FERTILIZER CHARACTERIZATION

Determination of Surface Area of Dicalcium Phosphate by Isotope Exchange

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The fineness of radioactive and nonradioactive dicalcium phosphate must be evaluated as one phase of a program for the characterization of the water-insoluble phosphate components of mixed fertilizers. The fineness of the phosphate grains generally lies below the practical sieve range. A technique for the rapid and fairly accurate estimation of surface area uses isotope exchange, whereby isotope ratios in biphase systems containing two elemental isotopes attain constancy in each phase at equilibrium. Determination of solution activity and concentration as the test sample reacts with a reagent solution containing the isotopes provides a measure of exchangeable phosphorus, which is compared with the phosphorus surface density, found by calibration of standard samples by gas adsorption measurements, to yield a measure of total surface area. Results for materials of similar surface quality generally agree with BET measurements within 10%.

A BROAD PROGRAM for the laboratory characterization of the water-insoluble components of mixed fertilizers is under way, with a view toward their agronomic evaluation under greenhouse and field conditions. The fertilizing potential of a phosphate compound intimately mixed with other salts, within limits prescribed by the specific soil and crop environment, is assumed to be determined by the thermodynamic solubility of the phosphate, its diffusibility, the influence of admixed salts, and the fineness of both the phosphate compound and the mixture. The fineness of the mixture generally lies within the sieve range and can be described adequately by ordinary sieve analysis. The size of the phosphate particles, on the other hand, normally falls in the subsieve range, thus necessitating the use of surface area measurement for fineness characterization. A rapid, reasonably accurate, and inexpensive method is needed for this purpose. Because the radioactive isotope exchange principle (5) offered promise as a basis for rapid surface measurement, its application to the determination of the surface area of routine preparations of dicalcium and basic phosphates has been studied in considerable detail. Only the work on dicalcium phosphate is presented at this time.

Measurement of Surface Phosphorus

The equilibrium condition in the exchange reaction between a phosphate salt and a solution containing phosphorus-32 is customarily indicated by the working equation:

$$\frac{\text{Total P (surface)}}{\text{Total P (solution)}} = \frac{P^{32} \text{ (surface)}}{P^{32} \text{ (solution)}} \quad (1)$$

Previous workers (4, 7) have sought to establish equilibrium between salt and solution prior to introduction of the radioactive isotope. The time consumed in this operation is unfavorable to its use in a rapid procedure. However, in instances in which the speed of exchange between solution and the accessible surface is much greater than that of other simultaneous processes, the surface equilibrium can be measured with the direct use of a solution of isotopes. This feature provides the basis for rapid measurement of surface phosphorus.

The isotope exchange technique is unique in its adaptability for use in measuring the surfaces of experimental phosphate salts which are labeled with radioactive phosphorus-32. The contacting solution in this case contains only nonradioactive phosphorus, which exchanges with the radioactive phosphorus on the accessible surface of the phosphate. The general principle is the same as with nonradioactive salts.

Experimental Factors. For nonradioactive material, the exchangeable phosphorus on the test surface is equal to the weight of sample, W, times the exchangeable phosphorus per unit weight of sample, E; the total phosphorus in solution at surface equilibrium is the product of the volume of solution, V, and the phosphorus concentration, C_e; the phosphorus-32 on the surface is proportional to the difference between the radioactivity of the reagent solution, Q_o, and that of the equilibrated solution, Q_e; and the phosphorus-32 in solution is proportional to Q_e, so that with proper preservation of counting conditions the ratio of surface phosphorus-32 to solution phosphorus-32 is $(Q_o -$

$Q_e)/Q_e$. Thus Equation 1 becomes:

$$\frac{WE}{VC_e} = \frac{Q_o - Q_e}{Q_e} \quad (2)$$

which upon rearrangement gives:

$$E = \frac{V}{W} C_e \frac{Q_o - Q_e}{Q_e} \quad (3)$$

Of these factors V, W, and Q_o are regulated by choice of initial conditions, whereas C_e and Q_e are found by measurement during the experiment. The first of the latter quantities is determined by chemical assay of the solution at the conclusion of the reaction, while the value for Q_e is taken from a graphical plot showing the count drop with time after the sample and solution are placed in contact (curve A, Figure 1).

A measure of Q_e may be obtained by extrapolation of the nearly horizontal branch of the curve to the axis of ordinates, as suggested by Rickson (6) for separation of the two indicated simultaneous processes of exchange. For the present needs the ordinate at the break of the curve is used, because it represents an exchange surface that would seem to approach more closely the usual reaction surface of the material. Aggregated samples that possess appreciable inside surface, which is slowly accessible to liquid through penetration of pores and cracks, yield rather steep curves for the second stage of the exchange reaction.

The quantity C_e depends on the concentration of the reagent solution and the speed and extent of adjustment between sample and solution. The attainment of a steady value of this factor during the reaction is not necessary, as the success of the exchange measurement depends on the constancy of E for different values of

V/W. This situation is illustrated by typical experimental results given in Table I. With the indicated variation in W/V, the equilibrium concentrations show an average deviation from the mean of 17.0%, whereas the corresponding figure for E is 5.5%. The indicated values for W/V and C_o, being developmental determinations, differ from those given in later discussion of the adopted procedure.

Measurement of exchangeable phosphorus in a radioactive sample involves additional factors which are associated with the circumstance that the initial direction of the exchange process is reversed. Thus, the phosphorus concentration of the reagent solution, C_o, replaces Ce in Equation 3. Furthermore, Q_o becomes the solution activity that would be obtained if all the phosphorus in solution were derived from the sample. This may be expressed as the product of the total phosphorus in solution at equilibrium, C_eV, and the apparent specific activity, k, of the sample. Finally, the count ratio must be inverted. Accordingly, for radioactive samples Equation 3 becomes:

$$E = \frac{V}{W} C_o \frac{Q_e}{kC_eV - Q_e} \qquad (4)$$

The apparent specific activity is the true specific activity of the material expressed in counts per gram of phosphorus. It is measured independently of the exchange reaction with use of a separate portion of the sample.
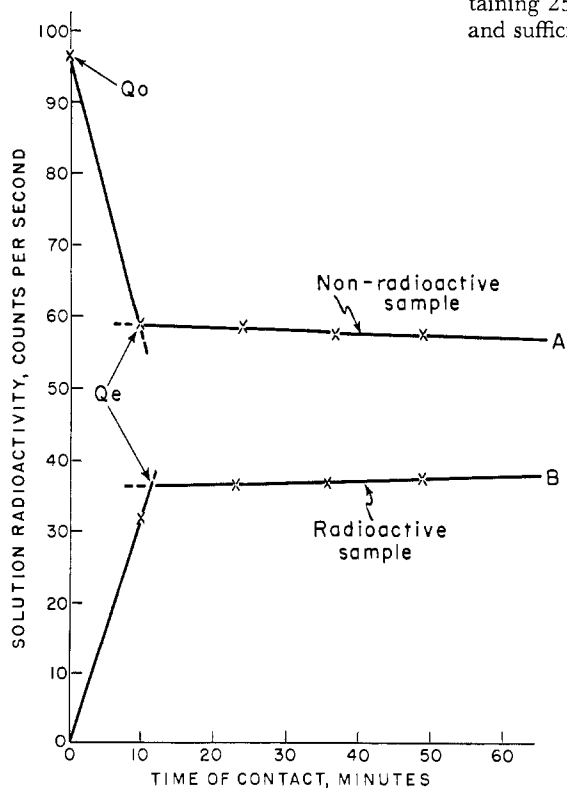
For the condition that Q_e is half of Q_o

Figure 1. Dependence of solution activity on time of contact with sample

Dicalcium Phosphate		W/V, G./100 Ml.	Co[a], γ P/Ml.	Ce, γ P/Ml.	E, γ P/G.
A.	Commercial, food grade −325 mesh (No. 2961-a)	3	17.4	32.6[b]	243[b]
		5	17.4	36.9	242
		10	17.4	31.0[b]	225[b]
	Same, after washing with 0.001M hydrochloric acid	3	18.3	34.0	217
		5	18.3	37.2	222
		7	18.3	40.4	226
	Same, −10 micron	3	19.6	33.6	497
		5	19.6	32.8	503
		7	19.6	31.7	480
B.	Laboratory preparation, 80% −100 mesh (No. 3101)	3	102.3	145	203
		5	102.3	168	204
		7	102.3	202	214
	Same, after washing with 0.001M hydrochloric acid	3	27.3	51.0	135
		5	27.3	48.3	135
		7	27.3	54.0	143

[a] Concentration of reagent solution.
[b] With use of a reagent comprised of a saturated solution of dicalcium phosphate, prepared from another portion of test material, results for C_e and E, respectively, were: 24.4 and 246 for $W/V = 3$ and 28.6 and 249 for $W/V = 10$.

or kC_eV, the count ratio is unity and the exchangeable phosphorus is given by the product of V/W and C_e or C_o, respectively, depending on whether the sample is nonradioactive or radioactive. When all the mentioned aspects of the measurement are considered, this balance of factors seems to represent the ideal condition for the determination. In routine practice, however, count ratios differing from unity by 50% or more are satisfactory.

Procedure. For nonradioactive samples the reagent is an aqueous solution of monopotassium phosphate containing 25 γ of phosphorus per milliliter and sufficient phosphorus-32 added as a phosphate salt in dilute hydrochloric acid (Catalog No. P-32-P-1, Oak Ridge National Laboratories, Oak Ridge, Tenn.), to yield an activity of approximately 100 counts per second per 25-ml. aliquot. The actual radioactivity, Q_o, is determined on an aliquot of this size by counting in a solution counter to a minimum of 10,000 counts. This latter figure is required to achieve a counting precision within 2%.

Two to 10 grams of the test sample (adjusted so that suitable count ratios are obtained) and 100 ml. of the reagent solution are placed in a polyethylene bottle and agitated on a wrist-action shaking apparatus for 3 minutes, time being counted from the moment the sample is wetted. About 35 ml. of the suspension is removed and centrifuged in a 50-ml. cellulose nitrate tube at approximately 10,000 × gravity for 1.5 minutes. The clarified liquid is passed through a vacuum filter, and a count is made on 25 ml. of the clear filtrate. The counted aliquot is returned to the centrifuge tube and agitated to gather the residue and thence to the polyethylene bottle for further agitation with the rest of the mixture. The solution is sampled and counted in the same manner three or more times at convenient intervals spread over 30 to 60 minutes, each count providing one point on the curve of solution radioactivity vs. time (Figure 1). The last-counted aliquot is analyzed for phosphorus, C_e, with the use of the photometric molybdivanadate procedure (1). Exchangeable phosphorus is calculated by substitution of the measured values of the several quantities in Equation 3.

For radioactive samples the reagent is the same as for nonradioactive materials, except that phosphorus-32 is not added and the phosphorus concentration, C_o, must be known accurately.

Table II. Relationship between Exchangeable Phosphorus and Surface Area of Various Dicalcium Phosphate Preparations

Lot No.	P:Ca, Mole Ratio	Method of Preparation[a]	Fineness, Mesh	Surface Area,[b] Sq. M./G.	Exchangeable P, γ/G.	E/S_b, γP/Sq. M.	Surface Area by Exchange,[c] Sq. M./G.
			Nonradioactive Material				
2961-a	1.002	A	−325	1.5	220	147	1.5
		A'	−10 microns	3.7	520	140	3.6
		A'	−325	1.6	240	150	1.7
3101	1.018	B	−100 (80%)	1.4	205	146	1.4
		B'	−100 (80%)	1.5	140	93	1.0
3167	0.981	B	−100 (92%)	7.2	1120	155	7.7
		B	−325	7.6	1290	169	8.9
2450	0.988	A	−100 + 325[d]	0.7	57	82	0.4
		A'	−100 + 325[d]	0.8	60	75	0.4
		A	−325	2.4	232	97	1.6
3165-c	0.903	B	−100 (65%)	13.5	1720	127	11.9
		B	−325	12.9	2220	172	15.3
			Radioactive Material				
R-42	0.973	B	−100 (65%)	1.6	327	204	0.8
		B	−325	2.5	695	278	1.8
R-125	0.937	C	−100	4.6	2445	532	6.2
R-127	0.938	C	−100	5.4	2200	407	5.6
R-126	0.957	D	−100	0.73	400	548	1.0

[a] A. Commercial. A'. Same, shaken with 0.001 M HCl for 1 hour and dried. B. Controlled addition of $Ca(OH)_2$ to H_3PO_4. B'. Same, shaken with 0.001 M HCl for 1 hour and dried. C. Addition of aqueous $(NH_4)_2HPO_4$ to aqueous $Ca(NO_3)_2.4H_2O$ at 100° C. D. Controlled addition of H_3PO_4 to $Ca(OH)_2$.

[b] BET gas adsorption technique employed. Measurements made by personnel of Bone Char Research Project, National Bureau of Standards, Washington, D. C.

[c] Found by division of values in column 6 by 145 γ of P per square meter for nonradioactive samples and by 395 γ of P per square meter for radioactive materials.

[d] Aggregates intentionally built up, to give free-flowing properties to material. Surface quality markedly different from other listed materials.

The details of the procedure depend upon the activity level of the sample. For samples of low specific activity (less than 100 millicuries per gram of phosphorus) the treatment is the same as described above. In the case of materials of high activity, such as freshly prepared labeled fertilizers (about 350 mc. per gram of phosphorus), 1-ml. portions of the clear filtrate are evaporated on metal planchets and counted under an end-window Geiger tube. The solution radioactivity in both instances rises with time (curve B, Figure 1) to provide a point of intersection for establishment of Q_e. The apparent specific radioactivity of the sample, k, is determined independently by count and phosphorus analysis of a clear aqueous extract of a separate portion of the sample. Exchangeable phosphorus is calculated by substitution of the measured values of the quantities in Equation 4.

Calibration of Exchangeable Phosphorus in Terms of Surface Area

The exchangeable phosphorus, E, is related to that part of the total surface of the sample that participated in the exchange, S_e, through a calibration factor, f', so that

$$E = f'S_e \qquad (5)$$

Comparison of the exchange surface with the surface, S_b, found by gas adsorption (2) is facilitated by the use of surface ratios. Thus, dividing both sides of Equation 5 by S_b yields

$$\frac{E}{S_b} = \frac{f'S_e}{S_b} \qquad (6)$$

Although the values of S_e and S_b are not in general the same, they can be made sensibly equal by suitable reduction of the particle size of the sample. When this condition is satisfied:

$$\frac{E}{S_b} = f' \qquad (7)$$

Experimentally, f' is the limit value of the ratio, E/S_b, when the particle size of the sample is decreased (3).

Ratios for several preparations of dicalcium phosphate are given in Table II. The range of ratios, E/S_b, obtained on the first listed material is 145 ± 5 γ of exchangeable phosphorus per square meter, which compares favorably with the counting precision. Since this figure includes both −325-mesh and −10-micron samples, it is to be regarded as a reliable limit value of E/S_b as defined by Equation 7.

The other nonradioactive materials exhibit a rather wide range of ratios, even in the −325-mesh preparations. This behavior is a consequence of differences in manufacturing technique, which are responsible for variations in certain properties, such as grain size, extent of aggregation, and chemical composition of the surface layer, that determine the general surface character of a material.

Thus, the calibration factor is influenced by the mode of preparation, in a manner disproportionate to any one measurable property of the material. A fair approximation of the surface area of these samples (Table II, last column) can, nevertheless, be obtained with the use of the calibration factor found for the first listed material. The approximate figure has practical value in process control, where measured areas that agree with gas-adsorption determinations within a precision of about 20% can be regarded as satisfactory.

The radioactive materials (Table II) show a greater exchange per unit of surface area than the nonradioactive samples. The increase arises in part, if not entirely, from the circumstance that some dissolution of the solid occurs when it is placed in contact with the phosphate solution. Hence, the measured solution activity (Q_e of Equation 4) is composed of both exchanged and dissolved phosphorus-32, and the apparent exchange is somewhat larger than the true exchange. However, surface areas may be approximated by use of a separate calibration factor which compensates, at least in part, for solid dissolution. Employment of the average E/S_b ratio of all tabulated radioactive preparations, 395 γ of phosphorus per square meter, yields surface areas found by exchange (last column) which agree with gas adsorption figures (fifth column) within 1.6 square meters per gram. This precision is satisfactory for process control in the manufacture of experimental fertilizers.

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Literature Cited

(1) Barton, C. J., *Anal. Chem.* **20,** 1068–73 (1948).
(2) Brunauer, S., Emmett, P. H., Teller, E., *J. Am. Chem. Soc.* **60,** 309–19 (1938).
(3) Hill, W. L., *Proc. 4th Tech. Session Bone Char* **1955,** in press.
(4) Olsen, S. R., *J. Phys. Chem.* **56,** 630–2 (1952).
(5) Paneth, F., Vorwerk, W., *Phys. Chem.* **101,** 445 (1922).
(6) Rickson, J. B., "Proceedings of Isotopes Techniques Conference," Oxford, 1951, vol. I, H. M. Stationery Office, London, 1953.
(7) Weikel, J. H., Jr., Neuman, W. F., Feldman, I., *J. Am. Chem. Soc.* **76,** 5202–7 (1954).