Application of Cation Exchange Resin to the Determination of Phosphorus in Foods

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Cation exchange resin was first used by Herlich and Rieman⁽¹⁾ for the determination of phosphorus in phosphate rocks. They converted the hydrochloric acid solution of phosphate into a mixture of hydrochloric acid and phosphoric acid by cation exchange and titrated directly with 0.1 *N* alkali using comparison buffers. Dijksman⁽²⁾ referred briefly to this method, and by the present authors the principle has been applied to the volumetric determination of phosphorus in foods⁽³⁾ and the gravimetric adaptation of the exchange technique has been investigated.⁽⁴⁾ However, it was found later that the volumetric method sometimes results in high values and that this was caused by the interference of carbonate in the concentrated alkali added before the titration. To avoid this difficulty in the present investigation the applicability of sodium regenerated cation exchange resin was examined as a substitute for the previously used hydrogen regenerated type and the following method is now recommended for the determination of phosphorus in foodstuffs.

Reagents

Hydrochloric acid; 20%.

Standard sodium hydroxide solution; 0.05 *N*: carbonate free.

Sodium chloride solution; 5%.

Methyl red indicator; 0.1% alcoholic solution.

Phenolphthalein-thymol blue indicator; to 1 part of 0.1% solution of thymol blue in 50% alcohol add 3 parts of 0.1% alcoholic solution of phenolphthalein.

Acetate buffer, *p*H 4.63; mix 17 ml. of 1.3 moles sodium acetate, 25 ml. of 1.0 mole acetic acid and 360 ml. of water. To 50 ml. of this solution add 3 drops of methyl red.

Borate buffer, *p*H 8.98; mix 130 ml. of 0.1 mole borax, 40 ml. of 0.1 mole hydrochloric acid and 280 ml. of water. To 60 ml. of this solution add 3 drops of methyl red and 6 drops of the phenolphthalein-thymol blue indicator. Each buffer solution should be contained in an Erlenmeyer flask similar in size and color to the one used in the titration.

Preparation of Exchange Column

Cation exchange resin; 100 to 200 mesh phenolmethylenesulfonic resin. Amberlite IR-100 or similar resins may be used. A resin synthetized in our laboratory was used in the present studies. Its total static exchange capacity was 2.28 milliequivalents per gram.

Six grams of the resin were suspended in the water and poured into an ordinary 25 ml. stopcock burette, the bottom of which had been plugged with absorbent cotton. Before each determination the exchanger was regenerated by pouring 100 ml. of sodium chloride solution through the column followed by 60 ml. of water in 3 portions. The rate of flow was adjusted by means of the stopcock to about 1 ml. per minute.

Hitherto, when using the exchange column, it was necessary to maintain the level of the solution several centimeters above that of the resin to prevent the formation of air bubbles between resin particles with the subsequent blocking of the column. However, in the case when the particle size is reduced to less than 100 mesh, the flowage stops automatically with the stopcock open when the solution reaches the bed level. The pressure drop caused by the small particle size did not obstruct the procedure, the maximum rate of flow being 3 ml. per minute under the experimental conditions. It is therefore necessary to regulate the rate of flow only once and thus the analyst is released from the continuous attention. For these reasons, the particle size of resin was reduced to 100-200 mesh. This made possible the simultaneous treatment of an increased number of samples without applying additional skill or the use of special apparatus.

Procedure

Weigh 5 g. of sample (or less in the case of phosphate-rich materials such as rice bran) into a porcelain crucible or a small Pyrex beaker and ash at 550 to 600°. Dissolve the ash in hydrochloric acid and evaporate to dryness on a water bath. Add 0.5 ml. of 20% hydrochloric acid and ca. 5 ml. of water, heat on a water bath, filter,

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(1) K. Herlich and W. Rieman, *Anal. Chem.*, **19**, 651 (1947).

(2) J. C. W. Dijksman, *Rec. trav. chim.*, **68**, 57 (1949).

(3) S. Kubo and C. Tsutsumi, *Report of the Food Research Institute (Tokyo)*, **3**, 72 (1950).

(4) *ibid.*, **3**, 83 (1950).

and wash with a small amount of water. Pass the filtrate and washings through the column at the rate of about 1 ml. per minute, collecting the filtrate in a 100 ml. Erlenmeyer flask. Wash with 25 ml. of water in 3 portions at the same rate and collect the washings in the same flask. The total volume will be about 50 ml. Add 3 drops of methyl red solution and adjust to *p*H 4.63 with 0.05 *N* sodium hydroxide solution using the acetate buffer. Usually less than 5 drops of the alkali will suffice for this purpose. Then add 6 drops of phenolphthalein-thymol blue indicator and titrate to *p*H 8.98 with 0.05 *N* alkali using the borate buffer. The titration is most preferably done under the light of a fluorescent lamp.

The phosphorus content of the sample is calculated from the volume of standard alkali required for the titration.

Experiments and Discussion

As would be expected from the exchange equilibrium of the resin, any hydrochloric acid solution of phosphates, after passing through an adequate amount of sodium type resin, shows an almost constant *p*H regardless of the amount of free hydrochloric acid present, providing that it lies within a certain concentration range. In these experiments some salts were added to standard potassium acid phosphate solutions, and to these were added 1, 3, 5 and 10 ml. of *N*-hydrochloric acid respectively. After passage through a 5 g. column of sodium type resin, the solutions were made up to the volume, *p*H were measured, and the phosphoric acid contents determined by titration. The results are given in Table 1.

Table 1

*p*H and Phosphoric Acid in the Effluents

	N-HCl added, ml.							
	1		3		5		10	
	*p*H	P[(a)]	*p*H	P	*p*H	P	*p*H	P
KH_2PO_4	4.9	4.13	4.7	—	3.9	—	—	—
〃 and Soln. A[(b)]	4.0	4.13	4.0	4.10	3.8	4.10	1.3	4.11
〃 and soln. B[(c)]	3.9	3.92	3.9	4.00	3.1	4.08	1.2	4.18

(*a*) ml. of 0.05 *N*-NaOH required for the titration. Theoretically expected value is 4.10.

(*b*) Solution A contains 10 mg. Ca and 6 mg. Mg as calcium chloride and magnesium sulfate respectively.

(*c*) Solution B contains 12 mg. Mg, 9 mg. Fe^{III} and 5 mg. Al as magnesium sulfate, iron alum and potassium alum respectively.

It is seen that when the amount of added hydrochloric acid is limited, the *p*H of the effluent always approximates to 4.0, and that the addition of only a few drops of 0.05 *N* alkali is necessary to adjust the *p*H 4.63. By eliminating the need for neutralization with concentrated alkali, as is required when the H-resin is employed, the method is simplified and carbonate interference is eliminated.

However, it is seen in Table 1 that when solution B is added, and at the same time, smaller amounts of hydrochloric acid are employed, the recovery of phosphorus is low even though cation exchange is complete. It is considered that the exchanged Fe^{III} or Al^{III} ion tends to adsorb some phosphoric acid, especially when the *p*H of the original solution is relatively high. The effects of the presence of ferric and ferrous iron and aluminum were studied, and from the results shown in Table 2, it is concluded that when smaller amounts of hydrochloric acid are used, only larger amounts of ferric iron will interfere with the accurate determination of phosphorus. Ferrous iron and aluminum showed no such tendency under the experimental conditions. However, in ordinary foodstuffs the contents of iron are not high enough to cause any difficulties. This can be said especially for cereals, beans, meat etc. where the iron levels are about the one hundredth that of phosphorus. Therefore, in practice, the interference of ferric iron can be

Table 2

Effects of Iron and Aluminum

(The figures represent the ml. of 0.05 *N*-NaOH required for titration. P present in each aliquot is 14.28 mg.)

	Fe or Al added, mg.	*N*-HCl added, ml.			
		0	1	3	5
KH_2PO_4	—	8.21	8.20	8.25	8.23
KH_2PO_4 and Fe^{II}	1		8.22	8.25	8.23
(Mohr's salt)	3		8.21	8.23	8.25
	5		8.25	8.24	8.29
KH_2PO_4 and Fe^{III}	1		8.24	8.25	8.26
(iron alum)	3		7.99	8.17	8.22
	5		7.71	8.04	8.19
KH_2PO_4 and Al	1		8.24	8.23	8.22
(potassium alum)	3		8.23	8.21	8.24

Table 3

Control Analysis

(The figures represent the ml. of 0.05 *N* NaOH required for titration.)

		N-HCl added, ml.			
		0	1	3	5
Sample	P added	P found			
Rice bran	8.10	8.07	8.12	8.10	8.14
Soybean	7.82	7.80	7.80	7.80	7.85

considered negligible, and this fact was confirmed by the following control analysis on soybean and rice bran.

A new method was adapted for the control analysis to prepare the sample solution. The sample (rice bran and soybean) was ashed, dissolved in hydrochloric acid, evaporated to dryness, redissolved, heated with dilute hydrochloric acid on a water-bath, and filtered to remove insoluble silica and carbon. The solution was passed through an enough amount of hydrogen regenerated cation exchanger to exchange all the cations in the solution. The resin was washed thoroughly with distilled water and then the adsorbed cations were effluated with 4% hydrochloric acid. The effluent was mixed with a known amount of phosphoric acid (nearly equivalent to the quantity in the original sample), evaporated to dryness, and redissolved in distilled water to a definite volume. By this means we obtained solutions which had the same mineral composition as the ash of the sample, their phoshorus contents being known.

Aliquots were taken and analysed by the above procedure and the values found were compared with the added amounts of phosphorus. As shown in Table 3, very satisfactory results were obtained on both rice bran and soybean.

From the above experiments and considerations, substitution of the sodium type exchanger for the hydrogen typeis recommended, since it results in a more simplified and accurate method of determination.

The pH values used for the end points in the procedure were taken from the potentiometric titration data of Herlich and Rieman.(1) The phenolphthalein used by them was replaced by phenolphthalein-thymol blue indicator because of its greater sensitivity. By this means even the color change resulting from the addition of half a drop of 0.05 N alkali can be detected in the ordinary Erlenmeyer flask.

Summary

A new volumetric determination of phosphorus in foods using a sodium type cation exchange resin was devised and critically investigated. The substitution of sodium for the hydrogen type exchanger eliminated errors resulting from the introduction of carbonate present in concentrated alkali. Moreover, the reduction of the resin particle size resulted in simplification of the procedure and reduced the skill necessary for its execution.

This method is accurate and applicable to the determination of phosphorus in ordinary foodstuffs, except when the sample contains unusually large amount of ferric iron. In such cases, the hydrogen type exchanger method(3) must be employed.

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