Effect of Shaking Procedures on the Neutral Ammonium Citrate Soluble Phosphate Fraction in Fertiliser Materials

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ABSTRACT

The effect of four types of shaker, extraction time and temperature on the quantity of phosphate extracted by neutral ammonium citrate was evaluated at two research laboratories. Six unprocessed phosphate rocks, and five partially acidulated and four fully acidulated phosphate fertilisers were investigated. Compared with the more than 10-fold variation in the solubility of the two reactive phosphate rock materials, Sechura and North Carolina, that resulted from using different types of shaker, the solubility of the unreactive phosphate rock materials and the partially and fully acidulated phosphate fertilisers in citrate was influenced to a much smaller degree by the action of the shaker. Sechura was less soluble in citrate than all four unreactive phosphate rock materials when either of the two horizontal shakers were used. This is totally at odds with the documented differences in the 'chemical reactivity' and agronomic effectiveness of these phosphate rock materials. Not until a wrist-action shaker was used did the solubility of Sechura and North Carolina exceed that of the unreactive materials and approach that obtained with a full end-over-end shake. The neutral
ammonium citrate procedure needs to include a more precise definition of the type of shaker and its speed. In laboratories where temperature-controlled extraction is not available, a 24-h shake at 20°C using an orbital or end-over-end apparatus could be an alternative to the standard 1-h extraction at 65°C.

Key words: Citrate soluble phosphate, phosphate rock, partially acidulated phosphate rock, single superphosphate, temperature, extraction, time of shaking.

INTRODUCTION

Neutral ammonium citrate is one of a number of chemical extractants which has been used extensively to determine the chemical quality of processed phosphate (P) fertilisers (Hoffman and Mager 1963; Hoffman and Breen 1964) and to assess the 'chemical reactivity' of phosphate rock (PR) materials (Chien and Hammond 1978; Mackay et al 1984). The neutral ammonium citrate procedure stipulates that during 1 h of extraction at 65°C the material under evaluation must remain continually dispersed in the citrate solution (AOAC 1980). The type, action and speed-setting of the shaker are not, however, specified.

In a cooperative research programme investigating the chemical and physical characteristics of a wide range of PR materials of varying reactivity (Syers et al 1986), different results for the amounts of P extracted by the neutral ammonium citrate method from PR materials were obtained between the two laboratories involved (Brown M W pers comm). In one laboratory, an end-over-end shaker and in the other a reciprocal (horizontal) water bath shaker had been used. The speed setting of the horizontal shaker was set according to the neutral ammonium citrate procedure, which stipulated that the material under evaluation must remain continually dispersed in the citrate solution during the 1-h shake. In the absence of any prior study, it had been assumed that as long as the dispersion of the material in the citrate solution was continually maintained, to avoid diffusion-limited dissolution of the PR, the action of the shaker should have little or no effect. The lack of agreement of results between the two laboratories when different shakers were used suggested that this assumption may have been incorrect.

Since a wide range of shakers with variable speed settings are available, the present study was initiated to investigate the effect that different types of shaker and their speed settings had on the amounts of P extracted by neutral ammonium citrate from a range of unprocessed PR materials and partially and fully acidulated phosphate fertilisers. The effect of time and temperature on the amounts of P extracted by this extractant was also studied.

MATERIALS AND METHODS

Phosphate materials

A summary of the origin and total phosphorus contents of each of the 15 phosphate fertiliser materials is presented in Table 1.
<table>
<thead>
<tr>
<th>Phosphate material</th>
<th>Abbreviation</th>
<th>Origin</th>
<th>Total P (%) absolute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Christmas Island phosphate rock</td>
<td>Xmas</td>
<td>Christmas Island, South Pacific</td>
<td>15.7</td>
</tr>
<tr>
<td>Nauru Island phosphate rock</td>
<td>Nauru</td>
<td>Nauru Island, South Pacific</td>
<td>16.6</td>
</tr>
<tr>
<td>Jordanian phosphate rock</td>
<td>Jordan</td>
<td>Jordan</td>
<td>13.9</td>
</tr>
<tr>
<td>North Florida phosphate rock</td>
<td>N Florida</td>
<td>North Florida, USA</td>
<td>14.6</td>
</tr>
<tr>
<td>North Carolina phosphate rock</td>
<td>N Carolina</td>
<td>North Carolina, USA</td>
<td>13.3</td>
</tr>
<tr>
<td>Sechura phosphate rock</td>
<td>Sechura</td>
<td>Sechura Desert, Peru</td>
<td>13.8</td>
</tr>
<tr>
<td>Partially acidulated Jordanian phosphate rock</td>
<td>PAPR J</td>
<td>Experimental material, FLRC, NZ</td>
<td>18.5</td>
</tr>
<tr>
<td>Partially acidulated North Carolina phosphate rock</td>
<td>PAPR NC</td>
<td>Experimental material, FLRC, NZ</td>
<td>17.8</td>
</tr>
<tr>
<td>Partially acidulated North Carolina phosphate rock plus elemental sulphur</td>
<td>PAPR NC + S</td>
<td>Commercial product, East Coast Fertilizer Co, NZ</td>
<td>15.6</td>
</tr>
<tr>
<td>Single superphosphate Jordanian phosphate rock physical mix</td>
<td>Longlife J</td>
<td>Experimental material, FLRC, NZ</td>
<td>11.8</td>
</tr>
<tr>
<td>Single superphosphate North Carolina phosphate rock physical mix</td>
<td>Longlife NC</td>
<td>Experimental material, FLRC, NZ</td>
<td>11.5</td>
</tr>
<tr>
<td>Single superphosphate</td>
<td>SSP 1</td>
<td>Commercial product, NZ</td>
<td>8.0</td>
</tr>
<tr>
<td>Single superphosphate</td>
<td>SSP 2</td>
<td>Commercial product, NZ</td>
<td>9.7</td>
</tr>
<tr>
<td>Single superphosphate made from Christmas Island phosphate rock</td>
<td>SSP Xmas</td>
<td>Experimental material, FLRC, NZ</td>
<td>10.6</td>
</tr>
<tr>
<td>Single superphosphate made from Nauru Island phosphate rock</td>
<td>SSP Nauru</td>
<td>Experimental material, FLRC, NZ</td>
<td>10.2</td>
</tr>
</tbody>
</table>
The materials used for this investigation were:

(a) Four unreactive phosphate rocks from Christmas and Nauru Islands and Jordan and North Florida.
(b) Two reactive phosphate rocks, one from North Carolina and the other from the Sechura deposit in Peru.
(c) Three partially acidulated phosphate rocks made from Jordan and North Carolina rocks. These products were made by adding 30% of the theoretical amount of phosphoric acid required to fully acidulate the phosphate rock. At this acid/rock ratio approximately 15–20% of the total P in the original phosphate rock is acidulated.
(d) Two single superphosphate/phosphate rock physical mixtures using Jordan and North Carolina phosphate rocks. These materials (known as 'longlife' in New Zealand) were manufactured by first acidulating a blend of Nauru and Christmas Island rocks with sulphuric acid in a similar manner to the production of single superphosphate. However, a slightly higher acid/rock ratio (0.6 rather than 0.58) was used, and the Jordan or North Carolina rock was added immediately ex-den in the ratio 30% phosphate rock to 70% single superphosphate by weight. The product was then granulated and stored.
(e) Two of the single superphosphate products were commercial products and two were experimental materials made at the Fertilizer and Lime Research Centre, Massey University.

Samples (250 g) of each 15 phosphate sources were ground to pass a 250-μm sieve before analysis.

Shaking methods

Four types of mechanical shaker were used:

(a) end-over-end at 30 revolutions per minute;
(b) orbital at 155 and 255 oscillations per minute;
(c) wrist action at approximately 100 oscillations per minute;
(d) reciprocal action (linear) at 100 oscillations per minute.

In addition, the investigations included:
(e) a vigorous handshake for 30 s every 15 min;
(f) no shake at all.

Time and temperature of extraction

The standard 1-h shake at 65°C was used for all shaking techniques. In addition the end-over-end method was investigated for:

(a) 2, 6, 16 and 24 h at 65°C; and
(b) 16 and 24 h at 20°C.

The orbital method was also evaluated for 1, 16 and 24 h at 20°C.
A summary of the different types of shakers, their speed settings and the different extraction times and temperatures is given in Table 2.

**Determination of ammonium citrate soluble phosphate**

The study was conducted at two separate laboratories: the Fertilizer and Lime Research Centre, Massey University, Palmerston North, and Ruakura Agriculture Centre, Hamilton. The latter is part of the MAFTech Division of the Ministry of Agriculture and Fisheries.

The neutral ammonium citrate soluble P fraction was determined as follows. At the Massey laboratory, duplicate 0.4-g samples were placed in 50-ml centrifuge tubes and extracted with 40 ml of neutral ammonium citrate solution which had a specific gravity of 1.09 at 20°C. For extractions at 65°C, the citrate solution was preheated. At the end of the shaking period, samples were immediately centrifuged at $12,064 \times g$ for 3 min and filtered through a 0.45-μm millipore filter. The concentration of P in the extract after dilution was determined by the molybdenum-blue method (Murphy and Riley 1962).

At the Ruakura laboratory, duplicate 0.5-g samples of each P source were placed in 100-ml conical flasks and extracted with 50 ml of citrate solution. Again the solution was preheated when necessary. At the end of the shaking period samples were immediately filtered through a Whatman No 2 paper. The concentration of P in the extract after dilution was determined by the vanadomolybdate method (Barney et al. 1959).

The amounts of P extracted by the citrate solution from 14 of the P sources following a 16-h orbital shake (255 oscillations per minute) at 20°C served as a standard against which the procedures of the two research laboratories were compared.

**TABLE 2**

<table>
<thead>
<tr>
<th>Shaking procedure</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>End-over-end</td>
<td>$65^a$</td>
<td>1, 2, 6, 16, 24</td>
</tr>
<tr>
<td>(30 revolutions min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>End-over-end</td>
<td>$20^a$</td>
<td>16, 24</td>
</tr>
<tr>
<td>(30 revolutions min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orbital</td>
<td>$65^a$</td>
<td>1</td>
</tr>
<tr>
<td>(155 oscillations min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orbital</td>
<td>$20^{a,b}$</td>
<td>1, 16, 24</td>
</tr>
<tr>
<td>(255 oscillations min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reciprocal</td>
<td>$65^b$</td>
<td>1</td>
</tr>
<tr>
<td>(100 oscillations min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wrist-action</td>
<td>$65^b$</td>
<td>1</td>
</tr>
<tr>
<td>Handshake</td>
<td>$65^a$</td>
<td>1</td>
</tr>
<tr>
<td>No shake</td>
<td>$65^a$</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ Analysis conducted at Fertilizer and Lime Research Centre.

$^b$ Analysis conducted at Ruakura Agriculture Centre.
compared. Good agreement was obtained between the two centres for the amounts of P extracted from the six PR materials following a 16-h orbital shake at 20°C despite the use of different extraction, filtration and dilution procedures and different colorimetric methods. When the comparison was extended to include the partially and fully acidulated P fertilisers, however, the solubility of these materials was consistently higher (2–6%) from the Ruakura Agriculture Centre. The analysis of fertiliser materials at both laboratories was completed over a short period to minimise the possible effects that slow reversion has on the citrate soluble P fraction in the partially and fully acidulated phosphate fertilisers. One exception was the analysis used to compare the two laboratories’ procedures. There was a 7-month interval between the time when the solubility of the partially and fully acidulated materials in citrate following a 16-h orbital shake at 20°C was measured at Ruakura and the time when the same analysis was completed at the Massey laboratory. The lower citrate solubility determinations of the acidulated materials at the Massey laboratory may reflect this slow reversion and explain the small systematic differences between laboratories for the processed materials.

RESULTS AND DISCUSSION

Type of shaker

The type of shaker and the action of the shaker had a much greater effect on the amounts of P extracted by the neutral ammonium citrate method from the reactive PR materials (Sechura and North Carolina) than from the four unreactive (Christmas, Nauru, Jordan and North Florida) materials (Fig 1a). As reactive PR

![Graph](image-url)

Fig 1. The effect that the type of shaker had on solubility of (a) phosphate rocks, (b) partially acidulated, and (c) fully acidulated phosphate fertilisers in citrate solution following the standard 1-h shake at 65°C.
materials, Sechura and North Carolina are suitable as direct application P fertilisers (Quin 1981; Gregg et al. 1987, 1988) while the four unreactive PR materials included in this study are of little agronomic value when applied directly to soils. With the no-shake, handshake and the two horizontal (orbital and reciprocal) shakers, less than 1.0% absolute P in the Sechura and North Carolina PRs was extracted. In fact the solubility of Sechura following a 1-h orbital or reciprocal shake was much less than
that of the four unreactive materials. The solubility of North Carolina was only marginally better than that of Sechura with the two horizontal shakers. The ranking of the six PR materials, based on their solubility in neutral ammonium citrate after a 1-h horizontal shake (Fig 1a), is totally at odds with the documented differences in the 'chemical reactivity' and agronomic effectiveness of these PR materials (Chien and Hammond 1978; Mackay et al 1984). Not until a wrist-action shaker, which travels through one-third of a revolution, was used did the amounts of P extracted from the two reactive PR materials exceed that of the unreactive PR materials and approach that obtained with a full end-over-end shake (Fig 1a).

The marked effect that the type of shaker had on the amount of P extracted by the citrate method is further highlighted by the difference in the solubility of two North Carolina samples of differing particle size composition following a 1-h horizontal (orbital) or end-over-end (wrist-action) shake (Table 3). The solubility of the coarser North Carolina II sample was increased more than fourfold when an end-over-end shaker was used in place of a horizontal shaker, while the solubility of the finer PR sample was influenced to a lesser degree by the action of the shaker. This was despite the fact that the speed setting or number of oscillations per minute chosen at which to run the horizontal shaker met the requirements set out in the neutral ammonium citrate procedure (AOAC 1980). The procedure states that during the 1-h shake the material under evaluation must remain continually dispersed in the citrate solution. Clearly the assumption made earlier that, provided this requirement was met, the action of the shaker should have little or no effect on the solubility of the PR was in fact incorrect. It would appear that the agitation with a horizontal shaker was insufficient to prevent localised saturation. This in turn would prevent potentially soluble material from dissolving. This was no more apparent than with Sechura and North Carolina, the two reactive PR materials. To avoid potential problems which could arise in future, a more precise definition of the type of shaker and its speed needs to be written into the neutral ammonium citrate procedure.

Compared with the more than 10-fold variation in the solubility of the phosphate rock materials that resulted from using different types of shaker during the standard 1-h shake at 65°C (Fig 1a), the type of shaker had a very minor effect on the

<table>
<thead>
<tr>
<th>Phosphate rock</th>
<th>Particle size (μm)</th>
<th>Total P extracted by:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 500</td>
<td>&lt; 250</td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>North Carolina I</td>
<td>99.9</td>
<td>97.0</td>
</tr>
<tr>
<td>North Carolina II</td>
<td>96.7</td>
<td>61.7</td>
</tr>
</tbody>
</table>

a Sample used in the present study and described in Table 1.
b Used in a previous study (Syers et al 1986).
solubility of the partially (Fig 1b) and fully (Fig 1c) acidulated phosphate fertilisers. A vigorous 30-s handshake every 15 min appears to be a suitable substitute for assessing the solubility or chemical quality of the partially and fully acidulated phosphate fertilisers in neutral ammonium citrate where an end-over-end shaker is not available. However, this alternative approach is totally unacceptable as a shaking technique when the evaluation includes phosphate rock materials of varying reactivity.

**Time and temperature of extraction**

All phosphate rock materials displayed a higher solubility when the extraction time on the end-over-end shaker at 65°C was increased in steps to 24 h (Fig 2a). Also in every case there was a high rate of increase in solubility between 1 and 2 h indicating that the standard 1-h shake should be exactly 60 min to achieve consistent results.

In contrast the increased extraction times have little effect on the solubility of partially or fully acidulated materials (Figs 2b,c).

Lengthening the time of extraction at 20°C from 1 to 16 h with the orbital shaker resulted in a very marked increase in the amounts of phosphate extracted from the PR materials (Fig 3a), and a much lesser effect on the solubility of the partially (Fig 3b) and fully (Fig 3c) acidulated phosphate fertilisers. Extending the time of extraction from 16 to 24 h with either an orbital (Fig 3) or end-over-end (Fig 4) shaker had only a small effect on the amounts of P extracted at 20°C from the PR materials, and little or no effect on the solubility of the partially and fully acidulated phosphate fertilisers.

The convenience associated with the extraction of phosphate fertilisers at room temperature (20°C) was the main reason for including an investigation of the effect of temperature on the amounts of P extracted by the neutral ammonium citrate. The amounts of P extracted from all phosphate materials at 20°C during a 16- and 24-h orbital (Fig 3) or end-over-end (Fig 4) shake approached the amounts of P extracted at 65°C with the standard 1-h end-over-end shake (Fig 1). In laboratories in which a wrist-action or end-over-end water bath shaker is not available, an orbital or end-over-end shaker operating at room temperature (20°C) appears to offer a suitable substitute for the standard 1-h end-over-end shake at 65°C, provided the time of extraction is 24 h.

**SUMMARY AND CONCLUSIONS**

Despite setting the speed of the two horizontal (orbital and reciprocal) shakers sufficiently fast enough to ensure that all the phosphate fertiliser materials evaluated remained continually dispersed in the neutral ammonium citrate solution during the standard 1-h shake, the amount of P extracted by the citrate solution from the reactive phosphate rock materials using these two shakers was much less than that obtained with an end-over-end shaker (Fig 5). In sharp contrast, the solubility of the unreactive phosphate rocks and the partially and fully acidulated phosphate fertilisers was influenced to only a minor degree by the action of the shaker (Fig 5). The neutral ammonium citrate procedure needs to include a more precise definition
Fig 2. The effect that extraction time had on solubility of (a) phosphate rocks, (b) partially acidulated, and (c) fully acidulated phosphate fertilisers using an end-over-end shaker at 65°C.
Effect of shaking on quantity of phosphate extracted

(c) Fully Acidulated

Fig 2—contd

(a) Phosphate Rocks

Fig 3. The effect that extraction time had on solubility of (a) phosphate rocks.
Fig 3—contd. (b) Partially acidulated, and (c) fully acidulated phosphate fertilisers using an orbital shaker at 20°C.
Fig 4. The effect that extraction time had on solubility of (a) phosphate rocks, (b) partially acidulated...
Fig 4—contd. (c) Fully acidulated phosphate fertilisers using an end-over-end shaker at 20°C.

Fig 5. The relative solubilities of a range of phosphate materials subjected to different types of shaker and different shaking times and temperatures. The data are presented as a percentage of the amount of P extracted following an end-over-end shake for the standard 1 h at 65°C (end 1/65). For the no-shake, reciprocal and handshake, phosphate materials were extracted for 1 h at 65°C and for the end-over-end (end 24/20) and orbital (orb 24/20), phosphate materials were extracted for 24 h at 20°C.

of the type, action and speed setting of the shaker. In laboratories in which a wrist-action or end-over-end water bath shaker is not available, a 24-h shake on an orbital or end-over-end shaker at room temperature (20°C) is an alternative to the standard 1-h end-over-end shake at 65°C.
ACKNOWLEDGEMENT

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REFERENCES


