



Understanding and Analysis of Cyanide Ion using Ion Exchange Chromatography with Amperometric Detection

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Today we will talk about.....

- Cyanide Ion
 - Understanding Cyanide Ion Species
 - Currently used EPA approved methods
 - Ion Chromatography with Amperometric Detection
- Summary

Understanding Cyanide Species

- **Free Cyanide**

- The form of cyanide that is bioavailable and known for its toxic effect on organisms.
- Free cyanide refers to either molecular hydrogen cyanide (HCN) or ionic cyanide (CN⁻).
- At a pH of 7 or less in water, free cyanide is present entirely as HCN.
- Above pH 11, free cyanide exists entirely as CN⁻.

- **Weak Acid Dissociated**

- Group of cyanide species that undergo dissociation and liberate free cyanide when refluxed under weakly acidic conditions (pH 4.5-6).
- Weak acid dissociable cyanide is determined analytically through weak acid distillation and analysis of liberated free cyanide

- **Total Cyanide**

- Total cyanide is an analytically defined term that refers to the sum total of all of the inorganic chemical forms of cyanide that dissociate and release free cyanide when refluxed under strongly acidic conditions.
- Total cyanide is determined analytically through strong acid distillation or UV radiation and exposure to strong acid followed by analysis of liberated free cyanide.

USEPA Methods

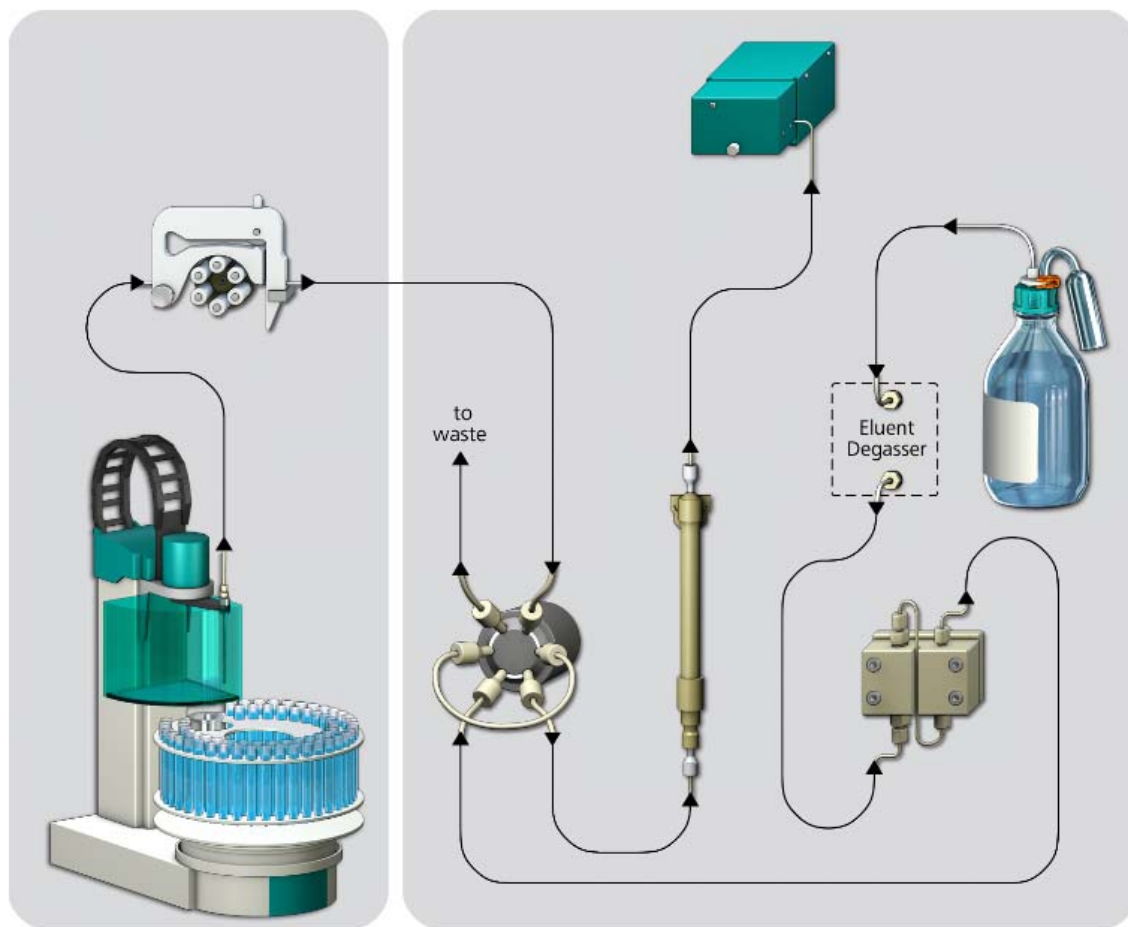
Cyanide	EPA Method	ASTM Method	SM (18 th & 19 th)	Other
	335.4	D2036 – A	4500CN - C	I-3300-85
		D2036 – B	4500CN – G	Kelada-01
		D6888	4500CN – E	QuikChem 10-204-00-1-X
			4500CN - F	OIA-1677, DW

- Semi-Automated FIA – Spectrophotometry
- Gas Diffusion – Amperometry
- Ion Chromatography - Amperometry

Major Interferences for Cyanide Analysis

- Sulfide Ion
 - Lead Acetate paper test
 - Reacts and detected as Cyanide analyte
- Thiocyanate ion
 - With appropriate pH and conditions, it can liberate Free Cyanide
- Mercaptans
 - During distillation, it can breakdown to interfere as Sulfide Ion

Ion Chromatography – Amperometric Detection



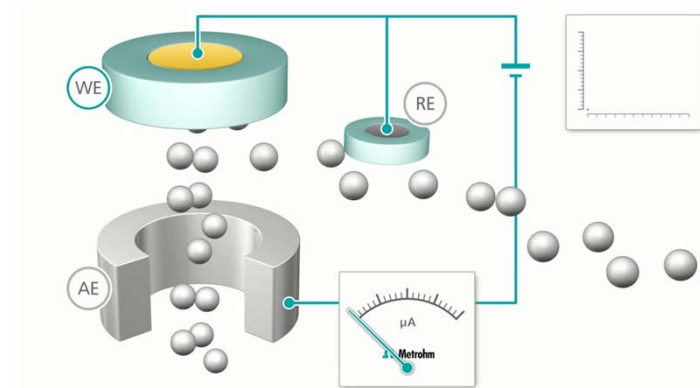
- Anion Exchange Column
- Isocratic IC System
- Amperometric Detection
 - Ag – WE
 - Solid State PD – RE
 - DC mode with 0.0 V

OR

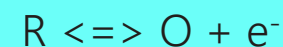
 - PAD mode

Measuring principle

- Three electrode system (reference, working, auxiliary electrode)
- Electric potential is applied between the reference and the working electrode
- Oxidation process on the working electrode surface (electron transfer)
- Current corresponding to the concentration of the substance is measured
- 5 – 10 % conversion on the working electrode



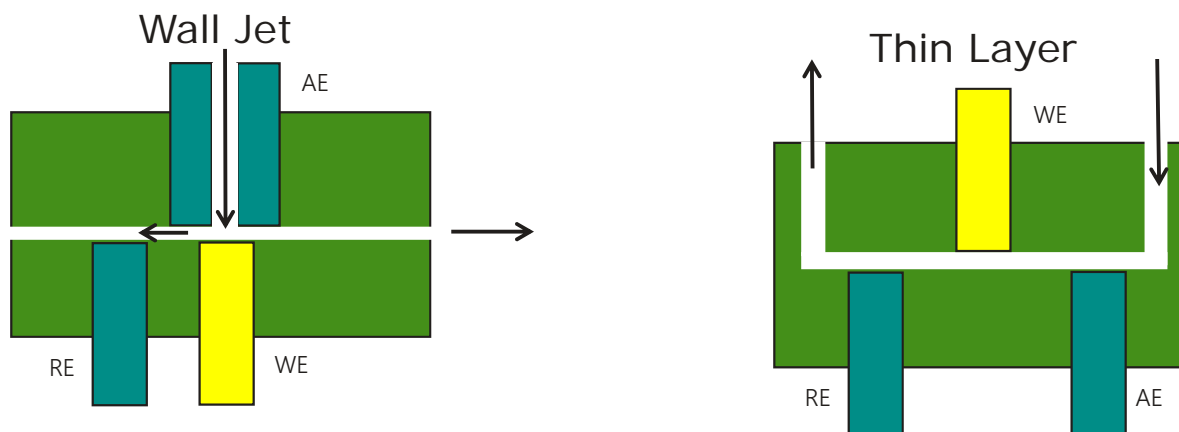
- ❖ oxidation or reduction
- ❖ electron transfer



Simple connection to any IC- or HPLC-system

Cells and Electrodes

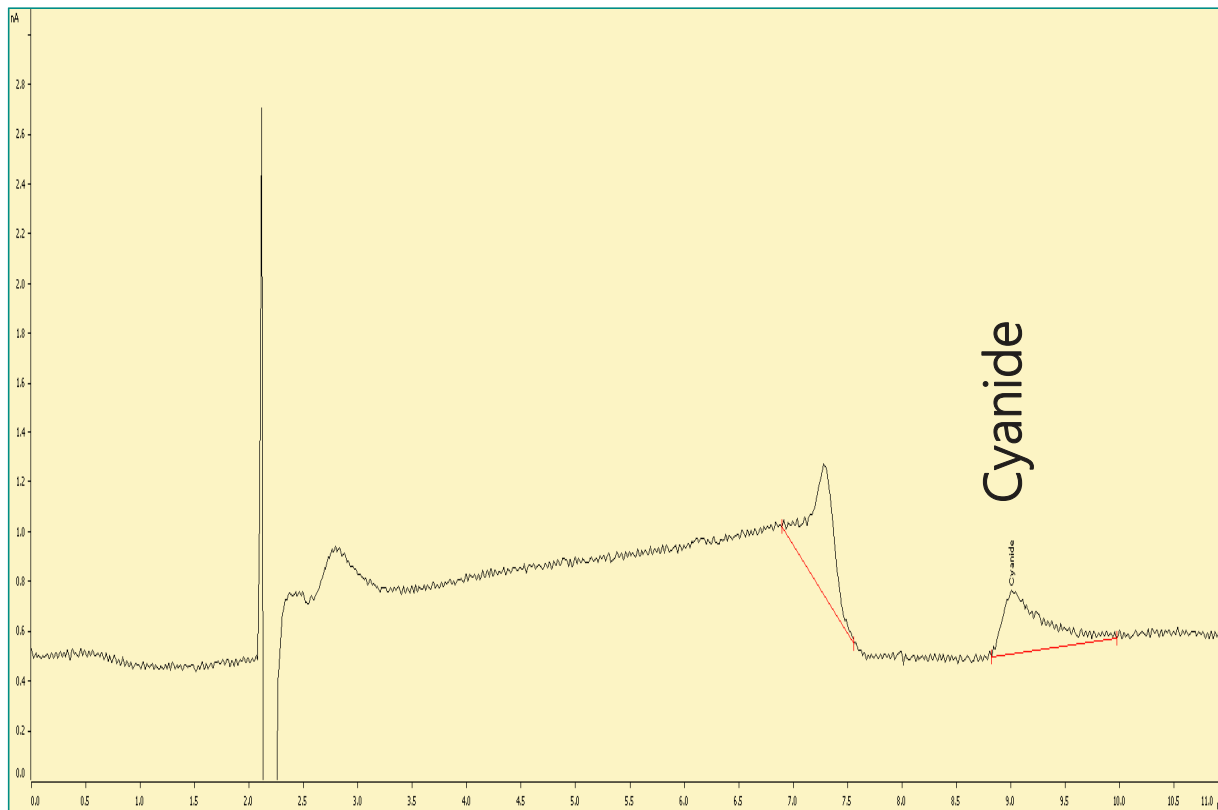
Positioning of electrodes in the cell



ASTM D2036 A – Cyanide Standard

Eluent flow	0.25 mls per minute
Eluent	100mM NaOH + 0.01mM EDTA
Column	ASUPP10-100 (2mm)
Column temperature	45 Deg.C
Sample volume	10 μ L
Detector	Amperometric (Ag WE)

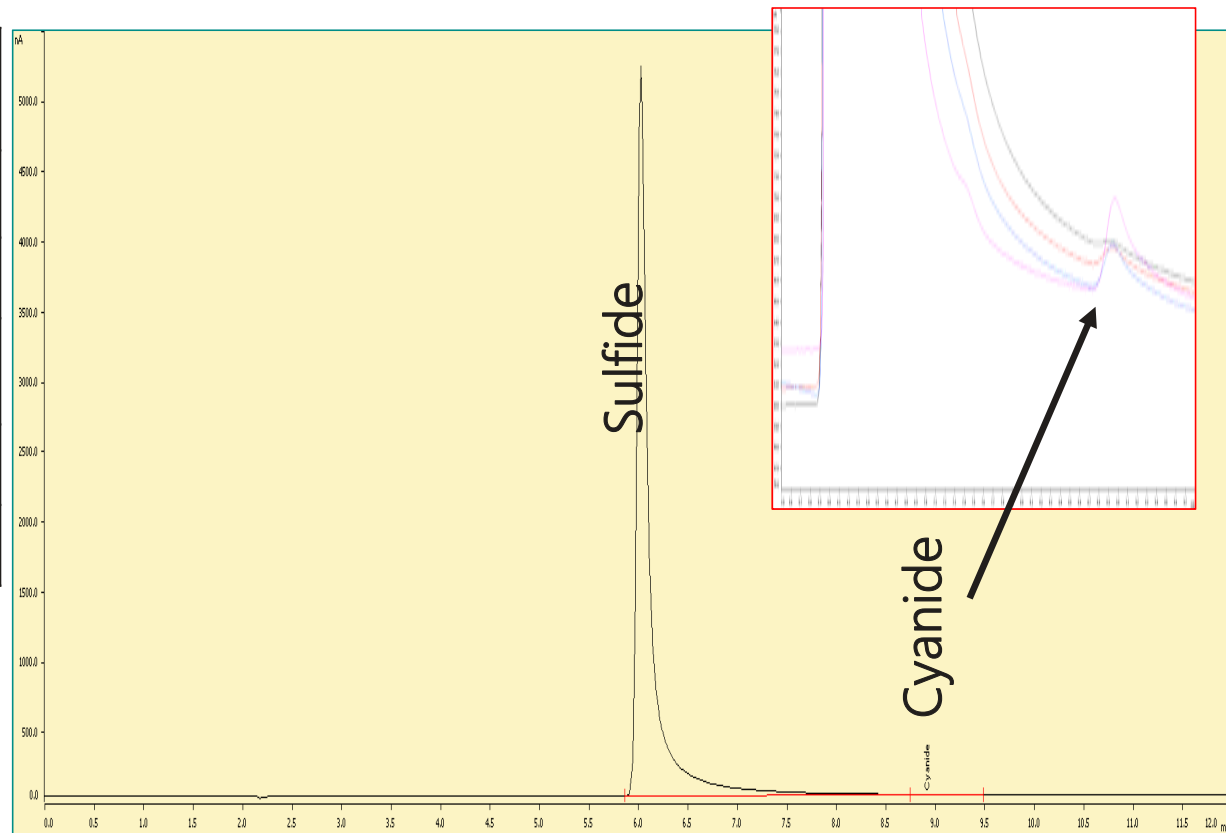
Component Name	Retention Time, mins	Concentration, μ g/L
Sulfide		
Cyanide	10	1



ASTM D2036 A – Cyanide with Sulfide Matrix

Eluent flow	0.25 mls per minute
Eluent	100mM NaOH + 0.01mM EDTA
Column	ASUPP10-100 (2mm)
Column temperature	45 Deg.C
Sample volume	10 μ L
Detector	Amperometric (Ag WE)

Component Name	Retention Time, mins	Concentration, μ g/L
Sulfide	6.0	20,000
Cyanide	10	2 - 20



Summary

- Ion Chromatography is better choice for the analysis of Cyanide in various matrices because
 - Chromatographically separates out Cyanide from interferences
 - Complete “Green Chemistry” approach as it eliminates toxic, hazardous chemicals like Pyridine
 - Larger linear dynamic range for calibration
 - More stable and rugged instrument calibration

Q&A

Thank You