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# Optimizing Metallographic Etchants for Ancient Gold and Silver Materials

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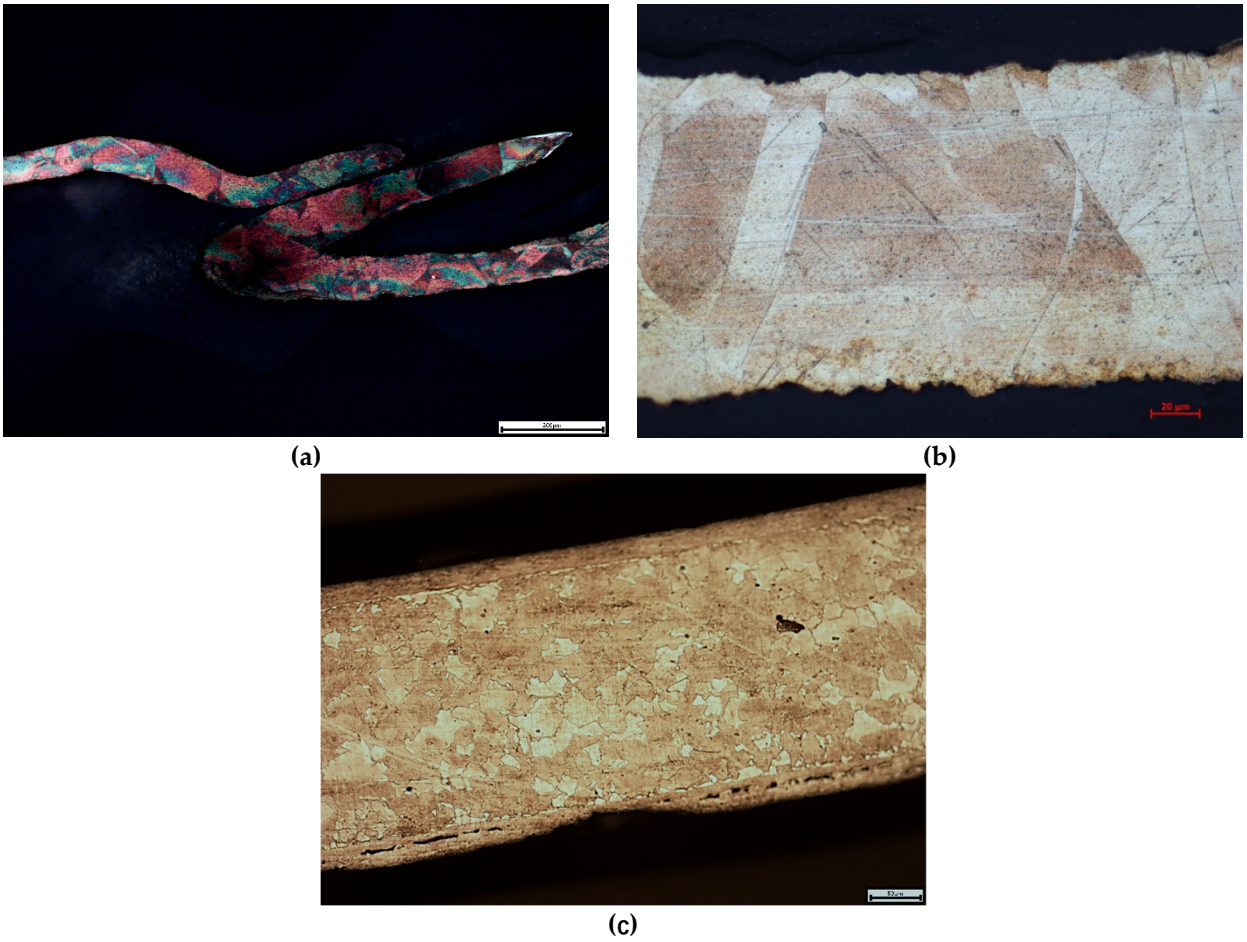
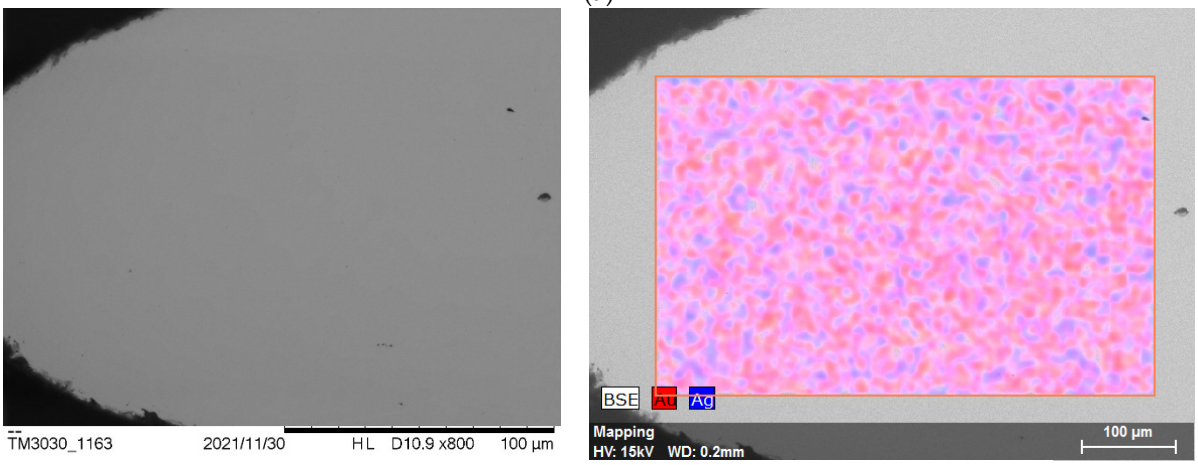
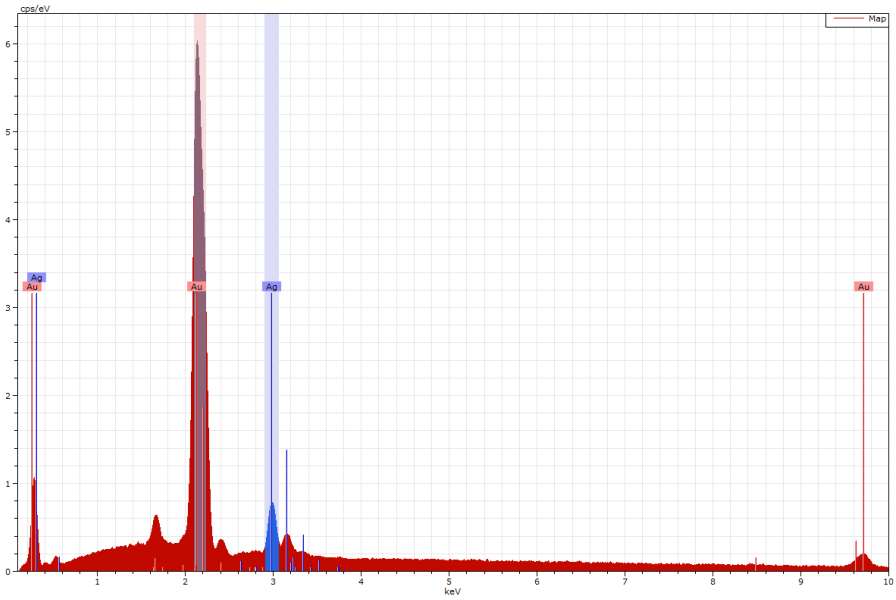



**Figure S1.** Problems with commonly used ancient gold / silver material etchants. (**a**) Problems with poorly defined metallographic images and blurred grain boundaries occur frequently when ancient gold material is etched with aqua regia (sample: gold mask from Sanxingdui site; scale bar: 200 μm); (**b**) Secondary scratches from re-polishing (scale bar: 20 μm); (**c**) Poor etching result due to etchant failure (etchant: ammonia + hydrogen peroxide; sample: silver bowl excavated in Yiwu City; scale bar: 50 μm).



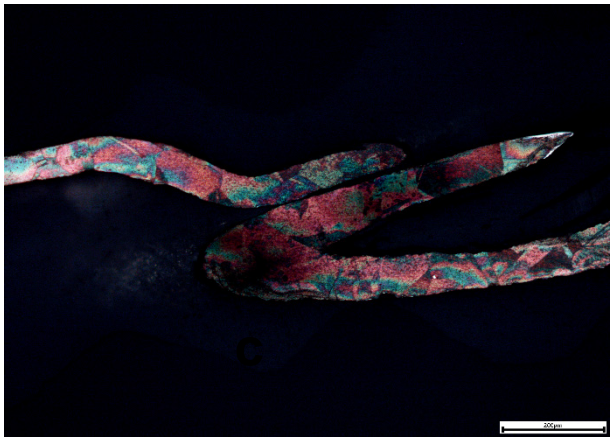
(**a**)



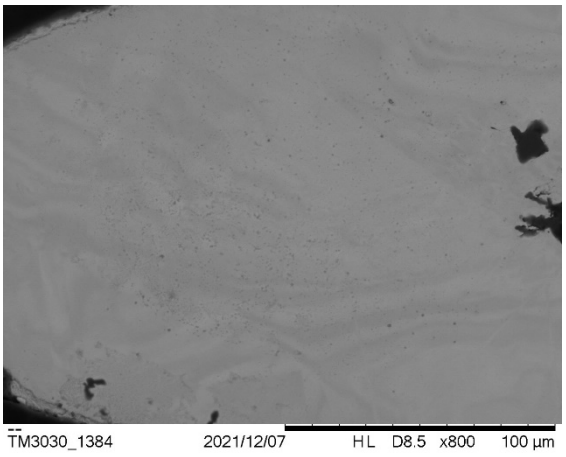




(**b**)

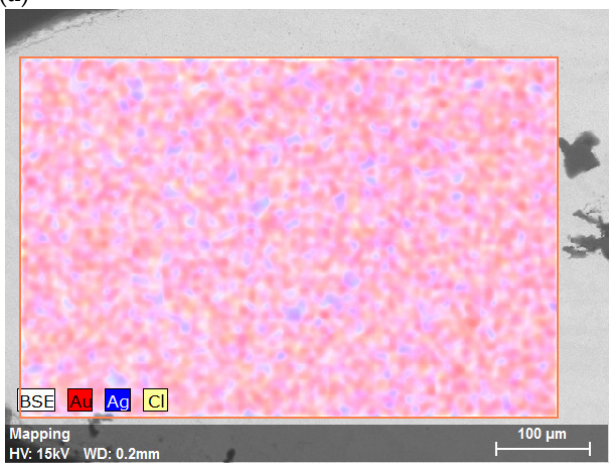
**Figure S2.** The ancient gold material used in this study. (**a**) The gold mask excavated from the sacrificial pit of the Sanxingdui site; (**b**) The region and spectrum of the SEM-EDS mapping analysis of the sample matrix.



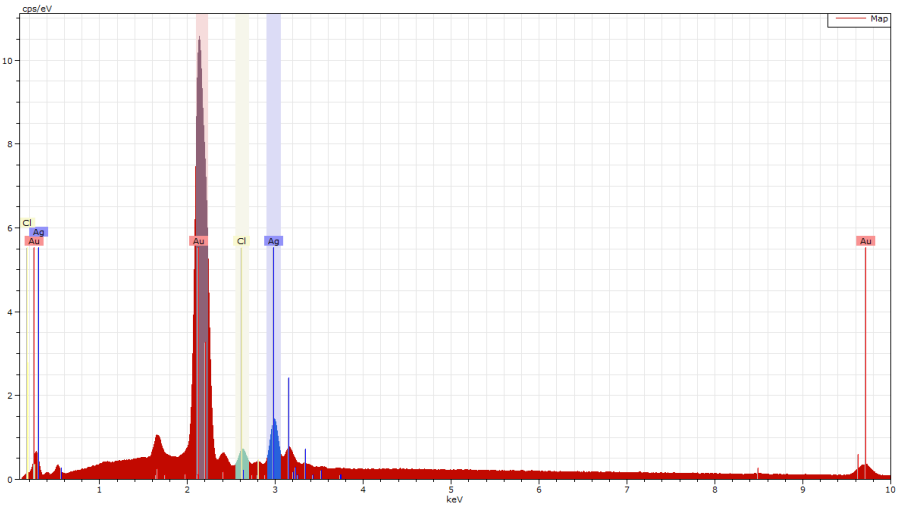
(**a**)




(**b**)




(**c**)




(**d**)

**Figure S3.** The AgCl "thin film" of the pure aqua regia-etched gold sample. (**a**) The gold mask sample from Sanxingdui site after etched by pure aqua regia (scale bar: 200 µm); (**b**)(**c**) The region of SEM-EDS mapping analysis; (**d**) The spectrum of the EDS result.

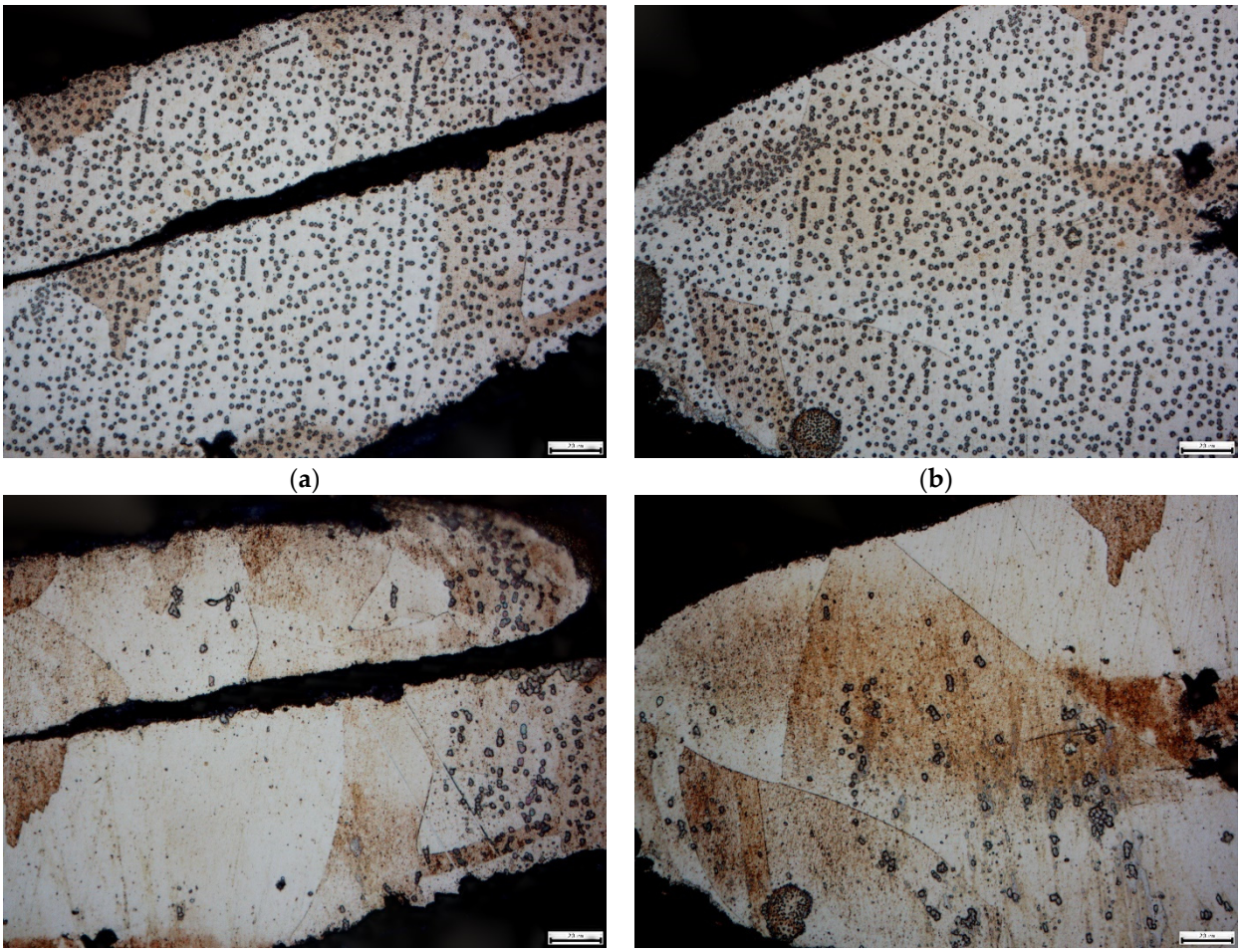
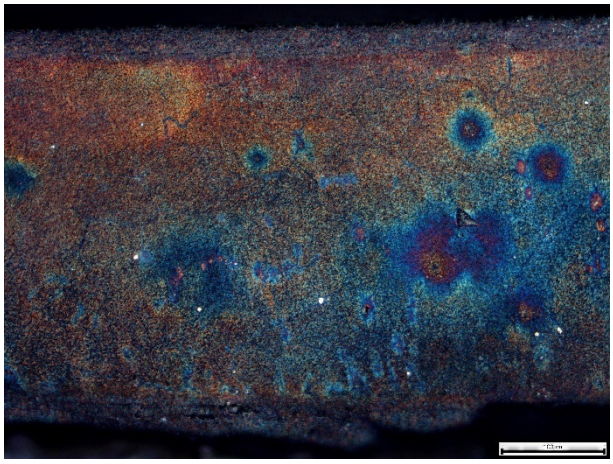
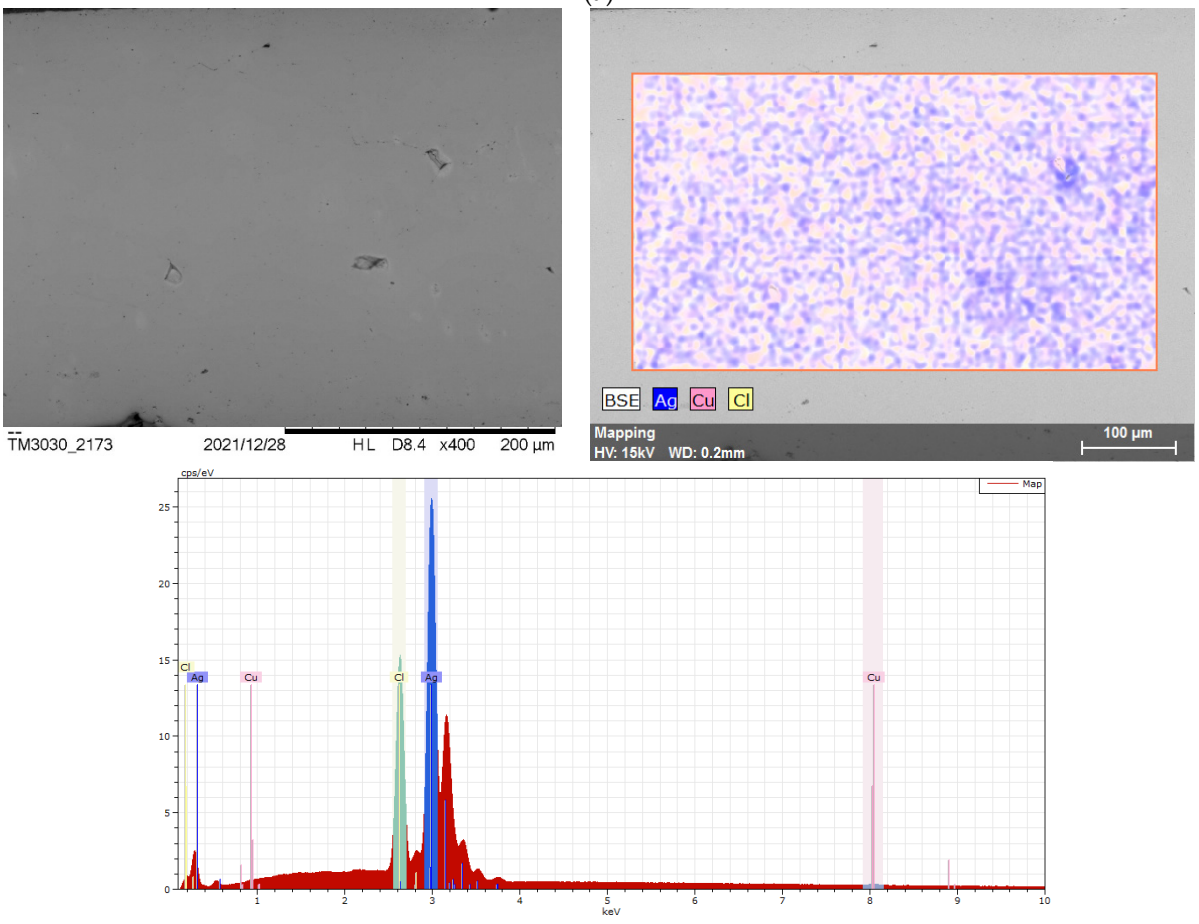


**Figure S4.** Comparison of the effectiveness of silver chloride impurities rubbed off (scale bar: 20 μm). (**a**)(**b**) Before rubbing (sample: gold mask from Sanxingdui site; etchant: 6 ml HCl + 2 ml $HNO_3$ and diluted to 20 ml; etching duration: 100s); (**c**)(**d**) After rubbing (gently wipe in the same direction for 15-20 seconds with a skimmed cotton swab).



(**a**)




(**b**)

**Figure S5.** The AgCl "thin film" of the diluted aqua regia-etched silver sample. (**a**) The silver bowl sample excavated in Yiwu City after etched by diluted aqua regia (etchant: 6 ml HCl + 2 ml $HNO_3$ and diluted to 12 ml; etching duration: 15 seconds; scale bar: 100 µm); (**b**) The region and spectrum of SEM-EDS mapping analysis (Ag 84.10%-Cl 15.13%-Cu 0.77%).

**Table S1.** Calculation process for $m_{AgCl_S_2O_3^{2-}}$, $m_{AgCl_CN^-}$, $m_{AgCl_Br^-}$ and $m_{AgCl_SCN^-}$.

(**a**) For $S_2O_3^{2-}$:

$$Ag^+ + S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)]^- \; ; \; \beta_1 = \frac{[Ag(S_2O_3)]}{[Ag][S_2O_3]} = 6.61 \times 10^8 \cdots\cdots (1)$$

$$Ag^+ + 2\,S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-} \; ; \; \beta_2 = \frac{[Ag(S_2O_3)_2]}{[Ag][S_2O_3]^2} = 2.88 \times 10^{13} \cdots\cdots (2)$$

According to (1)(2), the distribution of the coordination ions at each level can be obtained:

$$[Ag(S_2O_3)] = [Ag]\,\beta_1[S_2O_3] \; ; \; [Ag(S_2O_3)_2] = [Ag]\,\beta_2[S_2O_3]^2$$

Express the total concentration of the various forms of Ag-containing ions in the solution as $c_{Ag_S_2O_3}$, and the total concentration of the various forms of $S_2O_3^{2-}$-containing ions as $c_{S_2O_3}$:

$$c_{Ag_S_2O_3} = [Ag] + [Ag(S_2O_3)] + [Ag(S_2O_3)_2] = [Ag](1 + \beta_1[S_2O_3] + \beta_2[S_2O_3]^2) \cdots\cdots (3)$$

$$c_{S_2O_3} = [S_2O_3] + [Ag(S_2O_3)] + 2\,[Ag(S_2O_3)_2] = [S_2O_3] + [Ag]\,\beta_1[S_2O_3] + 2\,[Ag]\,\beta_2[S_2O_3]^2 \cdots\cdots (4)$$

According to the dissolution equilibrium, there is:

$$K_{sp} = [Ag][Cl] = 1.56 \times 10^{-10} \cdots\cdots (5)$$

Since $Ag^+$ released during the dissolution of AgCl is equal to $Cl^-$, and there are no other forms of $Cl^-$-containing ions in solution, so $[Cl] = c_{Ag_S_2O_3}$.

When the concentration of the ligand solution is 1 mol/L, it gives:

$$c_{S_2O_3} = 1\ mol/L$$

$$[S_2O_3] = 7.40 \times 10^{-3}\ mol/L \; ; \; c_{Ag_S_2O_3} = 4.97 \times 10^{-1}\ mol/L$$

$$m_{Ag_S_2O_3} = 712.3\ mg$$

(**b**) For $CN^-$:

$$Ag^+ + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^- \; ; \; \beta_2 = \frac{[Ag(CN)_2]}{[Ag][CN]^2} = 1.26 \times 10^{21} \cdots\cdots (1)$$

$$Ag^+ + 3\,CN^- \rightleftharpoons [Ag(CN)_3]^{2-} \; ; \; \beta_3 = \frac{[Ag(CN)_3]}{[Ag][CN]^3} = 5.01 \times 10^{21} \cdots\cdots (2)$$

$$Ag^+ + 4\,CN^- \rightleftharpoons [Ag(CN)_4]^{3-} \; ; \; \beta_4 = \frac{[Ag(CN)_4]}{[Ag][CN]^4} = 3.98 \times 10^{20} \cdots\cdots (3)$$

$$c_{Ag_CN} = [Ag] + [Ag(CN)_2] + [Ag(CN)_3] + [Ag(CN)_4]$$
$$= [Ag](1 + \beta_2[CN]^2 + \beta_3[CN]^3 + \beta_4[CN]^4) \cdots\cdots (4)$$

$$c_{CN} = [CN] + 2\,[Ag(CN)_2] + 3\,[Ag(CN)_3] + 4\,[Ag(CN)_4]$$
$$= [CN] + 2\,[Ag]\,\beta_2[CN]^2 + 3\,[Ag]\,\beta_3[CN]^3 + 4\,[Ag]\,\beta_4[CN]^4 \cdots\cdots (5)$$

$$K_{sp} = [Ag][Cl] = 1.56 \times 10^{-10} \cdots\cdots (6)$$

$$[Cl] = c_{Ag_CN} \cdots\cdots (7)$$

When the concentration of the ligand solution is 1 mol/L, it gives:

$$c_{CN} = 1\ mol/L$$

$$[CN] = 1.13 \times 10^{-6}\ mol/L \; ; \; c_{Ag_CN} = 5.00 \times 10^{-1}\ mol/L$$

$$m_{Ag_CN} = 7.15 \times 10^{-1}\ g$$

(**c**) For $Br^-$:

$$Ag^+ + Br^- \rightleftharpoons AgBr\ ;\ \beta_1 = \frac{[AgBr]}{[Ag][Br]} = 2.40 \times 10^4 \cdots\cdots\cdots (1)$$

$$Ag^+ + 2\ Br^- \rightleftharpoons [Ag(Br)_2]^-\ ;\ \beta_2 = \frac{[Ag(Br)_2]}{[Ag][Br]^2} = 2.14 \times 10^7 \cdots\cdots\cdots (2)$$

$$Ag^+ + 3\ Br^- \rightleftharpoons [Ag(Br)_3]^{2-}\ ;\ \beta_3 = \frac{[Ag(Br)_3]}{[Ag][Br]^3} = 1.00 \times 10^8 \cdots\cdots\cdots (3)$$

$$Ag^+ + 4\ Br^- \rightleftharpoons [Ag(Br)_4]^{3-}\ ;\ \beta_4 = \frac{[Ag(Br)_4]}{[Ag][Br]^4} = 5.37 \times 10^8 \cdots\cdots\cdots (4)$$

$$\begin{aligned} c_{Ag_Br} &= [Ag] + [AgBr] + [Ag(Br)_2] + [Ag(Br)_3] + [Ag(Br)_4] \\ &= [Ag](1 + \beta_1[Br] + \beta_2[Br]^2 + \beta_3[Br]^3 + \beta_4[Br]^4) \cdots\cdots\cdots (5) \end{aligned}$$

$$\begin{aligned} c_{Br} &= [Br] + [AgBr] + 2\,[Ag(Br)_2] + 3\,[Ag(Br)_3] + 4\,[Ag(Br)_4] \\ &= [Br] + \ [Ag]\,\beta_1[Br] + 2\,[Ag]\,\beta_2[Br]^2 + 3\,[Ag]\,\beta_3[Br]^3 + 4\,[Ag]\,\beta_4[Br]^4 \cdots\cdots\cdots (6) \end{aligned}$$

$$K_{sp_AgCl} = [Ag][Cl] = 1.56 \times 10^{-10} \cdots\cdots\cdots (7)$$

Since $Ag^+$ and $Br^-$ also have a solubility equilibrium, there is:

$$K_{sp_AgBr} = [Ag][Br] = 5.03 \times 10^{-13} \cdots\cdots\cdots (8)$$

When the concentration of the ligand solution is 1 mol/L, considering the conservation of Ag and Br throughout the reaction, it gives:

$$[Cl] - c_{Ag_Br} + c_{Br} = 1 \cdots\cdots\cdots (9)$$

$$[Br] = 3.21 \times 10^{-3}\ mol/L\ ;\ c_{Ag_Br} = 4.73 \times 10^{-8}\ mol/L$$

$$m_{Ag_Br} = 6.78 \times 10^{-6}\ g$$

(**d**) For $SCN^-$:

$$Ag^+ + SCN^- \rightleftharpoons AgSCN\ ;\ \beta_1 = \frac{[AgSCN]}{[Ag][SCN]} = 2.40 \times 10^4 \cdots\cdots\cdots (1)$$

$$Ag^+ + 2\ SCN^- \rightleftharpoons [Ag(SCN)_2]^-\ ;\ \beta_2 = \frac{[Ag(SCN)_2]}{[Ag][SCN]^2} = 2.14 \times 10^7 \cdots\cdots\cdots (2)$$

$$Ag^+ + 3\ SCN^- \rightleftharpoons [Ag(SCN)_3]^{2-}\ ;\ \beta_3 = \frac{[Ag(SCN)_3]}{[Ag][SCN]^3} = 1.00 \times 10^8 \cdots\cdots\cdots (3)$$

$$Ag^+ + 4\ SCN^- \rightleftharpoons [Ag(SCN)_4]^{3-}\ ;\ \beta_4 = \frac{[Ag(SCN)_4]}{[Ag][SCN]^4} = 5.37 \times 10^8 \cdots\cdots\cdots (4)$$

$$\begin{aligned} c_{Ag_SCN} &= [Ag] + [AgSCN] + [Ag(SCN)_2] + [Ag(SCN)_3] + [Ag(SCN)_4] \\ &= [Ag](1 + \beta_1[SCN] + \beta_2[SCN]^2 + \beta_3[SCN]^3 + \beta_4[SCN]^4) \cdots\cdots\cdots (5) \end{aligned}$$

$$\begin{aligned} c_{SCN} &= [SCN] + [AgSCN] + 2\,[Ag(SCN)_2] + 3\,[Ag(SCN)_3] + 4\,[Ag(SCN)_4] \\ &= [SCN] + \ [Ag]\,\beta_1[SCN] + 2\,[Ag]\,\beta_2[SCN]^2 + 3\,[Ag]\,\beta_3[SCN]^3 \\ &\quad + 4\,[Ag]\,\beta_4[SCN]^4 \cdots\cdots\cdots (6) \end{aligned}$$

$$K_{sp_AgCl} = [Ag][Cl] = 1.56 \times 10^{-10} \cdots\cdots\cdots (7)$$

$$K_{sp_AgSCN} = [Ag][SCN] = 1.18 \times 10^{-12} \cdots\cdots\cdots (8)$$

When the concentration of the ligand solution is 1 mol/L, it gives:

$$[Cl] - c_{Ag_SCN} + c_{SCN} = 1 \cdots\cdots\cdots (9)$$

$$[SCN] = 7.51 \times 10^{-3}\ mol/L\ ;\ c_{Ag_SCN} = 4.62 \times 10^{-8}\ mol/L$$

$$m_{Ag_SCN} = 6.62 \times 10^{-6}$$