The Cyanide Quick Reference Guide

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Reporting cyanide concentrations

There are three main categories for measuring and reporting cyanide:

1. Free (titratable) cyanide
- CN^-
- HCN (see Effect of pH and buffers)
- All CN^- complexed with Zn and Cd
- Some CN^- complexed with Cu

2. Weak Acid Dissociable (WAD) cyanide
- Titratable cyanide
- All CN^- complexed with Cu, Ag and Ni

3. Total cyanide
- WAD cyanide
- All CN^- complexed with Fe
- Some CN^- from Co, Pt and Au cyanide complexes
- SCN^- is included with some methods

Measured/reported values depend on the analysis method.

Cyanate (OCN^-) is not included in any of the determinations.

Note: Cyanide results are generally reported as mg/L CN^-, though free cyanide is typically reported as mg/L NaCN at gold operations.

Density of NaCN solutions (g/L)

[NaCN] (% w/w)	Temperature (°C)			
	0	10	20	30
5	1041	1039	1036	1033
10	1073	1070	1068	1065
15	1100	1098	1096	1093
20	1125	1123	1121	1118
25	1150	1148	1146	1144
30	1173	1171	1169	1167
Solubility (% w/w NaCN)	**29.7**	**32.4**	**36.5**	**41.8**

Free (titratable) cyanide measurement

Endpoint (EP) detection

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$

Potentiometric:

Can be used in a coloured solution. Provides more information about the titration and can more easily detect the EP in high copper and chloride solutions.

Visual indicators:
- Rhodanine - Initial cyanide solution must be colourless. Colour change is canary yellow to salmon pink. EP detection difficult in high chloride or copper solutions.
- Potassium Iodide - Can be used in a coloured solution. EP is indicated by a white precipitate of AgI. EP not as sharp as for rhodanine.

Recommended settings

$NaCN\ (mg/L) = mL\ AgNO_3$ at EP x Titration factor

NaCN Range (mg/L)	Volume of CN Solution (mL)	Recommended [$AgNO_3$]	Volume of $AgNO_3$ at EP (mL)	Titration Factor
<10	Use alternative method such as CN ion selective electrode, FIA or HPLC			
10 - 50	20	0.00103 M	2 - 10	5
50 - 100	10	0.00103 M	5 - 10	10
100 - 500	20	0.0103 M	2 - 10	50
500 - 2000	5	0.0103 M	2.5 - 10	200
30 %	5 (Diluted 200 fold)	0.0103 M (1.75 g $AgNO_3$ in 1 L)	7.5	40,000

Effect of pH and buffers

$HCN_{(aq)}$ is not titrated. If pH<10.5 then $HCN_{(aq)}$ is titrated when:
- Presence of buffer (eg CO_3^{2-}) which results in dissociation of some or all $HCN_{(aq)}$ to CN^- as titration proceeds ($HCN_{(aq)} \leftrightarrow H^+ + CN^-$ pKa = 9.2).
- Addition of NaOH to the titration to convert all $HCN_{(aq)}$ to CN^-.

Chloride ion interference

Cl^- will react with Ag^+. The titration EP is not as sharp, as Cl^- will begin to react with Ag^+ near the CN^- EP. This occurs for both colorimetric and potentiometric titrations.

Sulfide ion interference

S^{2-} will react with Ag^+. Removed by precipitating with Pb^{2+} before the titration. Can be quantified before cyanide by potentiometric titration.

Copper ion interference

Reduces EP sensitivity
- Potentiometric measures free CN^- and the fourth CN^- complexed with Cu (Figure 1).
- Rhodanine also measures a portion of the third CN^- complexed with Cu (Figure 2).

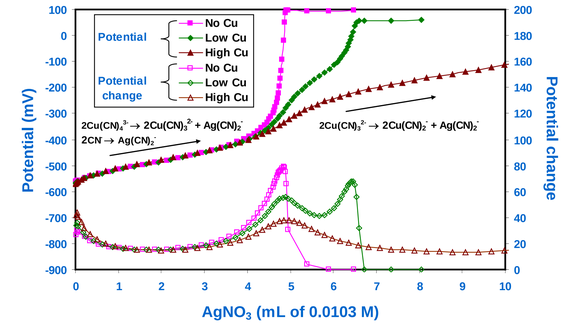

Figure 1: Potentiometric titration of 20 mL samples containing 250 mg/L NaCN; low Cu – 100 mg/L Cu as $Cu(CN)_3^{2-}$, high Cu – 500 mg/L Cu as $Cu(CN)_3^{2-}$.

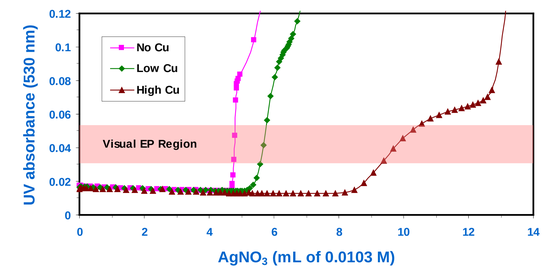

Figure 2: Rhodanine indicator absorbance of a silver nitrate titration of 20 ml samples for the same solutions as Figure 1.

Cyanide deportment

Analysis of cyanide species and degradation products such as SCN^-, OCN^- and metal cyanides is important to understand and quantify cyanide deportment. HPLC, ICP and other analysis methods are available.

FOR FURTHER INFORMATION
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