Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Bifunctional Organophosphorus Liquid-Liquid Extraction Reagents: Development and Applications

W. W. Schulz[a]; J. D. Navratil[b]
[a] ROCKWELL HANFORD ENERGY SYSTEMS GROUP RICHLAND, WASHINGTON [b] ROCKY FLATS PLANT ENERGY SYSTEMS GROUP GOLDEN, COLORADO

To cite this Article Schulz, W. W. and Navratil, J. D.(1984) 'Bifunctional Organophosphorus Liquid-Liquid Extraction Reagents: Development and Applications', Separation Science and Technology, 19: 11, 927 — 941

To link to this Article: DOI: 10.1080/01496398408068601

URL: http://dx.doi.org/10.1080/01496398408068601

SEPARATION SCIENCE AND TECHNOLOGY, 19(11 & 12), pp. 927-941, 1984-85

Bifunctional Organophosphorus Liquid–Liquid Extraction Reagents: Development and Applications

W. W. SCHULZ

ROCKWELL HANFORD
ENERGY SYSTEMS GROUP
RICHLAND, WASHINGTON 99352

J. D. NAVRATIL

ROCKY FLATS PLANT
ENERGY SYSTEMS GROUP
GOLDEN, COLORADO 80401

Abstract

American and Russian workers have evidenced great interest in the last decade in the potential application of certain neutral and acidic bifunctional organophosphorus compounds in solvent extraction processes. Triggering this interest is the ability of some carbamoylmethylenephosphorus (CMP) and carbamoylmethylenephosphine oxide (CMPO) compounds to extract trivalent actinides and lanthanides from strong HNO_3 (>1 M) solutions, a property which distinguishes them from monofunctional organophosphorus reagents. Investigators at several U.S. Department of Energy laboratories have concentrated on synthesis of novel CMP and CMPO reagents and on reactions and mechanisms involved in extraction of metal ions from aqueous nitrate media; application of selected CMP and CMPO reagants in solvent extraction and supported liquid membrane recovery of metal values from nuclear waste solutions have been proposed. This paper, based upon a book now in preparation, provides a brief overview of the current status of the development and application of bifunctional organophosphorus extractants.

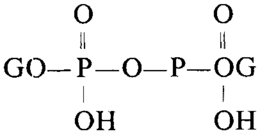
HISTORICAL INTRODUCTION

Use of neutral monofunctional organophosphorus compounds in liquid–liquid extraction systems dates from the middle 1940s when tri-*n*-butyl

0149-6395/84/1911-0927$3.50/0

phosphate (TBP) was first studied for its use in recovery and purification of uranium from impure concentrates (e.g., "yellow cake") (*1–3*). Such monofunctional reagents typically include, in addition to TBP, other organophosphates [$(RO)_3P(O)$], phosphonates [$(RO)_2RP(O)$], phosphinates [$(RO)R_2P(O)$], and phosphine oxides [$R_3P(O)$]. Today, these compounds are widely used as liquid–liquid extraction reagents in extractive metallurgy, analytical chemistry, and, of course, the nuclear fuel cycle.

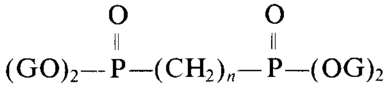
Throughout the 1950s, processes for liquid–liquid extraction of uranium from technical-grade phosphoric acid based upon the properties of alkyl pyrophosphoric acids (I) were proposed and tested (*4–8*).



$$\mathrm{GO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OG}$$

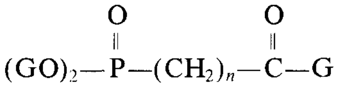
(I)

Chemists in the United States (*9–14*) and elsewhere (*15–18*) in the 1960s synthesized various neutral bifunctional (and tri- and tetrafunctional as well) organophosphorus compounds and characterized some of their chemical and physical properties (e.g., compounds such as II through VII). (In Compounds I through VII, the G's may be alkyl, cycloalkyl, aryl, substituted alkyl, substituted aryl, or mixed alkyl and aryl groups.)



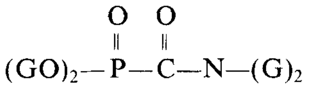
$$\mathrm{(GO)_2{-}\overset{\overset{O}{\|}}{P}{-}(CH_2)_{\mathit{n}}{-}\overset{\overset{O}{\|}}{P}{-}(OG)_2}$$

(II)



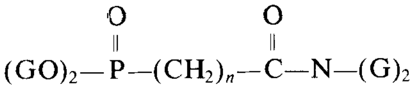
$$\mathrm{(GO)_2{-}\overset{\overset{O}{\|}}{P}{-}(CH_2)_{\mathit{n}}{-}\overset{\overset{O}{\|}}{C}{-}G}$$

(III)



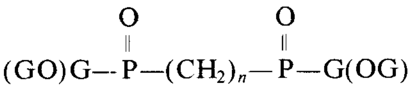
$$\mathrm{(GO)_2{-}\overset{\overset{O}{\|}}{P}{-}\overset{\overset{O}{\|}}{C}{-}N{-}(G)_2}$$

(IV)



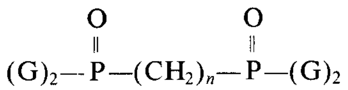
$$\mathrm{(GO)_2{-}\overset{\overset{O}{\|}}{P}{-}(CH_2)_{\mathit{n}}{-}\overset{\overset{O}{\|}}{C}{-}N{-}(G)_2}$$

(V)



$$\mathrm{(GO)G{-}\overset{\overset{O}{\|}}{P}{-}(CH_2)_{\mathit{n}}{-}\overset{\overset{O}{\|}}{P}{-}G(OG)}$$

(VI)



$$\mathrm{(G)_2{-}\overset{\overset{O}{\|}}{P}{-}(CH_2)_{\mathit{n}}{-}\overset{\overset{O}{\|}}{P}{-}(G)_2}$$

(VII)

Interest in neutral multifunctional organophosphorus extractants then waned, except in the Soviet Union where Russian scientists have sustained, to the present day, a substantial effort to synthesize and characterize many different multifunctional phosphine oxides (Type VII compounds).

Schulz and McIssac et al. (*19–22*), following an earlier suggestion of Siddall (*23*), demonstrated in the middle 1970s that certain neutral bifunctional organophosphorus reagents are particularly suitable for plant-scale removal and recovery of 3+ (e.g., Am) as well as 4+ and 6+ actinides from various highly acid nuclear fuel cycle waste liquors. (Removal of long-lived actinides from such wastes reduces potential hazards of long-term storage and/or disposal.) These studies stimulated a renaissance in the chemistry and application of neutral multifunctional organophosphorus reagents in liquid–liquid extraction systems which is still going on, particularly in the United States. Much new data concerning synthesis and purification of new compounds, their physical and chemical properties, and reaction mechanisms involved in extraction of HNO_3 and metal ions have evolved from this latest research.

Our goal in this paper is to provide the separations specialist with a brief overview of some of the salient features of the classes, synthesis, properties, and uses of both acidic and neutral multifunctional organophosphorus liquid–liquid extraction reagents. Review papers by O'Laughlin (*24*), Medved et al. (*25*), and Schulz and Navratil (*26*) provide much more detailed information on these topices.

CLASSIFICATION OF MULTIFUNCTIONAL ORGANOPHOSPHORUS EXTRACTANTS

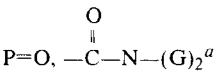
Definition

For application in liquid–liquid extraction systems, a multifunctional organophosphorus extractant is an organic compound which contains two, or more, functional (donor) groups (at least one of which contains a phosphorus atom*) potentially capable of reacting with selected metal ions to form stable organic-phase soluble species. Not unexpectedly, currently known multi-

---

*In this paper $\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}{=}\mathrm{O}$ (POOH) and $\mathrm{OH}{-}\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}{=}\mathrm{O}$ [$PO(OH)_2$] entities are considered to contain only a single donor group; this restriction is desirable to avoid considering compounds such as $(\mathrm{GO})_2\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}{=}\mathrm{O}$ as multifunctional organophosphorus extractants.

TABLE 1
Some Typical Combinations of Functional Groups in Multifunctional Organophosphorus Extractants

Number of groups	Functional groups
2	P=O, P=O
	P=O, C=O
	 $P{=}O,\ \overset{\overset{O}{\|}}{—C}—N—(G)_2$[a]
	P=S, P=S
	POOH, POOH
	POOH, P=O
	POOH, C=O
3	P=O, P=O, P=O
	POOH, POOH, POOH
	P—N, P—N, P—N[b]
	$PO(OH)_2$, $PO(OH)_2$, $PO(OH)_2$

[a] Carbamoyl group.
[b] Cyclotriphosphazene compounds.

functional organophosphorus extractants (Table 1) typically contain combinations of P=O, C=O, N → O, P=S, P—N, POOH, and $PO(OH)_2$ groups.

Classification

Major Types of Extractants

All multifunctional organophosphorus extractants can conveniently be divided into two broad groups: neutral compounds and acidic compounds.

Acidic extractants are those that contain at least one POOH or $P(OH)_2$ group in the molecule regardless of what other functional groups may be present. All other multifunctional organophosphorus extractants are classified as neutral extractants even though groups such as C(O)OH and S(O)OH may be present in the molecule or enolization of carbonyl groups may take place.

Paralleling the case with their monofunctional counterparts, most of the currently-known neutral multifunctional organophosphorus extractants can be assigned to one of three broad types (Table 2), namely, phosphonates, phosphinates, and phosphine oxides. (Cyclotriphosphazenes are a special class of neutral multifunctional organophosphorus reagents.) Similarly, the known multifunctional organophosphorus acidic extractants comprise phosphonic and pyrophosphoric acids.

Subclasses of Neutral Extractants

Neutral multifunctional phosphonate and phosphine oxide extractants can be further classified (Table 3) to reflect particular combinations of functional groups. In the type formulas listed in Table 3, BG stands for any group which

TABLE 2
General Classification of Multifunctional Organophosphorus Extractants

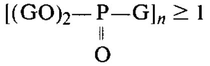
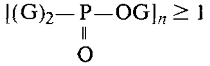
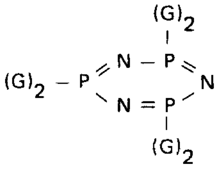
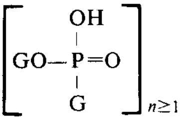
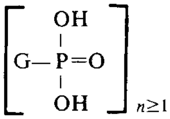
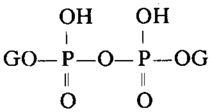
General classification	Class functional group
A. Neutral reagents	
Phosphonates	 $[(GO)_2{-}\underset{\overset{\|}{O}}{P}{-}G]_n \geq 1$
Phosphinates	 $[(G)_2{-}\underset{\overset{\|}{O}}{P}{-}OG]_n \geq 1$
Phosphine oxides	$[G_3P{=}O]_n \geq 1$
Cyclotriphosphazenes	
B. Acidic reagents	
Phosphonic acids	Type 1:  $\left[GO{-}\overset{OH}{\underset{G}{P}}{=}O\right]_{n\geq1}$
	Type 2:  $\left[G{-}\overset{OH}{\underset{OH}{P}}{=}O\right]_{n\geq1}$
C. Pyrophosphoric acids	 $GO{-}\underset{\overset{\|}{O}}{\overset{OH}{P}}{-}O{-}\underset{\overset{\|}{O}}{\overset{OH}{P}}{-}OG$

TABLE 3
Types of Multifunctional Phosphonate and Phosphine Oxide Extractants

General class	Name	Type formula[a]
Phosphonates	Diphosphonate	$(GO)_2$—P(O)—BG—P(O)—$(OG)_2$
	Ketophosphonate	$(GO)_2$—P(O)—BG—C(O)—G
	Carbamoylphosphonate	$(GO)_2$—P(O)—C(O)—N—$(G)_2$
	Carbamoylalkylphosphonate	$(GO)_2$—P(O)—BG—C(O)—N—$(G)_2$
Phosphine oxides	Phosphine oxides[b]	$(G)_2$—P(O)—BG—P(O)—$(G)_2$
	Carbamoylalkylphosphine oxides	$(G)_2$—P(O)—BG—C(O)—N—$(G)_2$

[a] BG = bridging group.
[b] Includes compounds containing ≥ two phosphoryl groups.

bridges the two functional groups while the G's are, typically, saturated alkyl or aryl or mixed alkyl–aryl groups but can also be substituted groups (e.g., methoxy, etc.).

Methylene and ethylene groups are typical bridging groups between the phosphoryl and carbonyl functional groups in the ketophosphonates and carbamoyl phosphonates and phosphine oxides. However, a large variety of unsubstituted and substituted alkyl and aryl groups has been used to bind two P=O groups in multifunctional phosphine oxides.

Nomenclature

Each of the 200 or so currently-known multifunctional organophosphorus extractants can be correctly designated by two or three different names. However, in recent times, most investigators have come to agree on a standard way of naming some types of these extractants. For example, carbamoylalkyl phosphonates [$(GO)_2P(O)(CH_2)C(O)N(G)_2$] and carbamoylalkylphosphine oxides [$(G)_2P(O)(CH_2)C(O)N(G)_2$] are conveniently named by citing, in order:

(1) The GO or G groups bound to the P=O group
(2) The G groups attachd to the N atom
(3) The alkyl groups, if any, connecting the phosphoryl and carbamoyl functions
(4) The type of compound, i.e., phosphonate or phosphine oxide

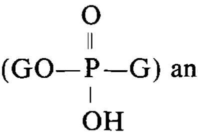
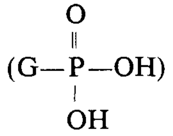
Illustrative of these rules are the names dibutyl-*N*,*N*-diethylcarbamoylmethylphosphonate [$(C_4H_9O)_2P(O)CH_2C(O)N(C_2H_5)_2$] and dibutyl-*N*,*N*-diethylcarbamoylmethylphosphine oxide [$(C_4H_9)_2P(O)CH_2C(O)N(C_2H_5)_2$].

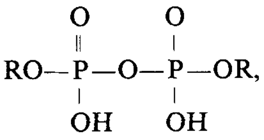
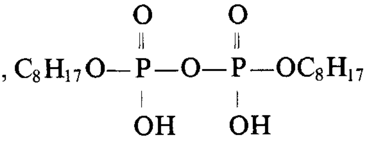
Diphosphonates are also conveniently named by indicating the two $(GO)_2$—P(O)— groups joined to the central bridging group. For example, $(C_4H_9O)_2P(O)CH_2P(O)(OC_4H_9)_2$ is tetrabutylmethylenediphosphonate. Other names for diphosphonates include polymethylenebis(dialkylphosphonates) (*25*), tetra-*p*-alkylpolymethylene diphosphonates (*12, 17, 27*), and bis(dialkyloxyphosphinyl)alkanes (*10, 28*).

Multifunctional organophosphorus extractants of the general formula $(RO)_2P(O)CH_2C(O)R'$ (R = alkyl, R′ = alkyl, aryl, . . .) are referred to as beta-ketophosphonates. The best known example of this type of extractant is dibutyl phenacylphosphonate $[(C_4H_9O)_2P(O)CH_2C(O)C_6H_5]$.

Multifunctional organophosphorus phosphine oxide extractants present different degrees of difficulty in naming them. Compounds involving two P=O groups separated by a simple bridging group (e.g., CH_2 or $(CH_2)_2$, etc.) are readily named; for example, $(C_8H_{17})_2P(OC)H_2P(O)(CH_8H_{17})_2$ is termed methylenebisdioctylphosphine oxide. Other phosphine oxide extractants containing complicated bridging groups connecting two or more PO groups are more difficult to name and can usually be named correctly in any of several ways. Further discussion and examples of the nomenclature of phosphine oxide extractants are outside the scope of this paper.

Acidic Extractants

Two types (Table 2) of multifunctional phosphonic acid extractants are known. Type 1  $\left(GO-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-G\right)$ and Type 2  $\left(G-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OH\right)$ compounds are termed by Marcus and Kertes (*29*) alkylalkylphosphonic and monoalkylphosphonic acids, respectively.

Alkylpyrophosphoric acids,  $RO-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-O-\underset{OH}{\underset{|}{\overset{O}{\overset{|}{P}}}}-OR$, are conveniently named by citing the two alkyl groups followed by the designation of a pyrophosphoric acid, e.g.,  $C_8H_{17}O-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-O-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OC_8H_{17}$ (dioctylpyrophosphoric acid). Some authors have chosen to name these compounds as esters of pyrophosphoric acid.

SYNTHESIS AND PURIFICATION

Neutral Compounds

The Michaelis-Becker reaction (Eqs. 1 and 2)

$$X(CH_2)X + 2MOP(OG)_2 \rightarrow (GO)_2P(O)(CH_2)(O)P(OG)_2 + 2MX \qquad (1)$$

$$(G')_2NCO(CH_2)X + MOP(OG)_2 \rightarrow (GO)_2P(O)(CH_2)_nC(O)N(G')_2 + MX \qquad (2)$$

and the Arbuzov rearrangement (Eq. 3)

$$(GO)_3P + (G')_2NCO(CH_2)X \rightarrow (GO)_2P(O)(CH_2)C(O)N(G')_2 + GX \qquad (3)$$

have been used to prepare (in 40 to 60% yield) diphosphonates and carbamoylphosphonates (*26*). Kim et al. (*30*) have discovered a phase-transfer-catalyzed Michaelis-Becker reaction which is not plagued by the side reactions typical of conventional Arbuzov and Michaelis-Becker syntheses which seriously limit yields and purities of crude products.

Two general methods for preparing phosphine oxides have been reported (*31*):

$$2(G_2)P(O)MgX + X(CH_2)_nX \rightarrow (G)_2P(O)(CH_2)_n(P)O(G)_2 \qquad (4)$$

$$2G_2POCl + (CH_2)_{n\geq 4}(MgX)_2 \rightarrow (G)_2P(O)(CH_2)_{n\geq 4}(O)P(G)_2 + MgCl_2 + MgX_2 \qquad (5)$$

Compounds which are solids at room temperature, such as phosphine oxides, can be readily purified by repeated recrystallizations, whereas with crude diphosphonates and carbamoylphosphonates several methods have been used (*26*). Vacuum distillation (0.001 torr, 110°C), high pressure liquid chromatography, and salt precipitation methods have been very successful in purifying carbamoylmethylphosphonates, with the latter method being preferred.

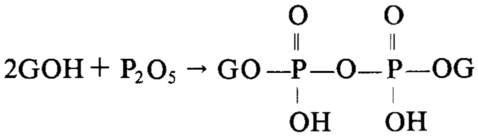
Acidic Compounds

Methylenediphosphoric acids can be prepared by hydrolysis of the corresponding tetra-alkyl esters with concentrated hydrochloric acid (*32*):

$$(RO)_2P(O)(CH_2)_nP(O)(OR)_2 + 4HCl \rightarrow (HO)_2P(O)(CH_2)_nP(O)(OH)_2 + 4RCl \qquad (6)$$

The reaction is almost quantitative (81–98% yields) and the acids can be purified by recrystallization from water.

The diesters of pyrophosphoric acid can be prepared by reaction of a 2:1 mole ratio of the corresponding alcohol and phosphorus pentoxide (*32*):



$$2GOH + P_2O_5 \rightarrow GO-\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-OG \qquad (7)$$

The reaction is carried out at 70°C for 30 min in the presence of kerosene, followed by distillation of the product *in vacuo* (0.5 torr) at 70°C.

COMMERCIAL AVAILABILITY

Exploitation of the extractive powers of many multifunctional organophosphorus extractants in analytical and especially plant-scale applications has been severely hampered by lack of reliable sources of reagents in desired quantities and purities at affordable prices. This situation is slowly changing in the United States as researchers discover and report on the properties of various neutral reagents. For example, in the United States, gram to kilogram amounts of various compounds such as dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP), dibutyl-*N*,*N*-diethylcarbamoylmethylphosphonate, and other bifunctional phosphonates are presently available from Columbia Organic Chemicals, Canton, South Carolina, and Alfa Products, Danvers, Massachusetts.

Various other companies (e.g., M&T Organics, Rahway, New Jersey; Mobil Chemicals, Richmond, Virginia) have, from time to time, expressed interest in marketing DHDECMP and certain other neutral bifunctional organophosphorus extractants.

SOLVENT EXTRACTION PROPERTIES

Phosphine Oxides

Systematic studies of the extraction properties of multifunctional phosphine oxide reagents have been largely confined to detailed investigations of the extraction of lanthanides, actinides, and mineral acids from aqueous mineral acid solutions. Most of the reported extraction work has been done at room temperature with dilute solutions of phosphine oxides in chlorinated carrier solvents. All investigators agree that phosphine oxides are considerably more powerful extractants for lanthanides and 3+, 4+, and 6+ actinides from mineral acid solutions than are monodentate phosphate esters, phosphonates, and phosphine oxides.

The predominant organic species for metal species extracted by diphosphine oxides (DPO) appear to be the disolvate formed:

$$M^{n} + nX + 2DPO \rightleftharpoons \overline{MX\cdot(DPO)_2} \tag{8}$$

Thus, Th(IV), Pa(V), U(VI), Pu(III, IV, VI), and Am(III) all form disolvates with various diphosphine oxide reagents. It is believed that lanthanides and other trivalent transplutonium elements also extract as disolvates.

Carbamoylmethylphosphonates

Various authors have observed that DHDECMP and other carbamoylmethylphosphonate (CMP) compounds extract trivalent actinides and lanthanides in a 3:1 stoichiometry:

$$M^{3+} + 3NO_3^- + \overline{3CMP} = \overline{M(NO_3)_3\cdot(CMP)_3} \tag{9}$$

Siddall (*11*, *12*) and other early investigators concluded (*20–23*) that CMP extractants behave as bidentate ligands. Recent detailed studies by Horwitz and co-workers (*33*) refute this conclusion. Thus, Horwitz et al. note that DHDECMP and the monodentate reagent dibutylphosphonate (DB[BP]) behave very similarly in their ability to extract Am(III) and Eu(III) from $Li(NO_3)_3$ solutions of low acidity. However, from HNO_3 solutions, DHDECMP extracts Am(III) and Eu(III) much more efficiently than does DB[BP]. Horwitz et al. ascribed this difference in extracting power to the ability of DHDECMP to reduce the direct attack of hydrogen ions on the metal—phosphoryl oxygen bonds by the protonation of the amide group. This latter process, according to Horwitz, resembles a buffering effect because it reduces the influence of HNO_3.

Ketophosphonates

Beta ketophosphonates [e.g., dibutylphenacylphosphonate (HDBPP), $(C_4H_9)_2P(O)CH_2C(O)C_6H_5$] can function both as a neutral adduct-forming agent through the P=O group and as a chelating anionic ligand (acidic extractant). Ceccaroli, Alstad, and Leroy (*34*) describe extraction of lanthanides from 1 *M* $NaClO_4$ solution by HDBPP by the following equilibrium regardless of whether the mechanism is acidic or neutral:

$$M^{3+} + x\overline{\mathrm{HDBPP}} + q\mathrm{ClO}_4^- \rightleftharpoons \overline{\mathrm{M[H(DBPP)}_{3-q}]_x\,(\mathrm{ClO}_4)_q} + (3-q)\mathrm{H}^+ \qquad (10)$$

The mechanism of the extraction is identified by the value of q as follows:

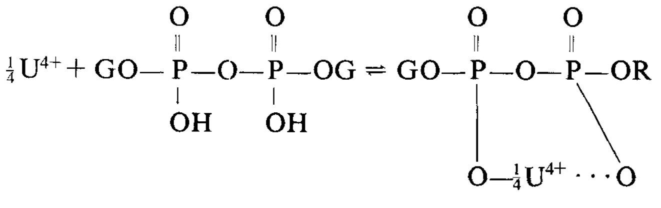
M	x	q	Mechanism
Eu, Gd, Tb, Tm	3	0	Acidic
La	4	1	Mixed
Gd	3 and 4	3	Neutral

Alkyl Pyrophosphoric Acids

Certain alkyl pyrophosphoric acids have been used to extract uranium from technical-grade phosphoric acid. Extraction of U(VI) proceeds according to (*35*)

$$UO_2^{2+} + 2G_2H_2P_2O_7 \rightleftharpoons UO_2(G_2HP_2O_7)_2 + 2H^+ \qquad (11)$$

Tetravalant uranium reacts with alkyl pyrophosphoric acids to form inner complexes with a stable six-membered ring:



(12)

APPLICATIONS

Analytical

Despite their strong extractive powers for certain metals from acidic media, application of multifunctional organophosphorus extractants to accomplish analytical separations has been relatively sparse. Some use has been made (Table 4) of neutral carbamoyl-type compounds to concentrate and separate small amounts of actinide elements from biological media and from nuclear waste solutions. Russian scientists conducted extensive investigations of the use of alkyl pyrophosphoric acids to extract Fe(III), Ga(III), Hf, In(III), Sb(III), Sc(III), Sn(II and IV), Tl(III), and Zr(IV) from mineral acid solutions. Procedures for separating the co-extracted metals by means of selective stripping procedures have been developed. Individual Russian papers (and reference cited therein) noted in Table 4 should be consulted for details of these analytical applications.

Nuclear

Dioctyl- and didecylpyrophosphoric acids have been used in commercial-scale recovery of uranium from technical-grade phosphoric acid solutions (*35*). Various phosphonic acids have been proposed and tested for similar use but none has reached plant-scale application.

DHDECMP has been evaluated for recovering americium and plutonium from NaCl–$MgCl_2$–KCl waste salts resulting from pyrochemical purification of plutonium metal at the Rocky Flats site (*42*). From nitric acid solutions of such salts, DHDECMP effectively extracts and separates plutonium and americium from contaminants such as Al, Mg, K, Na, and Zn. The extraction chromatographic Am–Pu recovery process employing DHDECMP performed very well in pilot-plant-scale tests; production-scale runs are currently in progress.

TABLE 4
Some Typical Analytical Applications of Multifunctional Organophosphorus Extractants

	Organic phase[a]			
Metal(s) extracted	Extractant	Diluent	Aqueous phase	Ref.
Neutral extractants:				
U, Np, Pu, Am	DHDECMP	Xylene	HNO_3 (nuclear waste)	*36*
TRU[b]	DBDECP	None	12 *M* HNO_3 (biological samples)	*37*
Lanthanides[c]	MHDPO or M(EH)DPO	CCl_4	9 *M* HNO_3 containing various rare earths	*38*
Acidic extractants:				
Ga(III)[d]	(2EH)PPA	Heptane	1–3 *N* H_2SO_4, HNO_3, $HClO_4$, or HBr	*39*
Fe(III)[e]	IAPPA[b]	Benzene	5 *N* HCl; 10 *N* HNO_3; 20 *N* H_2SO_4	*40*
Ti(IV)[g]	DOMPA	Octane	1–4 *N* H_2SO_4	*41*

[a] DHDECMP = dihexyl-*N,N*-diethylcarbamoylmethylphosphonate.
DBDECP = dibutyl-N,*N*-diethylcarbamoylphosphonate.
MHDPO = methylenebisdihexylphosphine oxide.
M(EH)DPO = methylenebisdi-2-ethylhexylphosphine oxide.
(2EH)PPA = di-2-ethylhexylpyrophosphoric acid.
IAPPA = diisoamylpyrophosphoric acid.
DOMPA = dioctylmethylenebisphosphonic acid.

[b] Am, Cm, Bk, Cf, and Es.

[c] Extraction chromatography: 10% MHDPO (or M(EH)DPO) on Plaskon as stationary phase; 9 *M* HNO_3 as mobile phase; 25°C.

[d] Ga selectively stripped from coextracted impurities (e.g., In, Tl, Bi, Sb, Sn, Ti, Zr, Hf, Sc) with oxalic acid solutions.

[e] Ti(III) solutions used to selectively strip Fe(II).

[f] Diisoamylphosphoric acid also present.

[g] Absorbance of yellow-colored DOMPA-Ti complex measured.

Other than the Rocky Flats site, process nuclear application of neutral multifunctional organophorous extractants has been sparse. Process flow sheets have been developed at several U.S. Department of Energy sites for removing small concentrations of plutonium, americium, and various other actinides from acidic waste streams produced during processing of both irradiated and unirradiated nuclear fuels (*26*). These processes have concentrated on use of DHDECMP; application of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide in such processes is currently being studied (*43*, *44*). None of these actinide removal processes has been tested on a plant scale.

REFERENCES

1. J. C. Warf, *J. Am. Chem. Soc., 71*, 3257 (1949).
2. T. C. Runion, *U.S. AEC Report ORNL-874*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1950.
3. T. C. Runion and J. H. Yeager, *U.S. AEC Report ORNL-890*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1950.
4. R. S. Long, U.S. Patent 2,866,880 (1980).
5. R. S. Long, D. A. Ellis, and R. H. Bailes, *Proc. 1st Int. Conf. Peaceful Uses At. Energy, Geneva, 1955*, Vol. 8, United Nations, New York, 1956, p. 77.
6. H. M. Heidt, D. E. Tynan, J. B. Adams, and R. Bart, *USAEC Report RMO-2042*, Arthur D. Little Co., San Françisco, California, 1955.
7. L. A. McClaine, P. Noble, and E. P. Bullwinkel, *J. Phys. Chem., 62*, 299 (1958).
8. D. Grdenic and B. Korpar, *J. Inorg. Nucl. Chem., 12*, 149 (1959).
9. J. J. Richard, K. E. Burke, J. W. O'Laughlin, and C. V. Banks, *J. Am. Chem. Soc., 83*, 1722 (1961).
10. J. E. Mrochek, J. W. O'Laughlin, H. Sakurai, and C. V. Banks, *J. Inorg. Nucl. Chem., 25*, 955 (1963).
11. T. H. Siddall Jr., *Ibid., 25*, 883 (1963).
12. T. H. Siddall Jr., *Ibid., 26*, 1991 (1964).
13. J. E. Mrochek and C. V. Banks, *Ibid., 27*, 589 (1965).
14. J. E. Mrochek, J. W. O'Laughlin, and C. V. Banks, *Ibid., 27*, 603 (1965).
15. H. Saisho, *Bull. Chem. Soc. Jpn.. 26*, 1991 (1964).
16. H. Saisho, *Ibid., 34*, 859 (1964).
17. J. Goffart and G. Duyckaerts, *Anal. Chim. Acta, 39*, 57 (1967).
18. J. Goffart and G. Duyckaerts, *Ibid., 48*, 99 (1969).
19. W. W. Schulz, *U.S. ERDA Report ARH-SA-203*, Atlantic Richfield Hanford Co., Richland, Washington, 1974.
20. W. W. Schulz and L. D. McIsaac, in *Transplutonium 1975* (W. Muller and R. Lindner, eds.), North-Holland, Amsterdam, 1976, p. 433.
21. W. W. Schulz and L. D. McIsaac, in *Proc. ISEC 77*, Canadian Inst. Min. Met., Toronto, Canada, 1978.
22. L. D. McIsaac, J. D. Baker, and J. W. Tkachyk, *U.S. ERDA Report ICP-1080*, Allied Chemical Co., Idaho Falls, Idaho, 1975.
23. T. H. Siddall Jr., U.S. Patent 3,243,254 (1966).
24. J. W. O'Laughlin, in *Prog. Nucl. Energy, Series IX Anal. Chem.*, Vol. 6 (D. C. Stuart and H. A. Elion, eds.), Pergamon, New York, 1966, p. 97.
25. T. Ya. Medved, Yu. M. Polikarpov, L. E. Bertina, V. G. Kossykh, K. S. Yidina, and M. I. Kabachnik, *Usp. Khim., 44*, 1003 (1975).
26. W. W. Schulz and J. D. Navratil, in *Recent Developments in Separation Science*, Vol. 7 (N. N. Li, ed.), CRC Press, Boca Raton, Florida, 1982. p. 31.
27. T. V. Healy and J. Kennedy, *J. Inorg. Nucl. Chem., 10*, 128 (1959).
28. J. A. Walmsley and S. Y. Tyree, *Inorg. Chem., 2*, 312 (1963).
29. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, New York, 1969.
30. K. M. Kim, N. V. Nguyen, and D. J. Cross, *J. Org. Chem., 46*, 5188 (1981).
31. K. Moedritzer and R. R. Irani, *J. Inorg. Nucl. Chem., 22*, 297 (1961).
32. D. A. Ellis, *U.S. AEC Report DOW-81*, Dow Chemical Co., Pittsburgh, California, 1952.

33. E. P. Horwitz, A. C. Muscatello, D. G. Kalina, and L. Kaplan, *Sep. Sci. Technol., 16*, 417 (1981).
34. B. Ceccaroli, J. Alstad, and M. J. F. Leroy, *Polyhedron, 1*, 257 (1982).
35. N. P. Galkin, B. N. Sudarikov, U. D. Veryatin, Yu. D. Shishkov, and A. A. Maidrov, *Technology of Uranium*, Israel Program for Scientific Translations, Jerusalem, 1966.
36. S. J. Johnson and W. I. Winters, *U.S. DOE Report ARH-SA-296*, Atlantic Richfield Hanford Co., Richland, Washington, 1977.
37. F. E. Butler and R. M. Hall, *Anal. Chem., 42*, 1073 (1970).
38. J. W. O'Laughlin and C. V. Banks, in *Solvent Extraction Chemistry* (D. Dyrssen, J. O. Liljenzin, and J. Rydberg, eds.), North-Holland, New York, 1967, p. 270.
39. I. S. Levin and N. A. Balakireva, *Russ. J. Anal. Chem. (Transl.), 22*, 1242 (1967).
40. Yu. B. Kletnik, *Ibid., 17*, 855 (1962).
41. H. Gorican and D. Grdenic, *Anal. Chem.,* 36, 230 (1964).
42. W. I. Yamada, L. L. Martella, and J. D. Navratil, *J. Less-Common Metals, 86*, 211 (1982).
43. E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason, and H. Diamond, *Sep. Sci. Technol., 17*, 261 (1982).
44. E. P. Horwitz and D. G. Kalina, *So'v. Extn. Ion Exch., 2*, 179 (1984).