

## CHEMICOMETALLURGICAL PROCESSES OF DEEP CONVERSION OF ORE, TECHNOGENIC, AND SECONDARY RAW MATERIALS

# Liquid Solvent Extraction of Arsenic from Acidic Process Solutions by Organophosphorus Extractants and Their Mixtures

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**Abstract**—An analytical review on methods for extracting arsenic from acidic solutions using various classes of industrial and advanced organophosphorus extractants and their mixtures is given. The states of arsenic(IV) and arsenic(V) in solutions of acids are described. Comparative data on the extraction of different forms of arsenic from acidic process solutions, including cutoff electrolytes of the copper industry, are given.

**Keywords:** arsenic, liquid solvent extraction, cutoff electrolyte, tri-*n*-butyl phosphate (TBP), di-(2-ethylhexyl)phosphoric acid (D2EHPA), Cyanex 923, Cyanex 301

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## INTRODUCTION

Arsenic is the most troublesome toxic impurity in the production of nonferrous metals [1]. During the processing of ores and ore concentrates, it accumulates in both the solid industrial products and process solutions. As a rule, recycling or further utilization of these solutions is impossible unless arsenic is removed from them. If arsenic can be extracted easily enough from weakly acidic or nearly neutral solutions, there are a limited number of methods that allow one to remove it from concentrated acid solutions. Liquid solvent extraction is among these methods.

In the process of copper electrolysis, impurities (including As, Sb, and Bi, the most harmful ones) move into an acidic electrolyte and can have a negative effect on the quality of cathodic copper. In connection with this, the problem of removing impurities and maintaining the optimal electrolyte composition in the production of copper is a key issue [2].

The most common method for refining the cutoff electrolyte from impurities is its regeneration in electrolyzers with insoluble anodes and the withdrawal of part of the electrolyte to the production of copper sulfate and nickel salts. The regeneration cycle involves up to 4% of the production baths refining up to 5% of the total electrolyte volume. In this process, copper and impurities such as As, Sb, and Fe are extracted and sulfuric acid is regenerated. However, the energy consumption in this process is 5–8 times higher than the energy consumed in the production baths and highly toxic AsH<sub>3</sub> may be released into the atmosphere. Moreover, the produced cathodic copper may be of low quality [3].

Liquid solvent extraction is a promising method for purifying electrolytes from arsenic, because it allows one to extract the latter from the electrolyte without acidity correction.

## IONIC STATES OF ARSENIC IN ACIDIC SOLUTIONS

The selection of a reagent for liquid solvent extraction depends primarily on the properties and ionic state of an extracted metal in the solution. Numerous studies suggest that arsenic is mainly present in the form of As(V) in process sulfuric acid solutions for copper electrolysis [4]. However, it is also capable of forming stable compounds of As(III), which is present in acidic solutions in the form of AsO<sup>+</sup> cations. At pH 2–11, As(III) exists in unionized form in the composition of weak acids HAsO<sub>2</sub> and H<sub>3</sub>AsO<sub>3</sub> (pK<sub>1</sub> = 10). As(V) forms a stronger acid, i.e., H<sub>3</sub>AsO<sub>4</sub>. In acidic solutions, arsenic acid is predominantly present in the form of unionized H<sub>3</sub>AsO<sub>4</sub> [5].

Modern extracting agents are capable of extracting both dissociated and weakly dissociated (or undissociated) compounds from solutions. The solubility of undissociated H<sub>3</sub>AsO<sub>4</sub> in water is determined by its hydration with a variable number of water molecules. Thus, an organic reagent immiscible with water should—entirely or partially—replace water molecules in the hydrated shell of H<sub>3</sub>AsO<sub>4</sub> to extract As(V) from a solution [5]. Reagents that form such complexes usually contain oxygen or sulfur atoms, which can provide an electronic pair for the formation of a solvate.

**Table 1.** Some physicochemical properties of commercially available extractants for As [14–20]

Brand	Main substance	Formula	Density, g/cm <sup>3</sup> (25°C)	Viscosity at T °C, cPs	Solubility in water, g/L	Flash point, °C
TBP	Tri- <i>n</i> -butylphosphate	(RO) <sub>3</sub> P=O	0.977	3.4 (25°C)	0.38	146
Hostarex PO 212	Di-2-methylpropyl-2-methylpropylphosphonate	R''P(O)(OR'') <sub>2</sub> R''- <i>iso</i> -C <sub>4</sub>	0.945	n/a	n/a	151
P507	2-Ethylhexyl-2-ethylhexylphosphonate	(R''O)R''P(O)OH	0.94–0.96	≤36 (25°C)	n/a	≥170
P204	Di-2-ethylhexylphosphoric acid (D2EHPA)	(R''O) <sub>2</sub> P(O)OH, R''- <i>iso</i> -C <sub>8</sub>	0.974–0.976	42 (25°C)	0.182	196
Cyanex 301	Bis(2,4,4-trimethylpentyl)dithiophosphonic acid	(R') <sub>2</sub> P(S)SH, R'- <i>iso</i> -C <sub>8</sub>	0.95	78 (24°C)	0.007	74
Cyanex 921	Trioctylphosphine oxide (TOPO)	R <sub>3</sub> P=O, R- <i>n</i> -C <sub>8</sub>	0.88	15 (55°C)	n/a	>110
Cyanex 923	Trialkylphosphine oxide (TAPO)	R <sub>3</sub> P=O, R- <i>n</i> -C <sub>6</sub> -C <sub>8</sub>	0.88	40 (25°C) 13.7 (50°C)	>0.01	182
Cyanex 925	Bis(2,4,4-trimethylpentyl)octylphosphine oxide	R' <sub>2</sub> RP=O, R- <i>n</i> -C <sub>8</sub> R'- <i>iso</i> -C <sub>8</sub>	0.88	11.7 (25°C)	0.02	n/a

The extraction of As(III) can proceed by a cation-exchange mechanism to some extent in accordance with its ionic state in acidic solutions (AsO<sup>+</sup>), but it is believed that the solvation extraction mechanism is predominantly implemented in the region of relatively high H<sub>2</sub>SO<sub>4</sub> concentrations.

Thus, As can be extracted from acidic electrolytes with polar oxygen- and sulfur-containing solvents, such as neutral organophosphorus compounds (esters of alkyl-phosphorus-containing acids, phosphine oxides, etc.) and their thiosubstituted derivatives. In addition, data on the extraction of As with various mixtures based on organophosphorus compounds are available [6].

#### EXTRACTION OF ARSENIC WITH FULLY ESTERIFIED ESTERS OF ALKYLPHOSPHORIC AND ALKYLPHOSPHONIC ACIDS

Among esters of alkyl-phosphorus-containing acids, tri-*n*-butyl phosphate (TBP)—which is manufactured and used on an industrial scale—is the most prominent one in technological applications.

The isolation of As by extraction with TBP was used at manufacturing sites in Belgium (Metallurgie Hoboken-Overpelt, a subsidiary of Union Minière), Australia (Copper Refineries Pty Ltd, Townsville), China (Shilu Copper Company), Japan (Hibi Kyodo Smelting Co. Ltd), Austria and Chile, and the former Soviet Union (PO Balkhashmed') [7–13].

Some physicochemical properties of TBP and other phosphorus-containing extractants are given in Table 1. The rapid kinetics of extraction and reextraction of arsenic (≤1 min) and relatively low viscosity is an advantage of TBP that allows one to use it both in the form of solutions and in the undiluted form [12]. Sometimes a small amount of high-molecular-weight aliphatic alcohols is added to the extractant as a modifier that prevents the formation of a third phase [6].

TBP efficiently extracts As(V) from solutions concentrated with sulfuric acid. In this case, As(III) is barely extracted. For undiluted TBP, the degree of extraction of As(V) increases from 44 to 67% with an increase in the acidity of the aqueous phase from 200 to 600 g/L H<sub>2</sub>SO<sub>4</sub>, [12]. For solutions with higher acidity, it is advisable to use 50% TBP in order to reduce H<sub>2</sub>SO<sub>4</sub> coextraction and the viscosity of the extracts.

The extraction of As with 50% TBP is a fairly selective process. For example, As(V) and a 10% H<sub>2</sub>SO<sub>4</sub> solution was predominantly extracted in one of the Chilean factories from the copper electrolyte solution with additions of up to 0.5–1.1 g/L Sb and 0.5–2.3 g/L Cl<sup>-</sup>, which contained 10 g/L As(V), 65 g/L Cu(II), 16 g/L Ni(II), 7.5 g/L Fe(II), 0.05 g/L Ca, and 600 g/L H<sub>2</sub>SO<sub>4</sub>. Since H<sub>2</sub>SO<sub>4</sub> is washed out from an extract better than As, the former can be removed at the stage of flushing with water at a high organics/water (O : W) ratio and then the water extraction is repeated at a lower O : W ratio in order to extract As. It was established [12] that the electrolyte additives (adhesives,

thiourea, etc.) and the presence of a dispersed solid phase ( $\text{Sb}_2\text{O}_3$ ) in concentrations of about 0.005 g/L have a small effect on the hydrodynamics of the process, which ensures rapid phase separation ( $\leq 5$  min).

In the classic version, the extraction of As with undiluted TBP is carried out in extractors of the mixer-settler type. Six extraction steps, two aqueous flushing steps for removing  $\text{H}_2\text{SO}_4$ , and five reextraction steps are usually sufficient for effective extraction. In addition, an extractant regeneration step that involves washing with an alkaline solution is needed to remove the TBP hydrolysis products [6, 11]. Processing a copper electrolyte under these conditions allows one to extract from it more than 90% of As and about 80% of Sb. According to a technological scheme, acidic flush water is returned to the stage of extraction and circulating organics are periodically withdrawn for alkaline regeneration by flushing with a 15% NaOH solution. Arsenic is precipitated from the obtained reextract in the form of slightly soluble salts and the filtrate is returned to the stage of reextraction.

Trials of the extraction of As with 100% TBP from mother lickers of the nickel plant of the 'Uralkhromed' industrial complex, which contained 68.8 g/L Ni, 2.4 g/L Cu, 3.2 g/L Fe, 18.5 g/L As, and 206 g/L  $\text{H}_2\text{SO}_4$ , were conducted [21]. The degree of extraction of As in five extraction steps was 93.5%. A solution containing 17.4 g/L As was obtained as a result of aqueous reextraction, which is suitable for the preparation of antiseptics.

Various types of extraction equipment can be used for implementing the extraction process with TBP. In [2, 9, 22], comparative results of scaled-up laboratory tests of the extraction of As with TBP from copper electrolytes in extraction apparatuses of several types are described. The results of semi-industrial trials of the extraction of As with undiluted TBP in centrifugal extractors are given in [9]. Before supplying to the extraction refining stage, an electrolyte with about 8 g/L As was filtered and adjusted in acidity to 180 g/L  $\text{H}_2\text{SO}_4$ . As a result, the degree of extraction of As in this equipment was 50% in two steps. In these semi-industrial trials, As could be removed from the electrolyte at a rate of 1 kg/h. Owing to high-performance equipment, the entrainment of organics at each stage did not exceed 0.05%.

On an industrial scale, the extraction refining stage to eliminate As by means of TBP was operated in the Copper Refineries Pty Ltd factory (Townsville, Australia), in which four extraction steps, two aqueous flushing steps, and three reextraction steps were used to extract As from an electrolyte solution containing 15–18 g/L As, 8 g/L Ni, and 0.06 g/L Sb. A 40–80% solution of TBP in Shellsol 2046 was used as an extractant. The degree of As extraction reached 50%. Copper(II) arsenate was precipitated from the reextract as a commercial product [3, 6].

A similar process was used in the Metallurgy Hoboken-Overpelt factory (Belgium) to extract  $\text{As}_2\text{O}_3$  as a final product [6]. According to the data from this manufacturer, the use of liquid solvent extraction for the removal of As reduces the cost of electrolyte refining by almost half compared to the scheme of deep electroextraction of copper and a fivefold cost savings are achieved when taking into account arsenic trioxide revenues [3].

In the Hibi Kyodo Smelting Co Ltd factory (Japan), arsenic was extracted with undiluted TBP from an electrolyte solution cooled to room temperature, which made it possible to attain an extraction efficiency of 80 to 90%. In particular, the As content in the raffinate decreased to 0.3 g/L after extracting it from a solution containing 3.8 g/L As, which corresponds to an extraction efficiency of 92.1%. The reextraction with hot water at O : W ratio = 4 : 1 ensured 10–20 g/L As for its concentration in the reextract. Arsenic was isolated from the resulting solution in the form of  $\text{As}_2\text{O}_3$  by reduction. The extraction with carbon tetrachloride was used to purify the raffinates from organic compounds [6].

The practice of industrial operation of TBP has revealed a number of problems: the impossibility to purify an electrolyte solution from Sb, Bi, and As(III); the contamination of electrolytes with organic impurities due to the high solubility of TBP; and the partial degradation of the extractant when operating in acidic media. Therefore, the possibility of As extraction with other organophosphorus extractants was considered.

A study of the properties of full esters of phosphoric acid with molecular weights higher than that for TBP [10] showed their low extraction efficiency for As. At the same time, a higher extraction ability of esters of alkylphosphonic acids with general formula  $(\text{RO})_2\text{P}(\text{O})\text{R}$ , in particular, dibutylbutylphosphonate (DBBF) and dipentylpentylphosphonate (DPPF), with respect to As was established. The degree of extraction of As(V) increases in sequence TBP < DPPF < DBBF, but  $\text{H}_2\text{SO}_4$  coextraction also increases. DBBF is stable in  $\text{H}_2\text{SO}_4$ , HCl and  $\text{HNO}_3$  solutions, but a third phase is formed in the extraction form concentrated acids, which requires that a modifier must be selected.

In [4, 23], the extraction of As(V) with di(2-ethylhexyl)methylphosphonate (D2EHMP) was studied. It was established that D2EHMP is similar to TBP in extraction properties: it is characterized by a rapid extraction kinetics and has satisfactory hydrodynamic properties in undiluted form. The degree of extraction of As(V) increases from 30 to 63% with an increase in the aqueous phase acidity from 0.5 to 3 mol/L  $\text{H}_2\text{SO}_4$ . At the same time, an increase in temperature to 40°C gives rise to a slight decrease in the degree of extraction of As(V), while the level of  $\text{H}_2\text{SO}_4$  coextraction decreases 1.7 times. The reextraction of As(V) from the D2EHMP phase is possible with water or a 5–10% aqueous solution of  $\text{Na}_2\text{SO}_4$ .

As was established in laboratory trials of the extraction of As from solutions of copper production with undiluted D2EHMP, a 95% extraction of As(V) and 10% coextraction of  $H_2SO_4$  can be achieved in six extraction steps from electrolytes containing 150 g/L  $H_2SO_4$ . A considerable excess of the organic phase is required for efficient extraction of As from a less acidic solution. In this case, 93% extraction of As and 34.2% coextraction of  $H_2SO_4$  are achieved in six extraction steps. Thus, D2EHMP and TBP are comparable in parameters as far as As extraction from acidic electrolytes is concerned.

As was claimed in the patent [24], As can be extracted with esters of alkylphosphonic ( $R_1P(O)(OR_2)OR_3$ ), alkylphosphonous ( $R_1P(OR_2)OR_3$ ), alkylphosphinous ( $R_1P(R_2)OR_3$ ), or alkylphosphinic ( $R_1P(O)R_2OR_3$ ) acids. Two options for extracting As from acid solutions are described: either together with Sb when using a mixed extractant containing an ester of an organophosphorus acid (TBP or Hostarex PO 212) and alkylated 8-hydroxyquinoline (Kelex-100) or selectively when using ester Hostarex PO 212 after the preliminary extraction of Sb with a mixture of Kelex-100 with D2EHPA. In particular, the proposed extractants were tested in As extraction from leaching solutions of a high-arsenic product (speisses) containing 90–120 g/L As, 30 g/L Cu, and 110–145 g/L  $H_2SO_4$ . Mixtures comprised of 20% Kelex-100, 30% Hostarex PO 212 (or 40% TBP), and 20–25% isodecanol in Escaid 100 allow one to extract 94–96% of As and Sb into the extract in seven extraction steps.

In accordance with the second option, 90–92% of Sb are initially removed from a solution containing 113.8 g/L As, 8.9 g/L Sb, 30 g/L Cu, and 150 g/L  $H_2SO_4$  in 4–7 extraction steps with a mixture comprised of 20–25% Kelex-100, 30% D2EHPA, and 20% isodecanol in Escaid 100 and then As is extracted with undiluted Hostarex PO 212. The authors noted that the proposed extractants are most effective for extracting As from solutions containing 5–100 g/L  $H_2SO_4$  or 5–400 g/L HCl. Arsenic can be extracted from the organic phases in the form of arsenous anhydride by reduction with  $SO_2$ .

Full esters of phosphorus-containing acids are tested as a carrier in the polymer membrane for separating As from acidic copper electrolytes [25]. The possibility of selective extraction of 5 g/L As (V) and a part of  $H_2SO_4$  from an electrolyte solution containing 220 g/L  $H_2SO_4$  in a membrane module that uses DBBF as a carrier was demonstrated.

#### ACIDIC ESTERS OF ALKYLPHOSPHORIC, ALKYLPHOSPHINIC, AND DITHIOPHOSPHINIC ACIDS

Acidic alkyl esters of phosphorus-containing acids, i.e., the so-called “organophosphorus acids” (OPA),

are also capable of extracting As. D2EHPA is a main commercially available representative of this class of extractants. Due to their relatively high viscosity, D2EHPA is used in the form of a solution in a diluent. The extraction equilibrium is achieved in the system quickly, within 3–5 min [22]. With an increase in the acidity of the aqueous phase from 1.5 to 4 mol/L  $H_2SO_4$ , the degree of extraction of As(V) with a 15% solution of D2EHPA in cyclohexane increases from 50 to 67%. At the same time, acid coextraction is insignificant. The extraction of As(V) with D2EHPA proceeds by a hydrate-solvate mechanism with the formation either of a mixture of mono- and disolvate complexes or of monosolvates and salt associates, depending on the mixture acidity.

Comparison of the extraction properties of D2EHPA with that for other organophosphorus compounds, including acidic esters of alkylphosphinic acids, such as isododecylphosphetic acid (IDDDPA) and diisooctylphosphinic acid (DIOPA), showed that As(V) extraction increases in the sequence TBP < DIOPA < IDDDPA < D2EHPA [22].

The reextraction of 80–90% As(V) in one step is possible from the D2EHPA-based extract with a solution of 90–130 g/L  $Na_2SO_4$  at O : W ratio = 1 : 1. Moreover, the phase separation time does not exceed 12–15 min at room temperature and decreases to 3–5 min at 35–40°C [22].

The trial results of the continuous extraction of As from processing solutions of copper-containing raw materials with a 50% solution of D2EHPA in cyclohexane in cascade extractors of the mixing–settling type are given in Table 2. As can be seen, the reextraction of As with a 10%  $Na_2SO_4$  solution proceeds more efficiently from more acidic extracts, as well as upon a decrease in the O : W ratio. In this case, no more than 34% of  $H_2SO_4$  contained in the extract goes to the reextract.

Acidic esters of thiosubstituted alkylated phosphorus-containing acids are also effective extractants for As. Unlike other extractants, sulfur-containing esters can form stable complexes with As(III), in which the latter serves as a cation component.

A solution of 0.25 mol/L of di-2-ethylhexyldithiophosphoric acid (D2EHDTPA) in heptane extracts As(III) from 1–12 N solutions of  $H_2SO_4$ , HCl, and HBr, as well as from solutions of 1–6 mol/L  $HNO_3$  with very high distribution coefficients ( $D_{As} \sim 10^3–10^4$ ). With an increase in the solution acidity, the degree of extraction significantly increases because of the increase in content of the extractable form of  $AsO^+$  in the aqueous phase. Extraction from weakly acidic, neutral, and alkaline solutions, in which As(III) is present in the form of arsenious acid and its anions, is barely taking place. By means of extraction with D2EHDTPA, As(III) can be quantitatively separated

**Table 2.** Results of the multistage extraction and reextraction of arsenic from process solutions with D2EHPA [22]

Solution type and impurity composition, g/L	Concentration, g/L		Extraction			Reextraction with 10% H <sub>2</sub> SO <sub>4</sub>		
	H <sub>2</sub> SO <sub>4</sub>	As	O : W	number of stages	E <sub>As</sub> , %	O : W	number of stages	E <sub>As</sub> , %
Mother solution of copper purification 45 Cu, 88 Ni, 2.6 Fe	57	10.8	1 : 1	10	67	1 : 1	4	67
			2 : 1	10	71	1 : 2	4	71
			4 : 1	6	93	1 : 4	4	92
Electrolyte I 17.5 Cu, 95 Ni, 2.2 Fe	110	11.3	1 : 1	10	84	1 : 1	4	83
Electrolyte II 1.6 Cu, 97 Ni, 3.2 Fe	149	10.2	1 : 1	10	96	1 : 1	4	95

from Ni, Co, Fe, Cd, Bi, Zn, Sn, and Ge, as well as from As(V).

Bis(2,4,4-trimethylpentyl)dithiophosphinic acid manufactured under the brand name Cyanex 301 is an extractant of the class of thiosubstituted alkylphosphinic acid esters, which is capable of effectively removing As(III) from acidic solutions. Due to the high viscosity, Cyanex 301 is used only in the form of diluted solutions. More concentrated forms of the extractant are used at elevated temperatures, but the As extraction efficiency somewhat decreases with an increase in the temperature. The kinetics of As(III) extraction is rapid and, as a result, equilibrium is achieved within 3 min [26]. Cyanex 301 is capable of extracting As(III) from mineral acids in a wide range of acid concentrations. The advantage of this extractant is the absence of coextraction of the mineral acids.

The extraction chemistry of As(III) has been studied only for weakly acidic solutions of HCl. It was established that As goes into the organic phase from such solutions in the form of a complex that contains  $\text{AsO}^+\text{Cl}^-$  and one molecule of the extractant [26]. A study of the dependence of the As(III) extraction efficiency on its concentration within the range of  $10^{-3}$ – $10^{-1}$  mol/L at pH 1 showed a relatively small extraction capacity of the extractant.

A study of the extraction of accompanying elements in the acidity range from 2 to 6 mol/L HCl showed that a 3.4% solution of Cyanex 301 in toluene quantitatively extracts Se(IV), Bi(III), Hg(II), and Cu(II) ions in a concentration of  $10^{-3}$  mol/L in the entire region of acidities, while the extraction of Sb(III) and Pb(II) ions is effective in the acidity ranges of up to 3 and 5 mol/L HCl, respectively, and then is significantly reduced; Ni(II) ions are extracted in noticeable amounts only at  $\text{pH} \geq 1$ . Similar dependences are established in sulfuric and nitric acids [26]. Thus, the extractant is characterized by a low selectivity with respect to As(III) extraction.

Difficulties at the reextraction stage is a serious drawback of Cyanex 301 as an extractant for As. Mineral acids cannot be used for reextracting As, but can

be used for reextracting Pb and Sb contaminants if the acid concentration exceeds 3–5 mol/L. Alkaline reextraction of As(III) with NaOH in a concentration of 1–2 mol/L is theoretically possible, but a stable emulsion is formed in the extract in the presence of Cu. To selectively extract As(III) in the presence of Se(IV), it was proposed to use a mixture comprised of 0.1 mol/L  $\text{KBrO}_3$  and 1 mol/L (HCl + KBr). The reextraction of As from the organic phase can also be accomplished by treating the latter with H<sub>2</sub>S at a pressure of 2–3 bar or with Na<sub>2</sub>S at 75–85°C [10].

In general, Cyanex 301 is among the most efficient extractants for As(III). However, its technological applicability is limited by issues of irreversible copper coextraction, a low selectivity, and difficulties at the stage of As reextraction. In our opinion, the issue of chemical stability of Cyanex 301 in the reextraction processes requires additional studies.

### TRIALKYLPHOSPHINE OXIDES AND TRIALKYLAMIDES OF PHOSPHORIC ACID

Extractants of the class of trialkylphosphine oxides, in particular, Cyanex 921–925, are of great interest to researchers because of their commercial availability, chemical stability, and ability to efficiently extract As from acidic media [9–11, 27–30].

Since trialkylphosphine oxides have a fairly high viscosity at room temperature (see Table 1) and Cyanex 921 (tri-*n*-octylphosphine oxide, TOPO) is a solid, these extractants are used in diluted form. Thus, it was proposed to use a solution of 2.0 mol/L TOFO in *p*-xylene for extracting As from copper electrolytes in the patent [30]. As was noted in [29], liquid Cyanex 923 (trialkylphosphine oxide, TAPO) can be used both in the form of solutions and in an undiluted form. However, solutions of TAPO are typically used in concentrations of no more than 50%. Hydrocarbon solvents containing an aromatic component are preferable for use as a diluent, but purely aliphatic compositions can also be used in some cases. In the latter case,

a third phase is formed in the extractant at high acidity ( $>300$  g/L  $\text{H}_2\text{SO}_4$ ), requiring the use of modifying agents. In general, the diluent type has a little effect on the efficiency of As extraction with phosphine oxides.

The processes of extraction and reextraction of As with phosphine oxides are characterized by rapid kinetics and, as a result, the equilibrium in the system is achieved within 5–7 min. The As extraction parameters decrease with an increase in the temperature, but a significant increase in the phase separation rate is simultaneously observed and, therefore, the extraction with TAPO is usually carried out at elevated temperatures.

As was reported in [28, 32], phosphine oxides somewhat better extract As(V) when compared to As(III). Moreover, with an increase in the  $\text{H}_2\text{SO}_4$  concentration to 200 g/L, the extraction efficiency of both forms, i.e., As(III) and As(V), with a 50% solution of Cyanex 923 (at 50°C) increases to 40 and 63%, respectively. Similar results were obtained in [31] for a 20% Cyanex 921, but a sharp decrease in the As extraction efficiency (from 90 to 30%) was detected upon an increase in the acidity of the aqueous phase above 2.5 mol/L  $\text{H}_2\text{SO}_4$ .

Unlike [28, 32], in [29], the As extraction efficiency with a 50% solution of Cyanex 925 increased neither at 50 nor at 20°C upon an increase in acidity. On the contrary, the As(V) extraction efficiency slightly decreased with an increase in the  $\text{H}_2\text{SO}_4$  concentration from 50 to 250 g/L. The differences are perhaps associated with the structure of hydrocarbon radicals—Cyanex 925 has branched radicals (in contrast to linear radicals in Cyanex 921 and Cyanex 923), which generally worsens As(V) extraction, although it makes it more selective owing to lower coextraction of impurities and  $\text{H}_2\text{SO}_4$ .

The reextraction of As from phosphine oxides proceeds better from more acidic extracts and at elevated temperatures, but even aqueous extraction is effective in the case of Cyanex 925.

As was shown in [31], the use of a 80% solution of Cyanex 921 in *p*-xylene allows one to selectively extract 87% As from a copper electrolyte in 3 steps at  $\text{O} : \text{W} = 1 : 1$ . An efficiency of 95.2% in one step of As extraction was achieved in the case of reextraction with a solution of 0.5 mol/L  $\text{Na}_2\text{SO}_4$  in a 10%  $\text{H}_2\text{SO}_4$  solution at 65°C. It was noted that a 50% solution of Cyanex 921 is ten times more efficient than a 50% solution of TBP as an extractant for As under comparable conditions.

As was found in [31, 32], 5% of Cyanex 921 and 30% of Cyanex 923 in the composition of polymeric liquid membranes can be used as carriers for As(V), ensuring the effective selective extraction of the latter from acidic solutions.

Thus, trialkylphosphine oxides of the Cyanex brand are promising extractants for removing As from

industrial solutions. In general, trialkylphosphine oxides are comparable to or superior to TBP with respect to the ability to extract As, but chemically more stable in acidic media, do not undergo hydrolysis, are less soluble, and can extract As of both oxidation states.

It should be noted that alternative extractants for removing As from acidic solutions are being constantly searched for and tested, for example, among derivatives of alkylated phosphorus-containing acids. Thus, the data on the extraction of As(V) with hexabutyltri- amide of phosphoric acid  $[(\text{C}_4\text{H}_9)_2\text{N}]_3\text{PO}$  (HBTAP, HBTA) are given in [4]. It was shown that a 1 M solution of HBTAP in kerosene extracts As(V) from acidic solutions more efficiently than TAPO in comparable concentration.

#### EXTRACTION OF ARSENIC WITH MIXTURES OF PHOSPHORUS-CONTAINING EXTRACTANTS

The development of formulations of extractant mixtures with synergistic properties is a way to improve the efficiency of liquid solvent As extraction. Typically, the available industrial reagents are used for this purpose. In particular, extractants of the Cyanex brands are among the most efficient extractants for extracting As, as mentioned above. Therefore, As extraction with a mixture of Cyanex 301 and Cyanex 925 for joint extraction of As(III) and As(V) from acidic electrolytes was studied in [5, 10]. Fifty-percent solutions of the Cyanex 925 + Cyanex 301 mixture and the individual reagents were used as extracting agents. The extraction equilibrium in the mixed extractant system was achieved within 5 min. It was found that a 50% solution of the Cyanex 925 + Cyanex 301 mixture in toluene extracts both forms As(III)/As(V). The individual extractants are noticeably worse at extracting As. In the extractions with a mixed reagent, the synergistic enhancement of the extraction efficiency was observed, which is achieved mainly by increasing the extraction of As(V) (Table 3). The aqueous reextraction of As at 50°C from an extractant based on the Cyanex 925 + Cyanex 301 mixture has proven inefficient. A stable emulsion is formed in reextraction with alkaline reagents. Thus, the problem of reextraction from the Cyanex 925 + Cyanex 301 mixtures requires additional studies.

In [4], the extraction of As together with Sb from sulfuric acid solutions with the mixtures of TBP or TAPO and acidic esters of phosphoric acids (OPA), in particular, D2EHPA or dioctylphenylphosphoric acid (DOPPA), is studied. A small synergistic effect was established in As extraction with the mixtures of OPA and TBP. The addition of 5–15% of OPA to TBP increases the extraction of As(V) from solutions containing 2.6 g/L As, 0.5 g/L Sb, 40 g/L Cu, 20 g/L Ni, and 200 g/L  $\text{H}_2\text{SO}_4$ . A further increase in the amount of OPA in the extractant up to 30% has a negative

**Table 3.** Effect of the organic phase composition on the parameters of As(III) and As(V) extraction with individual and mixed extractants based on Cyanex 925 and Cyanex 301 [33];  $C(\text{H}_2\text{SO}_4) = 150 \text{ g/L}$ ,  $C(\text{As}) = 0.625 \text{ g/L}$ ,  $T = 50^\circ\text{C}$ ,  $\text{O} : \text{W} = 1 : 1$ , and  $\tau = 5 \text{ min}$

Reagent content in octane	Distribution coefficient		Extraction efficiency, %	
	As(III)	As(V)	As(III)	As(V)
50 Cyanex 301	165.7	0.8	99.4	43.0
50 Cyanex 925	0.1	0.9	8.0	48.0
15 Cyanex 301	332.3	49.0	99.7	98.0
33 Cyanex 925				

effect on the extraction of As(V). The addition of OPA to a 40% solution of TAPO in kerosene has no effect on (D2EHPA) or decreases (DOPPA) the extraction of As(V). To solve the problem of the simultaneous extraction of Sb(III) and As(V), the following mixtures are promising: 80% TBP and 20% D2EHPA, which provide 80% extraction of Sb and 40% extraction of As; or 40% TAPO and 30% D2EHPA, which allow one to extract 80% Sb and 50% As.

In [34], a synergistic effect was established in the extraction of As(V) from sulfuric acid solutions (160–220 g/L  $\text{H}_2\text{SO}_4$ ) with the mixture of DBBP and D2EHPA in kerosene, but the process of As extraction is characterized by relatively slow kinetics. A DBBP solution in kerosene extracts As(V) from 2 mol/L  $\text{H}_2\text{SO}_4$  to some extent and D2EHPA does not extract As(V) at all at such acidity levels. If the mixture of 40% DBBP and 27% D2EHPA in kerosene is used, then the As extraction efficiency increases up to 40%, which is twice as high as the efficiency of the extraction with DBBP in a comparable concentration.

In [35], data on the effect of additions of acidic esters of phosphoric (P204) and phosphonic (P507) acids, as well as quaternary ammonium bases, tertiary carboxylic acids (V911), and aliphatic alcohols to 50% TBP are given. It was established that the mixture of TBP with D2EHPA (P204) exhibits the best extraction properties. A study of the properties of this compound showed that a decrease in the concentration of TBP to 40–45% ensures less  $\text{H}_2\text{SO}_4$  coextraction and quicker phase separation. The mixture composed of 10% P204 and 40% TBP in kerosene has been tested and implemented at the Shilu Copper Company factory (China) for the extraction of arsenic from copper electrolytes to produce 100 t/year copper arsenate from the reextracts [35].

## CONCLUSIONS

The extraction of As from acidic solutions with organophosphorus extractants is quite an effective way for extracting arsenic and is, accordingly, used in industry. The choice of a particular extractant or mixture of extractants depends on the requirements imposed on the degree of purification of solutions

from arsenic and on the process selectivity. In addition, the elemental composition of a solution should be taken into account in selecting an extractant; for example, the presence of copper in a solution is unacceptable when using dithiophosphinic acid, since copper compounds are irreversibly moved into the extractant phase.

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