

**Extraction Behavior and Purification of Germanium using an Undiluted Quaternary
Ammonium Ionic Liquid in Combination with a Complexing Agent**

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Supporting Information

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Properties of [A336][HSO₄]

Table S1 displays the density, viscosity and water content of the synthesized, water-saturated [A336][HSO₄] and compares these values with those of water-saturated [A336][Cl]. The water content of the synthesized ionic liquids was measured using a volumetric Karl Fischer titrator (Mettler–Toledo V30S). Densities and viscosities were measured on an Anton Paar DMA 4500 M density meter equipped with a Lovis 2000 ME microviscometer unit. From Table S1, it is evident that the properties of [A336][HSO₄] and [A336][Cl] are similar. However, the viscosity of [A336][HSO₄] is slightly higher, possibly caused by a hydrogen bond network between the hydrogensulfate anions.¹

Table S1: Properties of water-saturated ionic liquids at 25 °C.

	[A336][Cl]	[A336][HSO ₄]
Density (g cm ⁻³)	0.9010	0.9487
Viscosity (mPa·s)	72.65	132.85
Water content (wt%)	20.76	20.07

Extraction rate

Figure S1 displays the extraction efficiency of Ge(IV), As(III), Cu(II), Fe(III) and Zn(II) as a function of the contacting time. Extractions were performed on the synthetic zinc refinery leachate using undiluted [A336][HSO₄]. The data show that despite the high viscosity of the organic phase, equilibrium values are reached within 10 min. A contact time of 60 min is thus more than sufficient to study the equilibrium separation behavior of the extraction system.

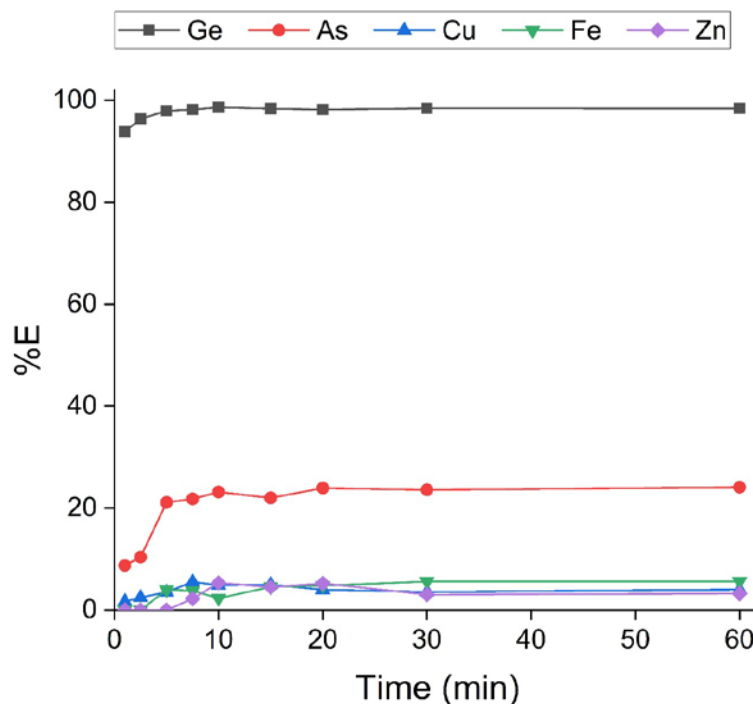


Figure S1: Extraction efficiency of 500 mg L⁻¹ Ge(IV), 30 g L⁻¹ Zn(II), 3 g L⁻¹ Fe(III), 1 g L⁻¹ Cu(II) and 1.5 g L⁻¹ As(III) using undiluted [A336][HSO₄] as a function of the contact time. Conditions: 1 mol L⁻¹ H₂SO₄, 5 equivalents of tartaric acid with respect to Ge(IV), 300 rpm, 22 °C.

Phase disengagement

Figure S2 shows different pictures of the phase disengagement process of the undiluted [A336][HSO₄] extraction system. The primary break of the emulsion occurs relatively quickly, i.e. within approximately 5 min, under gravity. However, complete phase separation, i.e. removal of entrainment, required overnight settling or centrifugation for several minutes.



Figure S2: Pictures of the phase disengagement process of undiluted $[A336][HSO_4]$ and the synthetic germanium containing leachate after equilibration. Left: directly after shaking.

Middle: after settling under gravity for 5 min. Right: after centrifugation for 5 min.

WDXRF calibration

The WDXRF system was calibrated with solutions prepared by mixing varying amounts of undiluted, water-saturated $[A336][Cl]$ and $[A336][HSO_4]$. A calibration curve was constructed by plotting the intensity of the Cl $K\alpha$ line (2.622 keV) as a function of the chloride content (Figure S3). The horizontal axis is defined as $(1 - \text{conversion})$ to obtain an upward trend. The data points ranging between $(1 - \text{conversion})$ 0.2 and 1.0 were fitted with a quadratic equation, while the remaining data points ranging from 0.0 to 0.2 were fitted with a linear equation. The use of two separate fittings resulted in a better overall fitting of the data points.²

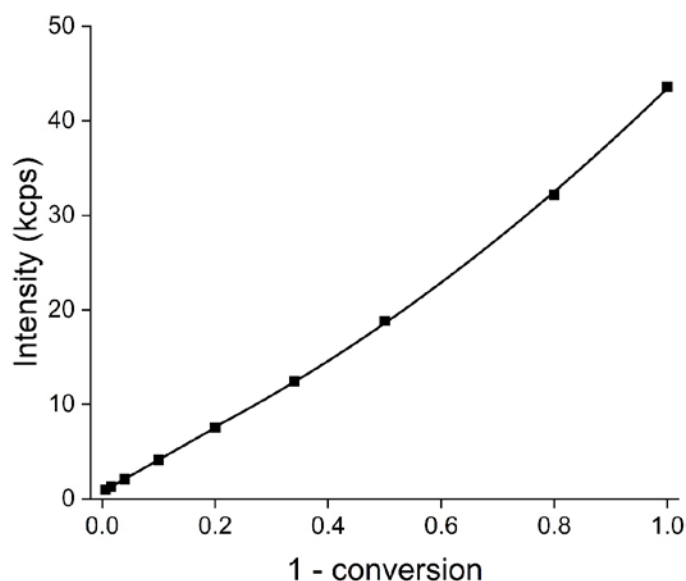


Figure S3: Calibration curve for the determination of chloride in undiluted, water-saturated [A336][HSO₄].

Influence of pH for the use of complexing agents

Figure S4 displays the extraction efficiency of 200 mg L⁻¹ Ge(IV) using undiluted [A336][Cl] as a function of the equilibrium pH for the three studied complexing agents *i.e.* tartaric acid, citric acid and catechol. The pH was adjusted by addition of either NaOH or H₂SO₄. Extractions were performed in the presence of 40 equivalents of complexing agent. For tartaric acid and citric acid only a limited influence of the pH was observed and the recovery of Ge(IV) is quantitative for most pH values. A slight decrease in the extraction efficiency of Ge(IV) could be observed at pH values <1. For catechol, a quantitative recovery of Ge(IV) could be obtained only at pH values >4. This is in agreement with literature reports, where the formation of an extractable anionic complex is shown to occur at pH >4.^{3,4} The observed sequence correlates well with the pK_{a1} values of the complexing agents: 9.45 for catechol, 3.13 for citric acid and 2.89 for tartaric acid. The decreasing extraction efficiencies at low pH are thus most likely caused by a more difficult deprotonation at increasing acidity.

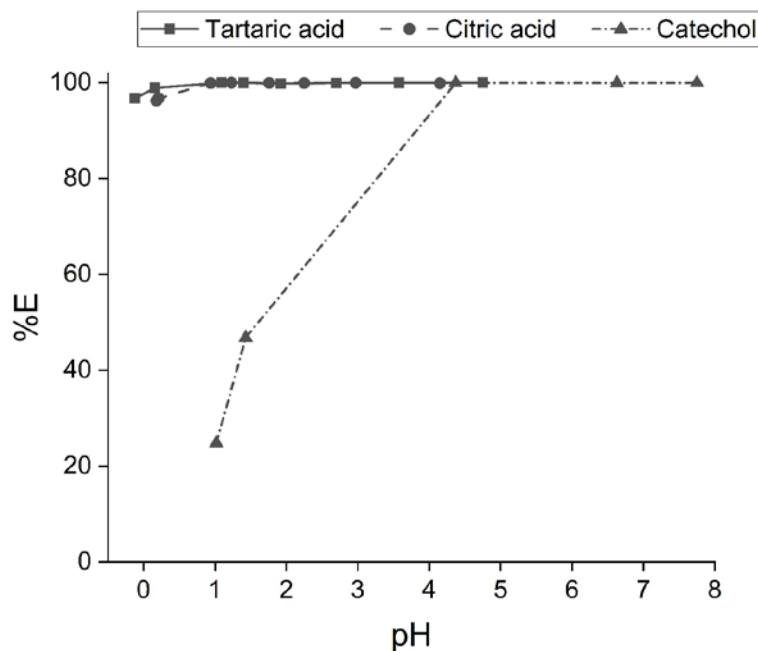
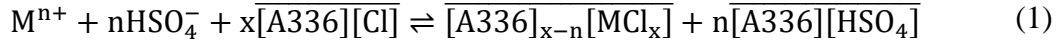


Figure S4: Extraction efficiency of 200 mg L⁻¹ Ge(IV) using undiluted [A336][Cl] as a function of the equilibrium pH and complexing agent (tartaric acid, citric acid, catechol). Conditions: 1 mol L⁻¹ H₂SO₄, 40 equivalents of complexing agent, 300 rpm, 60 min, 22 °C, O/A = 1.

Slope analysis derivations

Role of [A336][Cl]

If a metal ion M^{n+} is extracted from sulfuric acid media by [A336][Cl] as an anionic chloro complex, the extraction reaction can be written as in Eq. 1. Overbars denote species in the organic phase. The distribution ratio D and equilibrium constant K_{eq} can then be defined as in Eq. 2 and 3, respectively. After rearrangement, Eq. 4 can be obtained which shows that a plot of the logarithm of the distribution ratio D versus the logarithm of the [A336][Cl] concentration is linear under the condition of constant HSO_4^- and [A336][HSO₄] concentration. The slope of the plot in turn indicates the number of [A336][Cl] molecules involved in the extraction of the metal M^{n+} .



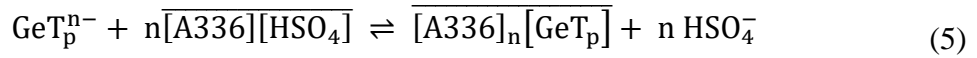
$$D = \frac{[\overline{[A336]_{x-n}[MCl_x]}}{[M^{n+}]} \quad (2)$$

$$K_{eq} = \frac{[\overline{[A336]_{x-n}[MCl_x]}}{[\overline{[A336][Cl]}]^x} \frac{[\overline{[A336][HSO_4]}]^n}{[M^{n+}][HSO_4^-]^n} = \frac{D[\overline{[A336][HSO_4]}]^n}{[\overline{[A336][Cl]}]^x [HSO_4^-]^n} \quad (3)$$

$$\log D = x \log [\overline{[A336][Cl]}] + \log K_{eq} + n \log \left(\frac{[HSO_4^-]}{[\overline{[A336][HSO_4]}}} \right) \quad (4)$$

Role of [A336][HSO₄] for Ge(IV) extraction

If Ge(IV) is extracted as an anionic tartaric acid complex using [A336][HSO₄], the corresponding extraction mechanism can be written according to Eq. 5, with T representing tartaric acid. The distribution ratio and equilibrium constant can then be written as in Eq. 6 and 7, respectively. Eq. 8, obtained after rearrangement of Eq. 7, shows that a plot of the logarithm of the distribution ratio D versus the logarithm of the [A336][HSO₄] concentration is linear at a constant HSO₄⁻ concentration. The HSO₄⁻ concentration can be kept relatively constant by working at a constant sulfuric acid concentration. The slope of the plot then indicates the number of [A336][HSO₄] molecules involved in the extraction of the anionic germanium tartrate complex.



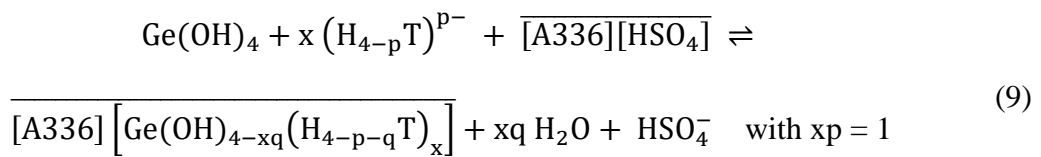
$$D = \frac{[\overline{[A336]_n[GeT_p]}}{[GeT_p^{n-}]} \quad (6)$$

$$K_{eq} = \frac{[\overline{[A336]_n[GeT_p]}}{[GeT_p^{n-}]} \frac{[HSO_4^-]^n}{[\overline{[A336][HSO_4]}]^n} = \frac{D[HSO_4^-]^n}{[\overline{[A336][HSO_4]}]^n} \quad (7)$$

$$\log D = n \log [\overline{[A336][HSO_4]}] + \log K_{eq} - n \log [HSO_4^-] \quad (8)$$

Role of tartaric acid for Ge(IV) extraction

If Ge(IV), present as Ge(OH)_4 in acidic aqueous solutions, complexes with tartaric acid to form an anionic complex which is extracted by a single $[\text{A336}][\text{HSO}_4^-]$ molecule, the corresponding extraction mechanism can be written according to Eq. 9. Tartaric acid is now represented by (deprotonated) H_{4-p}T . In order to fulfill the charge balance, the factor xp should equal 1. Again, the distribution ratio and equilibrium constants are defined in Eq. 10 and 11, respectively. Rearrangement results in Eq. 12, which shows that a plot of the logarithm of the distribution ratio D versus the logarithm of the tartaric acid concentration is linear under the condition that the extractant, i.e. $[\text{A336}][\text{HSO}_4^-]$, and the HSO_4^- concentration are kept constant. The latter can be achieved by working with a constant sulfuric acid concentration. The slope of such a plot represents the number of tartaric acid molecules that are involved in the complexation of Ge(IV), i.e. x . Subsequently, p can be calculated from the charge balance boundary condition. The parameter q , which defines the number of water molecules formed during the complexation, cannot be determined in this manner. However, literature reports on the Ge(IV)-tartaric acid complexation indicate a value of 2 for a monovalent germanium tartrate anion.⁵



$$D = \frac{[\text{A336}] [\text{Ge(OH)}_{4-xq} (\text{H}_{4-p-q}\text{T})_x]}{[\text{Ge(OH)}_4]} \quad (10)$$

$$K_{eq} = \frac{[\text{A336}] [\text{Ge(OH)}_{4-xq} (\text{H}_{4-p-q}\text{T})_x] [\text{HSO}_4^-]}{[\text{Ge(OH)}_4] [(\text{H}_{4-p}\text{T})^{p-}]^x [\text{A336}][\text{HSO}_4^-]} \quad (11)$$

$$= \frac{D[\text{HSO}_4^-]}{[(\text{H}_{4-p}\text{T})^{p-}]^x [\text{A336}][\text{HSO}_4]}$$

$$\log D = x \log[(\text{H}_{4-p}\text{T})^{p-}] + \log K_{eq} + \log[\text{A336}][\text{HSO}_4] - \log[\text{HSO}_4^-] \quad (12)$$

Reusability of the Ionic Liquid

Figure S5 shows that the scrubbing efficiency of As(III) using water progressively decreased throughout the various cycles of the separation process. Ge(IV), however, was not scrubbed and remained in the organic phase. The subsequent stripping of Ge(IV) using 2 mol L⁻¹ NaOH remained high throughout the process while As(III) showed a decreasing trend (Figure S6). The decreasing As(III) recoveries are caused by a small buildup of As(III), Zn(II), Cu(II) and Fe(III), due to an incomplete scrubbing and stripping of these elements.

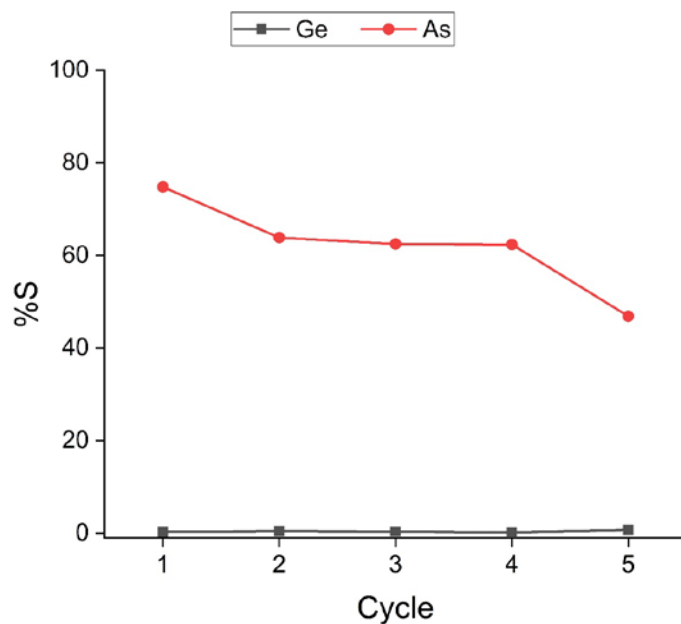


Figure S5: Scrubbing efficiency of Ge(IV) and As(III) from undiluted [A336][HSO₄] using water throughout five consecutive cycles of the separation process. Conditions: 300 rpm, 60 min, 22 °C, O/A = 0.33.

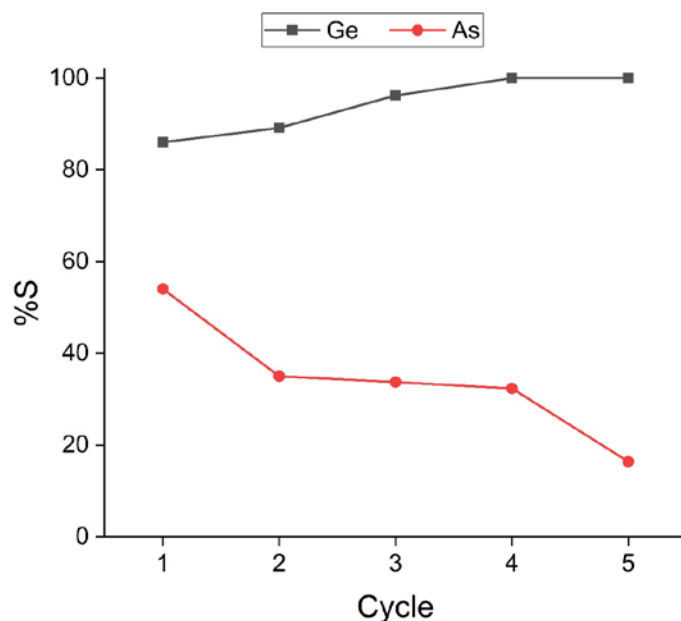


Figure S6: Stripping efficiency of Ge(IV) and As(III) from undiluted [A336][HSO₄] using 2 mol L⁻¹ NaOH throughout five consecutive cycles of the separation process. Conditions: 300 rpm, 60 min, 22 °C, O/A = 1.

References

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