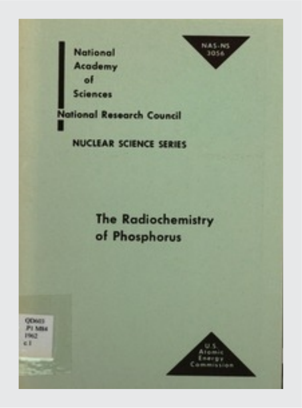

Radiochemistry of Phosphorus

DETAILS

42 pages | 6 x 9 | PAPERBACK
ISBN 978-0-309-36482-9 | DOI 10.17226/21554

AUTHORS

Mullins, William T.; Leddicotte, G. W.; Subcommittee on Radiochemistry; Committee on Nuclear Science; National Research Council

COMMITTEE ON NUCLEAR SCIENCE

L. F. CURTISS, *Chairman*
National Bureau of Standards

ROBLEY D. EVANS, *Vice Chairman*
Massachusetts Institute of Technology

J. A. DeJUREN, *Secretary*
Westinghouse Electric Corporation

C. J. BORKOWSKI
Oak Ridge National Laboratory

ROBERT G. COCHRAN
Texas Agricultural and Mechanical College

SAMUEL EPSTEIN
California Institute of Technology

U. FANO
National Bureau of Standards

HERBERT GOLDSTEIN
Nuclear Development Corporation of America

J. W. IRVINE, JR.
Massachusetts Institute of Technology

E. D. KLEMA
Northwestern University

W. WAYNE MEINKE
University of Michigan

J. J. NICKSON
Memorial Hospital, New York

ROBERT L. PLATZMAN
Laboratoire de Chimie Physique

D. M. VAN PATTER
Bartol Research Foundation

LIAISON MEMBERS

PAUL C. AEBERSOLD
Atomic Energy Commission

J. HOWARD McMILLEN
National Science Foundation

CHARLES K. REED
U. S. Air Force

WILLIAM E. WRIGHT
Office of Naval Research

SUBCOMMITTEE ON RADIOCHEMISTRY

W. WAYNE MEINKE, *Chairman*
University of Michigan

NATHAN BALLOU
Naval Radiological Defense Laboratory

GREGORY R. CHOPPIN
Florida State University

GEORGE A. COWAN
Los Alamos Scientific Laboratory

ARTHUR W. FAIRHALL
University of Washington

JEROME HUDIS
Brookhaven National Laboratory

EARL HYDE
University of California (Berkeley)

JULIAN NIELSEN
Hanford Laboratories

G. DAVID O'KELLEY
Oak Ridge National Laboratory

ELLIS P. STEINBERG
Argonne National Laboratory

PETER C. STEVENSON
University of California (Livermore)

DUANE N. SUNDERMAN
Battelle Memorial Institute

CONSULTANTS

HERBERT M. CLARK
Rensselaer Polytechnic Institute

JOHN W. WINCHESTER
Massachusetts Institute of Technology

CHEMISTRY

The Radiochemistry of Phosphorus

W. T. MULLINS and G. W. LEDDICOTTE

Oak Ridge National Laboratory
Oak Ridge, Tennessee

Issuance Date: March 1962

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Available as NAS-NS-3056 for $9.00 from

National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22161

Printed in the United States of America
USDOE Office of Scientific and Technical Information,
Oak Ridge, Tennessee

1962: latest printing May 1985

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of phosphorous is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of phosphorous which might be included in a revised version of the monograph.

CONTENTS

The Radiochemistry of Phosphorus

W. T. MULLINS and G. W. LEDDICOTTE
*Oak Ridge National Laboratory**
Oak Ridge, Tennessee

I. GENERAL REFERENCES ON THE INORGANIC AND ANALYTICAL CHEMISTRY OF PHOSPHORUS

Remy, H., Treatise on Inorganic Chemistry, Volume I, Elsevier, Amsterdam (1956).

Kleinberg, J., Argersinger, W. J., Jr., and Griswold, E., Inorganic Chemistry, Heath, Boston (1960).

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. L., Applied Inorganic Analysis, John Wiley and Sons, New York, 1958.

Wilson, C. L., and Wilson, D. W., Comprehensive Analytical Chemistry, Elsevier, Amsterdam, 1959.

Sienko, M. J., and Plane, R. A., Chemistry, McGraw-Hill, New York, 1957.

Charlot, G., and Bezier, D., Quantitative Inorganic Analysis, John Wiley and Sons, New York, 1957.

Sidgwick, N. V., The Chemical Elements and Their Compounds, University Press, Oxford, 1951.

Van Wazer, J. R., Phosphorus and Its Compounds: Volume I: Chemistry, Interscience, New York, 1958.

Hutchinson, E., Chemistry - The Elements and Their Reactions, Saunders, Philadelphia, 1959.

II. RADIOACTIVE NUCLIDES OF PHOSPHORUS

The radioactive nuclides of phosphorus that are of interest in the radiochemistry of phosphorus are given in Table I. This table has been compiled

---

*Operated for U. S. Atomic Energy Commission by Union Carbide Corporation.

from information appearing in reports by Strominger, et al.,$^{(1)}$ and by Hughes and Harvey.$^{(2)}$

TABLE I

THE RADIOACTIVE NUCLIDES OF PHOSPHORUS

Radio-nuclide	Half-life	Mode of Decay	Energy of Radiation	Produced By
P^{29}	4.6 s	β^+	γ 1.28, 2.42	Si-p-n, Si-d-n, P-γ-2n
P^{30}	2.55 m	β^+	β^+ 3.4 abs	Al-α-n, Si-p-n, Si-He^3-p, P-n-2n, P-γ-n, S-d-α, Cl-γ-α,n
P^{32}	14.3 d.	β^-	β^- 1.70	Si-d-γ, Si-d-p, Si-He^3-p P-d-p, P-n-γ, S-n-p, S-d-α, Cl-n-α, Cl-γ-α,n, Cl-d-pα
P^{33}	25.4 d	β^-	β^- 0.25 abs	S-n-p, S-γ-p, Cl-γ-α
P^{34}	12.4 s	β^-	β^- 5.1, 3.2	S-n-p, Cl-n-α

III. THE GENERAL CHEMISTRY OF PHOSPHORUS

Phosphorus is never found in nature as the element. The chief sources of phosphorus are phosphate rock, $Ca_3(PO_4)_2$, and apatite, $CaF_2 \cdot 3Ca_3(PO_4)_2$. It is usually obtained from these sources by mixing coke and sand with the crushed rock or ore and heating the mixture in an electric furnace. Since the temperature of the reaction is quite high, the phosphorus distills away from the reaction mixture and is trapped and condensed under water as yellow or white phosphorus.

A. Elementary Phosphorus

Phosphorus exists in at least three allotropic forms. The white phosphorus (or yellow phosphorus, if it is impure) obtained by a distillation of phosphorus has a melting point of 44°C. It dissolves in organic liquids, crystallizes in the cubic form, and burns spontaneously in air. When heated in the absence of air to a temperature of 250° C, it is converted to red phosphorus. The color and physical properties of red phosphorus depends upon the temperature and the length of the heating period. It will crystallize in the rhombohedral form, and it is stable in air at room temperature. Red phosphorus is insoluble in organic liquids. A black allotropic form of phosphorus is obtained by heating white phosphorus at 200° C and at a pressure of about 13,000 atmospheres. It is rhombohedral in form and is a good electrical conductor. Black phosphorus can be converted to red phosphorus by heating at temperatures above 500°.

B. The Chemical Compounds of Phosphorus

Phosphorus exhibits oxidation states of -3, -2, +1, +2, +3, +4, and +5. The principle oxidation state of phosphorus is +5; however, +3 compounds are not uncommon. Phosphorus can form compounds with hydrogen, oxygen, sulfur, the halogens, and nitrogen. It can react with certain metals to form phosphides. Table II lists many of the phosphorus compounds and gives information on their solubility in water and other agents. Some general information about these and other phosphorus compounds is given below. More specific information has been given in reviews by Van Wazer(3) and Hutchinson.(4)

Table II. Solubility of Phosphorus Compounds

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	PBr_3	Decomposes		Decomposes in alcohol; Soluble in ether, chloroform, CS_2 and CCl_4
	PBr_5	Decomposes		Soluble in CS_2, CCl_4 and benzene
Chlorides	PCl_2	Hydrolyzes		
	PCl_3	Decomposes	Decomposes	Soluble in ether, benzene, chloroform, CS_2 and CCl_4
	PCl_5	Decomposes		Decomposes in acid; soluble in CCl_4 and CS_2
Fluorides	PF_3	Decomposes		Decomposes in alkali; soluble in alcohol
	PF_5	Decomposes		
Iodides	P_2I_4	Decomposes		Soluble in CS_2
	PI_3	Decomposes	Decomposes	Very soluble in CS_2
Nitrides	P_3N_5	Insoluble	Very slightly soluble; Decomposes	Insoluble any solvent
Oxides	P_2O_3	Decomposes to H_3PO_3		
	P_2O_4	Very soluble to H_3PO_3	Decomposes	
	P_2O_5	Decomposes	Decomposes	Soluble in H_2SO_4; insoluble in acetone and NH_3
Oxy Salts	$POBr_3$	Decomposes		Soluble in H_2SO_4, CS_2, ether, benzene and chloroform
	$POBrCl_2$	Decomposes		
	$POCl_3$	Decomposes	Decomposes	Decomposes in alcohol and acid
	$P_2O_3Cl_4$	Decomposes		
	$POBr_2Cl$	Decomposes		
	POF_3	Decomposes		Decomposes in alcohol
	PON	Insoluble	Insoluble	Insoluble in acid and alkali
	$P_4O_6S_4$	Decomposes		Soluble in CS_2

1. Reactions with Hydrogen

The hydrogen compounds of phosphorus cannot be prepared by a direct union of the elements. Phosphine, PH_3, and diphosphine, P_2H_4, are usually formed by heating white phosphorus in the presence of aqueous sodium hydroxide or by hydrolyzing aluminum phosphide with sulfuric acid. PH_3 is extremely volatile and is inflammable in air. Phosphine is a toxic compound and is considerably less soluble in water than is ammonia. It is a much weaker base than ammonia, forming only a few phosphonium, PH_4^+, salts with the halides. These salts are strongly hydrolyzed in solution and exhibit strong acid characteristics. Diphosphine is not basic and forms no salt compounds.

2. Reactions with Oxygen

Phosphorus forms three oxide compounds with oxygen: the trioxide, P_2O_3, the tetroxide, P_2O_4, and the pentoxide, P_2O_5. The trioxide and the pentoxide are the most important of the oxygen compounds. Frequently, the formulas are written as P_4O_6 and P_4O_{10} because of the densities of their vapors.

The trioxide is produced by burning white phosphorus in a limited supply of oxygen. P_4O_6 is a colorless solid which melts at 24° and boils at 173°. P_4O_{10}, a colorless liquid, sublimes at temperatures above 360°. Phosphorus tetroxide, P_4O_8, is formed by heating P_4O_6 to temperatures above 200°. It is a solid, having a melting point higher than 180°. The pentoxide is formed by burning phosphorus in oxygen.

P_4O_8 reacts vigorously with water to form the oxyacid, phosphorous acid, H_3PO_3. H_3PO_3 can also be formed very slowly by reacting P_4O_6 with cold water. In hot water, the H_3PO_3 that forms rapidly decomposes to produce phosphoric acid and phosphine. P_4O_{10} also reacts vigorously with water to first produce meta-phosphoric acid, HPO_3, and then by a further hydrolysis reaction, orthophosphoric acid, H_3PO_4.

Phosphorous acid, H_3PO_3, can also be formed by reacting phosphorus halides, i.e., PCl_3, PBr_3, and PI_3 with water. H_3PO_3 is a colorless crystalline solid which melts at 73°. When heated above 200°, it decomposes to give phosphine and phosphoric acid. Phosphorous acid is an active reducing agent because it can be readily oxidized to phosphoric acid. Its alkali salts (such as NaH_2PO_3) will lose water when heated to 160° to give a pyrophosphite salt, e.g., $Na_2H_2P_2O_5$.

Hypophosphorous acid, H_3PO_2, is produced as transparent crystals by the reaction of barium salts of phosphorus with H_2SO_4. The crystals melt at 26.5°. H_3PO_2 and its salts, the hypophosphites, are strong reducing agents (P has an oxidation state of P^{+1} in these compounds) and can be used to reduce such elements as the halogens and Fe^{+3} ions, e.g., chlorine to chloride and ferric ions to iron.

Metaphosphorous acid, HPO_2, can be formed by burning phosphine in a limited supply of oxygen. Pyrophosphorous acid, $H_4P_2O_5$, is a colorless solid that is formed by heating alkaline hypophosphites, e.g., NaH_2PO_3, at 160°. $H_4P_2O_5$ melts at 38° and it will decompose when it is heated above 130°. HPO_2 and $H_4P_2O_5$ are rapidly converted to H_3PO_3 in the presence of water. The phosphorous acids contain phosphorus in the +3 oxidation state. All of these acids and their salts are reducing agents.

P_4O_{10}, at various degrees of hydration, reacts to form the series of oxyacids of phosphorus known as the phosphoric acids. Orthophosphoric acid, H_3PO_4, is formed by reacting P_4O_{10} with an adequate supply of water. H_3PO_4 is a colorless solid that melts at 142°C. It is very soluble in water. It will react with most of the metals to form orthophosphate salts, classified either as primary, secondary, or normal phosphates. The primary, or dihydrogen, phosphates, e.g., NaH_2PO_4, are soluble in water and yield slightly acid solutions. The secondary, or monohydrogen, phosphates, e.g., Na_2HPO_4, although only slightly soluble in water yield alkaline solutions. The normal, or triphosphates, e.g., Na_3PO_4, are more completely hydrolyzed in aqueous solution to yield alkaline solutions. The primary and secondary phosphates decompose rapidly when heated into metaphosphates and pyrophosphates. The triphosphates are stable toward heat.

H_3PO_4 loses water as it is heated to 250° C, and it is gradually converted to pyrophosphoric acid, $H_4P_2O_7$. Pyrophosphoric acid will crystallize from the melt as a colorless solid. The solid melts at 55°. $H_4P_2O_7$ can also be produced by strongly heating Na_2HPO_4. It yields two series of salts in its reactions with other elements;

namely, normal salts, such as $Na_4P_2O_7$ or $Mg_2P_2O_7$, and dihydrogen salts, such as $Na_2H_2P_2O_7$. The alkali metal salts of both series are soluble in most reagents; however, only the dihydrogen salts of other metal ions are readily soluble. $Mg_2P_2O_7$, magnesium pyrophosphate, is an accepted gravimetric weighing form for the quantitative determination of either phosphate ions, PO_4^{-3}, or magnesium, in many different types of sample materials.(5) The insoluble compound, $MgNH_4PO_4$, is first precipitated and then converted by heat into the pyrophosphate compound.

If $H_4P_2O_7$ is heated to 200°, it will lose water to form metaphosphoric, or glacial phosphoric, acid, HPO_3. The acid is very soluble in water and it will change slowly in cold water into orthophosphoric acid, H_3PO_4. In hot water (100°C) this change is very rapid. The salts of this acid are the metaphosphates, e.g., $(NaPO_3)_3$ or $(NaPO_3)_6$. Other complexes, having the formula, $(NaPO_3)_x$, are also known. The hexa metaphosphates, such as $(NaPO_3)_6$ form soluble complexes with many multivalent cations, e.g., $Na_2Ca_2P_6O_{18}$.

3. Reactions with Sulfur

Phosphorus and sulfur can combine directly with each other to form sulfur compounds. If white phosphorus is used, an explosive reaction occurs. When red phosphorus and sulfur are mixed, chemical combination occurs and proceeds quietly, and, according to the proportions used for each element, will form either P_4S_3, P_4S_5, P_4S_7, or P_4S_{10}. Tetraphosphorus trisulfide, P_4S_3, is the most important of the phosphorus sulfide compounds, being used chiefly in the manufacture of "strike-anywhere" matches. Phosphorus pentasulfide, P_4S_{10}, can be hydrolyzed to H_3PO_4, and this reaction with water makes it possible to use P_4S_{10} to introduce the group SH in the place of the hydroxyl group into organic compounds.

4. Reactions with the Halogens

Trivalent phosphorus can combine directly with all of the halogens to form the trihalides, PF_3, PCl_3, PBr_3, and PI_3. Pentavalent phosphorus will only form pentahalides with fluorine, chlorine, and bromine. The pentaiodide is not known; however, a tetraiodide, P_2I_4, can be formed by dissolving hydrogen and iodine in carbon disulfide. Several mixed halides of the type PF_2Br are also known.

The trihalide compounds react readily with water to form hydrogen halides and hypophosphorous acid, H_3PO_3. Since the trihalides contain phosphorus in the +3 oxidation state, they are easily oxidized. For example, PCl_3 reacts with air to room temperature to form the oxyhalide $POCl_3$ or mixed oxyhalides of the type, POF_2Cl. PCl_3 and PBr_3 can react with chlorine and bromine, respectively, to form the pentavalent halides, PCl_5 and PBr_5.

The pentahalide compounds are all rapidly attacked by water to form hydrogen halides and phosphoric acid, H_3PO_4. PF_5 is stable toward heat but PCl_5 and PBr_5 can easily dissociate into free halogen and the trivalent phosphorus halide when heated. The phosphorus pentahalide compounds can undergo hydrolysis to form oxyhalides of the type, POF_3, $POCl_3$, and $POBr_3$.

5. Reactions with Nitrogen

Phosphorus and nitrogen do not combine directly; however, a nitride, P_3N_5, can be formed by heating P_4S_{10} in an ammonia atmosphere at a temperature of 230°. P_3N_5 is a colorless solid which can be decomposed at 800° to give nitrogen and another nitride, PN. Hot water will hydrolyze both nitrides to form ammonia and oxyacids of phosphorus. The reactions of the phosphorus pentahalides with ammonia will produce phosphorus-nitrogen halides of the type, $PNCl_2$. All of these compounds will hydrolyze to produce ammonia and oxyacids of phosphorus.

6. Reactions with Metals

Phosphorus can also react directly with metals to form phosphides, e.g., Na_3P. Several metal phosphides, such as Ca_3P_2, can be prepared by reducing the corresponding phosphate with carbon. The metal phosphides are rapidly hydrolyzed by water or decomposed by acids to form phosphine and metallic ions.

IV. THE ANALYTICAL CHEMISTRY OF PHOSPHORUS

Phosphorus, after its separation from other chemical elements, is most frequently converted to orthophosphoric acid, and the orthophosphate ion determined gravimetrically. Such precipitating agents as magnesia mixture,(5) ferric chloride and ammonium acetate,(6,7) zirconyl chloride,(8) and molybdic acid,(5,9) barium acetate,(10) thallium acetate and silver nitrate,(11) and oxine(12) have been used to precipitate PO_4^{---}. The precipitation of the pyrophosphate ion, $P_2O_7^{----}$, with zinc sulfate has also been used in the gravimetric determination of phosphorus.(13-15) The compounds resulting from the reactions of these agents with PO_4^{-3} are as follows: ammonium magnesium phosphate, $NH_4MgPO_4 \cdot 6H_2O$; iron posphate, $FePO_4$; zirconyl hydrogen phosphate, $(ZrO)HPO_4$; ammonium phosphomolybdate, $(NH_4)_3(MoO_3)_{12}PO_4$; barium phosphate, $BaHPO_4$; silver thallium phosphate, Ag_2TlPO_4; oxinium 24-molybdo-2-phosphate, $6C_9H_7ON \cdot P_2O_5 \cdot 24MoO_3 \cdot 11H_2O$; and zinc phosphate, $ZnPO_4$.

Any one of the above gravimetric forms can be used in a carrier radiochemical procedure for radioactive phosphorus. However, it is not always necessary to obtain the phosphorus carrier and the radioactivity in a precipitible form before the radioactivity measurements. One of the phases obtained in a solvent extraction method or an aliquot of an eluate from an ion-exchange separation column could be used. Thus, the information that follows generally reports on current analysis ideas used in isolating and determining nonradioactive phosphorus. The same techniques can be easily applied to analytical determinations of radioactive phosphorus.

A. Separation by Precipitation

A complete separation of phosphorus from many other elements can be obtained by precipitating phosphorus in nitric acid solution as ammonium phosphomolybdate.(5,9) Sodium hydroxide will precipitate and completely separate iron, nickel, cobalt, trivalent chromium, titanium, and zirconium from phosphorus. The acid-sulfide elements can be easily separated by saturating a mineral acid solution with hydrogen sulfide. The volatility of arsenic and germanium chlorides can be used to separate these elements from phosphorus.

The ammonium phosphomolybdate precipitation is usually considered a preliminary separation method, since a stoichiometric composition of the phosphomolybdate compound is difficult to achieve. Thus, this compound is subsequently treated and the phosphorus precipitated in some other form. The most frequently used method involves a precipitation as magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, with magnesia mixture.(5) The phosphate compound is then ignited to magnesium pyrophosphate, $Mg_2P_2O_7$, in a muffle furnace at 1050 to 1100° C.

Arsenic, and moderate amounts of iron, aluminum, vanadium, zinc, tin, selenium, tellurium, titanium, or zirconium can interfere in the phosphate precipitation. However, arsenic may be removed by adding solid ammonium bromide to the solutions and boiling the solution to near dryness. The other elements can be complexed by adding citric acid to the solution before the addition of an excess of the magnesia mixture. Molybdenum, vanadium, and tungsten can also be separated from phosphorus by precipitating it with magnesia mixture at a low temperature and in the presence of tartrates.

Complete separations of iron, vanadium, zirconium, titanium, niobium, tantalum, and gallium from phosphorus can be obtained by precipitating these elements from ice-cold solutions containing free mineral or organic acids with cupferron.(16-18) Aluminum, beryllium, boron, manganese, nickel, and uranium can interfere in this separation.

B. Separation by Electrolysis

Although phosphorus cannot be separated from solution by electrodeposition, it can be effectively separated by electrolysis with a mercury cathode.(19-2 Chromium, iron, cobalt, nickel, copper, zinc, gallium, germanium, molybdenum, rhodium, palladium, silver, cadmium, indium, tin, rhenium, iridium, platinum, gold, mercury, thallium, and bismuth are readily deposited upon the mercury cathode from dilute sulfuric acid solutions. Phosphorus (and aluminum, titanium, vanadium, zirconium, and uranium) will not deposit on the cathode.

C. Separation by Volatility

Phosphorus can be liberated from an acid solution (HCl) as phosphine in a sweeping atmosphere of argon.(24,25) Generally applied to the determination of phosphorus in aluminum metal or its alloys, this separation frees phosphorus from many of the elements. Silicon and organic matter are the chief interferences; however, these can be removed by dehydration with perchloric acid.

D. Solvent Extraction Separations

P^{+5} can be partially extracted (about 15%) from a 21 M MHF solution with ethyl ether.(26) In such a system only Nb^{+5}, Ta^{+5}, and Re^{+7} are extracted greater than 50%; Sn^{+2}, Sn^{+4}, As^{+3}, As^{+2}, Te^{+4}, Ge^{+4}, Se^{+4}, V^{+3}, V^{+5}, Mo^{+6}, and Sb^{+3} will also partially extract. P^{+5} as $(NH_4)_2PO_4$ is partially extracted (about 21%) from an 8 $\underline{M}$ HNO_3 into ethyl ether.(27) Under these conditions, Au^{+3} is completely extracted while U^{+6}, Zr^{+4}, Th^{+4}, Tl^{+3}, Hg^{+2}, Cr^{+6}, Ce^{+4}, Bi^{+3}, and As^{+3} are extracted in varied concentrations.

Phosphorus as the heteropoly acid molybdephosphoric acid complex can be separated from molybdosilicic acid by extractions with ethyl acetoacetate,(28) ethyl acetate,(29) or butyl acetate.(30) It can also be extracted from steels with a mixture of 1-butanol (20% by volume) in chloroform.(31) Ether(32) and isobutanol(33) have also been used to extract phosphorus heteropoly acids from other elements.

The solubility of H_3PO_4 (and H_2SO_4) in ether can be used for the separation of phosphate.(34) PO_4 can be quantitatively extracted by converting it to H_3PO_4 by the addition of concentrated H_2SO_4 and extracting the H_3PO_4 with excess H_2SO_4 into ethyl ether. As, Sb, V, Zr, Mo, and U are partially or completely dissolved in the solvent mixture. Ag, Pb, Bi, Cu, Cd, Sn, Cr, Al, Ti, Th, Ca, Ba, Sr, Ni, Co, Mn, Zn, Mg, Na, K, and the rare earths are practically insoluble under these conditions.

A butanol-chloroform mixture has been used to extract P from a 5 $\underline{M}$ HNO_3 solution.(35) Mn, Si, Cr, and V do not interfere in this extraction.

Solvent extraction methods have also been used in the carrier-free separation of P^{32} (14.3 d) neutron-irradiated sulfur targets.(36-38)

E. Chromatographic Separations

1. Inorganic Absorbents

PO_4^{+3} has been separated from a mixture of at least 12 other anions by use of alumina columns pre-treated with nitric acid.(39) Kubli(42) has also extended this method to the separation of PO_4^{+3} from many other anions.

Carrier-free P^{32} (14.3 d) has been separated from neutron-irradiated elementary sulfur by adsorption either on a silica gel column from a CS_2 solution(41) or on alumina from an alkali solution.(42) The efficiency of adsorption of P^{32} was about 95%.

2. By Ion Exchange Resins

Samuelson and Runneberg(43) report that many applications using ion-exchange resin columns are possible for either the quantitative determination of phosphate ions on their separation from other elements and anions. These extensive studies should be consulted. In addition to these studies, exchange resin methods have been developed either to determine phosphate in rock,(44) phosphorus in copper and ferrous alloys(45) or to separate cations previous to the determination of phosphates.(46-49) Phosphorus (and sulfur and arsenic) have been separated from nickel and copper by ion exchange.(50) Theoretical studies on the elution of orthophosphate, pyrophosphate, tri-, meta-, and trimeta-phosphate from a Dowex 1-X10 resin column with different Cl^- concentrations and at different pH have been made by Benhenkang, et al.(52) Yoshino(53) has separated orthophosphates from arsenates by a similar method.

3. By Paper Chromatography

Phosphate ions, PO_4^{-3}, show a distinct rate of movement in paper chromatography systems using such solvents as butanol-HCl mixtures,(54) alcohol-HNO_3 mixtures,(55) and butanol-HBr mixtures.(56) Phosphate ions have been separated from ferrocyanide, ferricyanide, sulfide, arsenate, and iodide ions by use of butanol-ethanol-water mixtures as solvents.(57) Numberous anions of P^{+5} have been separated by Ebel and Volmar(58) using filter paper washed with HCl or treated with 8-hydroxyquinoline. Phosphates, phosphites, and hypophosphates have separated on HCl-washed paper using equal volumes of n-butanol, dioxan, and 1 N NH_4OH as a solvent.(59) Other studies concerned with phosphate mixtures included those investigated by Ebel,(60-62) Yamaguchi,(63) Gauthier,(64) Meissner,(65) Crowther,(66) and others.(67,68) Weil(69) has separated phosphor-organic compounds, e.g., phosphonous, phosphinic, and phosphinon acids, by paper chromatography.

Marinette, et al.,(70,71) Benson, et al.,(72) and Benson(73) have used silicic acid-impregnated paper and solvents such as phenol-distilled water (100 g to 40 g) and n-butanol-propionic acid-water mixtures to separate phosphorus as phosphatides. Benson, et al.,(72) and Benson(73) have separated the phosphatide components of a mixture on paper prior to an activation in a nuclear reactor.

V. DISSOLUTION OF SAMPLES CONTAINING PHOSPHORUS

Most of the methods used to decompose phosphorus-bearing materials produce phosphorus in the orthophosphate form.(74) Most of the phosphorus chemical salts are readily soluble in water or dilute acid. Most metals and alloys containing phosphorus must be put into solution with a strong oxidizing acid such as HNO_3 in order to prevent its loss as phosphine. If HF is used, it should be removed after dissolution by evaporation.

Rocks and minerals are usually fused with sodium carbonate or peroxide, and the melt extracted with water. Prolonged fusions with pyrosulfate can result in some loss of phosphorus by volatility.

Biological materials, such as tissues, body fluids, vegetation, etc., can be decomposed with HCl, HNO_3, HNO_3-H_2SO_4, or HNO_3-$HClO_4$ mixtures.(75,76) Compounds of phosphorus mixed with organic material must not be ignited in platinum unless good oxidizing conditions are maintained.(74)

If any of these dissolution techniques are used in a radiochemical separation of phosphorus radioactivity, the addition of inactive <u>phosphorus carrier</u> to the solubilizing mixture would assist in achieving an isotopic exchange between the radioactive and inactive phosphorus atoms.

VI. SAFETY PRACTICES

Chemical decomposition and processing of any sample material can be hazardous. Adequate safety precautions for processing any sample material have been recently described by Pieters and Creyghton.(77) This manual, as well as others on laboratory safety, should be consulted before any analysis is undertaken.

Whenever radioactive material is processed in a laboratory area, the needs for safe laboratory practices are greatly magnified. A discharge of radioactivity into a laboratory area by evolution or spillage can result in hazardous conditions for personnel and possible wide spread contamination throughout the laboratory area. Safe handling practices for processing radioactive materials appear in such sources as the Oak Ridge National Laboratory's Master Analytical Manual(78) and in the International Atomic Energy Agency's publication, entitled, "Safe-Handling of Radioisotopes."(79) Many other similar sources of information exist and should be consulted.

VII. COUNTING TECHNIQUES FOR THE RADIOACTIVE PHOSPHORUS ISOTOPES

The nuclear characteristics of the radioactive isotopes of phosphorus are summarized in Table I of this monograph.

The most frequently measured phosphorus radioisotope is P^{32} (14.3 d). It emits 1.70-Mev beta radiations in its decay, and its radioactivity can be measured by such counting techniques as Geiger-Mueller counting or proportional counting.(80,81) Generally, the sample material containing P^{32} must be processed radiochemically before the radioactivity measurements are made.

VIII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR PHOSPHORUS-32

Most of the radiochemical procedures that follow have been developed either to obtain 14.3 day P^{32} as a tracer,(82) or to separate it from fission products,(83) or to use P^{32} in the determination of stable phosphorus in a variety of sample materials by the radioactivation analysis method.(84,85) This analysis method has already been used to determine phosphorus in aluminum alloys,(87) niobium,(86) lead,(86) alumina,(86,87) aluminum phosphate,(86) biological materials,(88-97) graphite,(98) iodine,(99) silicon,(100,101) iron,(102-105) nickel(105) magnesium,(106) and organic compounds.(97)

Both carrier and carrier-free techniques have been used in these procedures. This information, as well as that concerned with the type of material analyzed, nuclear bombardment, method, time required for separation, and decontamination of P^{32} from other radioactivities, appears as part of each procedure.

Most of the procedures mentioned in the references are generally the same in that the phosphorus is first precipitated as the phosphomolybdate, and the final precipitate as $MgNH_4PO_4 \cdot 6H_2O$ with magnesia mixture. The procedures chosen for this monograph as illustrations of P^{32} radiochemical separations were based mostly on the matrix of the sample, the reactor facility used for irradiation, and the dissolution of the irradiated samples. The procedures used by Odeblad and others,(90,91) Reiffel(92) Schmeiser and Jerchel,(93) Spencer and others,(94) Tobias and Dunn,(95,96) Lvov and Naumova,(98) Herr,(102) Overman and Swartout,(103) Talbot and others,(104) Thompson,(105) and Dow(106) use techniques similar to those given in the procedures in this section.

PROCEDURE 1

Procedure Used In: Preparation of P^{32} tracer

Method: Precipitation

Type Material Analyzed: Copper

Type of Nuclear Bombardment:
- a. 60" cyclotron (37 Mev alphas, 9.5 Mev protons, 19 Mev deuterons)
- b. 184" cyclotron (388 Mev alphas, 348 Mev protons, 194 Mev deuterons)

Procedure By: Batzel (Reported by Meinke(82))

Separation Time: 2 hours

Chemical Yield of Carrier: 60%

Decontamination: Factor of 100 from all activities present except vanadium; probably a factor of 50 from vanadium.

Equipment Needed: Standard

Procedure:

1. Dissolve target in HNO_3. Add 5 mg P as PO_4^{-3} and neutralize most of free acid with NH_4OH.

2. Make 1 N in HNO_3 and add ammonium molybdate to the warm solution (50° C) (add 6 ml of molybdate for every 4 mg of P).

3. Allow to settle for 15 minutes. Centrifuge and wash with 1% HNO_3.

4. Dissolve with NH_4OH citrate solution and add HCl until the ppt that forms dissolves with difficulty.

5. Bubble SO_2 through the solution to reduce VO_3^- to VO^{++}. Add 2 ml of cold $MgCl_2$ mixture - allow to settle 5 minutes and add conc. NH_4OH until solution is 1/4 of original volume. Allow to settle for 15 min. Centrifuge and wash precipitate with 1:4 $NH_4OH:H_2O$.

6. Add 5 mg vanadium holdback carrier and repeat step (5).

7. Dissolve ppt in 1 N HNO_3.

8. Repeat (2) and (3).

9. Weigh as ammonium phosphomolybdate.

Remarks:

Vanadium co ppts with phosphorus if it is in V^{+5} state. It should be reduced to VO^{++} state and the cycle repeated two times in order to remove vanadium completely.

PROCEDURE 2

Procedure Used In: Separation from fission products

Method: Precipitation

Type Material Analyzed: Separation of phosphorus from fission products

Type of Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$ from P^{31} in fuel

Procedure By: Bonner, N. A., and Potratz, H. A., in report compiled by Kleinberg(83)

Separation Time: 7 hours

Chemical Yield of Carrier: 70-80%

Decontamination: Complete from fission products

Equipment Required: Standard

Procedure:

1. To the sample in a 40-ml Lusteroid centrifuge tube (Note 1), add 20 ml of 6 M HNO_3 and 1.0 ml of $(NH_4)_2HPO_4$ carrier solution. Heat the solu-

tion on a steam bath and add 2 ml of Zr carrier to precipitate zirconium phosphate. Continue heating for 3 to 5 min. Centrifuge and discard the supernate. Wash the precipitate with H_2O and discard the washings.

2. Dissolve the precipitate in 0.1 ml of conc. HF and add 5 ml of H_2O, 10 ml of 6 <u>M</u> HNO_3, 5 drops of 0.1% aerosol solution, and 5 ml of ammonium molybdate reagent. Heat the mixture on a steam bath for 2 to 5 min. Centrifuge and discard the supernate. Wash the ammonium phosphmolybdate precipitate with 10 ml of H_2O containing a few drops of aerosol (Note 2).

3. Dissolve the precipitate in 0.5 ml of conc. NH_4OH, add 10 ml of H_2O and 4 drops of 30% H_2O_2 (Superoxol) and stir thoroughly. Add 10 ml of conc. HCl and 2 ml of Zr carrier (Note 3), and heat on a steam bath for 5 min. Centrifuge and discard the supernate. Wash the precipitate with H_2O and discard the washings.

4. Dissolve the precipitate in 0.2 ml of conc. HF and add 10 ml of 3 <u>M</u> HCl, 0.5 ml of As carrier and a few drops of aerosol solution. Heat on a steam bath for 15 min. while bubbling H_2S through the solution. Centrifuge and transfer the supernate to a clean 40-ml Lusteroid centrifuge tube. Wash the precipitate with 1 to 2 ml of H_2O containing a few drops of aerosol solution. While the precipitate is being washed, pass H_2S through the original supernate which is being heated on a steam bath. Combine the supernate from the washing with the original supernate. Discard the As_2S_5 precipitate.

5. Add 2 ml of La carrier to the solution from Step 4. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the LaF_3 precipitate.

6. To the supernate, add 4 ml of conc. HNO_3 and 5 ml of ammonium molybdate reagent. Heat on a steam bath for 2 to 5 min., centrifuge, and discard the supernate. Wash the precipitate with 10 ml of H_2O containing a few drops of aerosol and discard the washings.

7 - 14. Repeat Steps 3 - 6 twice more.

15. Dissolve the ammonium phosphomolybdate precipitate in 1 ml of conc. NH_4OH and add 2 ml of citric acid solution (0.5 gm/ml). Add 10 ml of magnesia

mixture and conc. NH_4OH (dropwise) until the solution is just alkaline, then add 10 drops more. Swirl the solution for about 1 min. and if a precipitate does not begin to form, add an additional 5 drops of conc. NH_4OH. After precipitation begins, swirl the mixture for at least 1 min. and then add 4 additional ml of conc. NH_4OH. Allow the mixture to stand with occasional stirring for at least 10 min. Filter through a 15-ml fine, sintered glass funnel and wash the precipitate with a small amount of 1:20 NH_4OH. Dissolve the precipitate in a few drops of conc. HCl and a few milliliters of H_2O. Collect the filtrate in a 100-ml beaker.

16. Add 10 ml of magnesia mixture and just enough conc. NH_4OH to neutralize the HCl in the mixture. (One drop of NH_4OH in excess should cause the precipitate of $MgNH_4PO_4 \cdot 6H_2O$ to start forming.) Swirl for about 1 min. and then add 3 ml of conc. NH_4OH. Allow the mixture to stand for at least 10 min. Filter onto a weighed No. 42 Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate with small portions of 1:20 NH_4OH, 50% ethanol, and 95% ethanol. Pull air through the filter for 5 min, allow the precipitate to stand in the balance case for about 30 min., weigh, mount, and count (Note 4).

Notes:

1. If large amounts of $SO_4^{=}$ ion are present in the sample, the precipitation of zirconium phosphate is not complete.

2. If the ammonium phosphomolybdate precipitate shows a tendency to peptize, dilute NH_4NO_3 solution should be used for the wash.

3. The reagents should be added in the indicated order. If HCl is added before dilution with H_2O, ammonium phosphomolybdate reprecipitates.

4. 14.1d P^{32} is the isotope determined. This has a 1.71-Mev beta and no gamma.

PROCEDURE 3

Procedure Used In: Radioactivation analysis (Note 1)

Method of Separation: Precipitation

Element Separated: P^{32} (14.3 d)

Type of Material Bombarded: Niobium,(86) lead,(86) aluminia,(86) aluminum phosphate,(86) and biological materials.(86)

Type of Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$

Procedure By: Leddicotte(107)

Chemical Yield of Carrier: At least 65%

Time of Separation: 3 hours

Equipment Required: Standard

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 2) and comparator (Note 3) samples in a neutron flux of at least 6.5×10^{11} n/cm^2/sec for one (1) week longer (Note 4). Prepare the test and comparator sample for the irradiation either by wrapping each specimen in aluminum foil or placing it in quartz ampoule. Liquid samples should be irradiated in polyethylene bottles (Note 5).

B. Preparation of Irradiated Materials for Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 3) to a 25-ml volumetric flask. Dissolve the sample in water, and dilute to volume. Mix the solution well by carefully shaking it.

2. By means of a volumetric pipet, pipet a 1.00-ml aliquot of this solution into a 50-ml volumetric flask; then dilute the aliquot to 50 ml with water.

3. Shake the solution thoroughly; then pipet a 1.00-ml aliquot of it into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube, 2.00 ml of a standard carrier solution of known phosphorus concentration (Note 6). Also, add 1 ml each of holdback carriers of cobalt, copper, iron, and sodium (Note 7). Dilute the solution and adjust it to 1.0 M in HNO_3. Continue with Part C below.

II. Solid Test Sample

1. If the sample is a metal or alloy, quantitatively transfer the

irradiated test portion from the quartz tube or aluminum wrap to a 50-ml glass centrifuge tube, and then add, by means of a volumetric pipet, to the same centrifuge tube 2.00 ml of a standard carrier solution of known phosphorus concentration (Note 6). Also add 1 ml each of holdback carriers of cobalt, copper, iron, and sodium (Note 7). To this mixture, add dropwise enough concentrated mineral acid to completely dissolve the sample (Note 8). Dilute the solution and adjust it to 1.0 M in HNO_3. Continue with Part C below.

III. Liquid Test Samples

1. Pipet an aliquot of the irradiated portion into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same centrifuge tube 2.00 ml of a standard carrier solution of known phosphorus concentration (Note 6). Also add 1 ml each of holdback carriers of cobalt, copper, iron, and sodium (Note 7). Dilute the solution and adjust it to 1.0 M in HNO_3. Continue with Part C below.

IV. Organic Test Samples

1. If the sample is a tissue, vegetation, or a similar material, quantitatively transfer the irradiated test portion from the irradiation container to a 50-ml beaker. By means of a volumetric pipet, add to the same beaker 2.00 ml of a standard carrier solution of known phosphorus concentration (Note 6). Also add 1 ml each of holdback carriers of cobalt, copper, iron, and sodium (Note 7). Then add 3 ml of conc. H_2SO_4 and 4 ml of conc. HNO_3. Cover the beaker with a watch glass; then boil the solution for 15 minutes. Cool the solution, add to it 3 ml more of conc. HNO_3, and boil the solution for 15 minutes (or to fumes of SO_3). Repeat the addition of HNO_3 and the boiling until the sample is dissolved. Dilute solution to make it 1.0 M in HNO_3. Transfer to a 50-ml centrifuge tube; then continue with Part C below.

C. Radiochemical Separation of P^{32}.

1. Add 15 - 20 ml of molybdic acid reagent and heat with stirring over a flame until the yellow ammonium phosphomolybdate precipitate $(NH_4)_3\,P(Mo_3O_{10})_4$ occurs (Note 9 and 10). Centrifuge, discard the supernate, and wash the precipitate with 20 ml of 1 M HNO_3.

2. Dissolve the precipitate with 1 ml of conc. NH_4OH, adjust to a volume of 10 ml to 1 M HNO_3, and repeat step 1 twice for purity.

3. Dissolve the precipitate in 1 ml of conc. NH_4OH. Dilute the solution to 10 ml with water and make it slightly acid with HCl. Add 1 gram of citric acid (Note 11), stir well, and cool in an ice bath.

4. Add 10 - 20 ml of magnesia mixture (Note 12) and make basic with NH_4OH to precipitate $MgNH_4PO_4 \cdot 6H_2O$. Add 10 ml of 1:1 NH_4OH in excess. Allow to digest in ice bath for 30 minutes. Centrifuge and discard the supernate. Wash the precipitate with dilute NH_4OH.

5. Filter the precipitate on a tared filter disc of #42 Whatmans filter paper using a hirsch funnel. Wash with 95% alcohol, ether, and dry in a drying oven for 10 minutes at a temperature of 110° C.

6. Weigh the precipitate and mount for beta radioactivity measurement.

D. Measurement of P^{32} Radioactivity and Calculation of Stable Phosphorus Content of Test Sample

1. The P^{32} radioactivity in both the test and comparator samples are assayed by beta measurement only, using a Geiger-Mueller counter. A 30 mg/cm^2 Al absorber is used to shield sulfur and weaker beta energies.

2. Following the radioactivity measurements, correct the P^{32} radioactivity for decay (Note 13), dilution volume(s), and the sample weights (or volumes) of both the test and comparator samples. A simple ratio of these radioactivities becomes a measurement of the amount of stable phosphorus in the test sample:

$$\% \text{ P in Test Sample} = \frac{\text{Corrected } P^{32} \text{ radioactivity in test sample}}{\text{Corrected } P^{32} \text{ radioactivity in comparator sample}} \times 100$$

Notes:

1. This procedure can only be used to determine phosphorus in materials that are soluble in oxidizing reagents or in samples in which the phosphorus is in the form on PO_4^{---} for if the phosphorus is in a phosphide form, it is likely to go as a gas, PH_3, before ion exchange with the phosphorus carrier.

2. Solid test samples should weigh from 0.10 - 0.20 gram; liquid samples should have a volume of from 5 - 25 milliliters.

3. Use 0.025 to 0.030 grams of spectrographically pure $(NH_4)_2HPO_4$.

4. The limits of measurement for stable phosphorus by this procedure is 4×10^{-8} gram.

5. Irradiations of liquid, vegetation, or similar type sample materials must be made in an air-cooled or water-cooled reactor irradiation facility.

6. Standardized to contain at least 10 milligrams of phosphorus per milliliter.

7. Solutions of the ions of other elements may be added as holdback carriers; concentration equal to 5 milligrams of element per milliliter.

8. Soils, clays, and similar materials may require addition of HNO_3 or fusion.

9. Molybdic acid reagent is prepared by dissolving 25 grams of ammonium molybdate $(NH_4)_2MoO_4$ in 1 liter of water.

10. If the solution is too acid, the precipitate will not form. Use NH_4OH to make adjustment.

11. The citric acid is used to complex the Fe and prevent its precipitation with NH_4OH.

12. Magnesia mixture is prepared by dissolving 50 grams of $MgCl_2$ and 100 grams of NH_4Cl in 1 liter of water.

13. Decay measurements may be followed, if required.

PROCEDURE 4

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation

Element Separated: P^{32} (14.3 d)

Type of Material Analyzed: Aluminum and aluminum oxide(87)

Type of Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$

Procedure By: Foster and Gaitanis(87)

Separation Time: Several hours

Chemical Yield of Carrier: No statement made by authors(87)

Decontamination: No data presented by authors(87)

Equipment Needed: Standard

Procedure:

A. Irradiation of Sample Material

1. The samples and phosphorus standard were irradiated for 1 week in the graphite reactor at Oak Ridge, Tennessee. They were placed in the 14-Z position where the fast neutron population is very low. This minimizes the n,p production from $S^{32}(n,p)P^{32}$.

B. Chemical Separation

1. 1 gram of aluminum oxide activated sample, 0.013 gram of nonradioactive monoammonium dihydrogen phosphate carrier and 6 grams of boraxcarbonate flux mixture were added to a platinum crucible and heated for 30 minutes at the highest temperature of a Meker blast burner. After cooling the melt was dissolved in dilute nitric acid.

2. For the aluminum alloys, 2 grams of the metal, 0.25 grams of mercurous nitrate, and 0.013 gram of the carrier were dissolved in 100 ml of 1 to 1 nitric acid (Note 1).

3. For the aluminum oxide samples, the acidity was adjusted and the phosphorus was oxidized to phosphate with $KMnO_4$. The phosphorus was then precipitated as phosphomolybate using ammonium molybdate-citrate solution. This precipitate was dried and weighed; then 0.1 gram was transferred to a planchet and the beta radioactivity measured. After counting, the precipitate was dissolved and the phosphorus precipitated as magnesium ammonium phosphate which was ignited in that form.

4. For the aluminum alloys, after dissolution, most of the acid was removed by boiling, the solutions were gassed with H_2S, filtered, and boiled. The acidity was adjusted and precipitated as phosphomolybdate.

Notes:

1. No mention was made on the part of the author of any possible loss of PH_3 in the aluminum alloys. The HNO_3 probably oxidized it to PO_4^{---} without loss.

PROCEDURE 5

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation

Element Separated: P^{32} (14.3 d)

Type of Material Bombarded: Iodine

Type of Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$

Procedure By: James and Richards(99)

Separation Time: Several hours

Chemical Yield of Carrier: Not given by authors(99)

Decontamination: No information given

Equipment Needed: Standard

Procedure:

A. Irradiation of Sample Material

1. Approximately 0.5 grams samples of iodine were sealed in silica ampules and irradiated for 1 week in the pile at Harwell, together with 0.030 grams of diammonium hydrogen phosphate to act as a standard.

B. Chemical Separation

1. After one day of decay, the ampoules were crushed with a percussion mortar and the mixture transferred to 20 ml of H_2O containing 55 mgm of redphosphorus (Note 1) in suspension. The iodine is dissolved. The solution was warmed on a water bath until the iodine coloration disappeared. The residual red phosphorus was dissolved by adding an excess of inactive iodine and digesting on a water-bath overnight.

2. The fragments of silica was filtered off and the filtrate treated

with H_2O_2. The iodine crystals formed were filtered off and the excess iodine was extracted into chloroform.

3. The phosphate was then determined as the magnesium pyrophosphate. Their limits of detection is about 0.003 parts per million on a gram of sample.

Notes:

1. The amount of red phosphorus used was calculated beforehand in order to have an excess for the required reaction and to act as a carrier.

PROCEDURE 6

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation

Element Separated: P^{32} (14.3 d)

Type of Material Bombarded: Silicon

Type of Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$

Procedure By: James and Richards(100)

Separation Time: Several hours

Chemical Yield: Not stated by authors(100)

Decontamination: No information given by authors

Equipment Needed: Standard

Procedure:

A. Irradiation of Sample Material

1. On irradiation of a silicon sample, the following reaction takes place:

$$Si^{30}(n,\gamma)Si^{31} \xrightarrow{\beta^1} P^{31}$$

$$P^{31}(n,\gamma)P^{32}$$

Due to the fact that P^{32} is formed from the reaction on silicon, the authors derived an expression by irradiation at a certain position for a certain time (1 week) the amount of phosphorus that would be formed. The equation used is found in the original paper.(100)

B. Chemical Separation

1. After the silicon activity has decayed, the sample is dissolved in hydrofluoric-nitric acid mixture with disodium hydrogen phosphate present as a carrier. After complete removal of the silicon as the gaseous silicon tetrafluoride, the solution is reduced to small bulk, $HClO_4$ is added and taken to fuming to remove the HF. Dilute HCl is added to the solution and the phosphate is precipitated as $MgNH_4PO_4 \cdot 6H_2$ with magnesia mixture. The precipitate is allowed to digest 24 hours and is redissolved and reprecipitated as before in the presence of citric acid. It is centrifuged, filtered, ignited in a muffle furnace at 1,100° C to $Mg_2P_2O_7$. The $Mg_2P_2O_7$ is weighed, mounted, and counted for P^{32} radioactivity.

PROCEDURE 7

Procedure Used In: Radioactivation analysis (Note 1)

Method of Separation: Radiochromatographic

Element Separated: P^{32} (14.3 d)

Type Material Bombarded: Biological

Type Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$

Procedure By: Benson, et al.(88)

Separation Time: Several hours

Chemical Yield of Carrier: Carrier technique not used

Equipment Needed: Standard

Procedure:

Bovine blood serum, bovine spermatozoa, and green algae were extracted exhaustively with hot ethanol. The pooled extracts were concentrated to a small volume and taken up in chloroform. The solution was passed dropwise several times through a column of water to remove water soluble materials. An aliquot portion of the chloroform containing 100 μg of P was evaporated to dryness at room temperature and the residue taken up in 0.1 ml ethanol and 0.1 ml toluene. An equal volume of 0.2 N KOH in dry methanol was added and the solution warmed to 37° C for 15 minutes. Alcoholysis was complete in this time for the plant phospholipids. The animal phospholipids were treated with aqueous acetic acid and alcohol for 24 hours before alcoholysis in order to split plasmalogens (acetal lipids) which resist alkaline cleavage. The alkaline solution was acidified and decationized by adding acidic cation exchange resin (Dowex-50 H^+) after adding a drop of water. The suspension was separated by centrifugation. The resulting glycerophosphoryl esters were chromatographed two-dimensionally by acending or decending chromatography on 50 cm x 50 cm Sand S 589 White Ribbon analytical filter paper.

One microgram quantities of P^{31} as ammonium phosphate were placed at edges of the papers which were sealed in 150 cm polyethylene tubes. After 7 hours in the 5×10^{11} n/sec/cm^2 flux and six days decay, radioautographs were prepared. The reversed single coated x-ray film was exposed one to ten days to give the desired record of the location and relative intensity of the phosphate esters.

Notes:

1. This determination of phosphorus is unique due to the fact that the author not only determines phosphorus quantitatively, but also the phosphatides that are present.

PROCEDURE 8

Procedure Used In: Radioactivation analysis

Method of Separation: Ion exchange chromatography

Element Separated: P^{32} (14.3 d)

Type Material Bombarded: Biological tissue ash

Type Nuclear Bombardment: $P^{31}(n,\gamma)P^{32}$

Procedure By: Helwig, et al.(89)

Chemical Yield of Carrier: Not mentioned by the author

Equipment Needed: Standard

Procedure:

A. Preparation of the Ion-Exchange Columns

500 grams of commercially available anion-exchange resin was placed in a 9 cm dia column and washed with several liters of 0.5 M HCl, followed by several liters of 5.0 M HCl. The resin was stored in 5.0 M HCl until ready for use. The columns of about 1.4 cm cross-sectional area were packed down by air pressure with 12 to 24 cm of resin and equilibrated with 12.0 M HCl.

B. Application of Sample on Columns

The carrier salts were prepared by dissolving 0.625 g of Fe, 0.625 g of Zn, and 0.125 g of Co in moderately strong HCl. Radioactive tracers of Fe, P, Zn, and Co were then added to these salts and the solution heated to near dryness. A drop or two of HNO_3 was added to insure complete oxidation of the metals. The oxides were converted to chlorides with a few drops of conc. HCl and heated to dryness. The salts were then taken up in a 25-ml volumetric flask and diluted to volume with 12 M HCl.

A 2-ml aliquot of this solution was pipetted on to the resin bed and the P, Co, Fe, and Zn eluted from the column with 12 M, 4 M, 0.5 M, and 0.005 M HCl. The acid was fed to the folumn at a flow rate of 10-ml per cm per hour. Elution curves for P, Co, Fe, and Zn were obtained by collecting 1.67 ml aliquots of eluate continuously with an automatic sample collector, dried at 60° C in an oven, and counted.

Measurements were made by gross beta and gamma, using sodium iodide crystal for gamma measurements of the Fe, Co, and Zn and Geiger-Mueller counter for beta measurements of the P. The radioactivity measurements of the tracers were better than 98% recovery.

The phosphorus was eluted in the first 50 ml of 12 M HCl; nothing was eluted in the 6 M HCl; cobalt was eluted in the 4 M HCl between 150-175 ml; iron was eluted in the 0.5 M HCl between 210-240 ml; and zinc was eluted in the 0.005 M HCl between 260-275 ml with no cross contamination between the Co, Fe, or Zn. However, there seemed to be a slight contamination in the phosphorus fraction of some long-life components.

REFERENCES

1. Strominger, D., Hollander, J. M., and Seaborg, G. T., "Table of Isotopes," Rev. Mod. Phys. 30 (2), 613-1614 (1958).
2. Hughes, D. J., and Harvey, J. A., "Neutron Cross-Sections," Brookhaven National Laboratory, Upton, New York, Report No. BNL-325 (1958).
3. VanWazer, J. R., Phosphorus and Its Compounds, Volume I: Chemistry, Interscience, New York, 1958.
4. Hutchinson, E., Chemistry - The Elements and Their Reactions, Saunders, Philadelphia, 1959.
5. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., Applied Inorganic Analysis, pp. 698-709, John Wiley, New York, 1953.
6. Mohr, F., Z. Anal. Chem. 2, 250 (1863).
7. Raewsky, V., Compt. rend. 24, 681 (1847).
8. Stumper, R., and Mettelock, P., Compt. rend 224, 122 (1947).
9. Hundeshagen, F., Z. Anal. Chem. 28, 141-172 (1889).
10. Wackenroder, H., and Ludwig, H., Arch. Pharm. 56, 265 (1848).
11. Spacu, G., and Dima, L., Z. Anal. Chem. 120, 317 (1940).
12. Hecht, F., and Donau, J., Anorg. Mikro. Anal., Vienna 1940, 256.
13. VonKnorre, G., Z. angew. Chem. 5, 639 (1892).
14. Travers, A., and Chu, Y. K., Helv. Chim. Acta 16, 913 (1933).
15. Bell, R. N., Anal. Chem. 19, 97 (1947).
16. Baudisch, O., Chem. Ztg. 33, 1298 (1909).
17. Lundell, G. E. F., and Knowles, H. B., Ind. Eng. Chem. 12, 344 (1920).
18. Auger, V., Compt. rend. 170, 995 (1920).
19. Cain, J. R., J. Ind. Eng. Chem. 3, 476 (1911).
20. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., J. Ind. Eng. Chem. 15, 1064 (1923).
21. Brophy, D. H., J. Ind. Eng. Chem. 16, 963 (1924).

22. Maxwell, J. A., and Graham, R. P., Chem. Revs. 46, 471 (1950).

23. Chirnside, R. C., and Dauncey, L. H., Analyst 68, 175 (1943).

24. Ginsberg, H., Leichtmetall Analyse, p. 34, de Gruytes and Co., Berlin, 1945.

25. Grand, L., Revue de l'aluminum, 251, 171 (1958).

26. Bock, R., and Hernman, M., Z. anorg. u. allgem. Chemie, 284, 288 (1956).

27. Bock, R., and Bock, E., Z. anorg. Chem. 263, 146 (1950).

28. Stoll, K., Z. anal. Chem. 112, 81 (1938).

29. Hure, J., and Ortis, T., Bull. soc. chim. France, 834 (1949).

30. Kato, T., Techn. Repts, Tokyo Imp. Univ. 15, 70 (1950).

31. Wadelin, C., and Mellon, M. G., Anal. Chem. 25, 343 (1953).

32. Ging, N. S., Anal. Chem. 28, 1330 (1956).

33. Lueck, C. H., and Boltz, D. F., Anal. Chem. 28, 1168 (1956).

34. Cripps, F. H., AERE Report CRL/AE-49 (1955).

35. Wadelin, C., and Mellon, M. G., Anal. Chem. 25, 1668 (1953).

36. Korshunov, A. I., and Shafiev, A. I., Zhur. Neorg. Khim 3, 100-3 (1958).

37. Samsahl, K., Atompraxis 4, 14-17 (1958).

38. Poczynajlo, A., and Campbell, I. G., NP-7641, 1-12 (1958).

39. Schwob, G. M., and Dattler, G., Angew. Chem. 50, 691 (1957).

40. Kubli, H., Helv. Chim. Acta 30, 453 (1947).

41. Javanovic-Kovacevic, O. Z., Bull. Inst. Nuclear Sci. "Boris Kidrich" (Belgrade) 10, 51-9 (1960).

42. Veljkovic, S. R., and Milenkovic, S. M., Bull. Inst. Nuclear Sci. "Boris Kidrich" (Belgrade) 10, 61-9 (1960).

43. Samuelson, O., Ion Exchangers in Analytical Chemistry, pp. 146-148, John Wiley, New York, 1953.

44. Helrich, H., and Rieman, W., Anal. Chem. 19, 651 (1947).

45. Usatenko, V. I., and Datsenko, O. V., Chemical Abstracts 43, 5336g (1949).

46. Klement, R., Z. anal. Chem. 127, 2 (1944).

47. Klement, R., and Dmytruk, R., Z. anal. Chem. 128, 106 (1948).

48. Halm, R. B., Backer, C., and Backer, R., Anal. Chim. Acta 9, 223 (1953).

49. Yoshino, Y., Bull. Chem. Soc. Japan 26, 401 (1953).

50. Lure, Y. Y., and Filippova, N. A., Chemical Abstracts 44, 476c (1950).

51. Beukenkamp, J., Rieman, W., and Lindenbaum, S., Anal. Chem. 26, 505 (1954).

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

53. Yoshino, Y., Japan Analyst 3, 121 (1954).

54. DeCarvalho, R. G., Paper, Inter. Cong. of Analytical Chemistry, Lisbon, 1956.

55. Lederer, M., Anal. Chim. Acta 12, 146 (1955).

56. Kertes, S., and Lederer, M., Anal. Chim. Acta 15, 543 (1956).

57. DeLoach, W. S., and Drinkard, C., J. Chem. Educ. 28, 461 (1951).

58. Ebel, J. P., and Volmar, Y., Compt. rend. 233, 415 (1951).

59. Bonnin, A., and Sue, P., Compt. rend. 234, 960 (1952).

60. Ebel, J. P., Bull. Soc. chim. biol. 34, 321 (1952).

61. Ebel, J. P., Bull. Soc. Chim. France, 1953, 991, 998, 1089, and 1096.

62. Ebel, J. P., Mikrochim. Acta 1954, 679.

63. Yamaguchi, K., Chemical Abstracts 48, 3200-h (1954).

64. Gauthier, P., Bull. soc. chim. France, 1955, 881.

65. Meissner, J., Z. anorg. u. all gem. Chem. 281, 293 (1955).

66. Crowther, J. P., Anal. Chem. 26, 1383 (1954).

67. Lederer, M., Australian J. Sci. 11, 174 (1949).

68. Long, A. G., Quayle, J. R., and Stedman, R. J., J. Chem. Soc. 1951, 2197.

69. Weil, T., Helv. Chim. Acta 38, 1274 (1955).

70. Marinetti, G. V., Erbland, J., Albrecht, M., and Stotz, E., Biochim et Biophys. Acta 25, 585 (1957).

71. Marinetti, G. V., Erbland, J., and Kochen, J., Fed. Proc. 16, 837 (1957).

72. Benson, A. A., Maruo, B., Flipse, R. J., Yurow, H. W., and Miller, W. W., Proceedings, 2nd UN Geneva Conference 24, 289, Pergamon, London (1959).

73. Benson, A. A., Methods in Enzymology VI, January, 1960.

74. Hillebrand, W. F., et al., op. cit., pp. 695-696.

75. Yamagata, N., and Yamagata, T., Bull. Chem. Soc. Japan 31, (9), 1063 (1953).

76. Yamagata, N., Yamagata, T., Matsuda, S., Tajima, E., Watanake, S., Anal. Abs. 6 (5), 1849 (1959).

77. Pieters, H. A. J., and Cryghton, J. W., Safety in the Chemical Laboratory, Academic Press, New York, 1957.

78. Leddicotte, G. W., Reynolds, S. A., and Corbin, L. T., Safety, Method No. 50150, ORNL Master Analytical Manual, TID-7015, Section 5 (1960).

79. International Atomic Energy Agency, Safety Series No. 1, Safe Handling of Radioisotopes, Vienna, 1958.

80. Reynolds, S. A., Record of Chemical Progress 16, 99 (1955).

81. Price, W. J., Nuclear Radiation Detection, McGraw-Hill, New York, 1958.

82. Meinke, W. W., Chemical Procedures Used In Bombardment Work at Berkeley, U. S. Atomic Energy Commission Report, AECD-2738.

83. Kleinberg, J., "Collected Radiochemical Procedures," Los Alamos Scientific Laboratory Report LA-1721, 2nd Ed., March, 1960.

84. Boyd, G. E., Anal. Chem. 21, 335 (1949).

85. Leddicotte, G. W., Pure and Applied Chemistry 1, 61-80 (1960).

86. Leddicotte, G. W., Mullins, W. T., Bate, L. C., Emery, J. F., Druschel, R. E., and Brooksbank, W. A., Paper 927, Proc. Intern. Conference Peaceful Uses Atomic Energy, Geneva, 1958.

87. Foster, E. M., and Gaitanis, C. D., Anal. Chem. 27, 1342 (1955).

88. Benson, A. A., Maruo, B., Flipse, R. J., Yurow, H. W., and Miller, W. W., Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva 24, 289, Pergamon, 1959.

89. Helwig, H. L., Ashikawa, J. K., and Smith, E. R., UCRL-2655 (1954).

90. Odeblad, E., and Tobias, C. A., Arch. Biochem. Biophys. 9, 452 (1954).

91. Odeblad, E., Westin, B., and Malmford, K. G., Acta Radiol. 49, 137 (1958).

92. Reiffel, L., and Stone, C. A., J. Lab. Clin. Med. 49, 286 (1957).

93. Schmeiser, K., and Jerchel, D., Angew. Chem. 65, 490 (1953).

94. Spencer, R. P., Mitchell, T. G., and King, E. R., Am. J. Roentgenol. Radium Theraphy Nuclear Med. 79, 1053 (1958).

95. Tobias, C. A., and Dunn, R. W., Science 109, 109 (1949).

96. Tobias, C. S., Wolfe, R., Dunn, R., and Rosenfeld, I., Unio. Internationalis Contra Cancrum Acta 7, 874 (1952).

97. Winteringham, F. P. W., Bridges, P. M., and Hellyer, G. C., Biochem. J. 59, 13 (1955).

98. Lvov, A. A., and Naumova, I. I., Atomnaya Energ. 6, 468 (1958).

99. James, J. A., and Richards, D. H., Nature 176, 1026 (1955).

100. James, J. A., and Richards, D. H., Nature 177, 1230 (1956).

101. Kant, A., Cali, J. P., and Thompson, H. D., Anal. Chem. 28, 1867 (1956).

102. Herr, W., Arch. Eisenhuttenw. 26, 523 (1955).

103. Overman, R. T., and Swartout, J. A., "The Use of the Uranium Reactor in Radiochemical Studies," USAEC Report 2245 (1948).

104. Talbot, J., Albert, P., Caron, M., and Chaudron, G., Rev. Met. 50, 817 (1953).

105. Thompson, B. A., Anal. Chem. 31, 1492 (1959).

106. Dow Chemical Report COO-85 (1951).

107. Leddicotte, G. W., "Phosphorus, Neutron Activation Analysis (Isotopic Carrier) Method," Method No. 511600; to be issued in the Oak Ridge National Laboratory Master Analytical Manual.