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

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To cite this Article Gupta, Bina and Mudhar, Niti(2006) 'Extraction and Separation of Germanium Using Cyanex 301/Cyanex 923. Its Recovery from Transistor Waste', Separation Science and Technology, 41: 3, 549 — 572
To link to this Article: DOI: 10.1080/01496390500525021
URL: http://dx.doi.org/10.1080/01496390500525021

Separation Science and Technology, 41: 549–572, 2006
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ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500525021

Extraction and Separation of Germanium Using Cyanex 301/Cyanex 923. Its Recovery from Transistor Waste

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Abstract: The extraction of Ge(IV) from HCl, HNO_3 and H_2SO_4 media in toluene solution of Cyanex 301 and Cyanex 923 is investigated. It is almost quantitatively extracted (~95%) in Cyanex 301 and Cyanex 923 at 8 $molL^{-1}$ HCl but the extractions from H_2SO_4 and HNO_3 are poor in the entire investigated range of acid molarity. Detailed investigations were carried out from HCl medium. Based on the slope analysis data the extracting species is identified as $GeCl_4{\cdot}2R$ (R = Cyanex 301/Cyanex 923). The extraction of Ge(IV) is higher and comparable in diluents like toluene, n-hexane and kerosene (160–200°C) and there is no correlation between the dielectric constant and the percent extraction. The extractants are stable towards prolonged acid contact and there is negligible loss in their extraction efficiency even after recycling them for several cycles. The extraction behavior of commonly associated metal ions namely As(V)/(III), Sn(IV), Tl(III), In(III), Ga(III), Fe(III), Al(III), Hg(II), and Cu(II) has also been investigated. Based on the partition data conditions for attaining some binary and ternary separations involving Ge(IV) have been optimized. The separation data have been fused to develop a scheme for the recovery (93%) of pure germanium (~99%) from semi conductor waste.

Keywords: Liquid-liquid extraction, germanium, cyanex 301, cyanex 923, separations, recovery

Received 15 June 2005, Accepted 22 November 2005

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INTRODUCTION

Germanium is one of the premier hi-tech metals with a growing demand in the semi-conductor industry. It is getting improbable to meet the demand of the metal from its natural resources and thus it becomes important to develop methods to recover it from electronic waste. It is estimated that about one-fourth of germanium consumed comes from recycled waste of electronic and optical devices. In view of the complexity of the waste material and the purity of the metal desired, solvent extraction seems to be an ideal choice for the recovery of germanium. Carbon tetrachloride (1, 2), high molecular weight amines (3) and chelating agents (4–8) have been used for the extraction of Ge(IV) but they often require strict control of aqueous phase variables and the phase separation is rather slow. Wang and Yang (9) studied the synergistic extraction of Ge(IV) using P_{507} and N_{601}. TOPO (10) has been used for the extraction chromatographic separation of Ge(IV) from other elements.

In the last two decades the alkylphosphorus extractants of Cyanex series have come up on the forefront as useful extractants mainly because of their poor aqueous solubility and higher extraction power. Out of these bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), its disulphur analogue bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and Cyanex 923 (a mixture of four trialkyl phosphine oxides namely $R_3P=O$, $R'R_2P=O$, $R'_2RP=O$, and $R'_3P=O$, R is n-octyl and R' is n-hexyl) have gained more prominence. It may be important to explore these extractants for the extraction and separation of Ge(IV) followed by their evaluation for the recovery of the metal from waste materials. It was observed that Cyanex 272 is a poor extractant for Ge(IV) and the present studies are confined to Cyanex 301 and 923.

As a first step conditions for the separation of germanium from some of the commonly associated metal ions found in different matrices have been optimized. In this context the extraction of Ge(IV) and the associated metal ions such as As(V)/(III), Sn(IV), Tl(III), In(III), Ga(III), Fe(III), Al(III), Hg(II), and Cu(II) has been investigated. The effect of different aqueous and organic phase variables on the extraction of Ge(IV) has been studied. The composition of the extracting species is proposed. Based on the distribution data, some important binary and ternary separations of Ge(IV) have been achieved. The separation data have been utilized for the recovery of germanium from the solution of semiconductor waste. The loading and recycling capacity and hydrolytic stability of the extractant are evaluated.

EXPERIMENTAL

Reagents and Materials

Stock solutions of the metal ions were prepared by dissolving their nitrates/chlorides/sulphates in double distilled water containing a minimum amount of the corresponding mineral acid and standardized by the usual complexometric titrations. The chemicals and the organic solvents used were of Analytical/Guaranteed grade from Thomas Baker/E. Merck, India. Kerosene of boiling fraction 160–200°C was used. Cyanex 301 (Av. Mol. Wt. 322, assay 77%) and Cyanex 923 (Av. Mol. Wt. 348, assay 93%) were obtained as gift samples from Cytec Inc., Niagara Falls, Ontario (Canada). The germanium diode waste was obtained from a repair shop in local market.

Procedure

An Atomic Absorption Spectrometer (GBC-Avanta) and an Inductively Coupled Plasma–Mass Spectrometer (Perkin Elmer) were used for the determination of concentration of metal ions in the aqueous phase. A constant temperature shaking water bath (Julabo, Germany) was used for the temperature controlled studies.

For the partition studies equal volumes of the aqueous (metal ion solution in mineral acid) and organic phase (Cyanex 301/Cyanex 923 in appropriate diluent) were shaken at room temperature ($25 \pm 3^\circ$C) for five minutes to ensure complete equilibration. The two phases were separated and a suitable aliquot of the aqueous phase was assayed for the metal ion concentration. The experimental conditions for the various studies are mentioned along with the corresponding data. Based on three observations, the value of percent extraction of Ge(IV) at about 80% extraction exhibits a coefficient of variation of $\pm 3\%$.

RESULTS AND DISCUSSION

Effect of Equilibration Time

The equilibration time for Ge(IV) was varied from thirty seconds to thirty minutes. Results indicate that the equilibrium in both the extractants was achieved in about two minutes and prolonged shaking has no adverse effect on the partition of Ge(IV). In all the studies five minutes shaking time was observed.

Effect of Metal Ion Concentration

To study the effect of metal ion concentration on the partition of Ge(IV), its concentration was varied from 10^{-4} to $5 \times 10^{-2}\,\mathrm{molL}^{-1}$ keeping the HCl and extractant concentration constant at $8\,\mathrm{molL}^{-1}$ and $0.5\,\mathrm{molL}^{-1}$, respectively. The plots (Fig. 1) indicate a linearity in the metal ion concentration range of 10^{-4}–$2.7 \times 10^{-2}\,\mathrm{molL}^{-1}$ for Ge(IV). The linearity suggests that the extracting species do not change in this range of metal ion concentration. Beyond the quoted range of concentration the loading conditions start setting

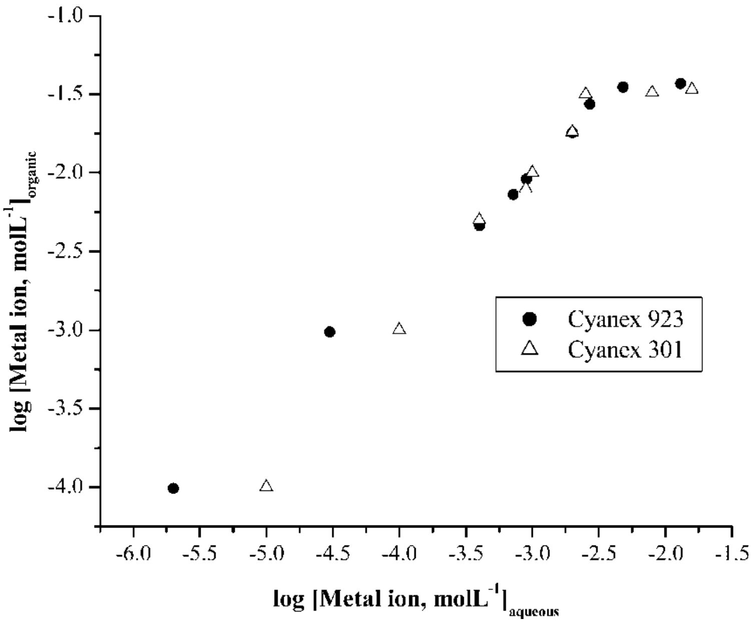


Figure 1. Effect of concentration of metal ion on the extraction of Ge(IV) from hydrochloric acid using Cyanex 301/923. Conditions: [HCl] = 8 molL^{-1}; [Cyanex] = 0.5 molL^{-1} Cyanex 301/923; [Metal ion] = 10^{-4}–5×10^{-2} molL^{-1}.

in. The results indicate that both Cyanex 301 and Cyanex 923 can hold the metal ion up to one- eighteenth of their molar concentration.

Effect of the Nature of Diluent

A number of solvents namely toluene, n-hexane, kerosene (160–200°C), xylene, chloroform, benzene, chlorobenzene, and nitrobenzene were employed to discern the effect of varying nature of the organic diluents on the extraction of Ge(IV). The results are given in Table 1. No correlation between dielectric constant and percent extraction was observed. As apparent from the data the extraction of Ge(IV) is higher and comparable in toluene, n-hexane, and kerosene. The results also suggest that kerosene can be used for commercial purposes without affecting the results. In all other studies toluene was used as a diluent.

Effect of Concentration of Extractant

The effect of varying Cyanex 301 and Cyanex 923 concentration (1×10^{-2}–0.5 mol L^{-1}) on the distribution of Ge(IV) (1×10^{-3} mol L^{-1}) was investigated

Table 1. Effect of the nature of diluent on the extraction of 1.0 × 10^{-3} molL^{-1} Ge(IV) at 5.0 molL^{-1} HCl using 0.5 molL^{-1} Cyanex 301/923

Diluent	Dielectric constant	Extraction (%)	
		Cyanex 301	Cyanex 923
Toluene	2.2	56 ± 1	28 ± 1
n-Hexane	2.0	57 ± 1	28 ± 1
Kerosene	2.0	57 ± 1	30 ± 1
Xylene	2.2	41 ± 1	29 ± 1
Benzene	2.2	37 ± 1	22 ± 1
Chloroform	4.9	40 ± 1	3 ± 1
Chlorobenzene	5.7	42 ± 1	24 ± 1
Nitrobenzene	35.7	44 ± 1	15 ± 1

at 7.0 mol L^{-1} HCl (Fig. 2). With increasing extractant concentration an increase in the extraction of Ge(IV) was observed. Log-log plots between extractant concentration and distribution ratio in the case of both the extractants give a straight line with a slope value of two thereby indicating the involvement of two molecules of Cyanex 301/Cyanex 923 in the extracting species.

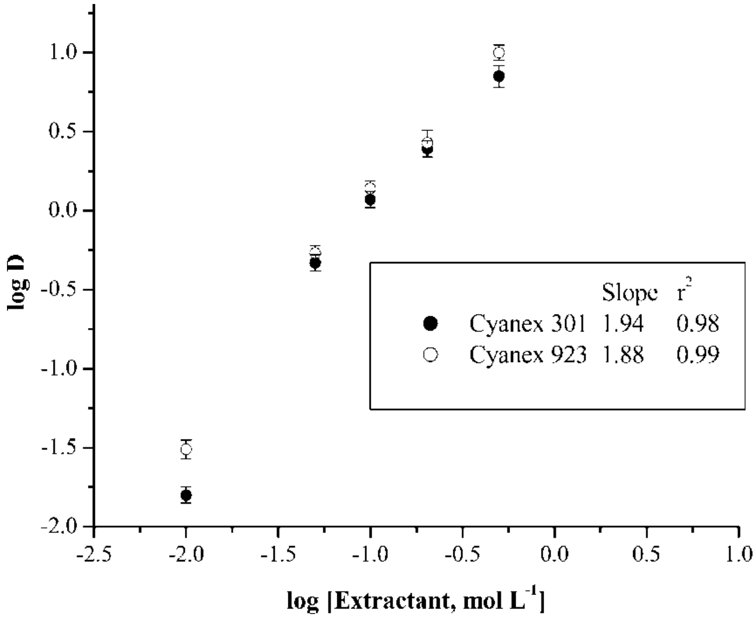


Figure 2. Effect of concentration of Cyanex 301/923 on the extraction of Ge(IV) from hydrochloric acid. Conditions: [Metal ion] = 1.0 × 10^{-3} molL^{-1}; [HCl] = 7 molL^{-1}; [Cyanex 301/923] = 1 × 10^{-2}–0.5 molL^{-1}.

Effect of Cl^- Ion Concentration

In order to identify the extracting Ge(IV) chloro species, the effect of Cl^- ion concentration on the distribution of Ge(IV) has been investigated. The Cl^- ion concentration was varied (1 to 6 $molL^{-1}$) by using LiCl maintaining the acidity of the aqueous phase at 2 $molL^{-1}$ HCl and extractant concentration at 0.5 $molL^{-1}$ Cyanex 301/923. Linear log-log plots of $[Cl^-]$ vs. D with a slope of around four in the case of both the extractants suggest the extraction of neutral germanium tetrachloride by solvation and the extracting species is $GeCl_4 \cdot 2R$ (R = Cyanex 301/Cyanex 923) (Fig. 3). It has been reported earlier that Cyanex 301 at higher acidity instead of a cation exchanger can behave as a solvating molecule (11).

Thus the equilibrium treatment in both the cases can be presented as

$$Ge^{4+}_{aq} + 2R_{org} + 4Cl^-_{aq} \leftrightarrow GeCl_4 \cdot 2R_{org}$$

$$R = \text{Cyanex } 301/923$$

$$K = \frac{[GeCl_4 \cdot 2R]_{org}}{[Ge^{4+}]_{aq}\,[R]^2_{org}\,[Cl^-]^4_{aq}}$$

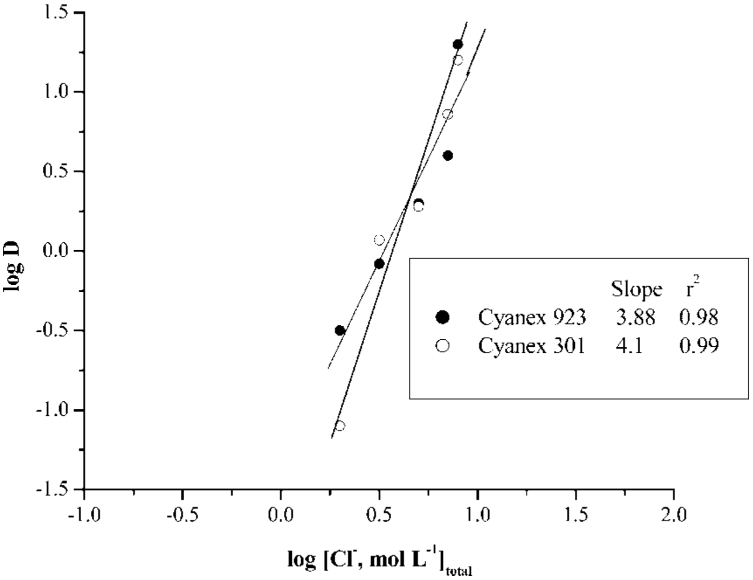


Figure 3. Effect of chloride ion concentration on the extraction of Ge(IV). Conditions: [Metal ion] = $1.0 \times 10^{-3}\,mol\,L^{-1}$; [Cyanex 301/923] = $0.50\,mol\,L^{-1}$; [HCl] = $2.0\,mol\,L^{-1}$.

where distribution ratio $D = [GeCl_4 \cdot 2R]_{org}/[Ge^{4+}]_{aq}$ assuming that metal ion in aqueous phase mainly exists as Ge^{4+} and in organic phase as $GeCl_4 \cdot 2R$.

$$\log K = \log D - 4\log[Cl^-]_{aq} - 2\log[R]_{org}$$

where K = extraction constant.

Effect of Temperature

The effect of temperature on the extraction of Ge(IV) has been investigated at $5.0\,\mathrm{molL^{-1}}$ HCl using $0.5\,\mathrm{molL^{-1}}$ Cyanex 301/Cyanex 923 (Fig. 4). The temperature of the solutions was maintained constant by keeping them in a thermostatic water bath ($\pm 0.1°C$). The plot between 1000/T and log K indicates that the extraction of Ge(IV) increases with the rise in temperature. The results reveal the process to be endothermic. The value of ΔH as calculated from vant Hoff's equation $-\ln k = \Delta H/R.\ 1/T$ is 49 and $55\,\mathrm{kJ\,mol^{-1}}$for Cyanex 301 and Cyanex 923, respectively. All other studies were carried out at room temperature ($25 \pm 3°C$).

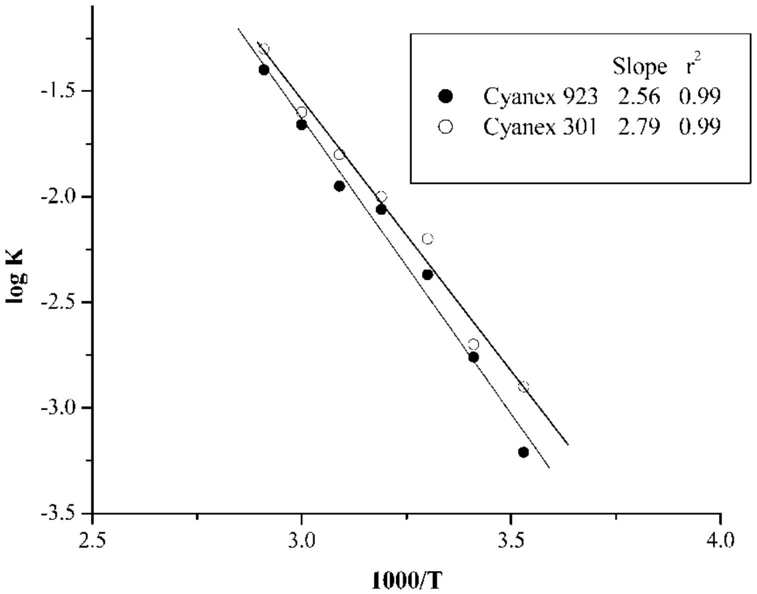


Figure 4. Effect of temperature on the extraction of Ge(IV). Conditions: [Metal ion] = $1.0 \times 10^{-3}\,\mathrm{molL^{-1}}$; [HCl] = $5.0\,\mathrm{molL^{-1}}$; [Cyanex 301/923] = $0.5\,\mathrm{molL^{-1}}$.

Extraction Behavior

The extraction behavior of Ge(IV) ($1 \times 10^{-3}\,\mathrm{molL}^{-1}$) in toluene solution of Cyanex 301 from HCl, HNO_3 and H_2SO_4 media ($1 \times 10^{-2} - 8\,\mathrm{molL}^{-1}$) is shown in Fig. 5. The extraction of Ge(IV) from HCl medium is low (~8%) up to $1\,\mathrm{molL}^{-1}$ acidity but increases beyond this and gets quantitative at $8\,\mathrm{molL}^{-1}$ HCl. The extraction of Ge(IV) is relatively poor from both sulphuric and nitric acid media in the investigated acidity range. The effect of different variables on extraction was studied from HCl medium.

The extraction behavior of commonly associated metal ions ($1 \times 10^{-3}\,\mathrm{molL}^{-1}$) namely As(V)/(III), Sn(IV), Tl(III), In(III), Ga(III), Al(III), Fe(III), Hg(II), and Cu(II) from 1×10^{-2} to $8\,\mathrm{molL}^{-1}$ HCl with $0.5\,\mathrm{molL}^{-1}$ Cyanex 301 solution is shown in Fig. 6. The extraction of Ga(III) and Al(III) decreases with the increasing acid molarity, attains a minimum around $0.5\,\mathrm{molL}^{-1}$ HCl and thereafter increases slightly. The extraction of Sn(IV), As(III), Hg(II), and Cu(II) show more or less quantitative extraction in the entire investigated range of acid molarity. The percent extraction of In(III) and Fe(III) is almost quantitative up to $5\,\mathrm{molL}^{-1}$ HCl.

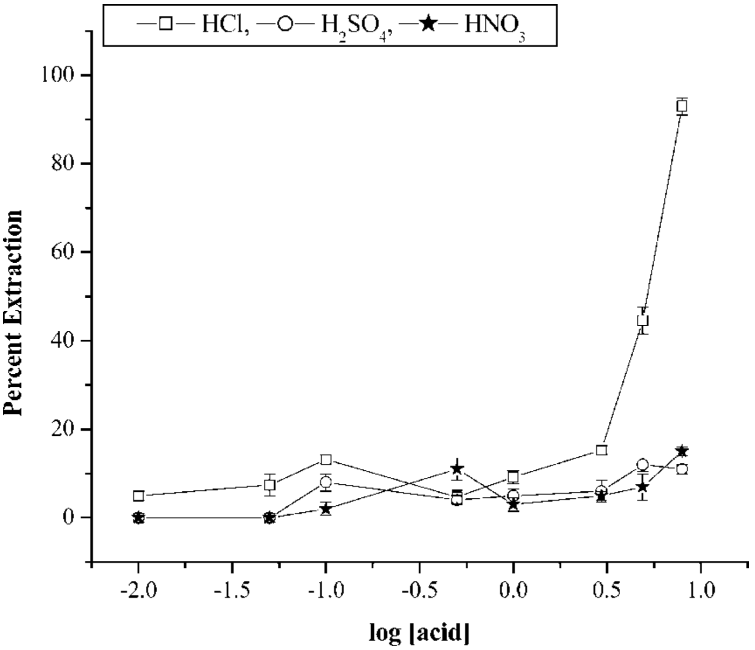


Figure 5. Effect of concentration of different acids on the extraction of Ge(IV) using Cyanex 301. Conditions: [Metal ion] = $1.0 \times 10^{-3}\,\mathrm{molL}^{-1}$; [Cyanex 301] = $0.5\,\mathrm{molL}^{-1}$; [$HCl/HNO_3/H_2SO_4$] = 1.0×10^{-2}–$8\,\mathrm{molL}^{-1}$.

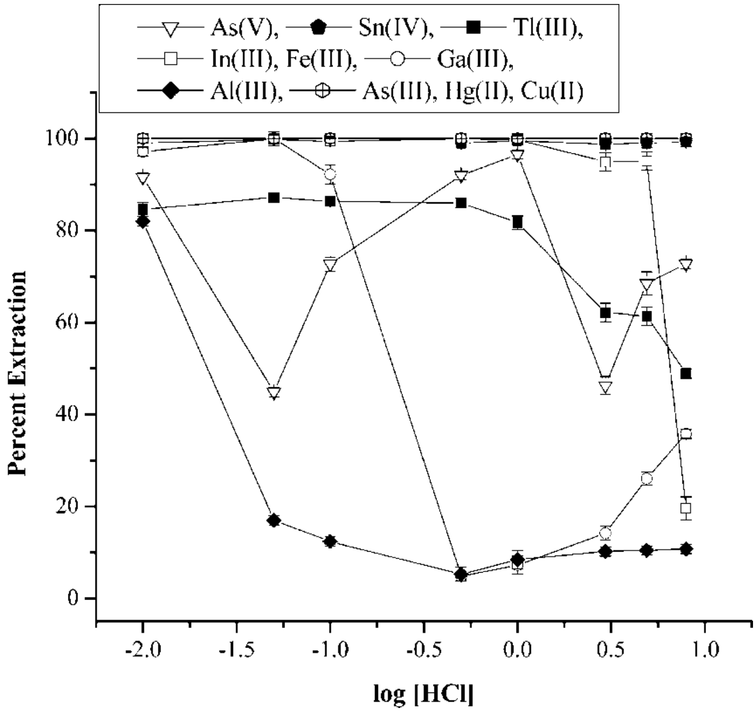


Figure 6. Effect of concentration of hydrochloric acid on the extraction of associated metal ions using Cyanex 301. Conditions: [Metal ion] = 1.0×10^{-3} molL^{-1}; [Cyanex 301] = 0.5 molL^{-1}; [HCl] = 1.0×10^{-2}–8 molL^{-1}.

On increasing the acidity beyond 5 molL^{-1} the extraction of In(III) and Fe(III) decreases up to ~20%. The extraction of Tl(III) is around 85% up to 1 molL^{-1} acid and thereafter it decreases. The extraction of As(V) is almost quantitative but shows two maxima at 1×10^{-2} molL^{-1} and 1 molL^{-1} HCl.

The extraction of Ge(IV) using Cyanex 923 from HCl, H_2SO_4, and HNO_3 indicates that the extraction is highest from HCl medium than H_2SO_4 and HNO_3 (Fig. 7). The extraction from HCl medium is negligible up to 0.5 molL^{-1} HCl, increases beyond this and attains a value ~96% at 8 molL^{-1} HCl.

The extraction of Sn(IV), Tl(III), In(III) and Hg(II) in Cyanex 923 is quantitative in the studied range of acidity (Fig. 8). Cu(II) shows negligible extraction up to 1 molL^{-1} HCl increasing to around 80% at 5 molL^{-1} HCl followed by a decreasing trend. As(V)/(III) exhibits less extraction at lower acid molarity which increases slightly beyond 5 molL^{-1} HCl. The extraction of Ga(III) decreases with increasing acid molarity and starts increasing beyond 0.1 molL^{-1} HCl, attaining a quantitative value at 3 molL^{-1} HCl. In the extraction behavior of Fe(III) two

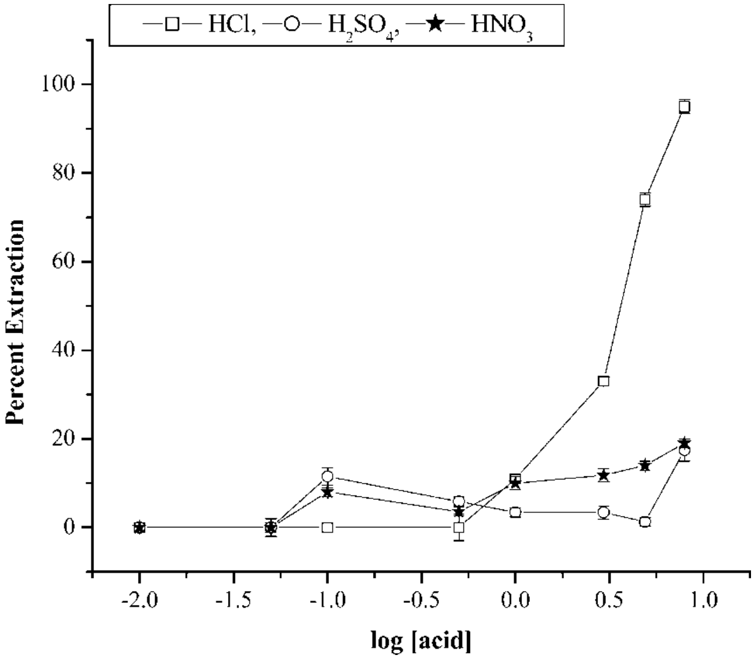


Figure 7. Effect of concentration of different acids on the extraction of Ge(IV) using Cyanex 923. Conditions: [Metal ion] = 1.0×10^{-3} $molL^{-1}$; [Cyanex 923] = 0.5 $molL^{-1}$; [$HCl/HNO_3/H_2SO_4$] = 1.0×10^{-2}–8 $molL^{-1}$.

maxima corresponding to ~85% extraction at 5×10^{-2} and 3 $molL^{-1}$ HCl are observed. The extraction of Al(III) is poor at low acidity, increasing slightly at higher acidity.

Figure 9 indicates that Ge(IV) is poorly extracted in Cyanex 272 from $HCl/HNO_3/H_2SO_4$. Therefore extraction studies for associated metal ions were not carried out with Cyanex 272.

Stripping

Various stripping reagents were tried for the back extraction of Ge(IV) from the loaded organic phase. The results are given in Table 2. The results suggest that Ge(IV) is effectively stripped using 0.1 $molL^{-1}$ citric acid, 0.5 $molL^{-1}$ HCl, 0.1 $molL^{-1}$ oxalic acid, 0.1 $molL^{-1}$ tartaric acid, and 3% H_2O_2 from Cyanex 301 and for Cyanex 923 0.1 $molL^{-1}$ HCl, 0.5 $molL^{-1}$ HCl, 1 $molL^{-1}$ H_2SO_4, 0.1 $molL^{-1}$ tartaric acid, 0.3 $molL^{-1}$ ammonium thiocyanate and 3% H_2O_2 are effective. In all the studies 0.5 $molL^{-1}$ HCl is used for the stripping of Ge(IV) from both the extractants unless otherwise mentioned.

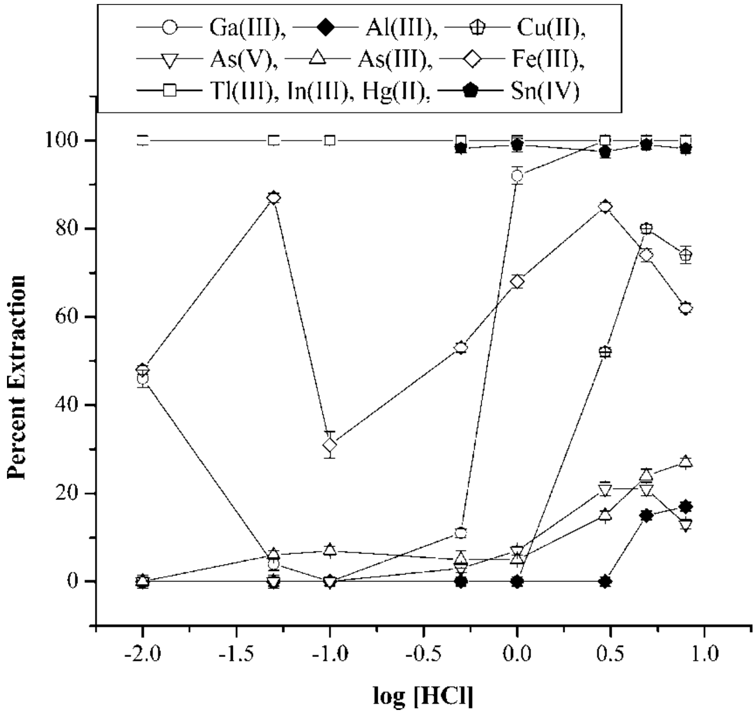


Figure 8. Effect of concentration of hydrochloric acid on the extraction of associated metal ions using Cyanex 923. Conditions: [Metal ion] = 1.0×10^{-3} molL^{-1}; [Cyanex 923] = 0.5 molL^{-1}; [HCl] = 1.0×10^{-2}–8 molL^{-1}.

Hydrolytic Stability and Regeneration Power of Cyanex 301 and Cyanex 923

The stability and regeneration capacity of Cyanex 301 and Cyanex 923 were assessed for their potential as a commercial extractant. A 0.5 molL^{-1} toluene solution of Cyanex 301/Cyanex 923 was kept in contact with 8 molL^{-1} HCl for 50 days with intermittent shaking. A known aliquot of the extractant solution was removed periodically after every five days, washed thoroughly with water and employed for the extraction of Ge(IV) at 8 molL^{-1} HCl. An insignificant change (2–3%) in the percent extraction of Ge(IV) has been observed even after a contact of fifty days. Sole et al. (12) and Modolo and Odoj (13) have also observed the stability of Cyanex 301 against acids and reported that H_2SO_4 has no detrimental effects while HNO_3 causes the disintegration of the extractant.

The studies on the successive extraction (from 8 molL^{-1} HCl) and stripping (with 0.5 molL^{-1} HCl) of Ge(IV) have revealed negligible change (2–3%) in the percent extraction/stripping of the metal ion up to fifteen cycles for Cyanex 301 and Cyanex 923 (Fig. 10). The regeneration power of Cyanex

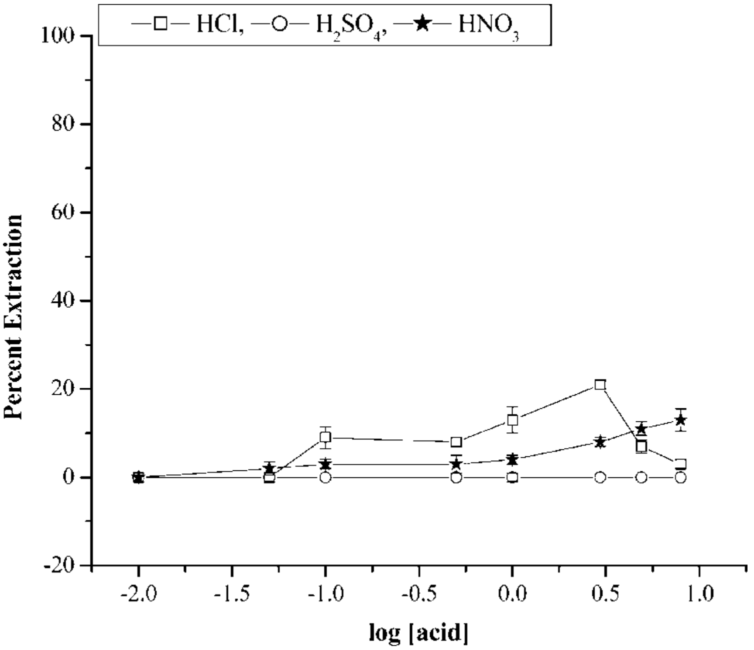


Figure 9. Effect of concentration of different acids on the extraction of Ge(IV) using Cyanex 272. Conditions: [Metal ion] = 1.0×10^{-3} molL^{-1}; [Cyanex 272] = 0.5 molL^{-1}; [$HCl/HNO_3/H_2SO_4$] = 1.0×10^{-2}–8 molL^{-1}.

Table 2. Effect of stripping reagents on the extraction of Ge(IV) using 0.5 mol L^{-1} Cyanex 301/923 at 8.0 mol L^{-1} HCl

Strippant used	Percent stripped (Cyanex 301)	Percent stripped (Cyanex 923)
0.1 mol L^{-1} Oxalic acid	[a]100	[a]89
0.1 mol L^{-1} Citric acid	[b]100	[b]100
0.1 mol L^{-1} Tartaric acid	[a]100	[b]100
3% H_2O_2	[a]100	[b]100
0.5 mol L^{-1} HCl	[a]100	[b]100
0.1 mol L^{-1} HCl	[b]85	[b]100
0.1 mol L^{-1} EDTA	[a]94	[a]90
1.0 mol L^{-1} HCl	[a]90	[a]88
0.5 mol L^{-1} H_2SO_4	[a]87	[a]89
0.5 mol L^{-1} HNO_3	[a]77	[a]87
0.3 mol L^{-1} NH_4SCN	—	[b]99

[a] Stripped using three volumes.
[b] Stripped using two volumes.

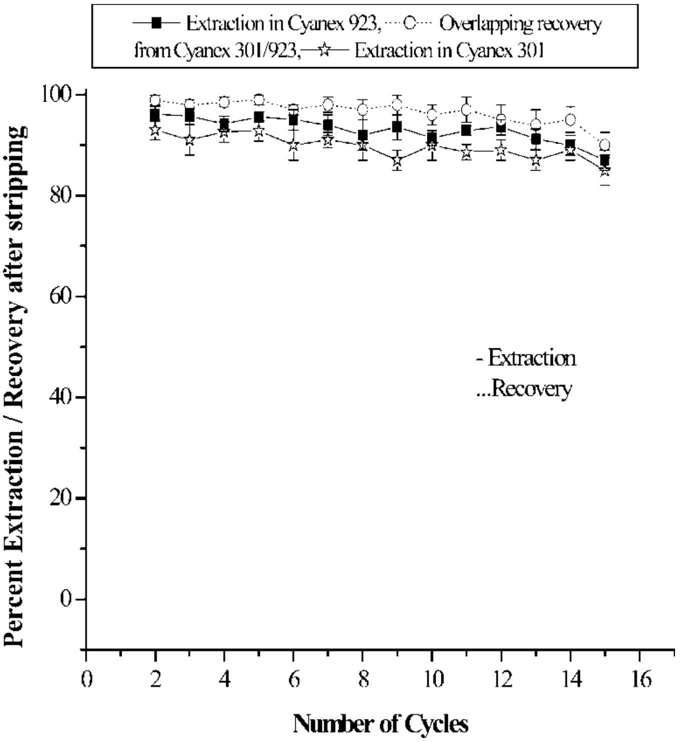


Figure 10. Variation in the extraction/recovery of Ge(IV) in successive cycles. Conditions: [Metal ion] = 1.0×10^{-3} molL^{-1}; [Cyanex 301/923] = 0.5 molL^{-1}; [HCl] = 8 molL^{-1}; Strippant = 0.5 molL^{-1} HCl.

301/923 towards 3% H_2O_2 was also assessed and insignificant change in percent extraction/stripping of the metal ion was observed up to fifteen cycles.

SEPARATIONS OF Ge(IV)

The partition data on different metal ions suggest that Ge(IV) can be conveniently separated from most of the commonly associated metal ions from HCl medium either by selective extraction or stripping. A number of binary and ternary separations have been achieved.

Binary Separations

Cyanex 301

The separation of Ge(IV) from As(V)/Sn(IV)/Tl(III)/In(III)/As(III), Fe(III)/Hg(II)/Cu(II) has been achieved at 0.5 molL^{-1} HCl by selectively extracting the latter metal ion leaving Ge(IV) in the aqueous phase. The separation of Ge(IV) from Ga(III) is achieved at 5×10^{-2} molL^{-1} HCl. Ga(III) gets extracted leaving behind Ge(IV) in the aqueous phase. Ga(III) is stripped by washing the organic phase with three volumes of 0.5 molL^{-1} HCl. For the separation of Ge(IV) from Al(III) the acidity of the aqueous phase is adjusted to 1×10^{-2} molL^{-1} acid thus, extracting Al(III) and leaving Ge(IV) in the aqueous phase. The extracted metal ions have been stripped from the organic phase using appropriate stripping reagents. In all the above separations the metal ions extracted in the organic phase are easily stripped using simple reagents but all of them fail to strip Cu(II). Cu(II) is stripped with concentrated HNO_3 which disintegrates the extractant.

Cyanex 923

The separation of Ge(IV) from Sn(IV)/Tl(III)/In(III)/Hg(II) is attained by extracting the latter metal ion at 0.5 molL^{-1} HCl using 0.5 molL^{-1} Cyanex 923. Ge(IV) remains unextracted in the aqueous phase. The separation of Ge(IV) from Ga(III) is attained at 1 molL^{-1} HCl. At this acid molarity Ge(IV) is poorly extracted while Ga(III) is quantitatively extracted in the organic phase. The separation of Ge(IV) from Fe(III) is attained by twice extracting Fe(III) into the organic phase at 5×10^{-2} molL^{-1} acid molarity. As(V)/(III) are separated from Ge(IV) at 8 molL^{-1} HCl. As(V)/(III) coextracted with Ge(IV) is stripped using 8 molL^{-1} HCl solution. The separation of Ge(IV) from Al(III) is achieved by extracting Ge(IV) at 8 molL^{-1} HCl leaving Al(III) in the aqueous phase. The coextracted Al(III) is removed by equilibrating the loaded organic phase with 8 molL^{-1} HCl before stripping Ge(IV). Ge(IV)-Cu(II) separation was achieved by selective stripping. Both the metal ions were first extracted at 8 molL^{-1} HCl followed by the selective stripping of Ge(IV) using 0.3 molL^{-1} NH_4SCN and Cu(II) with 2 molL^{-1} NaOH.

The conditions of separation and percent recovery of the metal ions from Cyanex 301/923 are listed in Table 3.

Ternary Separations

Various ternary separations have been carried out from hydrochloric acid media using 0.5 molL^{-1} Cyanex 301 and Cyanex 923 and are listed in Table 4.

Cyanex 301

The separations involving Ge(IV)-Ga(III)-In(III) were achieved by extracting Ga(III)-In(III) quantitatively at 5×10^{-2} molL^{-1} HCl. Ga(III) was stripped from the organic phase with three volumes of 0.5 molL^{-1} HCl followed by the recovery of In(III) with 1 molL^{-1} oxalic acid. Ternary separations involving Ge(IV)-Fe(III)-Cu(II) and Ge(IV)-As(V)-Hg(II) were carried out at

Table 3. Binary separations of Ge(IV) using 0.5 mol L^{-1} Cyanex 923/Cyanex 301

Metal ions	Molar ratio ($\times 10^{-3}$) mol L^{-1}	Acid molarity mol L^{-1}	Extractant	Metal ion remained in aqueous phase (%)	Meta ion transferred into organic phase (%)	Metal ion stripped[a] from organic phase (%)
Ge(IV)-Fe(III)	1 : 10	0.5	Cyanex 301	95 ± 1.2, Ge	97 ± 1.10, Fe	98 ± 1.0, Fe
	10 : 1			93 ± 1.5, Ge	99 ± 0.89, Fe	99 ± 0.91, Fe
Ge(IV)-As(V)	1 : 10	0.5	Cyanex 301	94 ± 1.5, Ge	90 ± 1.0, As	98 ± 0.85, As
	10 : 1			95 ± 1.1, Ge	92 ± 1.1, As	99 ± 1.0, As
Ge(IV)-Sn(IV)	1 : 10	0.5	Cyanex 301	96 ± 1.5, Ge	98 ± 1.2, Sn	98 ± 1.0, Sn
	10 : 1			95 ± 1.3, Ge	99 ± 0.75, Sn	99 ± 1.0, Sn
Ge(IV)-As(III)	1 : 10	0.5	Cyanex 301	96 ± 1.2, Ge	99 ± 0.8, As	97 ± 1.1, As
	10 : 1			95 ± 1.5, Ge	99 ± 1.0, As	99 ± 1.0, As
Ge(IV)-Tl(III)	1 : 10	0.5	Cyanex 301	99 ± 0.75, Ge	92 ± 1.5, Tl	95 ± 1.3, Tl
	10 : 1		(2 vol)	98 ± 0.91, Ge	95 ± 1.2, Tl	94 ± 1.1, Tl
Ge(IV)-In(III)	1 : 10	0.5	Cyanex 301	99 ± 1.0, Ge	98 ± 1.0, In	98 ± 0.81, In
	10 : 1			99 ± 0.85, Ge	99 ± 0.83, In	97 ± 1.0, In
Ge(IV)-Cu(II)	1 : 10	0.5	Cyanex 301	98 ± 1.0, Ge	99 ± 1.0,Cu	95 ± 1.1, Cu
	10 : 1			97 ± 1.5, Ge	99 ± 1.0, Cu	96 ± 1.0, Cu
Ge(IV)-Hg(II)	1 : 10	0.5	Cyanex 301	98 ± 1.0, Ge	99 ± 1.0, Hg	98 ± 1.1, Hg
	10 : 1			99 ± 1.0, Ge	99 ± 1.0, Hg	97 ± 1.0, Hg
Ge(IV)-Ga(III)	1 : 10	5×10^{-2}	Cyanex 301	92 ± 1.5, Ge	97 ± 1.2, Ga	98 ± 0.91, Ga
	10 : 1			91 ± 1.2, Ge	98 ± 1.0, Ga	97 ± 1.1, Ga
Ge(IV)-Al(III)	1 : 10	1×10^{-2}	Cyanex 301	93 ± 1.3, Ge	81 ± 1.2, Al	95 ± 1.5, Al
	10 : 1			92 ± 1.0, Ge	83 ± 1.3, Al	96 ± 1.1, Al

(*continued*)

Table 3. Continued

Metal ions	Molar ratio $(\times 10^{-3})$ mol L^{-1}	Acid molarity mol L^{-1}	Extractant	Metal ion remained in aqueous phase (%)	Meta ion transferred into organic phase (%)	Metal ion stripped[a] from organic phase (%)
Ge(IV)-In(III)	1 : 10	0.5	Cyanex 923	99 ± 1.0, Ge	97 ± 1.5, In	94 ± 1.5, In
	10 : 1			99 ± 1.0, Ge	98 ± 1.0, In	97 ± 1.0, In
Ge(IV)-Tl(III)	1 : 10	0.5	Cyanex 923	99 ± 1.0, Ge	98 ± 1.0, Tl	99 ± 1.0, Tl
	10 : 1			99 ± 1.0, Ge	97 ± 1.5, Tl	95 ± 1.5, Tl
Ge(IV)-Sn(IV)	1 : 10	0.5	Cyanex 923	99 ± 1.0, Ge	99 ± 1.0, Sn	99 ± 1.0, Sn
	10 : 1			99 ± 1.0, Ge	99 ± 1.0, Sn	98 ± 1.5, Sn
Ge(IV)-Cu(II)	1 : 10	8.0	Cyanex 923	24 ± 1.0, Cu	96 ± 1.0, Ge	(i) 95 ± 1.5, Ge
					75 ± 1.5, Cu	(ii) 75 ± 1.0, Cu
	10 : 1			25 ± 1.0, Cu	95 ± 1.0, Ge	(i) 94 ± 1.0, Ge
				74 ± 1.5, Cu		(ii) 72 ± 1.1, Cu
Ge(IV)-Hg(II)	1 : 10	0.5	Cyanex 923	99 ± 1.0, Ge	99 ± 1.0, Hg	98 ± 1.5, Hg
	10 : 1			99 ± 1.0, Ge	99 ± 1.0, Hg	99 ± 1.0, Hg
Ge(IV)-Ga(III)	1 : 10	1.0	Cyanex 923	93 ± 1.0, Ge	97 ± 1.5, Ga	98 ± 1.0, Ga
	10 : 1			95 ± 1.0, Ge	98 ± 1.0, Ga	99 ± 1.0, Ga
Ge(IV)-Al(III)	1 : 10	8.0	Cyanex 923	80 ± 1.0, Al	96 ± 1.0, Ge	(i) 19 ± 1.0, Al
						(ii) 99 ± 1.0, Ge
	10 : 1			81 ± 1.0, Al	97 ± 1.0, Ge	(i) 17 ± 1.1, Al
						(ii) 99 ± 1.0, Ge
Ge(IV)-Fe(III)	1 : 10	5×10^{-2}	Cyanex 923	95 ± 1.0, Ge	97 ± 1.0, Fe	98 ± 1.0, Fe
	10 : 1		(2 vol)	98 ± 1.0, Ge	97 ± 1.0, Fe	99 ± 1.0, Fe

Ge(IV)-As(V)	1 : 10	8.0	Cyanex 923	80 ± 1.0, As	93 ± 1.5, Ge	(i) 19 ± 1.0, As (ii) 97 ± 1.0, Ge
	10 : 1			84 ± 1.0, As	95 ± 1.0, Ge	(i) 13 ± 1.0, As (ii) 98 ± 1.0, Ge
Ge(IV)-As(III)	1 : 10	8.0	Cyanex 923	72 ± 1.0, As	96 ± 1.0, Ge	(i) 27 ± 1.0, As (ii) 99 ± 1.0, Ge
	10 : 1			71 ± 1.5, As	95 ± 1.0, Ge	(i) 27 ± 1.0, As (ii) 99 ± 1.0, Ge

(i) and (ii) indicate the order in which they are stripped from the organic phase.

Cyanex 301

[a] Fe(III) stripped using 8 mol L^{-1} HCl (two volumes)

Tl(III)/In(III)/Ga(III) stripped using 1.0 mol L^{-1} oxalic acid

As(V)/As(III)/Sn(IV) stripped using 2.0 mol L^{-1} NaOH

Cu(II) stripped using concentrated HNO_3

Ge(IV) stripped using 0.5 mol L^{-1} HCl (three volumes)

Hg(II) stripped using 0.1 mol L^{-1} sodium thiosulphite (two volumes).

Cyanex 923

[a] Ga(III) stripped using 0.1 mol L^{-1} HCl (two volumes)

In(III) stripped using 1.0 mol L^{-1} H_2SO_4

Tl(III)/Fe(III) stripped using 0.1 mol L^{-1} oxalic acid

Ge(IV) stripped using 0.5 mol L^{-1} HCl (three volumes)/0.3 mol L^{-1} NH_4SCN

As(V)/As(III)/Al(III) stripped using 8 mol L^{-1} HCl

Sn(IV) stripped using 2.0 mol L^{-1} NaOH

Hg(II) stripped using 7.0 mol L^{-1} HNO_3 (two volumes).

Table 4. Some important ternary separations of Ge(IV) from associated metal ions in hydrochloric acid medium using 0.5 mol L^{-1} Cyanex 301/923 (toluene)

Metal ions	Molar ratio ($\times 10^{-3}$ mol L^{-1})	HCl mol L^{-1}	Extractant mol L^{-1}	Metal ion remaining in the aqueous phase (%)	Metal ions recovered[a] from the organic phase (%)
Ge(IV):In(III):Ga(III)	1 : 1 : 10	5×10^{-2}	Cyanex 301	98 ± 0.81, Ge	(i) 99 ± 0.82, Ga (ii) 97 ± 1.0, In
	1 : 10 : 1			99 ± 0.82, Ge	(i) 99 ± 0.75, Ga (ii) 97 ± 1.2, In
	10 : 1 : 1			99 ± 0.93, Ge	(i) 99 ± 0.83, Ga (ii) 98 ± 1.0, In
As(V):Ge(IV):Hg(II)	1 : 1 : 10	0.5	Cyanex 301	98 ± 0.85, Ge	(i) 99 ± 1.0, Hg (ii) 99 ± 0.78, As
	1 : 10 : 1			98 ± 0.95, Ge	(i) 99 ± 0.72, Hg (ii) 99 ± 1.0, As
	10 : 1 : 1			97 ± 1.3, Ge	(i) 99 ± 0.83, Hg (ii) 99 ± 0.72, As
Ge(IV):Fe(III):Cu(II)	1 : 1 : 10	0.5	Cyanex 301	98 ± 1.2, Ge	(i) 99 ± 1.0, Fe (ii) 97 ± 1.2, Cu[a]
	1 : 10 : 1			96 ± 1.3, Ge	(i) 99 ± 0.78, Fe (ii) 99 ± 1.0, Cu[a]
	10 : 1 : 1			98 ± 0.91, Ge	(i) 99 ± 0.83, Fe (ii) 99 ± 1.1, Cu[a]
Ge(IV):In(III):Ga(III)	1 : 1 : 10	(i) 0.1 (ii) 1.0	Cyanex 923	99 ± 0.72, Ge	(i) 99 ± 0.83, In (ii) 99 ± 1.0, Ga
	1 : 10 : 1			99 ± 0.83, Ge	(i) 99 ± 0.87, In (ii) 99 ± 0.95, Ga
	10 : 1 : 1			98 ± 1.2, Ge	(i) 99 ± 0.91, In (ii) 97 ± 1.5, Ga

Ge(IV):Ga(III):Hg(II)	1 : 1 : 10	(i) 0.1 (ii) 1.0	Cyanex 923	97 ± 1.5, Ge	(i) 99 ± 1.0, Hg (ii) 98 ± 1.1, Ga
	1 : 10 : 1			98 ± 1.3, Ge	(i) 96 ± 1.5, Hg (ii) 99 ± 0.82, Ga
	10 : 1 : 1			99 ± 0.82, Ge	(i) 96 ± 0.91, Hg (ii) 97 ± 1.3, Ga
Ge(IV):As(III):Fe(III)	1 : 1 : 10	(i) 5×10^{-2} (ii) 8.0	Cyanex 923 (2 vol)	84 ± 1.3, As	(i) 99 ± 0.78, Fe (ii) 99 ± 0.90, Ge
	1 : 10 : 1			85 ± 1.0, As	(i) 99 ± 1.0, Fe (ii) 99 ± 0.83, Ge
	10 : 1 : 1			85 ± 0.89, As	(i) 99 ± 0.78, Fe (ii) 98 ± 0.91, Ge

(i) and (ii) indicate the order of extraction/stripping of elements from the organic phase.

Cyanex 301

[a]Ga(III) stripped using 0.5 mol L^{-1} HCl (three volumes)
In(III) stripped using 1.0 mol L^{-1} oxalic acid
Fe(III) stripped using 8.0 mol L^{-1} HCl
Cu(II) stripped using concentrated HNO_3
Hg(II) stripped using 0.1 mol L^{-1} sodium thiosulphite (two volumes).
As(V)/Sn(IV) stripped using 2.0 mol L^{-1} NaOH

Cyanex 923

[a]In(III) stripped using 1.0 mol L^{-1} H_2SO_4
Ga(III) stripped using 0.1 mol L^{-1} HCl (two volumes)
Hg(II) stripped using 7.0 mol L^{-1} HNO_3
Fe(III) stripped using 0.1 mol L^{-1} oxalic acid
As(III) stripped using 8.0 mol L^{-1} HCl
Ge(IV) stripped using 0.5 mol L^{-1} HCl (two volumes).

0.5 molL^{-1} HCl by extracting Fe(III)-Cu(II) and As(V)-Hg(II) in the organic layer. Fe(III) and Cu(II) were stripped using two volumes of 8 molL^{-1} HCl and concentrated HNO_3, respectively. Hg(II) and As(V) were recovered using 0.1 molL^{-1} sodium thiosulphite and 2 molL^{-1} NaOH, respectively.

Cyanex 923

The separation of Ge(IV)-Ga(III)-In(III)/Hg(II) were achieved by extracting In(III)/Hg(II) 0.1 molL^{-1} HCl leaving Ge(IV)-Ga(III) in the aqueous layer. In(III) and Hg(II) were then recovered using 1 molL^{-1} H_2SO_4 and 7 molL^{-1} HNO_3, respectively. The acidity of the remaining aqueous phase containing Ge(IV) and Ga(III) was adjusted to 1 molL^{-1} HCl and subjected to extraction with 0.5 molL^{-1} Cyanex 923. Around 90% of Ga(III) was extracted leaving Ge(IV) in the aqueous layer. Ga(III) was stripped using 0.1 molL^{-1} HCl. For Ge(IV)-Fe(III)-As(III) separation the aqueous phase at 5×10^{-2} molL^{-1} HCl was contacted twice with 0.5 molL^{-1} Cyanex 923 to extract Fe(III) which was then stripped using 0.1 molL^{-1} oxalic acid. Ge(IV)-As(III) separation was achieved by extracting Ge(IV) at 8 molL^{-1} HCl. As(III) coextracted with Ge(IV) was recovered by washing the organic layer with 8 molL^{-1} HCl followed by recovery of Ge(IV) from the organic phase using 0.5 molL^{-1} HCl.

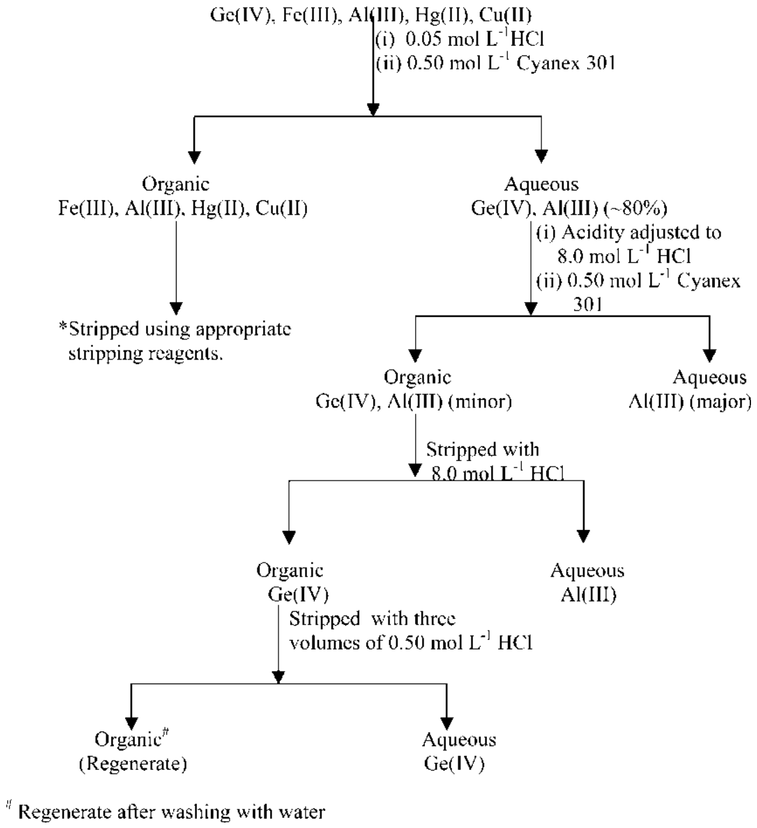
The above binary and ternary separations attained using Cyanex −301 and −923 provide a database for the purification of germanium and evolving a scheme for the recovery of the metal from different matrices. As a representative case a scheme has been developed for the recovery of germanium from semiconductor waste.

Recovery of Ge(IV) from Germanium Diodes

The semiconductor waste was sorted out to obtain the germanium coated portion. In order to optimize the appropriate strength of the acid to leach maximum germanium in solution this portion was left overnight in contact with 5 mL of 2, 6, and 12 molL^{-1} HCl and it was observed that overnight contact with 2 molL^{-1} HCl is sufficient to leach the maximum amount of germanium. In order to recover germanium 0.1 g of the waste was left in contact with 10 mL of 2 molL^{-1} HCl. The solution was filtered and the filtrate was made up to 1 liter keeping the overall acidity to 5×10^{-2} molL^{-1}. The solution contained germanium as the major component along with mercury, iron, aluminium and copper.

Recovery of Ge(IV) Using Cyanex 301

The diode waste was contacted with equal volume of 0.5 molL^{-1} Cyanex 301. Fe(III), Hg(II), and Cu(II) were quantitatively extracted in the organic phase with around 20% Al(III). Ge(IV) remained unextracted in the aqueous phase.

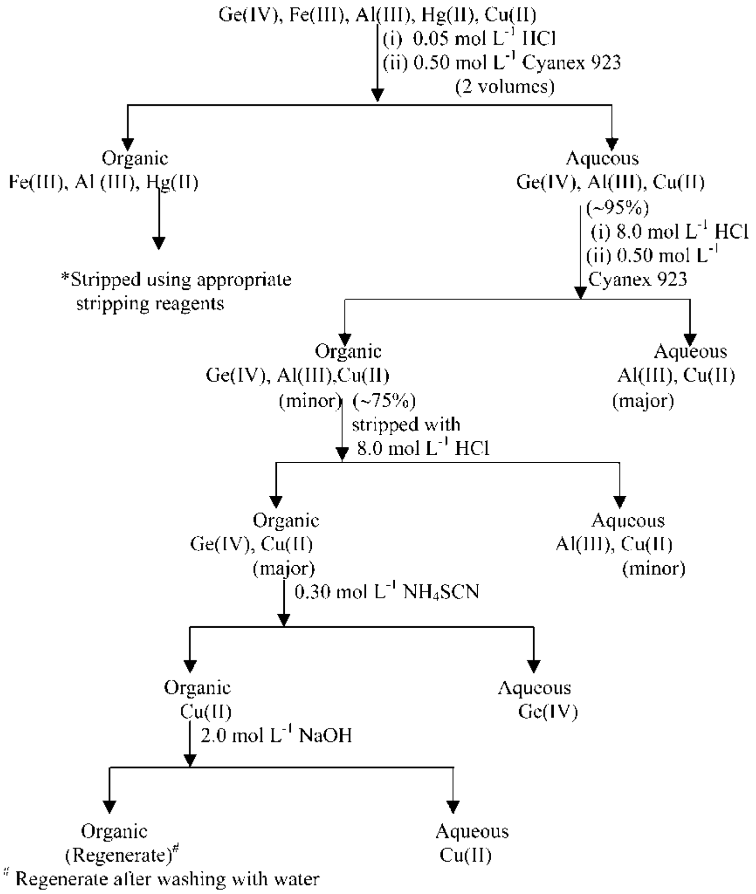


Flowsheet 1. Recovery of Ge(IV) from semiconductor waste using 0.5 mol L^{-1} Cyanex 301. *Note:* Stripping of Cu(II) with concentrated HNO_3 degenerates the extractant.

The extracted metal ions were stripped using appropriate stripping reagents as mentioned in Table 3. The acidity of the aqueous phase was then adjusted to 8 molL^{-1} HCl and contacted again with an equal volume of 0.5 molL^{-1} Cyanex 301. Ge(IV) was quantitatively extracted along with some amount of Al(III). The loaded organic phase was first scrubbed with 8 molL^{-1} HCl to strip Al(III) followed by the recovery of Ge(IV) from the organic layer (Cyanex 301) using three volumes of 0.5 molL^{-1} HCl (Flowsheet 1).

Recovery of Ge(IV) Using Cyanex 923

The diode waste solution B was equilibrated twice with equal volume of 0.5 molL^{-1} Cyanex 923. Fe(III) and Hg(II) were quantitatively extracted



Flowsheet 2. Recovery of Ge(IV) from semiconductor waste using 0.5 $\mathrm{molL^{-1}}$ Cyanex 923.

along with Al(III) [~5%]. Ge(IV), Cu(II) and major portion of Al(III) remained in the aqueous phase. The acidity of the aqueous phase was adjusted to 8 $\mathrm{molL^{-1}}$ HCl and equilibrated with an equal volume of 0.5 $\mathrm{molL^{-1}}$ Cyanex 923. Ge(IV) was quantitatively transferred to the organic phase along with 75% of Cu(II) and minor portions of Al(III). The coextracted Al(III) was stripped using 8 $\mathrm{molL^{-1}}$ HCl. Subsequently Ge(IV) was selectively recovered using 0.3 $\mathrm{molL^{-1}}$ NH_4SCN followed by the stripping of Cu(II) with 2 $\mathrm{molL^{-1}}$ NaOH (Flowsheet 2).

The concentration of the metal ions before and after extraction are given in Table 5. In both the cases more than ninety percent germanium was recovered with a purity around 99%. In the case of Cyanex 923 the organic layer can be regenerated by washing with water. However, Cyanex 301

Table 5. Recovery of Ge(IV) from Semiconductor Waste using Cyanex 301/923

Metal ions	Composition of initial solution concentration (mg L^{-1})	Composition of final solution Concentration (mg L^{-1})		Percent recovery of Ge(IV)	
		Cyanex 301	Cyanex 923	Cyanex 301	Cyanex 923
Ge	30 ± 2	28 ± 1	29 ± 1	93 ± 2	94 ± 2
Fe	24 ± 1	<0.01	<0.01		
Al	11 ± 1	0.2 ± 0.02	0.2 ± 0.02		
Hg	5 ± 0.5	<0.01	<0.01		
Cu	2 ± 0.2	<0.01	<0.01		

Note: '±' refers to the standard deviation

cannot be reused because HNO_3 used for stripping copper degenerates the extractant.

CONCLUSIONS

The investigations conducted herein bring forth the potential of Cyanex 301 and Cyanex 923 for the separation and recovery of Ge(IV). A quantitative extraction of metal ion is achieved from HCl medium. The extraction of Ge(IV) in both the extractants proceeds via a solvation mechanism. Both the extractants possess a reasonable loading capacity. Ge(IV) is conveniently separated from As(V)/(III), Sn(IV), Tl(III), In(III), Ga(III), Fe(III), Al(III), Hg(II) and Cu(II) by selective extraction/stripping. The developed conditions of separation have been successfully extended to recover pure germanium from semiconductor waste matrix. The process for the recovery of Ge(IV) using Cyanex 301 and Cyanex 923 is more or less similar but the latter scores over the former because of the problem encountered in the stripping of copper. Moreover, Cyanex 923 has a lower cost than Cyanex 301. However, for a matrix without copper both the extractants can be equally efficient. Apparently in terms of kinetics of extraction and hydrolytic stability both the extractants appear reasonably well placed.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. S.N. Tandon for his fruitful discussions. The financial support by the Department of Science and Technology (DST), New Delhi, India is gratefully acknowledged. The authors are thankful to Cytec Canada Inc. for the gift samples of Cyanex 301 and Cyanex 923.

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