S 68. *Preparation of Carrier-free ^{32}P from Pile-irradiated Sulphur. Part I. Adsorption of ^{32}P on Ferric Hydroxide and Dialysed Iron.*

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The removal of radio-phosphate on ferric hydroxide in alkaline solution, and on dialysed iron in acid solution, has been investigated. On ferric hydroxide, the efficiency of adsorption of radio-phosphate decreases with increase of pH from 10·5 to 13·0. The presence of sulphate ion has little effect on the adsorption. On dialysed iron in the pH range 1·0—4·0, phosphate adsorption in the presence of sufficient sulphate to complete precipitation of the radio-phosphate has been measured. The amount of phosphate adsorbed is decreased if the sulphate concentration is increased beyond the minimum required for precipitation of the dialysed iron. This effect decreases markedly with increase of pH. Radio-phosphate can be selectively adsorbed by dialysed iron from solutions containing chromium and aluminium at pH 2·0. The relationship between concentration of radio-phosphate and the amount of ferric hydroxide or dialysed iron required for maximum recovery of radio-phosphate has been determined.

The preparation of carrier-free radio-phosphorus by irradiation of carbon disulphide with fast neutrons has been described by Fermi *et al.* (*Proc. Roy. Soc.*, 1934, **146**, *A*, 483; 1935, **149**, *A*, 522; Chiewitz and Hevesy, *Nature*, 1935, **136**, 754; Erbacher and Philipp, *Ber.*, 1936, **69**, 893). Although carbon disulphide is a convenient target material when a radium–beryllium source of fast neutrons is used, yet sulphur itself has many advantages in pile irradiations.

The extraction of radio-phosphorus from pile-irradiated sulphur has been described by Cohn (Isotope Branch Circular No. C-1, U.S.A.E.C., 7.1.47; cf. Hevesy, " Radio-active Indicators," Interscience Publishers Inc., New York, 1948, 3). The present work has been concerned with the losses observed at the various stages of the Cohn method and with adapting that method for production purposes at Harwell. The method can be divided conveniently into four stages : (1) the extraction of the radio-phosphorus from the molten irradiated sulphur by boiling nitric acid; (2) separation of the phosphate formed from anionic impurities, *e.g.*, sulphate, by precipitation of ferric hydroxide with ammonia in the solution; (3) removal of the ferric ion, and (4) removal of other cationic contaminants on an ion-exchange column. However, if large amounts of cations are present, particularly chromium and aluminium, significant amounts of radio-phosphorus are retained in the ion-exchange column, and Cohn recommends that this stage be replaced by the usual purification by phosphomolybdate; this requires addition of carrier phosphate.

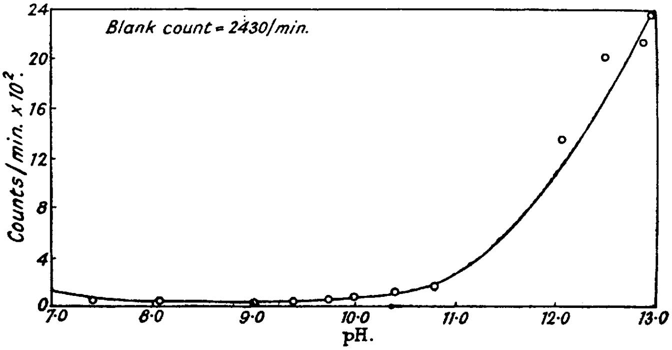
As it was desired to prepare the radio-phosphate on a production scale in stainless-steel vessels, it appeared that a new method for the separation of the radio-phosphate from chromium, etc., would have to be worked out. The results obtained on the precipitation of radio-phosphate on ferric hydroxide could be explained on the basis of the well-known preferential electrostatic adsorption of tervalent as compared with bivalent ions on a colloidal surface. The lack of adsorption of the phosphate at pH 13·0 could then be ascribed to the ferric hydroxide being amphoteric in character and having an isoelectric point somewhere above pH 13·0, *i.e.*, that any charge on the particles of ferric hydroxide was very small at pH 13·0 or indeed even reversing its sign somewhere in this region.

It seemed likely that, by choosing another positively charged sol, selective adsorption of the radio-phosphate might be induced in weakly acid solutions. The sol selected would have to be capable of easy removal from the phosphate and be reasonably stable at about pH 1·0—2·0 where both chromium and aluminium would still be present in solution as cations and not as finely dispersed colloids. Dialysed iron, which is electropositively charged in the desired range of pH and can be dissolved in concentrated hydrochloric acid, seemed to be an ideal choice. Determinations of the adsorption of radio-phosphate in acid solution by dialysed iron were therefore carried out.

EXPERIMENTAL.

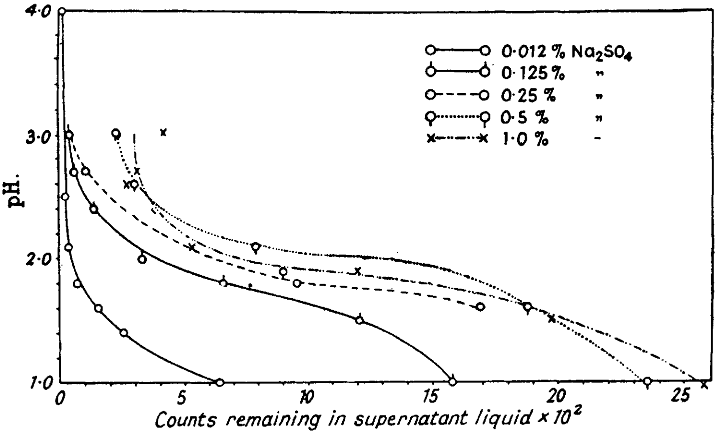
The following experiments were designed to investigate the effect of one or more variables on the adsorption of radio-phosphate on ferric hydroxide or on dialysed iron, the variables being pH, sodium sulphate concentration, ferric hydroxide or dialysed iron concentration, and radio-phosphate concentration. In most cases appropriate amounts of a variable were pipetted into 15-ml. centrifuge tubes containing known amounts of radio-phosphate and ferric alum or dialysed iron. The precipitation of the ferric hydroxide or dialysed iron was induced by adding respectively a known concentration of alkali or sodium sulphate solution. Variation of hydrogen ion concentration was accomplished by adding decreasing amounts of hydrochloric acid, ammonium hydroxide solution, or sodium hydroxide solution. The precipitate was centrifuged off, and the number of disintegrations per minute of the radio-phosphate remaining in the supernatant liquid was determined by evaporating a definite volume to dryness on an aluminium tray, which was then placed in a standard position under the window of a Geiger–Müller counter situated in a lead castle of conventional design. No corrections for self-absorption of the β-rays in the samples were made. All concentrations quoted in the tables were the final concentrations of the particular variable after addition of all reactants and before removal of the precipitate by centrifugation. The results of the first table are plotted in Fig. 1, and some of those in the fourth table in Fig. 2.

FIG. 1.



Precipitation of $^{32}PO_4'''$ *on* $Fe(OH)_3$.

FIG. 2.



Adsorption of $^{32}PO_4'''$ *on dialysed iron.*

Effect of pH *on adsorption of radio-phosphate on ferric hydroxide.*

Tube no.	Counts/ min.	pH of supernatant liquid.	Final concn. of alkali.
1	2368	12·98	0·2N-NaOH
2	2119	12·53	0·1N-NaOH
3	1009	11·12	0·05N-NaOH
4	36	8·10	0·025N-NaOH
5	124	10·80	7·5% NH_4OH
6	109	10·44	3·75% „
7	70	10·09	1·87% NH_4OH
8	60	9·74	0·93% „
9	41	9·43	0·47% „
10	35	9·11	0·23% „
11	64	7·67	0·12% „
12	2328	2·36	0·06% „
Blank	2430	—	—

(*Note.*—Total amount of Fe present as hydroxide = 0·5 mg./ml. All values of pH were determined electrometrically by means of the Cambridge Alka electrode.)

Radio-phosphate remaining after ferric hydroxide precipitation.

Concn. of Fe (mg./ml.) before centrifuging.	Activity (in counts/min.) * remaining after precipitation.								
0·16	55,535	25,944	13,470	5462	2668	1331	601	382	198
0·32	12,427	5,884	2,425	1378	526	272	177	88	71
0·625	3,740	1,821	798	338	237	91	68	30	18
1·25	759	385	195	109	94	61	16	99	6
2·50	341	156	143	54	26	19	95	80	4
5·0	238	111	32	104	15	13	12	50	18
10·0	54	17	127	13	4	3	6	12	2
Concn. of radio-phosphate before centrifuging (in μc./ml.)	200	100	50	25	12·5	6·25	3·17	1·6	0·8

* 1000 Counts/min. = 0·67 μc./ml.

Effect of pH *and sulphate concentration on the adsorption of radio-phosphate on ferric hydroxide.*

(Blank count on radio-phosphate = 559 cts./min.)

Final concn. of alkali.	Final concentration of sodium sulphate, %.							
	7·5.		3·75.		1·87.		0·94.	
	Cts./min.	pH.	Cts./min.	pH.	Cts./min.	pH.	Cts./min.	pH.
0·2N-NaOH	388	12·78	346	12·86	396	12·98	367	13·03
0·1N-NaOH	432	12·46	341	12·56	396	12·43	352	12·65
0·05N-NaOH	481	11·93	317	11·79	346	12·00	324	12·12
0·025N-NaOH	405	11·20	181	11·61	119	10·66	162	10·84
3N-NH_4OH	146	11·10	90	10·81	52	10·84	—	—
1·5N-NH_4OH	106	10·8	52	10·66	55	10·62	37	10·43
0·75N-NH_4OH	62	10·6	25	10·52	30	10·54	24	10·21
0·375N-NH_4OH	48	10·4	24	10·25	17	10·28	17	9·89
0·19N-NH_4OH.........	22	10·15	14	10·04	11	9·98	16	9·65
0·095N-NH_4OH	12	9·96	13	9·79	10	9·76	7	9·29
0·048N-NH_4OH	14	9·07	0	9·54	2	9·36	2	8·98
0·024N-NH_4OH	—	—	4	9·10	4	8·96	0	8·68

Effect of sulphate concentration on the adsorption of radio-phosphate by dialysed iron in the pH *range* 1·0—4·0.

(Blank count on radio-phosphate = 6000 cts./min.)

Final Na_2SO_4 concn., %.	Activity (in cts./min.) in 0·1 ml. of supernatant liquid.													
	Cts./ min.	pH.	Cts./ min.	pH.	Cts./ min.	pH.	Cts./ min.	pH.	Cts./ min.	pH.	Cts./ min.	pH.	Cts./ min.	pH.
1·0	2411	1·0	1975	1·5	1192	1·9	525	2·1	258	2·6	304	2·7	406	3·0
0·5	2350	1·0	1874	1·5	887	1·9	782	2·1	299	2·6	261	2·7	223	3·0
0·25	—	—	1691	1·5	946	1·8	820	2·0	—	—	102	2·7	40	3·0
0·125	1481	1·0	1210	1·5	681	1·6	324	2·0	136	2·4	60	2·7	43	2·9
0·062	1102	1·0	686	1·5	418	1·6	332	1·9	88	2·3	51	2·6	19	2·9
0·031	420	1·0	385	1·5	182	1·6	98	1·9	29	2·2	29	2·6	42	2·9
0·016	638	1·0	250	1·4	151	1·6	66	1·8	36	2·1	28	2·5	16	4·4
Final concn. of HCl:	0·1N.		0·05N.		0·025N.		0·0125N.		0·0062N.		0·0031N.		H_2O	

Effect of radio-phosphate concentration and dialysed iron concentration on the adsorption of radio-phosphate at pH 2·4.

(1000 Counts/min. = 3·76 μc./ml.; pH of all tubes = 2·3.)

Dialysed Fe concn. (mg./ml.) before centrifuging.	Activity (in cts./min.) in 0·02 ml. of supernatant liquid.								
0·39	31899	13624	4758	2393	230	161	802	54	18
0·78	13476	5320	2797	451	119	58	27	18	16
1·56	10039	1852	793	284	49	19	14	17	12
3·12	2253	723	301	132	39	17	8	7	10
6·25	724	230	95	114	13	12	9	6	9
12·5	141	65	64	99	—	21	9	7	8
25	125	75	112	102	18	16	23	11	7
Concn. of radio-phosphate before centrifuging (μc./ml.):	215	107·4	53·7	26·85	13·42	6·71	3·35	1·67	0·83

Adsorption of Cations on Dialysed Iron.—A solution was prepared containing 233 mg. of $Al_2(SO_4)_3,18H_2O$ and 157 mg. of $Cr(NO_3)_3,9H_2O$ in 100 ml. of water, the pH being adjusted to 2·0. A 5-ml. sample was pipetted into each of 2 centrifuge tubes containing 1·0 ml. of 0·5% dialysed iron. Precipitation occurred immediately. The precipitate was centrifuged off, re-suspended in 5 ml. of N/50-hydrochloric acid, and centrifuged off, and the washing repeated, the addition of a trace of ammonium sulphate being required to prevent peptising on the second washing. The precipitate was then dissolved in 1 ml. of 7N-hydrochloric acid and diluted to 5 ml., 0·1 ml. of this solution being taken for spectroscopic analysis. Less than 1 p.p.m. of Cr and less than 1 p.p.m. of Al were found.

The experiment was repeated, using 20 mc. of ^{32}P in 2 l. of N/100-acid containing contaminants from stainless-steel apparatus. 5 Ml. of commercial dialysed iron were used for precipitation, and the precipitate (containing 95% of the radio-phosphorus), after being washed twice, was dissolved in 20 ml. of 8N-hydrochloric acid and analysed spectrographically after the iron had been removed by extraction with *iso*propyl ether. The analysis is compared with an analysis of a similar amount of the commercial dialysed iron—which was rather impure—after extraction of the iron by the same method :

	Fe.	Mn.	Cr.	Al.	Ni.	
Radioactive sample	<2	20	3	1	<2	p.p.m.
Blank sample	<2	20	4	1	<2	

Discussion.—The amounts of ^{32}P present in the above experiments as radio-phosphate are of the order of 10^{-10}—10^{-12} g., and it has not been possible to estimate how much inactive phosphate, up to say 10^{-7} g., may be associated with the so-called carrier-free material. As indicated in the introduction, the ferric hydroxide shows marked adsorption of radio-phosphate at hydrogen-ion concentrations up to about pH 10·5—11·0; above pH 11·0 the adsorption falls rapidly to zero (cf. Cohn, *loc. cit.*). The suggested explanation of this effect, outlined above, is partly borne out by the fact that the observations obtained with a stable positively charged sol in slightly acid solution were of a remarkably similar nature. In the case of dialysed iron, the addition of an anion of lower valency was essential in order to complete precipitation, as the concentrations of radio-phosphate were far below the precipitation concentrations. Sulphate was chosen as it would certainly be present in any digestion of sulphur with nitric acid, and it was essential to know precisely to what extent the adsorption of sulphate would compete with that of phosphate in acid solution. It will be seen from the fourth table and Fig. 2 that, with dialysed iron, the effect of sulphate ion decreases with decreasing acidity, but with ferric hydroxide (see third table) the effect of sulphate ion is very small even in high concentration. From the second table a rough proportionality is observed between the amount of radio-phosphate present before centrifuging and the amount left in the supernatant liquid, but this does not hold for radio-phosphate adsorbed by increasing amounts of iron.

As expected, no adsorption of chromium and aluminium is observed, but dialysed iron of greater purity than that commercially available would have to be prepared. Preliminary trials with purified materials have shown exactly similar results. The use of dialysed iron will permit the preparation of carrier-free radio-phosphate even under conditions of high chromium and aluminium contamination. The results reported above show that, radio-phosphate being used as a tracer, it should be possible to make quantitative observations on the amounts of phosphate adsorbed on colloid surfaces. Further work on this aspect of the results is in progress.

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