*The Preparation of Phosphorus-32 in a High Specific Activity Using the Szilard-Chalmers Effect**

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It is desirable that reference sources of radioactive isotope be of a high purity and also of a high specific activity, particularly in the case of β-ray emitters. In the case of phosphorus-32, the carrier-free source has usually been prepared by the (n, p) reaction on a sulfur target. However, this source is often contaminated with a considerable amount of phosphorus-33, which is produced by the (n, p) reaction on the sulfur-33 in the target. It is possible to prepare phosphorus-32 free from phosphorus-33 by the use of the (n, γ) reaction of phosphorus-31; however, its specific activity is considerably less than the product of the (n, p) reaction.

The Szilard-Chalmers process is considered to be an effective method for preparing phosphorus-32 of a high specific activity, which then furnishes a stock solution for the preparation of the reference sources. In this paper the process for the preparation of phosphorus-32 in a high specific activity using the Szilard-Chalmers effect will be studied with several inorganic phosphorus compounds.

Experimental

Target Materials. — The sodium dihydrogen phosphate, disodium hydrogen phosphite and sodium hypophosphite used were guaranteed reagents from the Wako Chemicals Co. The disodium hydrogen phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate and tripotassium phosphate were guaranteed reagents from the Kanto Chemicals Co. Each of these hydrated salts was dehydrated, dried, and analyzed as has been previously reported.[1]

Neutron Irradiation.—The salts were irradiated in the JRR-1 reactor (a water-boiler type, operated at 40 kW.). The salts, sealed in a polyethylene tube in the presence of air, were irradiated at an ambient reactor temperature. After irradiation, the samples were stored in a Dewar vessel cooled with dry ice for about one week.

The Preparation of the Ion Exchange Resin Column. — Strongly basic anion exchange resin (Diaion SA 100, 100~200 meshes) was washed with a large excess of concentrated hydrochloric acid and redistilled water and was then made into a column 0.8 cm. in diameter and 10 cm. long. The column was washed with 50 ml. of a chloride solution (eluting agent I in Fig. 1) before use.

Separation Procedure. — The irradiated sample was dissolved in an equimolar mixture of a 0.025 M potassium chloride solution and 0.025 M hydrochloric acid, and the concentration of the sample was made 0.1 M. In order to find the best conditions for separating orthophosphate and pyrophosphate ions, the following items were studied: the concentrations andmixing the ratio of the chlorides, the concentration of the irradiated salt in the sample solution, and the composition of the eluting agent. The separation of complex phosphate mixtures by the ion exchange method has been studied by several other workers,[2-7] and several different procedures have been proposed. However, in the present experiment, some improvement of the separation process was necessary because trace amounts of complex polyphosphate ion had to be separated from a large amount of orthophosphate, orthophosphite or hypophosphite ions. From the orthophosphate containing a trace amount of pyrophosphate ions, e. g., 1 μM of pyrophosphate in 0.1 M of orthophosphate, the pyrophosphate was

TABLE I. VOLUME OF THE ELUTING AGENT I REQUIRED FOR COMPLETE ELUTION OF ORTHOPHOSPHATE IONS

Orthophosphate concentration	Volume of sample solution	Required volume of eluting agent I*
M	ml.	ml.
0.1	10	55
0.1	50	135
0.1	100	220
0.5	10	120
1	10	210
1	50	230
1	100	420

* Pyrophosphate was eluted from 80 ml. to 250 ml.

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1) H. Baba, K. Tanaka and K. Yoshihara, This Bulletin, 36, 928 (1963).

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3) S. Lindenbaum, T. V. Peters and W. Rieman, *Anal. Chim. Acta.*, 11, 530 (1954).

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5) J. P. Ebel and N. Busch, *Compt. rend.*, 242, 647 (1956).

6) M. Matsuhashi, *J. Biochem.*, 44, 65 (1957).

7) H. J. Weiser, Jr., *J. Am. Oil Chemists' Soc.*, 34, 124 (1957).

cleanly separated by eluting it with 0.025 M of an equimolar chloride mixture solution. To avoid the incomplete separation between orthophosphate and pyrophosphate ions caused by the tailing of the former, the total aliquot of the sample solution was made 10 ml. per column for each run. The tailing of orthophosphate ions was influenced by the concentration of irradiated salt in the sample solution and the volume of the sample solution, as is shown in Table I. The overall separation procedure is shown in Fig. 1. It was

Irradiated target
Dissolve in 0.025 M KCl+0.025 M HCl mixed solution (prepare 0.1 M of sample solution)
↓ Each 10 ml. of sample solution to each column
Anion exchange resin column (0.8 cm. in diameter×10 cm. long of Diaion SA 100, 100~200 meshes, flow rate 0.8 ml./min.)
Eluting agent I, 60 ml. of 0.025 M KCl +0.025 M HCl mixed solution
Eluting agent II, 50 ml. of 8 M HCl solution
↓
8 M HCl fraction
Boiled and concentrated
Adjusted acidity, total activity and assayed
↓
Product

Fig. 1. Separation procedure with ion exchange resin.

found that when orthophosphate, orthophosphite or hypophosphite containing trace amounts of pyrophosphate and higher polyphosphate ions in a chloride solution was passed through the column, the pyrophosphate and higher polyphosphates were adsorbed on the resin column, while the orthophosphate, orthophosphite and hypophosphite ions were completely eluted with 60 ml. of the chloride solution. The adsorded polyphosphate ions were eluted with an 8 M hydrochloric acid solution.

The Chemical Analysis of Phosphorus.—For the analysis of phosphorus, the sample solution was evaporated to fuming with sulfuric acid after the addition of 5 ml. of concentrated nitric acid, 1 ml. of 40% perchloric acid, and 0.5 ml. of concentrated sulfuric acid. The residual sulfuric acid solution was then diluted to a 1 N acid solution. The trace amounts of phosphorus were analyzed by the colorimetry reported by Gaitanis.[8] The ammonium phosphomolybdate, formed by the addition of ammonium molybdate to the pretreated sample solution in 1 N sulfuric acid, was extracted with benzene. The solvent phase extracted was shaken with a stannous chloride solution, and the absorbancy of the solvent phase was measured at 735 mμ. The macroamounts of phosphorus, on the other hand, were analyzed by gravimetry with an ammonium phosphomolybdate precipitate.

8) M. J. Gaitanis, "Master Analytical Manual," Section 1-12, TID-7015 (1957).

Radioactivity Measurements.—The sample solution was evaporated in a glass planchet 2.5 cm. in diameter and was counted with a thin-end window-type G. M. gas flow counter. The decay rate was measured by the G. M. counter in its constant geometry. The 2π-β counter, whose efficiency was corrected by a 4π-β counter for phosphorus-32 activity, was used for the absolute measurement of phosphorus-32 activity. In this absolute measurement, small portions of the sample solution were dropped on a stainless steel disk covered with a thin Ducocement film, weighed, evaporated to dryness, and counted.

Results and Discussion

The distribution of the chemical species containing phosphorus-32 in neutron-irradiated phosphorus compounds has been studied by many workers,[9-23] and also the fragmentation of chemical species induced by the thermal neutron capture of phosphorus-31 in phosphates has been discussed. However, many questions still remain. In the present experiment, it was found that phosphorus-32 could be recovered in the polyphosphate fraction with specific activities considerably higher than those of the original irradiated salts, such as orthophosphates, orthophosphite, or hypophosphite.

The recoveries and enrichment factors obtained by the ion exchange method for several irrradiated samples are shown in Table II. All the samples were irradiated for 2 hr. in the same capsule in the pneumatic tube (the nominal neutron flux, 0.64×10^{12} n./cm^2·sec.) of the JRR-1. Each value shown in the table is the average of three separate experiments. It may be seen in the table that the recovery is higher for the orthophosphates, except tripotassium phosphate, than those for sodium orthophosphite and sodium hypophosphite. The residual activity in the resin

9) W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940).
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17) R. F. C. Claridge and A. G. Maddock, "Proceedings of the Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Prague (1961), p. 475.
18) L. Lindner and G. Harbottle, ibid. (1961), p. 485.
19) T. R. Sato and H. H. Strain, ibid. (1961), p. 503.
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21) K. Yoshihara and T. Yokoshima, This Bulletin, **34**, 123 (1961).
22) R. F. C. Claridge and A. G. Maddock, *Trans. Faraday Soc.*, **57**, 1392 (1961); **59**, 935 (1963).
23) H. Baba, *Nippon Genshiryoku Gakkaishi*, **5**, 917 (1963).

TABLE II. RECOVERY AND ENRICHMENT FACTOR

Target material	Recovery %	Enrichment factor
NaH_2PO_4	57.6±0.6	$(2.1\pm0.7)\times10^3$
Na_2HPO_4	62.2±1.6	$(2.3\pm0.5)\times10^3$
Na_3PO_4	54.3±1.3	$(4.2\pm0.8)\times10^3$
KH_2PO_4	52.4±1.0	$(8.7\pm1.4)\times10^3$
K_2HPO_4	49.6±2.6	$(1.8\pm0.3)\times10^2$
K_3PO_4	40.7±1.9	$(8.0\pm2.5)\times10^2$
Na_2HPO_3	42.4±1.4	$(4.8\pm0.1)\times10^2$
NaH_2PO_2	25.4±1.6	$(4.4\pm0.6)\times10^2$

column after elution with 8 M hydrochloric acid was found to be less than 0.1% of the total activity.

Experiments were than carried out in order to observe the fluctuations in the preparation of phosphorus-32 with a high specific activity when several samples of the same salt were separately irradiated. The results obtained in the case of potassium dihydrogen phosphate are shown in Table III. The recoveries are within a range of deviation of less than 2 per cent, whereas the enrichment factors show considerable fluctuations. The polyphosphate

TABLE III. RECOVERY AND ENRICHMENT FACTOR OBTAINED BY THE TREATMENT OF IRRADIATED KH_2PO_4

Irradiation condition	Recovery %	Enrichment factor
2 hr. No. 16 hole of JRR-1	50.0	7.6×10^3
	54.4	9.7×10^3
	52.9	1.1×10^4
	56.8	4.6×10^3
	57.2	1.8×10^3
	av. 54.2±1.2	$(6.6\pm1.5)\times10^3$
15 hr. No. 12 hole of JRR-1	38.1	4.4×10^3
	41.9	4.1×10^3
	42.2	4.4×10^3
	41.4	5.4×10^3
	43.0	8.6×10^3
	43.5	1.1×10^4
	av. 41.6±0.8	$(6.3\pm1.0)\times10^3$

in unirradiated samples was also separated by the ion exchange method, and the phosphorus amounts in the polyphosphate fraction were determined by colorimetry. The amount of phosphorus per gram of sample adsorbed on the resin column, which was detected as the polyphosphate fraction, is shown in Table IV for the unirradiated samples. There was not much difference between the amounts adsorbed on the resin column for the unirradiated and irradiated samples. However, the amount of the polyphosphate formed by neutron irradiation in a reactor seemed to be of the order of the values to be expected from the results

TABLE IV. AMOUNTS OF PHOSPHORUS IN THE FRACTION OF POLYPHOSPHATE (MAINLY PYROPHOSPHATE) CONTAINED IN TARGET MATERIALTS

Target material	μg. as P / 1 g. of target materials
NaH_2PO_4	53
Na_2HPO_4	35
Na_3PO_4	18
KH_2PO_4	15
K_2HPO_4	250*
K_3PO_4	120
Na_2HPO_3	40
NaH_2PO_2	10

* approximate value.

of the polyphosphate formation by gamma irradiation.[24]

The recoveries obtained under different irradiation conditions are shown in Table V, where the irradiation time dependence of the recovery is specifically shown. The neutron flux and other irradiation conditions, for example, the intensity of gamma rays, vary with their position in a reactor. However, the

TABLE V. EFFECT OF IRRADIATION TIME IN A REACTOR

Target material	Irradiation time	Irradiation hole of JRR-1*	Percentage recovery	Enrichment factor
NaH_2PO_4	30 min.	16	50.0	1.8×10^3
	60 min.	16	50.8	1.8×10^3
	120 min.	16	57.6	2.2×10^3
	300 min.	2**	53.8	2.0×10^3
	15 hr.	12	54.7	2.4×10^3
Na_2HPO_4	30 min.	16	61.9	3.1×10^3
	60 min.	16	60.2	2.4×10^3
	120 min.	16	62.2	2.3×10^3
	300 min.	2	67.4	2.2×10^3
	15 hr.	12	63.5	3.4×10^3
KH_2PO_4	30 min.	16	53.8	1.9×10^4
	60 min.	16	50.0	1.0×10^4
	120 min.	16	54.2	6.6×10^3
	300 min.	2	42.4	5.7×10^3
	15 hr.	12	43.5	1.1×10^4
K_2HPO_4	30 min.	16	46.6	4.7×10^2
	60 min.	16	41.4	2.4×10^2
	120 min.	16	49.6	1.8×10^2
	300 min.	2	43.9	2.2×10^2
	15 hr.	12	42.9	3.0×10^2

* No. 16- a pneumatic tube, No. 2- a horizontal hole, No. 12- a vertical hole.

** No. 2 and No. 16 holes are placed in symmetrical position of JRR-1 reactor.

24) K. Tanaka, This Bulletin, 37, 1032 (1964).

recovery was not much affected by the irradiation time for several orthophosphates in the time range of 30 min. to 15 hr.

The product obtained by treating the potassium dihydrogen phosphate was evaporated to dryness, and an analysis of the radiochemical purity was made. The gross decay curve was measured for the time more than ten times the half life of phosphorus-32. The decay rate for the curve was constant and was exactly the same as for phosphorus-32 (14.3 day). The absorption curves of radiation with an aluminum disk were also obtained for this product. The curves obtained 150 days after irradiation were compared with those 20 days after irradiation. The two curves were the same. No weak β-ray emitters could be detected for the product.

The products thus prepared were radiochemically pure, no gamma ray peaks were observed by scintillation spectrometry with a NaI crystal, and the total solids which were detected after the evaporation of the product solution were less than 0.1 mg./ml. The specific activity higher than 1 mc./mg. could be prepared, even in irradiations of total neutrons of approximately 2×10^{15}.

Summary

A process has been developed for obtaining phosphorus-32 free from phosphorus-33 and with a high specific activity. Phosphorus-32 has been prepared by an anion exchange method, in which a chloride solution containing 0.025 M of potassium chloride and 0.025 M of hydrochloric acid of neutron irradiated phosphate was passed through the column of a strongly basic anion exchanger, and the adsorbed phosphorus-32 has been eluted with 8 M hydrochloric acid. The anhydrous orthophosphate shows a good recovery compared with several orthophosphates, sodium orthophosphite and sodium hypophosphite. The recovery is not much affected by the irradiation time. Enrichment factors higher than 10^3 have been obtained.

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