Chemical Separation and Chromatographic Methods

Separations Based on Complexation Reactions

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Masking

Masking is a pseudo-separation method in which a species (interferent) is prevented from participating in a chemical reaction in the analyte's determination by binding it with a masking agent in an unreactive complex.

Technically, masking is not a separation technique because the analyte and interferent are never physically separated from each other. Masking can, however, be considered a pseudo-separation technique.

Complexation reactions

In **complexation reactions**, several ligands react with a metal atom to form a coordination complex. This is achieved by providing lone pairs of the ligand into empty orbitals of the metal atom and forming dipolar bonds. The ligands are Lewis bases, they can be both ions and neutral molecules.

In chemistry, a **coordination complex**, consists of an atom or ion (usually metallic), and a surrounding array of bound molecules or anions, that are in turn known as ligands or complexing agents.

Coordination refers to the "coordinate covalent bonds" (dipolar bonds) between the ligands and the central atom. Originally, a complex implied a reversible association of molecules, atoms, or ions through such weak chemical bonds.

Masking agent is the reagent used to bind the species to be masked in an unreactive complex.

A wide variety of ions and molecules have been used as **masking agents**, and, as a result, selectivity is usually not a problem.

Selected Masking Agents

Masking Agent	Species Which Can Be Masked
CN^-	Ag, Au, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pd, Pt, Zn
SCN^-	Ag, Cd, Co, Cu, Fe, Ni, Pd, Pt, Zn
NH_3	Ag, Co, Cu, Fe, Pd, Pt
F^-	Al, Co, Cr, Mg, Mn, Sn, Zn
$S_2O_3^{2-}$	Au, Cd, Co, Cu, Fe, Pb, Pd, Pt, Sb
tartrate	Al, Ba, Bi, Ca, Ce, Co, Cr, Cu, Fe, Hg, Mn, Pb, Pd, Pt, Sb, Sn, Zn
oxalate	Al, Fe, Mg, Mn, Sn
thioglycolic acid	Cu, Fe, Sn

Example

Suggest a masking agent for the analysis of **Al** in the presence of **Fe**. Repeat for the analysis of **Fe** when **Al** is an interferent.

To find a suitable masking agent, we look for a species that binds with the interferent but does not bind with the analyte.

Oxalate, for example, is an inappropriate choice because it binds with both **Al** and **Fe**. From the Table we find that thioglycolic acid is a selective masking agent for **Fe** in the presence of **Al** and that $\mathbf{F^-}$ is a selective masking agent for **Al** in the presence of **Fe**.

Example

Show that **CN^-** is an appropriate masking agent for **Ni^{2+}** in a method where nickel's complexation with **EDTA** is an interference.

The relevant reactions and formation constants are

$$Ni^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons NiY^{2-}(aq) \quad K_1 = 4.2 \times 10^{18}$$

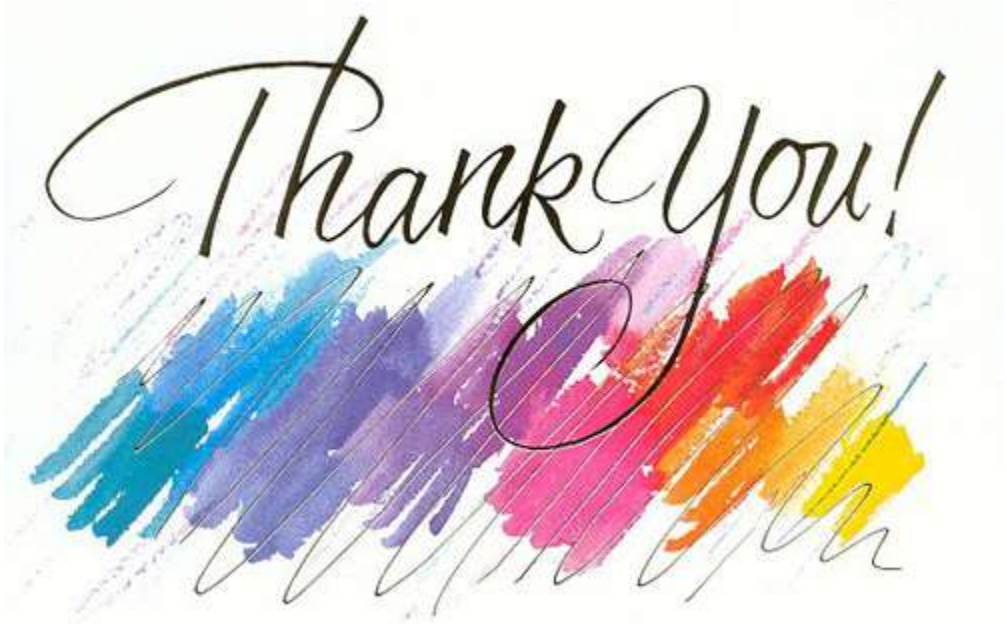
$$Ni^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Ni(CN)_4^{2-}(aq) \quad \beta_4 = 1.7 \times 10^{30}$$

where **Y^{4-}** is an abbreviation for **EDTA**. Cyanide is an appropriate masking agent because the formation constant for the **$Ni(CN)_4^{2-}$** is greater than that for the **Ni–EDTA** complex. In fact, the equilibrium constant for the reaction in which **EDTA** displaces the masking agent is very small, indicating that **$Ni(CN)_4^{2-}$** is relatively inert in the presence of **EDTA**.

$$Ni(CN)_4^{2-}(aq) + Y^{4-}(aq) \rightleftharpoons NiY^{2+}(aq) + 4CN^-(aq)$$

$$K = \frac{K_1}{\beta_4} = \frac{4.2 \times 10^{18}}{1.7 \times 10^{30}} = 2.5 \times 10^{-12}$$

As shown in the Example, we can judge a masking agent's effectiveness by considering the relevant equilibrium constants.


Thank You!