate.

To illustrate the effect of calcium carbonate on finely ground Langebaan rock (21 per cent P₂O₅), four separate five gram samples containing increasing amounts of CaCO₃ were shaken with two per cent citric acid according to the Wagner procedure. The results obtained are shown in Table 4.

TABLE 4. Depression of citric solubility by lime (calcium carbonate)

Langebaan Rock (g)	Calcium carbonate added (g)	Citric soluble P ₂ O ₅ (%)	Citric solubility (%)
5	Nil	7.60	36.2
5	0.05 (1%)	7.05	33.6
5	0.25 (5%)	6.10	29.0
5	0.50 (10%)	5.20	24.0
5	0.75 (15%)	4.50	21.4
5	1.00 (20%)	3.80	18.1

Pot experiments

Pot experiments were carried out in a green house at Bellville, Cape, to compare

(1) The availability of the citric acid insoluble residue of finely ground Langebaan rock with that of the material.

- (2) Availability with citric solubility of finely ground Langebaan rock in the presence of lime (calcium carbonate).
- (3) Availability with citric solubility of finely ground Reno (Gafsa) and Langebaan rock and superphosphate when applied at
 - (a) equal rates.
 - (b) equal totals of phosphoric oxide.

(1) Availability of citric acid insoluble residue.

In Table 1 it was shown that the insoluble residue of Langebaan rock is soluble in citric acid. A pot experiment was conducted to determine the availability of this residue to the plant.

TABLE 5. Analysis of Langebaan rock and insoluble residue used in the experiment

	Original (%)	Residue (%)
Total phosphoric oxide (P ₂ O ₅)	20.10	17.10
Citric soluble phosphoric oxide (P ₂ O ₅)	7.55	6.05
Citric solubility	37.56	35.38
Calcium oxide (CaO)	29.40	25.76
Matrix carbon dioxide (-CO ₂)	2.59	2.07
Fluorine (F)	1.56	1.31
Insolubles	39.80	48.58

Physical State: 18 per cent retained on 100 mesh and 50 per cent retained on 200 mesh.

Free (adventitious) calcium carbonate was removed from the original sample by shaking with a solution of triammonium citrate at pH 8.1. Two soils from the Fesantekraal area in the Cape were selected for the experiment.

TABLE 6. Analysis of soils used in the experiment

Type	No 1	No 2
	Gravelly loam	Sandy loam
Phosphorus soluble in 0.1N HCl	2.2 ppm	7.0 ppm
Phosphorus soluble in NH ₄ F-.025N HCl	2.9	7.6
Potassium (exchangeable)	0.003%	0.012%
Calcium (")	0.014%	0.045%
Magnesium (")	0.002%	0.008%
Hydrogen (")	nil	1.3 me
pH	5.7	5.2

The soils were packed in 60 lb pots. Each treatment was replicated five times. The pots were sown to mealies (Early Wisconsin) on 3rd January, 1965 and thinned at intervals until six plants were left. These were harvested above ground on 19th March, 1965. The stems and leaves were weighed, dried at 65°C, weighed again and phosphorus determined. The results given in Table 7 are the average for five pots of each treatment.

TABLE 7. Availability of insoluble residue of Langebaan rock

Treatment	Control	Original	Residue
Weight added (g)	Nil	5.80	6.80
Total P added (mg)	Nil	507.5	507.5
cs P added (mg)	Nil	191.1	179.6
Citric solubility %	—	37.6	35.4
Soil No 1 — Dry weight (g)	26.4	54.8	58.0
P absorbed on dry basis (mg)	26.6	45.6	46.4
Soil No 2 — Dry weight (g)	95.2	110.5	102.8
P absorbed on dry basis (mg)	85.9	101.7	104.9

The experiment demonstrates clearly that the difference in availability between the original rock and the citric acid insoluble residue is negligible. If the Wagner method presented a true reflection of availability this residue should be unavailable to plants.

(2) Availability of Langebaan rock in the presence of free lime (calcium carbonate).

It was shown in Table 4 that the presence of free calcium carbonate depresses the citric solubility of Langebaan rock. Ten per cent calcium carbonate reduces the citric acid soluble phosphoric oxide (P₂O₅) from 7.60 per cent to 5.2 per cent and the percentage solubility of P₂O₅ from 36.2 to 24.0. A pot experiment was conducted with Langebaan rock in the presence of ten per cent free calcium carbonate to assess the significance of this depression in terms of availability.

The conditions of the experiment and the soils used were identical to those in (1) above.

TABLE 8. Availability of Langebaan rock in presence of free lime

Treatment	Control	No CaCO ₃	0.58 g CaCO ₃
Weight added (g)	Nil	5.80	5.80
P added (mg)	Nil	507.5	507.5
cs P added (mg)	Nil	191.1	131.5
Citric solubility %	—	37.6	25.9
Soil No 1 — Dry weight (g)	26.4	54.8	53.2
P absorbed on dry basis (mg)	26.6	45.6	41.6
Soil No 2 — Dry weight (g)	95.2	110.5	112.5
P absorbed on dry basis (mg)	85.9	101.7	103.5

The result of this experiment demonstrate that the depression in citric solubility by free calcium carbonate does not necessarily indicate a corresponding loss in availability. No allowance is made for this factor in the official method. It is another example where the Wagner method when applied to rock phosphate breaks down.

(3) Availability as a function of citric solubility at equal rates of fertilizer application and equal totals of phosphoric oxide.

TABLE 9. Analysis of fertilizers used in the experiment

Fertilizer	Total P ₂ O ₅ %	Citric soluble P ₂ O ₅ %	Citric solubility %
Super-phosphate	19.1	19.1	100.0
Reno rock phosphate	28.6	12.4	43.4
Langebaan rock phosphate	21.1	7.0	33.2

Physical state: (1) Superphosphate: powder and applied as such
(2) Reno: 90% minus 325 mesh (as received)
(3) Langebaan: milled to 90% minus 325 mesh

Note: Free CaCO₃ was not removed from Reno and Langebaan rock.

The soil was a dark sandy loam obtained from George, Cape.

TABLE 10. Analysis of soil used in the experiment

Phosphorus — soluble in 0.1N HCl	5.4 ppm
Phosphorus — soluble in NH ₄ F — .025 N HCl	5.4
Potassium — (exchangeable)	0.009%
Calcium — (")	0.072%
Magnesium — (")	0.017%
Hydrogen — (")	3.6 me/100 g
Total base exchange capacity	8.9 me/100 g
Degree base saturation	59%
pH	5.2

The soil was packed in 60 lb pots. Each treatment was replicated eight times. The pots were sown to wheat (Kenia Sökkies) in June, 1963. The experiment was allowed to run to completion. Ears and chaff were harvested in November, weighed at 65°C, weighed again and phosphorus determined.

The respective treatments and the results of the experiment are given in Tables 11 (a) and (b). Dry weights and P absorbed represent the average for eight pots of each treatment.

TABLE 11 (a) At equal weights of fertilizer application (500 lb per morgen)

Treatment	Control	Super	Reno	Langebaan-rock
Weight added (g)	Nil	3.5	3.5	3.5
Total P added (mg)	„	290	437	323
cs P added (mg)	„	290	190	113
Citric solubility %	„	100.0	43.4	35.0
Dry weight of 36 plants (g)	19.7	66.8	61.1	61.7
P absorbed on dry basis per pot (mg)	17.61	98.65	96.79	85.28

TABLE 11 (b) At equal weights of total phosphorus

Treatment	Control	Super	Reno	Langebaan-rock
Weight added (g)	Nil	3.5	2.4	3.2
Total P added (mg)	„	290	300	290
cs P added (mg)	„	290	130	102
Citric solubility %	„	100.0	43.4	35.2
Dry weight of 36 plants (g)	19.7	66.8	58.8	58.7
P absorbed on dry basis per pot (mg)	17.61	98.65	88.0	80.24

The experiment illustrates that availability is not a function of citric solubility.

Summary and conclusions

The development and application of Wagner's method for the determination of the availability of phosphatic fertilizers is reviewed. Experimental results are given which show that

- (a) The citric acid insoluble residue of Langebaan rock phosphate is soluble in a fresh solution of citric acid.
- (b) Four successive extractions of a variety of mineral phosphates with 2 per cent citric acid removed
 - (i) 68 per cent to 98 per cent of the phosphoric oxide in fluorapatites of sedimentary origin (rock phosphates). Langebaan rock falls in this category.
 - (ii) 22 per cent to 28 per cent of the phosphoric oxide in crystalline apatites, e.g. Phalaborwa phosphate.
 - (iii) 2.3 per cent of the phosphoric oxide in an aluminium phosphate.
- (c) Weight of material taken affects the citric solubility of Langebaan rock. Any solubility can be obtained by varying the weight taken.
- (d) Free (adventitious) calcium carbonate (lime) has the effect of depressing the citric solubility of Langebaan rock.

Results of a series of pot experiments carried out to interpret some of the above findings in terms of availability are also given.

- (a) The difference in availability between the citric acid insoluble residue of Langebaan rock and that of the original material is negligible.
- (b) The availability of a rock phosphate to plants is not a function of its solubility in two per cent citric acid according to the Wagner method. This finding is in agreement with the results obtained by workers overseas.

Registration of an acceptable rock phosphate fertilizer should be confined to its total phosphoric oxide and fineness on a prescribed screen.

Opsomming

DIE BEPERKINGS VAN SITROENSUUR-OPLOSBAARHEID AS 'N MAATSTAF VAN TOEGANKLIKHEID VAN ROTSFOSFAAT

Volgens die Wagner-metode is rotsfosfaat slegs gedeeltelik oplosbaar in 'n twee persent sitroensuur-oplossing. Dit word bewys dat die residu oplosbaar is in 'n vars sitroensuur-oplossing en beskikbaar is aan plante. Rotsfosfate van sedimentêre oorsprong is feitlik heeltemal oplosbaar in vier agtereenvolgende ekstraksies met twee persent sitroensuur in vergelyking met die ongeveer 25 persent oplosbaarheid van stollings-apatiete. Poteksperimente word beskryf wat aandui dat sitroensuur-oplosbaarheid nie gekorreleer is met toeganklikheid nie. Enige oplosbaarheid van 'n rotsfosfaat in sitroensuur kan verkry word deur verskillende ander gewigte te neem vir die bepaling.

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