Alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s as extractants for gold in hydrochloric acid medium

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This study describes the alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s as potential reagents for solvent extraction of Au(III) and some other metal ions from chloride medium. The Au(III) selectivity can be improved to a practicable viability by an appropriate selection of the bis-phosphonate structure. The alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s possesses extraction properties ideal for its use in the solvent extraction of Au(III) from hydrochloric acid medium. Au(III) extraction by this reagent proceeds through formation of a 1:1 metal-ligand complex, typical of a organophosphorus solvating extractant. The extraction, selectivity, stripping, and kinetic data suggest that methane-1,1-diyl bis(O,O-diisopropyl phosphonate) is a highly promising reagent for the commercial recovery of Au(III) from HCl leach sources and can be recommended for pilot-plant trials, using thiourea as the stripping agent.

INTRODUCTION

The extraction of gold from acidic media involving new reagents may have potential application in the processing of gold bearing deposits that are not amendable to cyanide leaching [1], in the recovery and removal of gold from precious metal concentrates, and in the recovery of gold from electronic wastes [2–5].

The ion-exchange type amine reagents [1, 6–9] and solvating extractants like phospholenes [10], cyanex-923 [11] and cyanex-471 [13] have been studied widely for the concentration of gold from low-grade hydrochloric acid solutions. The widely known organophosphorus compounds like the phosphates, phosphonates, phosphinates, phosphine oxides are capable of solvating $AuCl_4^-$ species from both acidic and alkaline media, but often suffer from low distribution of gold in the organic phase [4, 5], probably because of the insufficient basicity in the P = O bond of the organophosphorus molecule. However, it will be expected that the bifunctional phosphonic acid derivatives and its analogues can provide better extraction efficiency owing to the simultaneous attraction by the two P = O groups on $AuCl_4$ and the distance between the two P = O groups in the bis-molecule that could effectively be utilized to improve the selectivity towards a particular solvate.

Some bisphosphonates have been studied in the extraction of uranium and rare-earth metals [13], but there is no report on their use for precious metal extraction. This work reports the

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extraction behavior of a series of synthetic diphosphonates such as the alkane-α, ω-diyl bis(O,O-dialkylphos-phonate)s, towards Au(III) in hydrochloric acid medium, and its application towards gold recovery.

EXPERIMENTAL

Reagents. The extractants used in this study are presented in Table 1. The commercially available alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s reagents were methane-1,1-diyl bis(O,O-diethyl phosphonate) [MBDEP], ethane-1,2-diyl bis(O,O-diethyl phosphonate) [EBDEP] both of which were obtained from Aldrich Chemicals; methane-1,1-diyl bis(O,O-diisopropyl phosphonate) [MBDIPP], ethane-1,2-diyl bis(O,O-diisopropyl phosphon-ate) [EBDIPP] were obtained from Lancaster Chemicals; tri-n-butyl phosphate [TBP] from KANTO Chemicals; and tri-n-octyl phosphine oxide [TOPO] from DOJINDO Chemicals.

The following alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s: ethane-1,2-diyl bis(O,O-dibutyl phosphonate) [EBDBP], propane-1,3-diyl bis(O,O-dibutyl phosphonate) [PBDBP], butane-1,4-diyl bis(O,O-dibutyl phosphonate) [BBDBP] were synthesized by a known method [14–16]. The synthesis products were purified by flush chromatography. The physical properties of the synthetic compounds were found to possess specific gravity values in the range of 1.04 to 1.09 and are high-boiling free-flowing liquids [15, 17].

The analytical and spectral data were obtained for the synthetic products, which conformed to the structures and compositions shown in Table 1 as follows.

EBDBP: ^{1}H-NMR (CDCl$_3$) δ, ppm = 0.94 (t, 12H, CH$_3^-$); 1.41 (m, 8H, MeCH$_2^-$); 1.69 (m, 8H, MeCCH$_2^-$); 2.43 (t, 4H, –PCH$_2^-$); 4.11 (m, 8H, –OCH$_2^-$). FTIR, cm^{-1}: 1249 (νP = O), 1011, 1059 (P-O-C$_4$H$_9$). Found: C, 51.81; H, 9.08%. Cald: C, 52.16; H, 9.73%.

PBDBP: ^{1}H-NMR (CDCl$_3$) δ, ppm = 0.94 (t, 12H, CH$_3^-$); 1.39 (m, 8H, MeCH$_2^-$); 1.65 (m, 8H, MeCCH$_2^-$); 1.88 (t, 4H, –PCH$_2^-$); 2.23 (m, 2H, –PCCH$_2$CP$^-$); 4.04 (m, 8H, –OCH$_2^-$). FTIR, cm^{-1}: 1251 (νP = O), 1014, 1061 (P-O-C$_4$H$_9$). Found: C, 52.98; H, 10.01%. Cald: C, 53.26; H, 9.88%.

BBDBP: ^{1}H-NMR (CDCl$_3$) δ, ppm = 0.91 (t, 12H, CH$_3^-$); 1.26 (m, 8H, MeCH$_2^-$); 1.47 – 1.89 (m, 16H, PCH$_2$CH$_2$CH$_2$CH$_2$P$^-$, MeCCH$_2^-$); 3.89 (m, 8H, –OCH$_2^-$). FTIR, cm^{-1}: 1248 (νP = O), 1024, 1064 (P-O-C$_4$H$_9$). Found: C, 53.76; H, 10.26%. Cald: C, 54.29; H, 10.02%.

Stock solutions and other metal ions were prepared by dissolving their chloride salts. All other materials used were of reagent grade quality.

Solvent extraction studies. A 10-mL solution of the organic phase containing the extractant dissolved in the appropriate diluent (such as 1,2-dichloroethane [DCE]) was shaken with an equal volume of the metal ion solution contained in a 50-

Table 1. Extractants used in the study

Structure	R_n	Ligand
$(CH_3CH_2)_2 - O - P(=O) - R_n - P(=O) - O - (CH_2CH_3)_2$	-CH$_2$- -(CH$_2$)$_2$-	MBDEP EBDEP
$[(CH_3)_2CH_2]_2 - O - P(=O) - R_n - P(=O) - O - [CH_2(CH_3)_2]_2$	-CH$_2$- -(CH$_2$)$_2$-	MBDIPP EBDIPP
$[CH_3(CH_2)_3] - O - P(=O) - R_n - P(=O) - O - [(CH_2)_3CH_3]_2$	-(CH$_2$)$_2$- -(CH$_2$)$_3$- -(CH$_2$)$_4$-	EBDBP PBDBP BBDBP
$R_n - P(=O) - R_n$ with R_n	-(CH$_2$)$_3$CH$_3$	TBP
$R_n - O - P(=O) - O - R_n$ with O-R$_n$	-(CH$_2$)$_7$CH$_3$	TOPO

mL stoppered glass tubes, using a mechanical shaker. After a predetermined time, the two phases were allowed to separate and the concentration of the metal ion in the aqueous phase was measured by atomic absorption spectrophotometry. The percent extraction and the distribution ratio of the concerned metal ion were calculated by equating mass balance between the two phases.

RESULTS AND DISCUSSION

Since the extraction properties of solvating reagents are known to be highly dependent on the aqueous acidity, the influence of increasing concentrations of different acid solutions on the extraction of Au(III) was studied, with special attention to MBDIPP as the representative of the alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s. Figure 1 shows the effect of acids on the extraction of Au(III). The most favorable condition for gold extraction was seen to be from hydrochloric acid medium. The extraction of Au(III) increases rapidly with the aqueous acid concentration, reaching an optimum value above 4 M HCl. The extraction process in HCl medium is regulated by the dissociation of the $HAuCl_4$ species. Madi et al. [10] have found that the equilibrium constants of Au(III) extraction (from 0.5 to 1.5 M HCl) with phospholenes are dependent on the ionic strength of the aqueous medium. This result could be correlated by stating that the extraction of Au(III) from HCl medium at low ionic strength, using phosphoryl ligands is dependent on both [H+] and the total ionic concentration of the aqueous phase, which in turns defines the concentration of the extractable $AuCl_4^-$ species. However, with sufficient increase in HCl concentration, the metal/ligand attractions become independent of the $HAuCl_4/AuCl_4^-$ equilibrium, providing enhanced extraction of the metal in the organic phase. So, a high concentration of HCl in the aqueous feed would favor quantitative extraction of Au(III) from the specified medium.
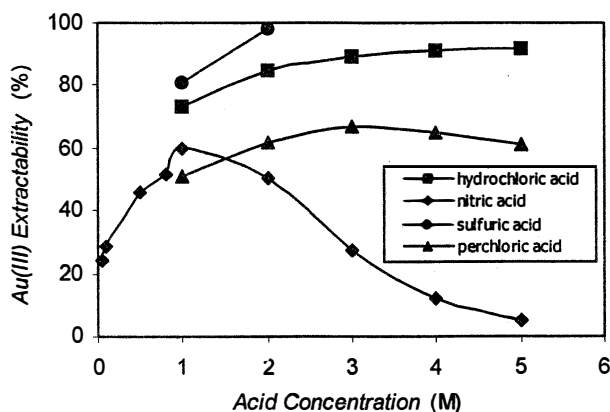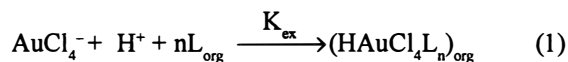

Fig. 1. Effect of acids on the metal ion extraction with MBDIPP. [MBDIPP] = 5.0 × 10^-3 M in DCE, [Au(III)] = 1.0 × 10^-4 M, [Acid] = 1~6 M HCl, phase ratio = 1, shaking time = 1 h.

In hydrochloric acid medium, the equilibrium of Au(III) extraction with solvating extractants has been defined [10] as:

$$AuCl_4^- + H^+ + nL_{org} \xrightarrow{K_{ex}} (HAuCl_4L_n)_{org} \qquad (1)$$

where L denotes the ligand molecule, the subscript 'org' refers to the species in the organic phase. The K_{ex} is the extraction constant at equilibrium and can be defined as

$$K_{ex} = \frac{[HAuCl_4L_n]_{org}}{[AuCl_4^-][H^+][L]_{org}^n} \qquad (2)$$

From the definition of the distribution ratio (D), that of Au(III) is

$$D = \frac{C_{org/t}}{C_{aq/t}} \qquad (3)$$

By equating $C_{aq/t} = [HAuCl_4] + [AuCl_4^-]$ and by substituting equation 3 in equation 2, the extraction equation becomes:

$$\log D = \log K_{ex} + \log [H^+] + n \log [L]_{org} - \log \{([H^+]/K_a) + 1\} \qquad (4)$$

where Ka is the dissociation constant of $HAuCl_4$. Under a given acid concentration, the plot of log D against log [L] should produce a straight line with the slope (n) defining the stiochiometry of the extraction process.

The composition of the Au(III)-ligand complex was determined by the slope ratio method, in which the log D vs. log [L] plots were obtained for Au(III) extraction with different alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s, TOPO and TBP, as shown in Fig. 2. In all reagents, the slope value in each curve is close to one, indicating that Au(III) is extracted in the organic phase as 1:1 Au-ligand complexes, for both the alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s and the monofunctional TBP and TOPO. At higher concentrations (~5 M) gold exists almost exclusively as a tetrachlorocomplex $AuCl_4^-$ [11, 18]. With the analogy of other phosphoryl reagents, the extraction of gold in the present case may be defined as the solvation of the $AuCl_4^-$ species by the P = O in the phosphonate molecule [10, 11].

As evident from Table 1, the alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s contain two P = O groups at equivalent positions, which can interact with Au(III) through coordination or solvation. In both cases, the basicity available at the P = O bonds will determine the extent of attraction with the Au(III). The resulting strength of the metal/ligand bond and the geometrical requirements involved therein will be regulated by the spatial separation between the P = O centers in the bis-molecule. Using a 5 M HCl in the aqueous phase, the extraction of Au(III) in the presence of potential interfering ions was further studied, using the different phosphonate derivatives. The extraction of the different metal ions are presented in Table 2.
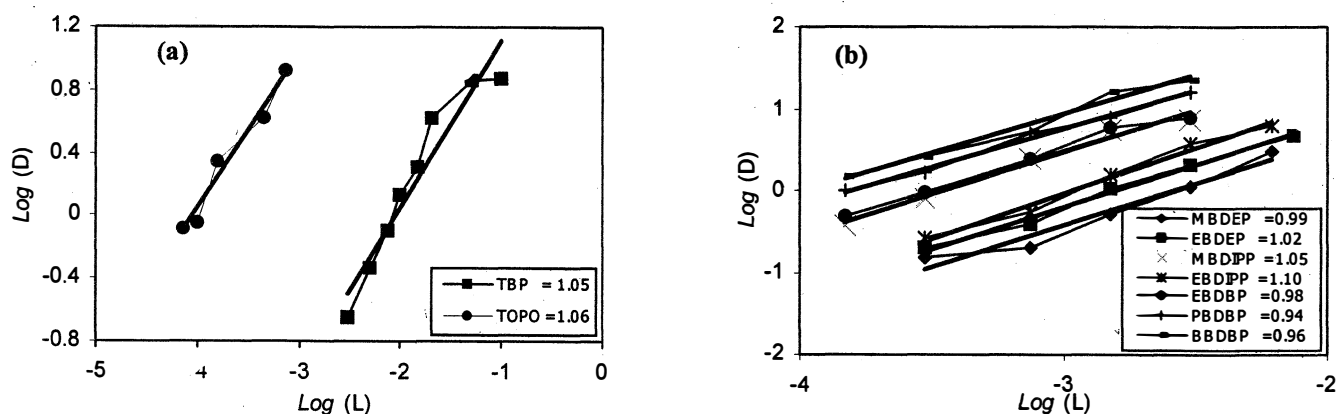
Fig. 2. Determination of Au(III)-ligand complex stoichiometry by the slope ratio method. Plots of log D vs. log (L), using ligands: a) monofunctional phophonates, and b) alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s, [ligand] = $1.0 \times 10^{-4} \sim 3.0 \times 10^{-3}$ M in DCE, [Au(III)] = 1.0×10^{-4} M in 5M HCl, phase ratio = 1, shaking time = 1 h.

Table 2. Extraction of metal ions in 5M HCl using bis(alkylphosphonate)s and monofunctional trialkylphosphates.

Ligand	% Extractability				
	Au(III)	Pd(II)	Ag(I)	Pt(IV)	Cu(II)
MBDEP	62.3	0.0	0.6	37.3	0.0
EBDEP	70.6	0.0	0.0	29.6	0.0
MBDIPP	91.8	0.0	0.0	21.1	0.0
EBDIPP	90.2	0.0	0.1	29.5	0.8
EBDBP	91.3	7.6	6.8	0.1	0.2
PBDBP	97.6	1.7	1.2	42.3	0.2
BBDBP	99.3	0.0	1.4	52.6	0.7
TBP	22.1	0.0	2.2	23.2	1.6
TOPO	92.1	15.3	23.0	38.1	5.4

[Ligand] = 5.0×10^{-3} M in DCE; [Metal ion] = 1.0×10^{-4} M in 5 M HCl; phase ratio = 1; shaking time = 1 h.
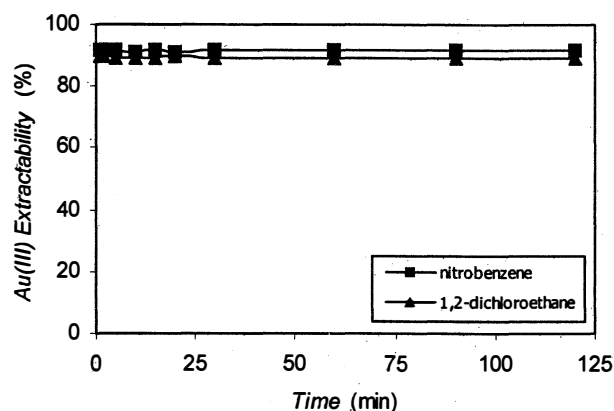

Fig. 3. Effect of shaking time on the extraction of Au(III). [MBDIPP] = 2.0×10^{-2} M in DCE and in nitrobenzene, [Au(III)] = 1.0×10^{-4} M in 5M HCl, phase ratio = 1, shaking time = 1 h.

For Au(III), the extractability increases greatly with the increase in the chain length that connect the P = O centers. The order of Au(III) extractability with the present ligands; e.g., in BBDBP > PBDBP > EBDBP and in EBDEP > MBDEP, can immediately be interpreted on the basis of a solvation process [10], where the accommodation of the large $AuCl_4^-$ species by the two P = O groups will be favored by a larger cavity size of the ligand. The Au(III) extractability is also dependent on the alkyl group attached to the phosphonate, as illustrated in n-butyl > isopropyl > methyl-containing ligands in EBDBP > EBDIPP > EBDEP, respectively.

Au(III) and Pt(IV) are co-extracted in greater amount while the co-extraction of Pd(II), Ag(I) and Cu(II) with Au(III) occur only to a very little extent or even negligible. It was seen that the degree of Au(III) extraction of alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s is comparable to TOPO. However comparing EBDEP and MBDIPP with TOPO, the co-extraction of Au(III), Ag(I), Pd(II), Pt(IV) and Cu(II) is unavoidable with TOPO. This may appear a big disadvantage when the recovery of gold from industrial wastes and precious metal concentrates are considered [2]. The observed Au(III) extractability with alkane-α, ω-diyl bis(O,O-dialkylphosphonate)s also indicated a great advantage over the monofunctional TBP, if the separation of gold from Au-Pt mixture is considered.

The kinetics of any solvent extraction process is important for its commercial application. The equilibration time for the extraction of Au(III) using MBDIPP was measured in 1,2-dichloroethane (DCE) and nitrobenzene. The results are presented in Fig. 3. In both diluents, the extraction of gold reaches equilibrium in less than 1 min providing a transfer of nearly 90% into the organic phase. The kinetic characteristics of MBDIPP, coupled with its high extraction selectivity for Au(III) would probably justify for use in continuous-extraction gold recovery systems [6].

Table 3. Effects of permittivity of various organic solvents on the extraction of Au(III).

Organic Solvents	Permittivity	Au(III) Extractability, %
carbon tetrachloride	2.24	0.0
chloroform	4.81	0.2
chlorobenzene	5.71	4.0
1,2-dichloroethane	10.65	68.4
nitrobenzene	35.70	90.0

[MBDIPP] = 5.0×10^{-3} M; [Au(III)] = 1.0×10^{-4} M in 0.5 M HCl; phase ratio = 1; shaking time = 60 min.

Table 4. Back-extraction of Au(III) from the Au(III)-ligand complex with various reagents.

Reagents	% Au(III) Back-extracted
H_2O	0.0
HNO_3	0.8
HCl	9.3
H_2SO_4	0.0
$HClO_4$	10.6
Sodium Thiocyanate (NaSCN)	87.7
Thiourea (H_2HCSNH_2)	100

Extraction conditions: [MBDIPP] = 2.0×10^{-2} M in DCE, [Au(III)] = 1.0×10^{-4} M in 5 M HCl, Phase Ratio = 1, Shaking Time = 1 h.
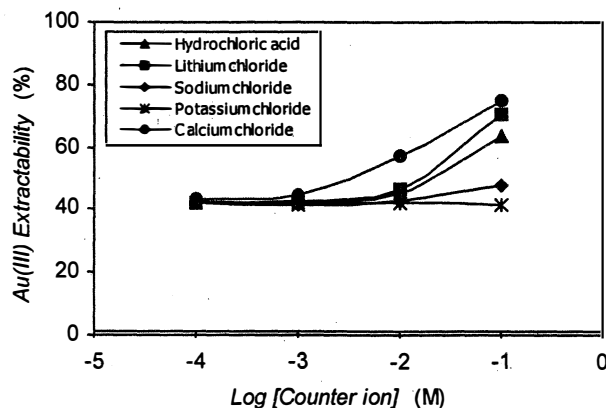Back-extraction conditions: [reagent] = 1 M, phase ratio = 1, Shaking Time = 1 h.

Fig. 4. Effect of counter ions on the extraction of Au(III). [MBDIPP] = 5.0×10^{-2} M in DCE, [Au(III)] = 1.0×10^{-4} M, [Counter ion] = $10^{-4} \sim 10^{-1}$ M, phase ratio = 1, shaking time = 1 h.
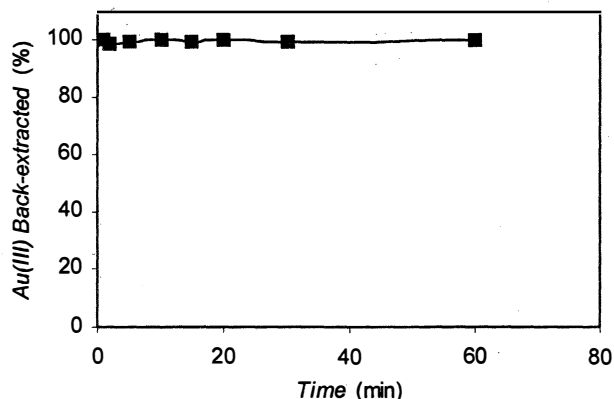

Fig. 5. Effect of shaking time on the back-extraction of Au(III) from the organic phase. Extraction conditions: [MBDIPP] = 2.0×10^{-2} M in DCE, [Au(III)] = 1.0×10^{-4} M in 5 M HCl, phase ratio = 1, shaking time = 1 h. Back-extraction conditions: [thiourea] = 1 M, phase ratio = 1.

Since the reagents under study, extract gold as ion-pair, it is essential to assess the solute-diluent relations in the organic phase. Table 3 shows the influence of diluent on the extraction of $AuCl_4^-$. The extraction order is: nitrobenzene > 1,2-dichloroethane > chlorobenzene. There was no extraction in carbon tetrachloride and chloroform. It is therefore understood that diluents with high electric constants are needed to solubilize the MBDIPP-HAuCl$_4$ complex. In consideration of the availability of commercial diluents to be used in the gold recovery using MBDIPP, a preferentially aromatic diluent like Exxon Aromatic®150 [19] containing nitrobenzene could be considered.

Solvent extraction processes based on solvating extractants are known to be highly dependent on the presence of counter ions that ultimately affect the ionic strength of the aqueous feed solutions and also salting out effect. Fig. 4 gives the effect of some alkali metal chlorides on the extraction of Au(III). It is seen that larger ions of small hydration degree like Na$^+$ and K$^+$ destabilizes the Au(III)-MBDIPP complex whereas the presence of Li$^+$ with large hydration degree greatly enhances the extractability.

Almost quantitative stripping of Au(III) from the Au(III)-MBDIPP complex loaded in DCE was possible in 1 min contact with 1.0 M thiourea, as illustrated in Fig. 5. The results of Au(III) stripping with various reagents are compared in Table 4.

The above result show that the bifunctional bis(dialkyl-phosphonate)s; namely the alkane-α, ω-diyl bis(O,O-di-alkylphosphonate)s are better reagents for extraction of gold from hydrochloric acid medium than the monofunctional trialkylphosphates. A separation method based on extraction of Au(III) with MBDIPP could be tried for the recovery of the metal from industrial wastes dissolved in hydrochloric acid.

ACKNOWLEDGEMENT

REFERENCES

1. Argiropoulos, G., Cattrall, R. W., Hamilton, I. C., and Paimin, R. *Proceedings of the International Solvent Extraction Ion Exchange Conference* (ISEC '96, Melbourne). 1, 123 (1996).

2. Mooiman, M. B. *Precious Metals.* 17, 411 (1993).

3. Muir, D. *Chemistry in Australia.* 348 (1992).

4. Rimmer, B. F. *Chem, Ind.* 63 (1974).

5. Demopoulos, G. P. *J. Metals.* 13 (1986).

6. Pareau, D., Stambouli, M., and Durand, G. *Proceedings of the International Solvent Extraction Ion Exchange Conference* (ISEC '96, Melbourne). 1, 653 (1996).

7. Villacescusa, I., Miralles, N., DePablo, J., Salvado, V., and Sastre, A. M. *Solvent Extr. Ion Exch.* 11, 613 (1993).

8. Alguacil, F. J. and Caravaca, C. *Hydrometallurgy.* 34, 91 (1993).

9. Sato, T. and Yamamoto, M. *Bull. Chem. Soc. Jpn.* 55, 90 (1982).

10. Madi, A., Miralles, N., Cortina, J. L., Arnaldos, J., and A. Sastre. *Proceedings of the International Solvent Extraction Ion Exchange Conference* (ISEC '96, Melbourne). 1, 463 (1996).

11. Martinez, S., Sastre, A., Miralles, N., and Alguacil, F. J. *Hydrometallurgy.* 40, 77 (1996).

12. Salvado, V., Hidalgo, M., Masana, A., Munoz, M., Valiente, M., and Muhammed, M. *Solvent Extr. Ion Exch.* 8, 491 (1990).

13. Dey, A. K., Khopkar, S. M., and Chalmers, R. A. *Solvent Extraction of Metals.* (Van Nostrand Reinhold Company, London, 1970).

14. Kosolapoff, K. *Organophosphorus Compounds.* (John Wiley, New York, 1950).

15. Sliles, A. R. *Esters of Alkane Diphosphonic Acids.* US Patent No. 2, 957, 904 (1960).

16. Chowdhury, D. A. and Kamata, S. *Solvent Extr. Ion Exch* 15, 231 (1997).

17. Cade, J. A. *J. Chem. Soc.* 2266 (1959).

18. Edwards, I. and TeReile, W. A. M. *In* T.C. Lo, M. H. Baird, and C. Hanson *Handbook of Solvent Extraction.* (John Wiley, New York, 1983).

19. Viring, M. J. and Wolfe, G. A. *Proceedings of the International Solvent Extraction Ion Exchange Conference* (ISEC '96, Melbourne). 1, 311 (1996).