An example of precipitation separation using pH.

R. Corn – Chem M3LC. Fall 2016.

Barium Oxalate : $Ba(C_2O_4)_{(s)}$: Ksp = 1.1×10^{-6}

Lead Oxalate: $Pb(C_2O_4)_{(s)}$: Ksp = 8.5×10^{-9}

Oxalic Acid is a diprotic: $H_2C_2O_4$: $pK_1 = 1.25$; $pK_2 = 4.14$

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Separation of 1.00 mM Pb^{2+} and 1.00 mM Ba^{2+}:

$[Ba^{2+}] = 1.00$ mM

$[Pb^{2+}] = 1.00$ mM

To remove 99% of the Pb^{2+}

$[Pb^{2+}] = 0.01$ mM $= 10^{-5}$ M

We will use a solution with a total oxalic acid concentration (C^{tot}) of 0.100M.

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At what pH will 99% of the Lead Oxalate be precipitated?

$Ksp = [Pb^{2+}] [C_2O_4{}^{2-}]$

$8.5 \times 10^{-9} = (1 \times 10^{-5}) [C_2O_4{}^{2-}] = (1 \times 10^{-5}) \alpha_{C_2O_4{}^{2-}} (0.100)$

$\alpha_{C_2O_4{}^{2-}} = 8.5 \times 10^{-3} = 1/(1 + [H^+]/K_2 + [H^+]^2/K_1K_2)$

$1/(8.5 * 10^{-3}) = 1 + x/(10^{-4.14}) + x^2/(10^{-5.39})$

(note that 5.39 = 1.25 + 4.14)

solving the quadratic yields:

pH = 2.13

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At what pH will the Barium Oxalate start to precipitate?

$Ksp = [Ba^{2+}] [C_2O_4^{2-}]$

$1.1 \times 10^{-6} = (1 \times 10^{-3}) [C_2O_4^{2-}] = (1 \times 10^{-3}) \alpha_{C_2O_4^{2-}} (0.100)$

$\alpha_{C_2O_4^{2-}} = 1.1 \times 10^{-2} = 1/(1 + [H^+]/K_2 + [H^+]^2/K_1K_2)$

$1/(1.1 \times 10^{-2}) = 1 + x/(10^{-4.14}) + x^2/(10^{-5.39})$

solving the quadratic yields:

pH = 2.23

Thus, in a (narrow) pH range of 2.13 to 2.23 we can plate out 99% of the lead oxalate in solution without precipitating barium oxalate!