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DETERMINATION OF PHOSPHORUS-32 IN AQUEOUS ENVIRONMENTAL SAMPLES

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Abstract - An improved method for isolating and beta counting ^{32}P in aqueous environmental samples at the Savannah River Laboratory is described. Interference from ^{131}I is eliminated by a chloroform extraction and from ^{95}Zr-^{95}Nb by anion exchange with *"Dowex"* 1-X8 resin.* ^{32}P is separated from interferences such as ^{141}Ce, ^{144}Ce, ^{51}Cr, ^{137}Cs, and ^{140}Ba-^{140}La by extraction as phosphomolybdic acid with hexanol. This solvent is mixed with liquid scintillator and counted.

Three improvements made in the method are: (a) using HCL gas to adjust the sample to 12M HCl to shorten the procedure, (b) replacing pentanol with hexanol to increase the extraction of phosphomolybdic acid, and (c) counting ^{32}P by liquid scintillation instead of on planchets.

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Decontamination of ^{32}P from interferences is about 10^4, and recovery is at least 85%. Analyses of control spikes during the past 30 months shows the method to have a sensitivity of 14 pCi/ℓ and a precision of 11% when using a 50 ml sample.

INTRODUCTION

Phosphorus-32, on an activity basis, is not a major pollutant from nuclear reactors. It is, however, of special concern in environmental monitoring of reactors because of its short half-life and its ease of assimilation and retention in the food web. Phosphorus-32 is formed by the neutron activation of stable ^{31}P in the phosphate-containing compounds used as corrosion inhibitors in nuclear reactor systems.

At the Savannah River Plant, ^{32}P (a beta emitter) has been monitored since mid-1965. Measurements are continuing on a regularly scheduled basis to assure that releases of this radionuclide are less than established limits. Table I lists the beta emitters monitored at the Savannah River Plant. Plant effluents are held in retention basins and analyzed to verify that the levels of radionuclides are within discharge limits.

The key problem in measuring phosphorus-32 in environmental samples is separating the ^{32}P from all the other radionuclides in the sample. ^{32}P is a pure beta emitter; it cannot be measured by the more convenient gamma ray spectroscopy. Since beta emitters do not have finite energies, beta spectroscopy is both difficult and imprecise. In general, therefore, beta emitters are chemically separated and then counted by a gross-counting technique.

Beta emitters may be determined by counting a precipitate, a solution, or a gas. Precipitate counting is frequently avoided because of the risk of self-absorption. Solutions are generally counted using liquid scintillation techniques because of their convenience and sensitivity. Gas counting is restricted to volatile isotopes and compounds of those isotopes.

In an examination of existing methods, the precipitation of benzidine phosphate or bismuth phosphate[1] for the radiochemical separation of phosphorus-32 was not feasible because of coprecipitation of other contaminants in our samples. The classical ammonium molybdophosphate method likewise was unsatisfactory owing to considerable contamination present in the final product. The method based on the precipitation of zirconium phosphate[2,3] was unsatisfactory because of contamination by zirconium-95 present in samples. An existing procedure used at this laboratory[4] was modified to shorten the procedure, improve the recovery, and substitute liquid scintillation counting for precipitate counting. Other variations of this procedure have been used at other locations,[5,6,7] but the recovery and decontamination factors were lower than in this procedure. An extensive review of the extraction of phosphomolybdic acid, the key technique used in our procedure, has been published.[8]

EXPERIMENTAL

In our modified procedure, ^{131}I is removed by solvent extraction, ^{95}Zr-^{95}Nb are removed by anion exchange, and ^{141}Ce, ^{144}Ce, ^{51}Cr, ^{137}Cs, and ^{140}Ba-^{140}La are separated by extraction.

IODINE-131 REMOVAL

Iodine-131, if present, is removed by extraction with chloroform. After iodine carrier is added (as iodide), the sample is treated with sodium pyrosulfite (metabisulfite), $Na_2S_2O_5$, to reduce all iodine species to the iodide state. Then the sample is treated with sodium nitrite, $NaNO_2$, to oxidize the iodide to elemental iodine. The elemental iodine is then extracted with chloroform.

ZIRCONIUM-95/NIOBIUM-95 REMOVAL

Zirconium-95 and its daughter element, niobium-95, are removed by anion exchange on "Dowex" 1-X8 (100 to 200 mesh) as shown in Figure 1. Hydrogen chloride gas is bubbled into the sample to adjust the concentration to 12M and form the anion complex of Zr-Nb. This technique avoids the evaporation of a sample of 50 to 200 ml and subsequent dissolution in concentrated hydrochloric acid.

The anion exchange resin is conditioned by slurrying about 5 g of "Dowex" 1-X8 (100-200 mesh) in 5 ml of concentrated HCl. The slurry is poured into a glass ion exchange column (Figure 2) and washed with 20 ml of concentrated HCl. The sample is then passed through the column at a rate of 3 ml/min. The column is rinsed twice with 20 ml of concentrated HCl.

EXTRACTION OF PHOSPHORUS-32

The ^{32}P is separated from the remaining beta and gamma emitters by extraction as the phosphomolybdic acid (Figure 1). The sample and washings are adjusted to 1.3M nitric acid to form the phosphomolybdic acid which is extracted into a 1:3 solution of hexanol in toluene. Hexanol was substituted for the traditional pentanol because of its greater insolubility in water (Table II). This substitution increased the recovery of ^{32}P significantly. The organic phase is combined with a liquid scintillation mixture and counted.

REAGENTS

Note: Use analytical reagent grade chemicals unless otherwise specified.

Iodine carrier, sodium iodide, 20 mg I/ml.

Dissolve 2.36 g NaI in water, and dilute to 100 ml.

Sodium hydroxide - sodium metabisulfite (0.2N NaOH-0.01N $Na_2S_2O_5$).

Dissolve 0.8 g NaOH and 0.1 g $Na_2S_2O_5$ in water, and dilute to 100 ml.

Sodium hydroxide, 2N

Dissolve 8.0 g NaOH in water, and dilute to 100 ml.

Sulfuric acid, concentrated.

Sodium nitrite, 20%

Dissolve 20 g $NaNO_2$ in 80 ml water.

Chloroform

"Dowex" 1-X8, 100 to 200 mesh anion exchange resin.

Hydrogen chloride gas, technical grade, 99.0% min.

Hydrochloric acid, concentrated.

Phosphorus carrier, 0.25 mg P/ml [sodium phosphate (tribasic)].

Dissolve 307 mg $Na_3PO_4 \cdot 12\ H_2O$ in water, and dilute to 100 ml.

Ammonium hydroxide, 6M.

Dissolve 17.1 ml of concentrated NH_4OH in water, and dilute to 100 ml.

Ammonium molybdate reagent, 10%.

Dissolve 10 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water, and dilute to 100 ml.

Nitric acid, 8M.

Dissolve 50.3 ml concentrated HNO_3 in water, and dilute to 100 ml.

Hexanol-toluene, 1:3 mixture.

Dissolve 20 ml of hexanol in 60 ml of toluene.

Nitric acid, 1.3M

Dilute 8.2 ml of concentrated HNO_3 to 100 ml with water.

PROCEDURE

Note: If iodine is absent, begin at step 1 and omit steps 2 through 9;

If iodine is present, omit step 1 and begin at step 2.

1. Place 50 ml of sample in a 100 ml centrifuge tube that is cooled in a beaker of ice water; add 1.0 ml of phosphorus carrier (0.25 mg/ml).
2. Place 50 ml of sample in a 250 ml separatory funnel; add 1.0 ml of phosphorus carrier (0.25 mg/ml).
3. Add 1 ml of iodine carrier (20 mg I/ml).

4. Add 3 ml of 0.2N NaOH-0.01N $Na_2S_2O_5$ reagent.

5. Test to make sure solution is alkaline; add 2N NaOH if necessary.

6. Adjust pH of sample to 2 by adding concentrated H_2SO_4 dropwise.

7. Add 50 µl of 20% $NaNO_2$.

8. Add 20 ml $CHCl_3$ and extract iodine. Discard $CHCl_3$ and repeat extraction.

9. Transfer aqueous solution to a 100 ml centrifuge tube cooled in a beaker of ice water.

10. Bubble HCl gas into the sample; as the HCl dissolves it forms a heavy phase in the bottom of the tube. Bubble in HCl gas until the heavy phase fills the tube (about 25 minutes).

11. Prepare an anion exchange column by slurrying about 5 g of "Dowex" 1-X8 (100-200 mesh) in 5 ml of concentrated HCl. Pour into an ion exchange column of about 1 inch diameter (resin will be about 1½ inches deep). Wash the column with 20 ml of concentrated HCl.

12. Pour the sample into the column and let it flow through at a rate of about 3 ml/minute to remove Zr-Nb.

13. Rinse the centrifuge tube with 20 ml of concentrated HCl; add the rinses to the "Dowex" ion exchange resin in the column.

14. Repeat Step 13.

15. Combine the washes and sample in a beaker and evaporate to 5 to 10 ml. Do not allow the sample to go to dryness.

16. Dilute the sample to 40 ml.

17. Adjust the pH to 7.5 with 6M NH_4OH.

18. Add 6 ml of 10% solution of $(NH_4)_2MoO_4$.

19. Wait 2 minutes.

20. Adjust to 1.3M using 9 ml of 8M HNO_3.

21. Add 15 ml of a 1:3 mixture of hexanol and toluene (to extract ^{32}P).

22. Shake 1 minute in a separatory funnel and drain off the aqueous layer into a secondary separatory funnel.

23. Add 5 ml of the 1:3 mixture of hexanol and toluene to the aqueous layer, and shake 1 minute; discard the aqueous layer.

24. Combine the organic phases, wash with 25 ml of 1.3M HNO_3, and discard the aqueous layer.

25. Remove 15 ml of the organic phase and combine this with 10 ml of scintillator mix for counting ^{32}P.

26. 15 ml represents 75% of original sample.

RESULTS AND DISCUSSION

This improved method for isolation and beta counting ^{32}P in aqueous environmental samples at the Savannah River Laboratory has been used successfully for nearly 3 years. The decontamination of ^{32}P from interferences is about 10^4, and the recovery of ^{32}P from spiked samples is at least 85%. The analysis of control spikes during this period shows the method to have a sensitivity of 14 pCi/l and a precision of 11% when using a 50 ml sample.

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Table I. Beta Emitters Monitored at the Savannah River Plant

Isotope	Beta Energy, MeV (max.)	Half-Life
^{3}H	0.0186	12.262 years
^{35}S	0.167	87.9 days
^{89}Sr	1.463	52.3 days
^{90}Sr	0.546	27.7 years
^{90}Y	2.27	64.0 hours
^{91}Y	1.54	58.0 days
^{147}Pm	0.224	2.62 years

Table II. Comparison of Solubility of Pentanol and Hexanol

Solvent	Solubility
Pentanol	2.7 g/100 ml at 22°C
Hexanol	0.59 g/100 ml at 20°C

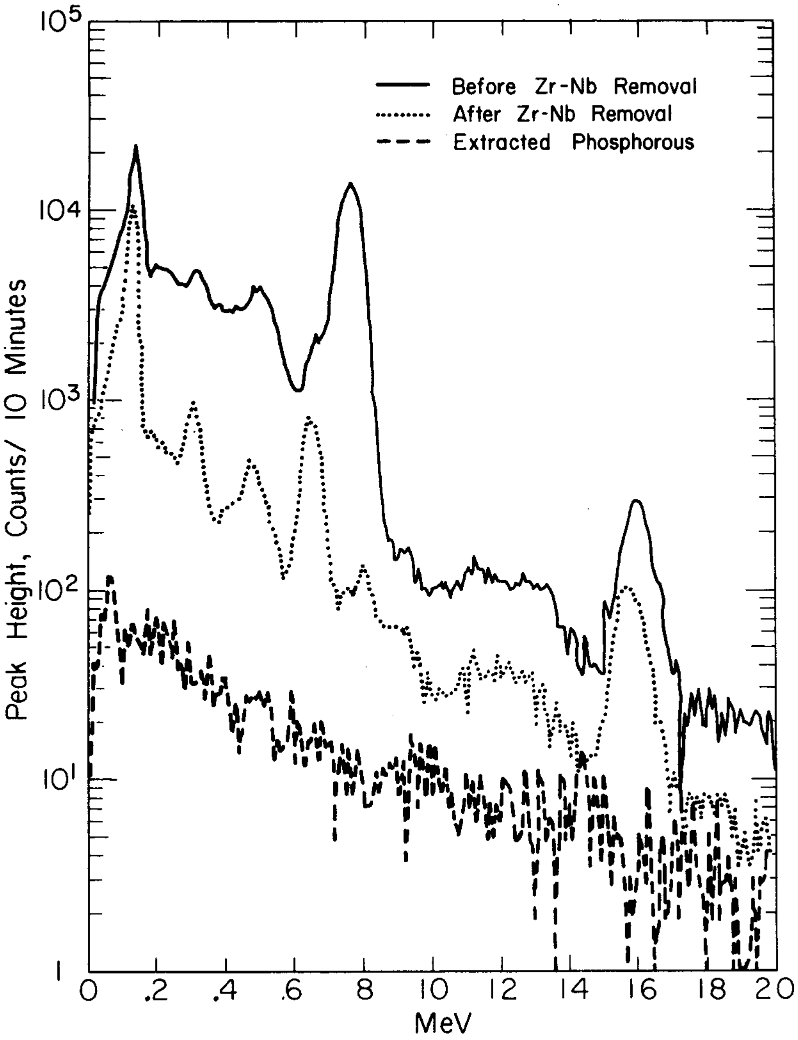

FIGURE 1. Spectra of an Aqueous Environmental Sample Containing ^{32}P

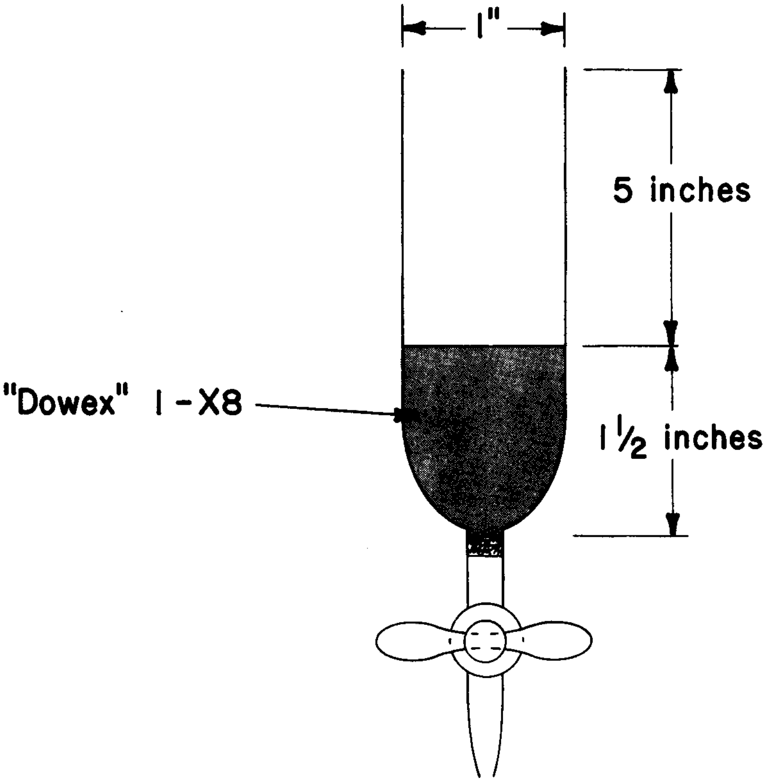

FIGURE 2. Anion Exchange Column