

Supporting Information

75As Nuclear Magnetic Resonance Spectroscopic Investigation of the Thioarsenate Speciation in Strongly Alkaline Sulfidic Leaching Solutions

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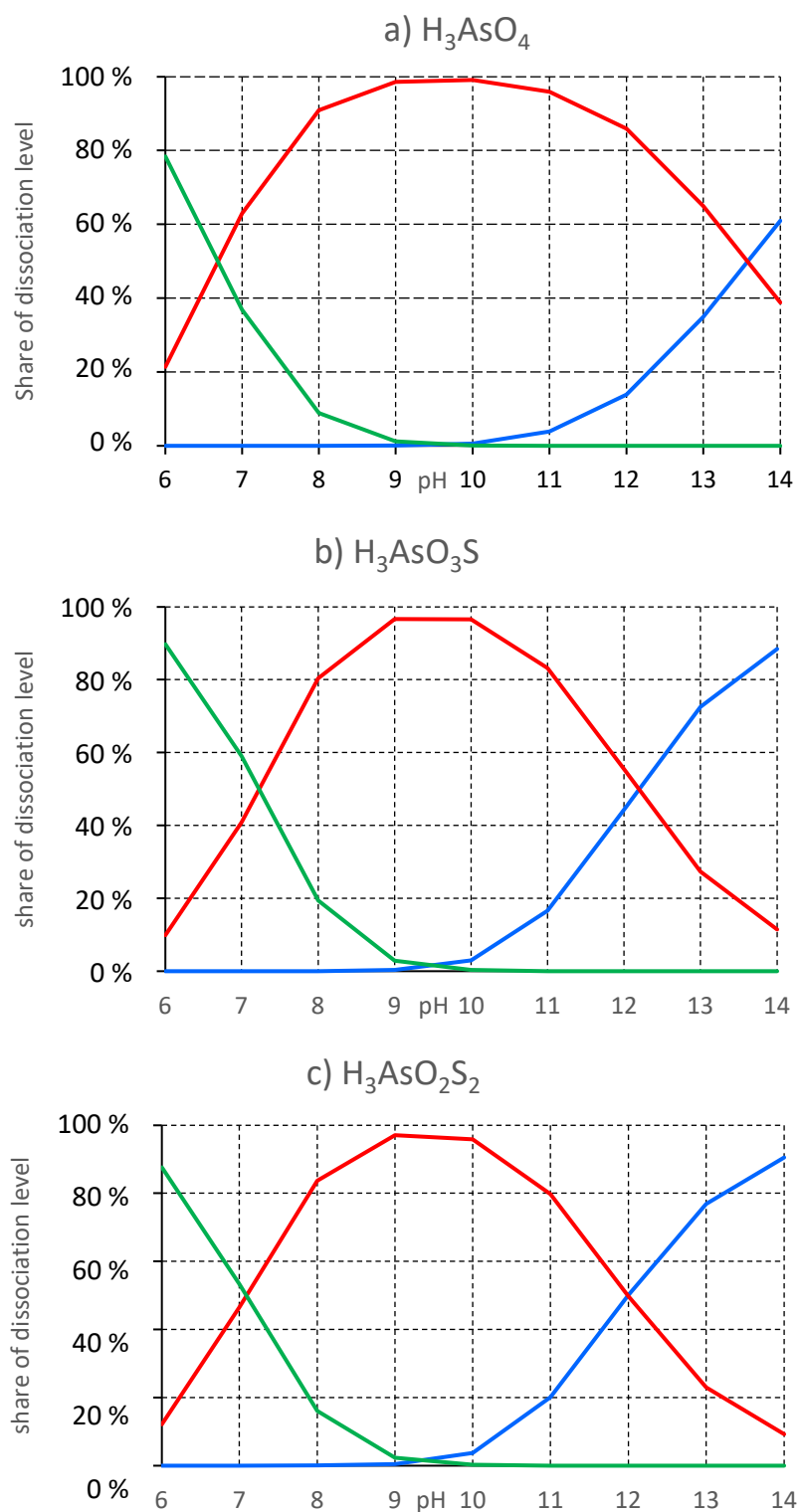
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Table S1. Dissociation constants for arsenate, tetrathioarsenate and oxothioarsenates

Compound	pK ₁	pK ₂	pK ₃	Reference
H ₃ AsO ₄	2.25	6.94	11.59	[43]
H ₃ AsO ₃ S	3.3	7.2	11	[44]
H ₃ AsO ₂ S ₂	2.44	7.1	10.9	[44]
H ₃ AsOS ₃	/	/	10.8	[44]
H ₃ AsS ₄	/	/	5.2	[44]

Figure S1. Species distribution diagrams for the dissociation equilibria of a) H_3AsO_4 , b) $\text{H}_3\text{AsO}_3\text{S}$, c) $\text{H}_3\text{AsO}_2\text{S}_2$ as a function of pH with the dissociation levels H_2AsX_4^- , HAsX_4^{2-} , AsX_4^{3-} ($\text{X} = \text{O}, \text{S}$). H_3AsX_4 was not plotted for clarity as the concentration in the pH range under consideration was essentially zero. The solutions were assumed to be 1 M in arsenic. The calculations were performed with PHREEQC [53]



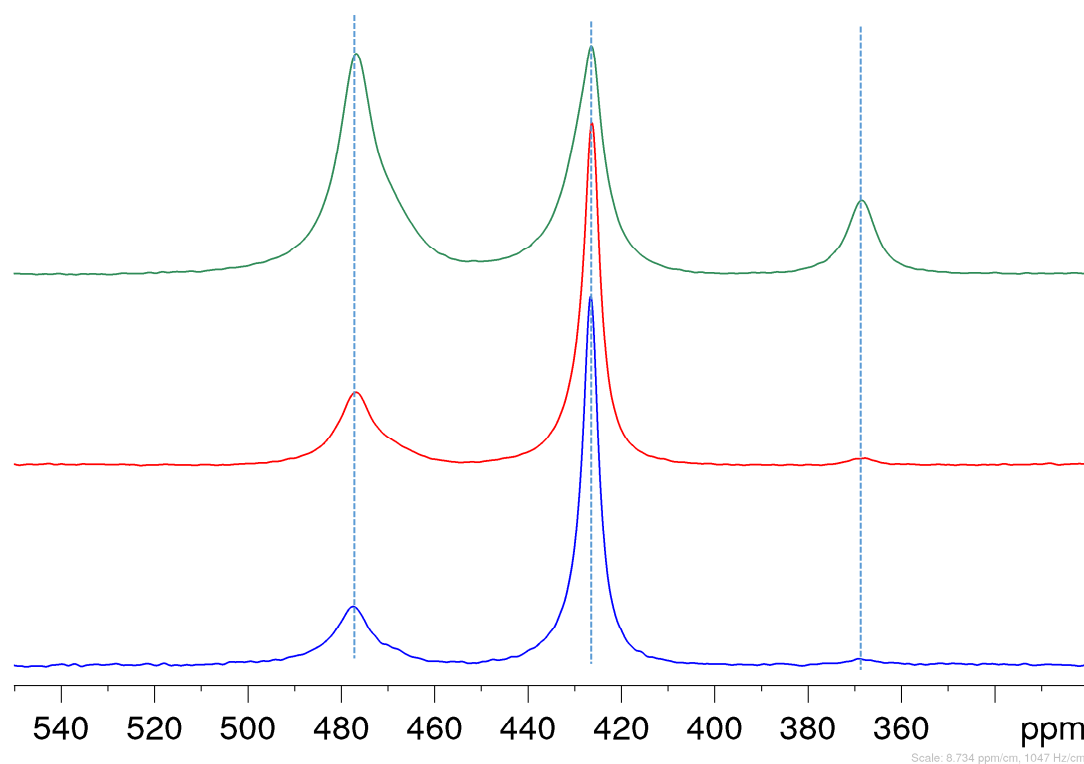


Figure S2. Stack plot of the ^{75}As NMR spectra of a solution with As : OH = molar 1 : 8 ratio (0.125 M As in 1 M NaOH) within **1 h**, after **3 h** and **6 d** after preparation.

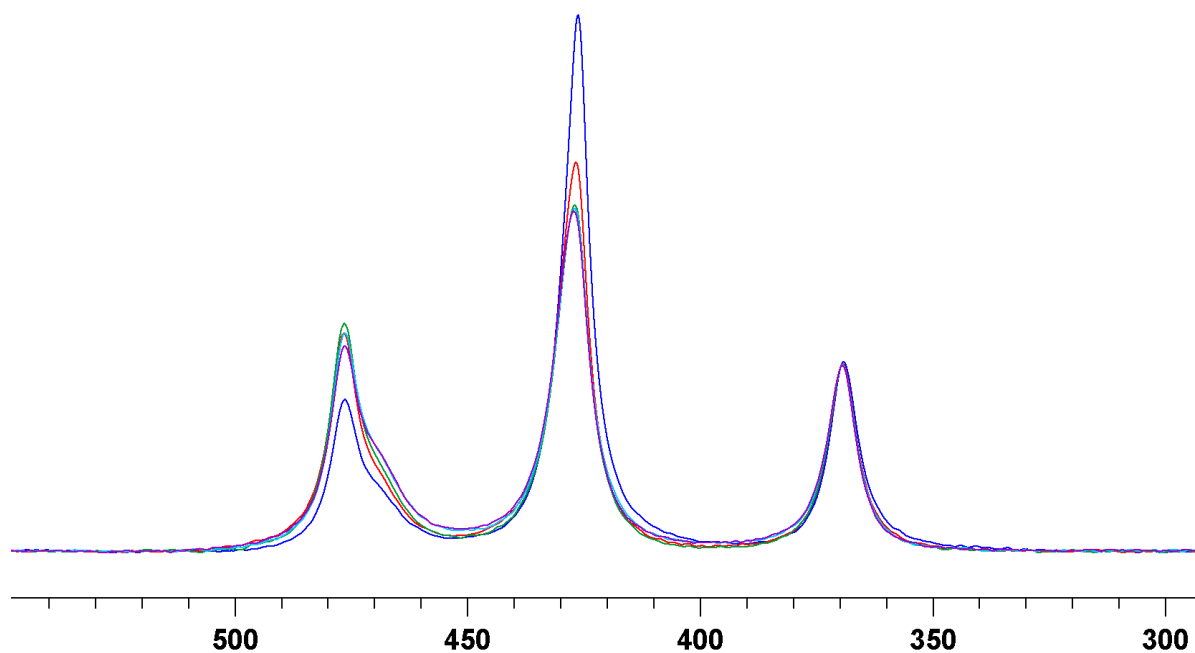


Figure S3. ^{75}As NMR spectra of a 0.3 M As solution (0.12 mol As_2S_5 + 0.06 mol Na_3AsO_4 in 2M NaOH) within 1 h, and after 5, 10, 15, 20 h after preparation. For better comparability, the spectra were scaled to the same intensity for the arsenate signal at 370 ppm.

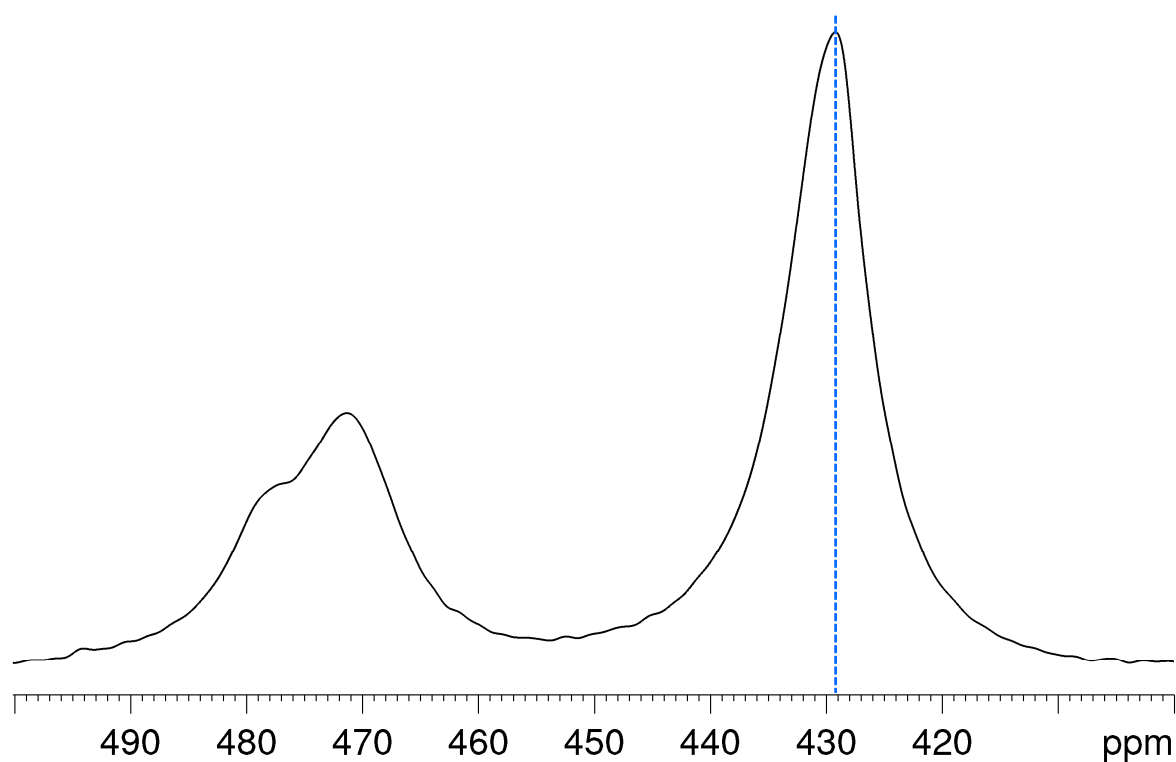


Figure S4: Section of the ^{75}As NMR spectrum of a 0.3 M As solution (0.12 mol As_2S_5 + 0.06 mol Na_3AsO_4 in 2M NaOH) at 358 K (NS = 8192). Note the pronounced asymmetry of the signal at about 429 ppm.

References

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