

Total Cyanide may not always be free, but it is often available – cyanide methods and interferences

William Lipps
Analytical & Measuring Instrument Division
August, 2017

Regurgitated



Contents

Fundamental CN Chemistry

Sampling and Sample Preservation

Methods and Interferences

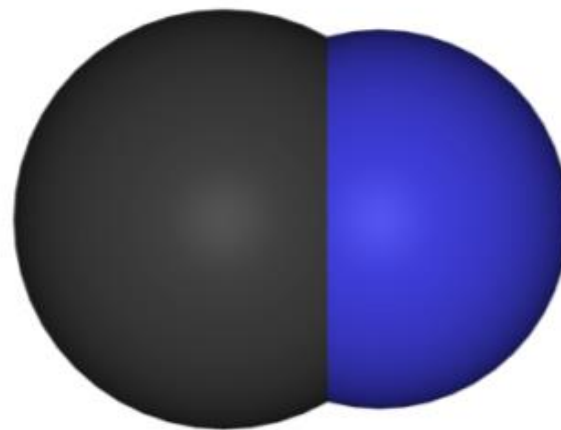
Conclusion

Contents

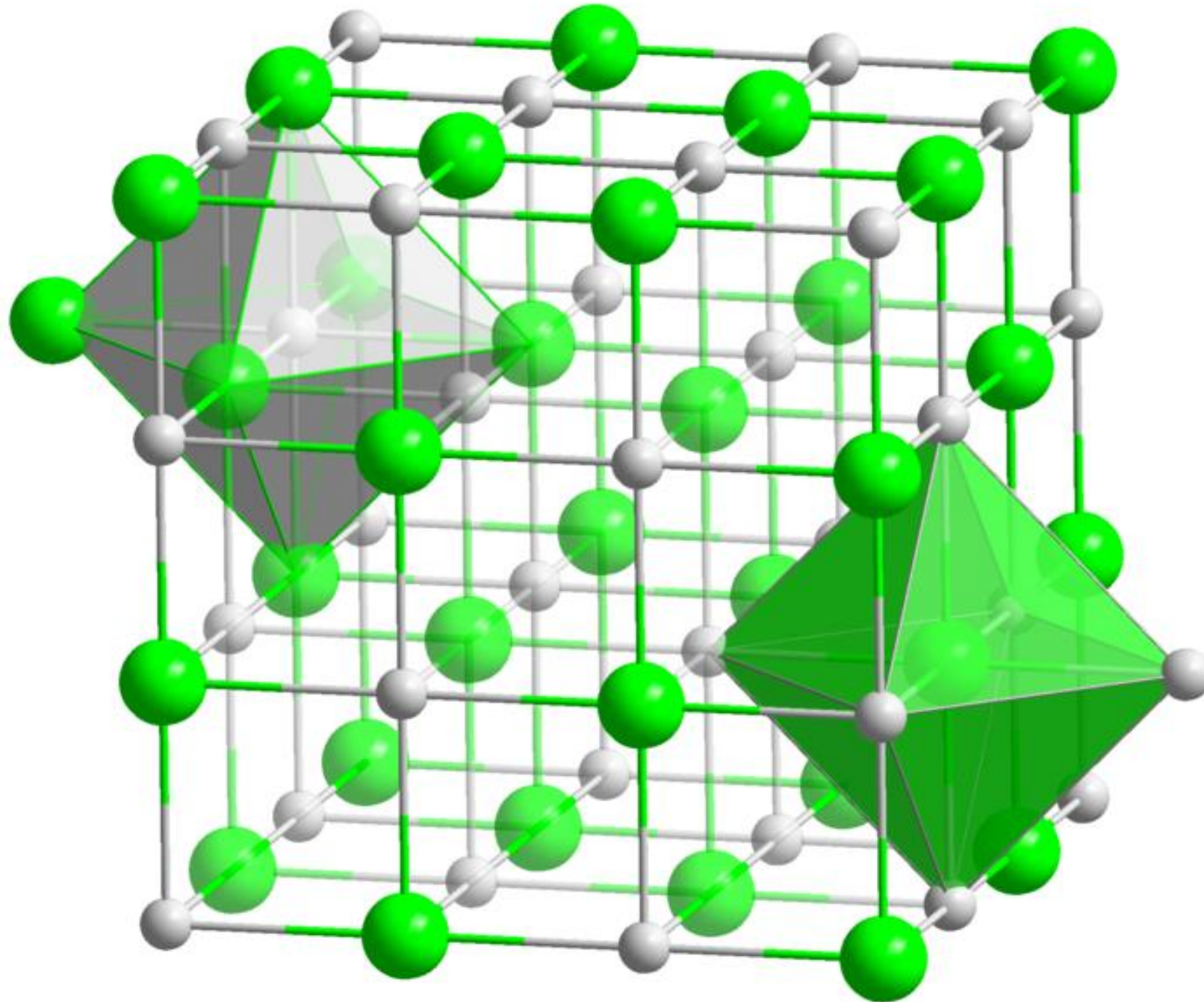
Fundamental CN Chemistry

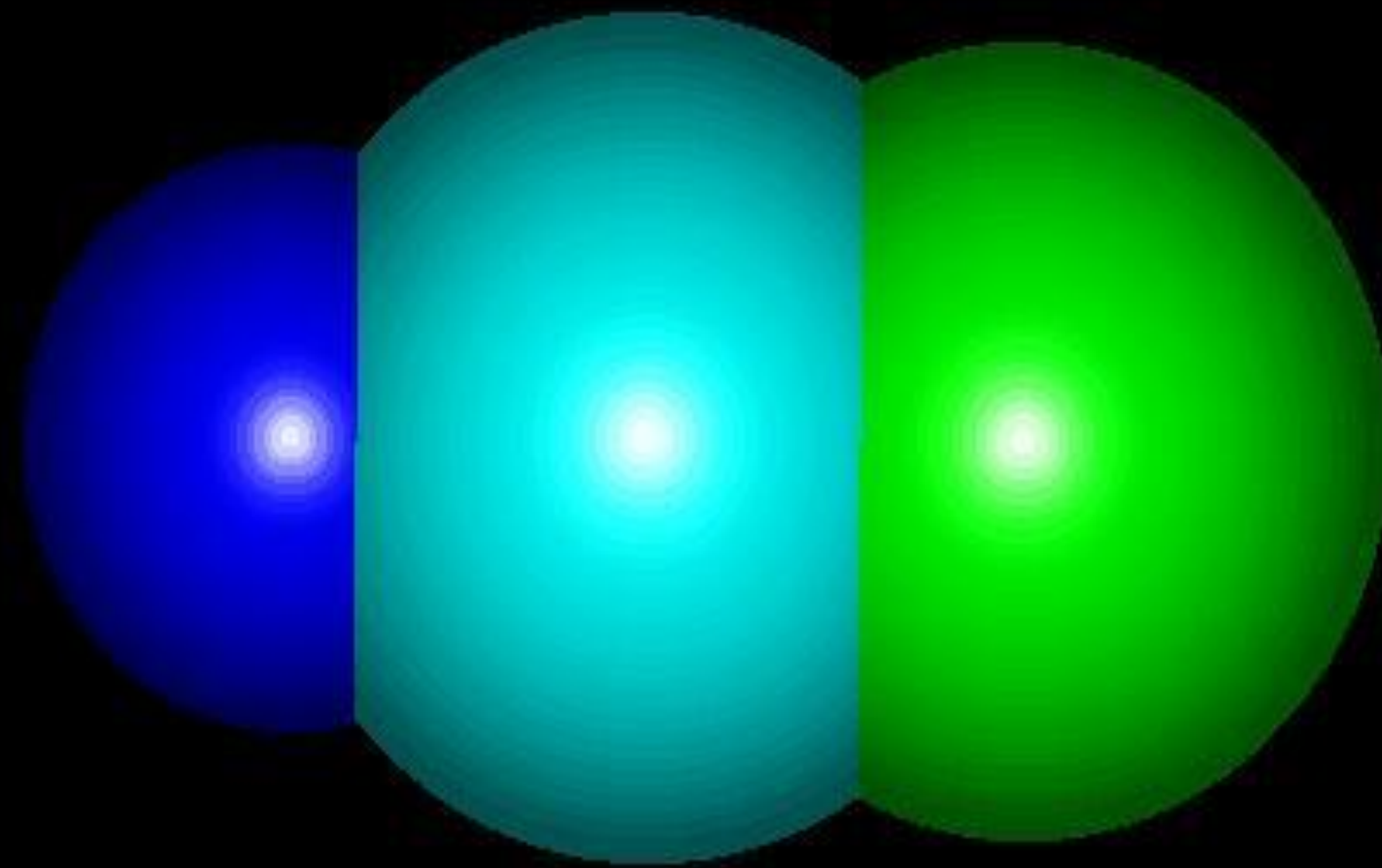
A generalized summary of cyanide and its metal – cyanide species

- **Transition metals - strong bonds**
- **Alkali metals - ionic bonds**



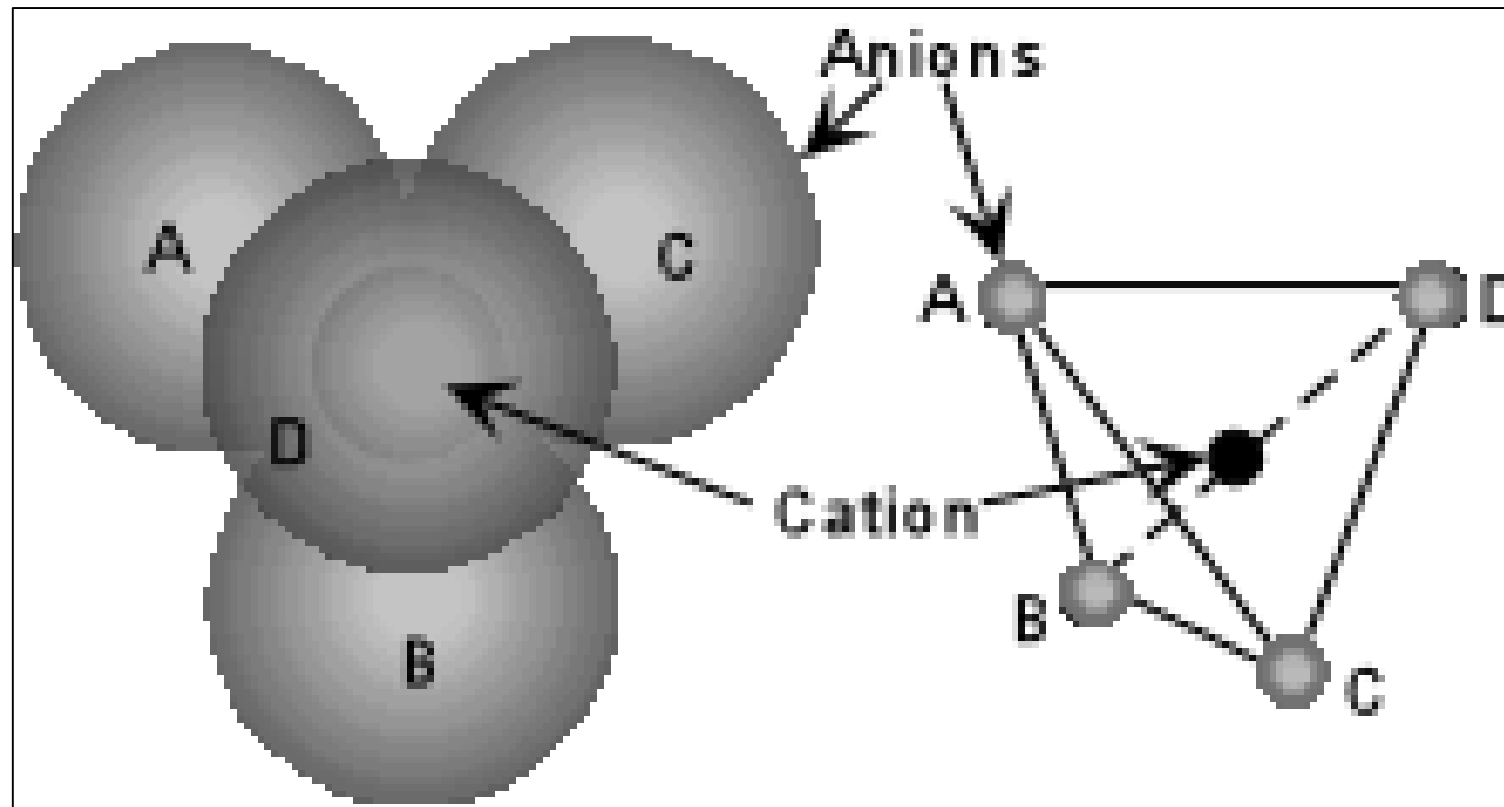
Alkali and alkaline earth metals form water soluble salts with the cyanide anion





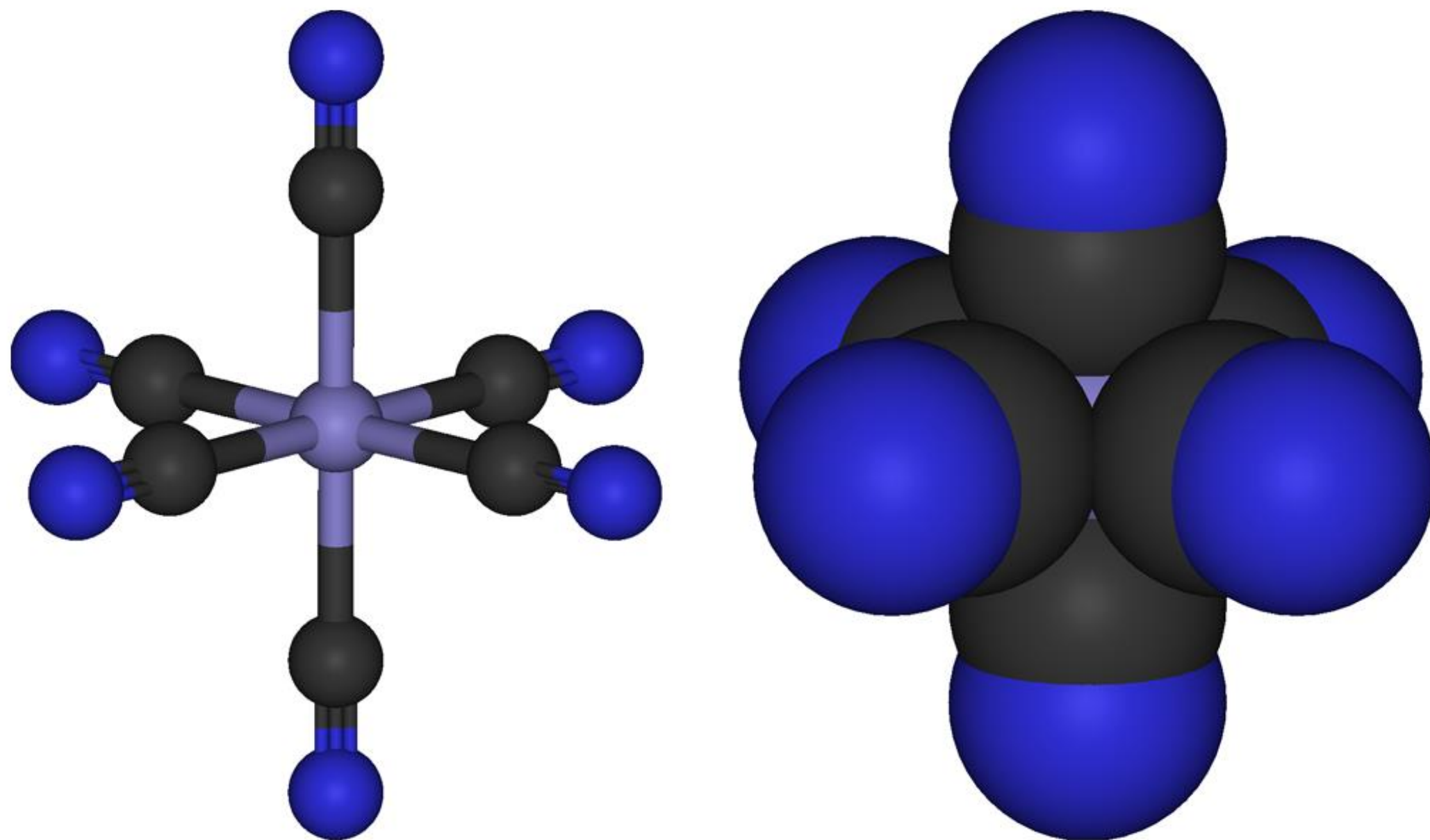
Get your Free CN here

A tetragonal coordination complex anion with CN ligands

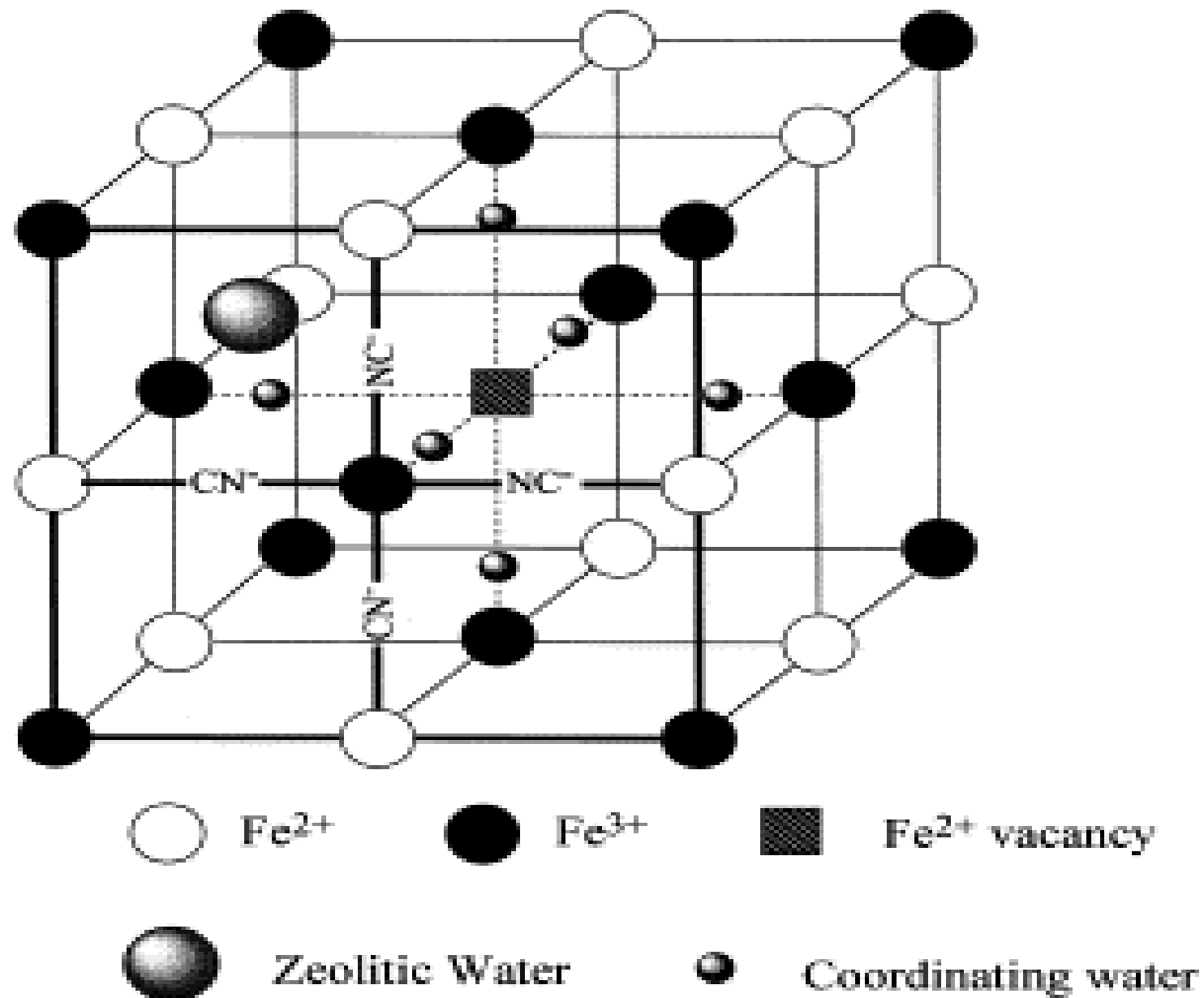


Zn, Cd, Cu, Ni, Hg

Iron and Cobalt CN are hexagonal coordination complexes with CN ligands



If a metal-cyanide complex forms a salt with a transition metal it is not soluble



Bonds between the metal and cyanide are moderate to strong

$[\text{Hg}(\text{CN})_4]^{-2}$	Weak
$[\text{Cd}(\text{CN})_4]^{-2}$	
$[\text{Zn}(\text{CN})_4]^{-2}$	
$[\text{Ag}(\text{CN})_2]^{-}$	
$[\text{Cu}(\text{CN})_4]^{-3}$	Moderate
$[\text{Ni}(\text{CN})_4]^{-2}$	
$\text{Hg}(\text{CN})_2$	
$[\text{Fe}(\text{CN})_6]^{-4}$	Strong
$[\text{Fe}(\text{CN})_6]^{-3}$	
$[\text{Co}(\text{CN})_6]^{-3}$	



Cyanide methods measure the various cyanide “species” dissolved in water

Total Cyanide

Fe

Co

Available Cyanide

Ag

Hg

Ni

Cu

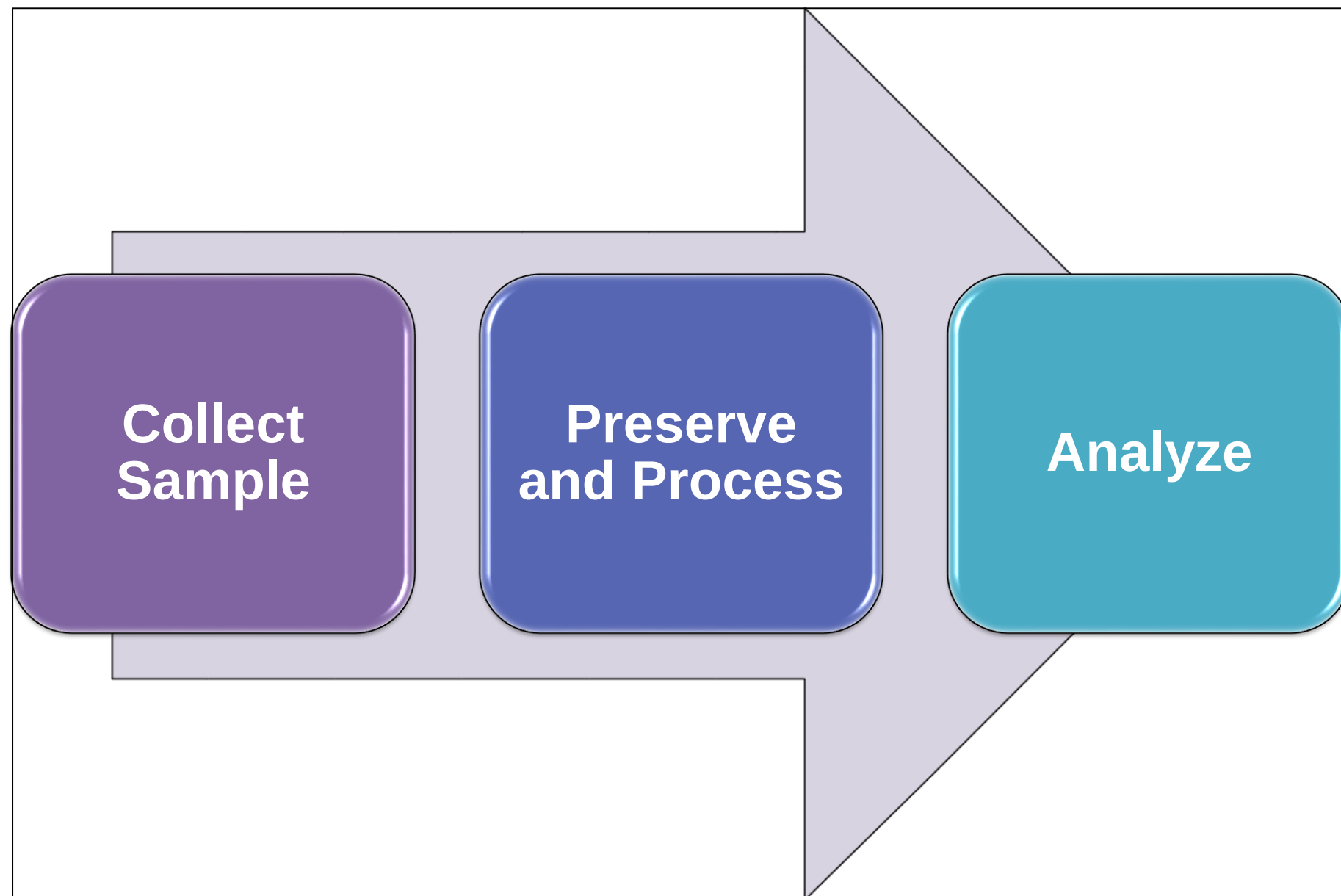
Zn

Cd

Free Cyanide

CN⁻

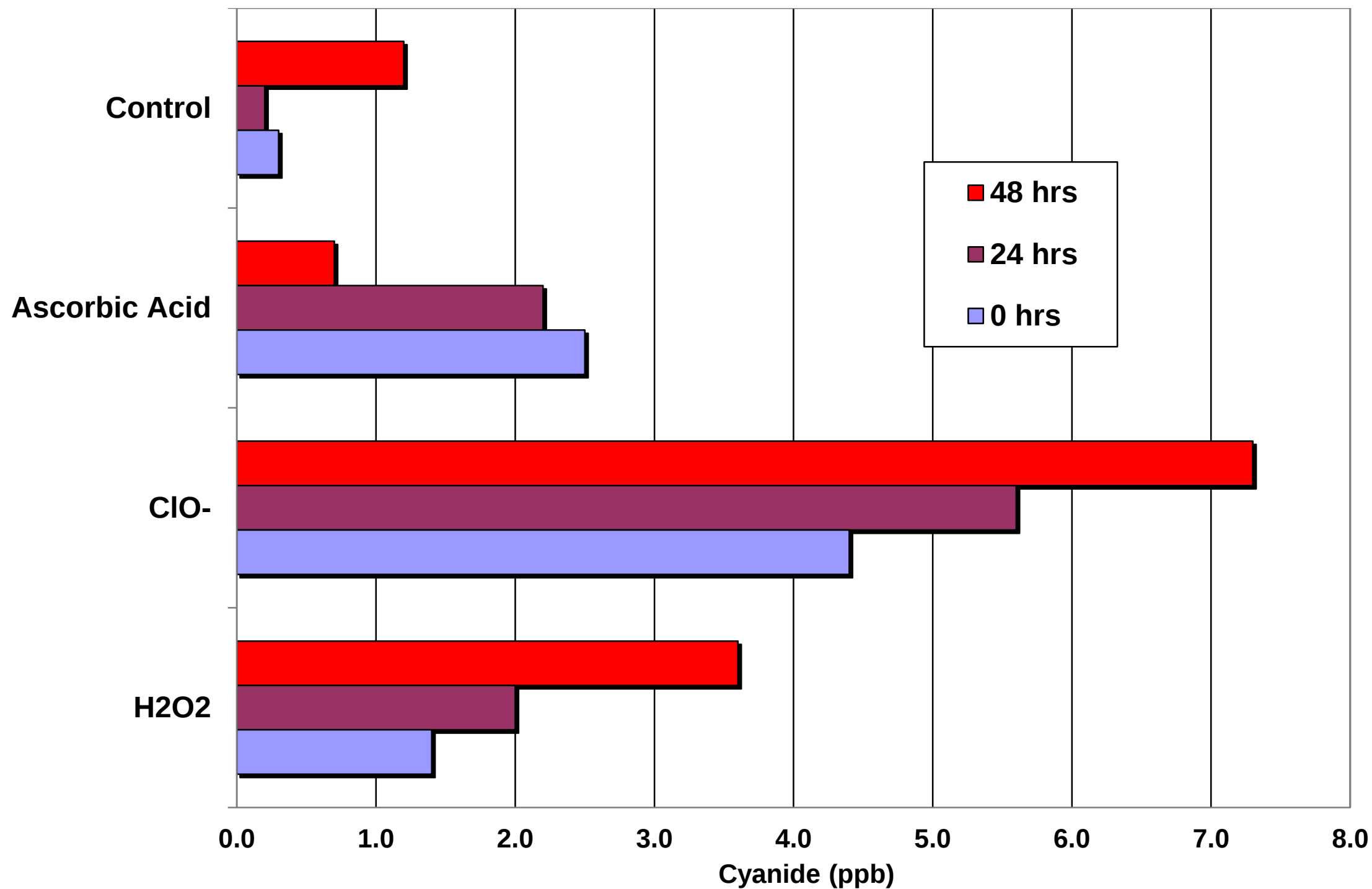
HCN



Contents

Sampling and Sample Preservation

Cyanide formation after preservation at pH 12



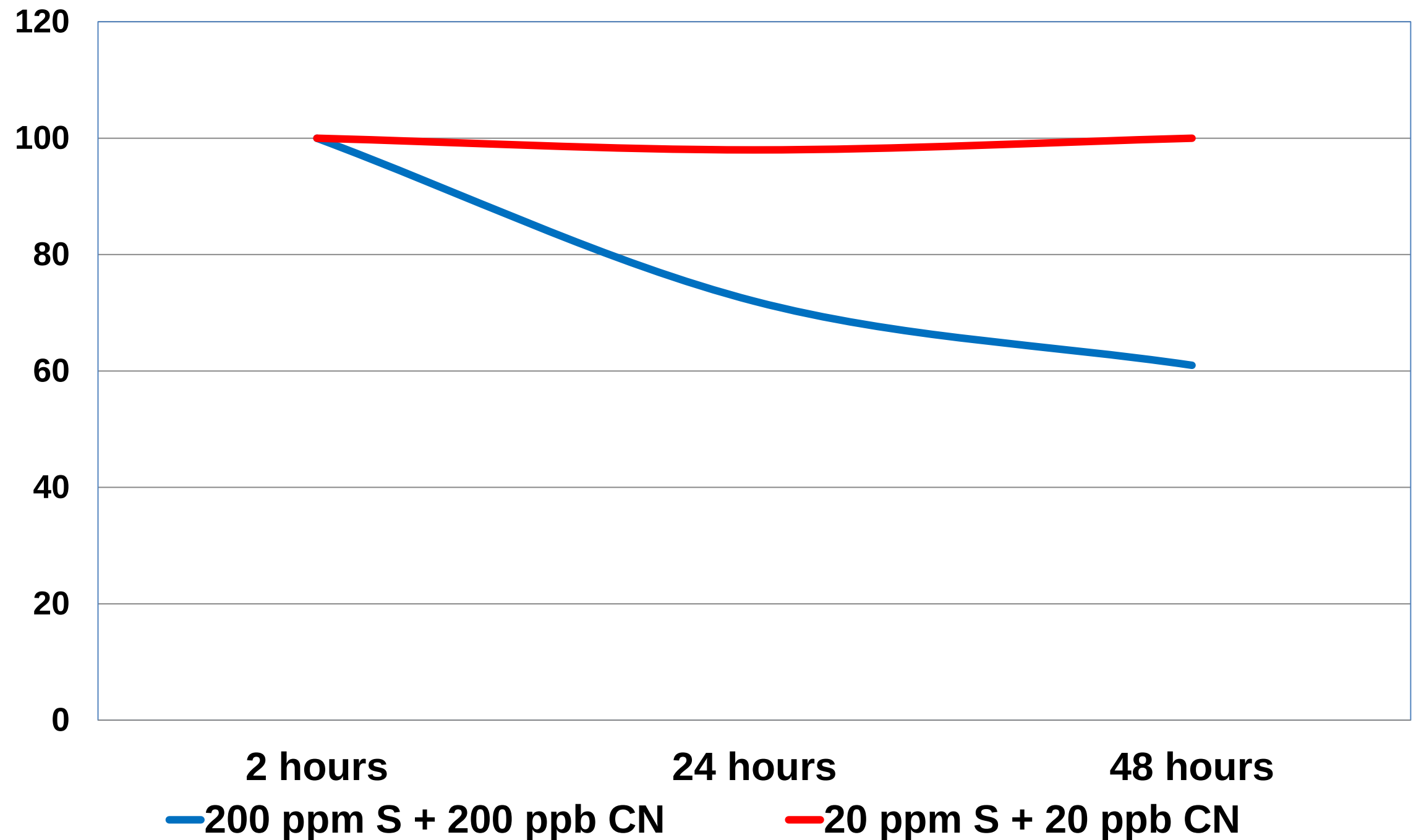
Store samples at 2 – 6 °C in the dark at pH 11



Sulfide reacts with free cyanide lowering its concentration

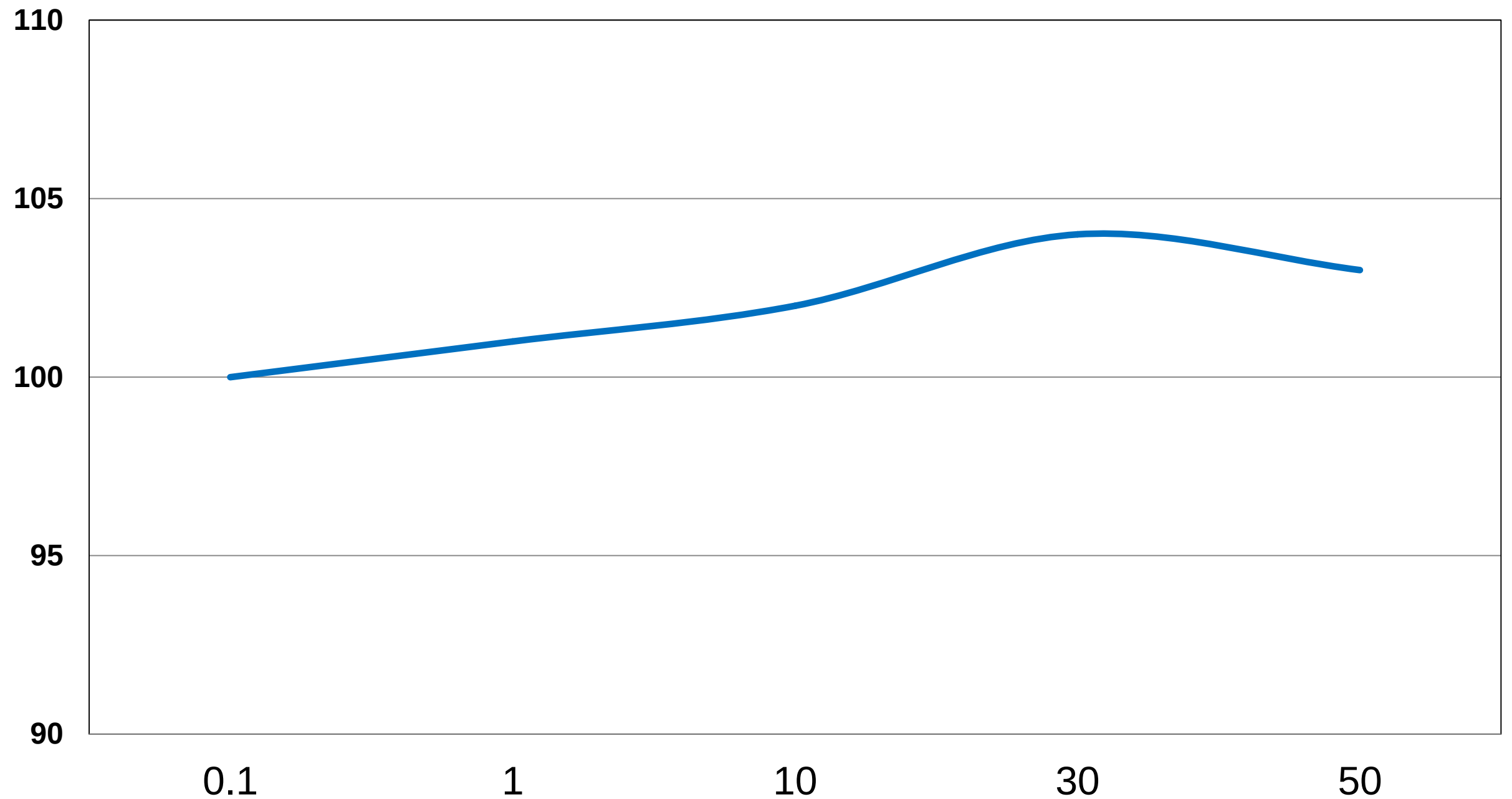


Holding Time Study – Sulfide Bearing Samples



Recovery of 100 ppb CN in up to 50 ppm Sulfide using on-line sulfide abatement

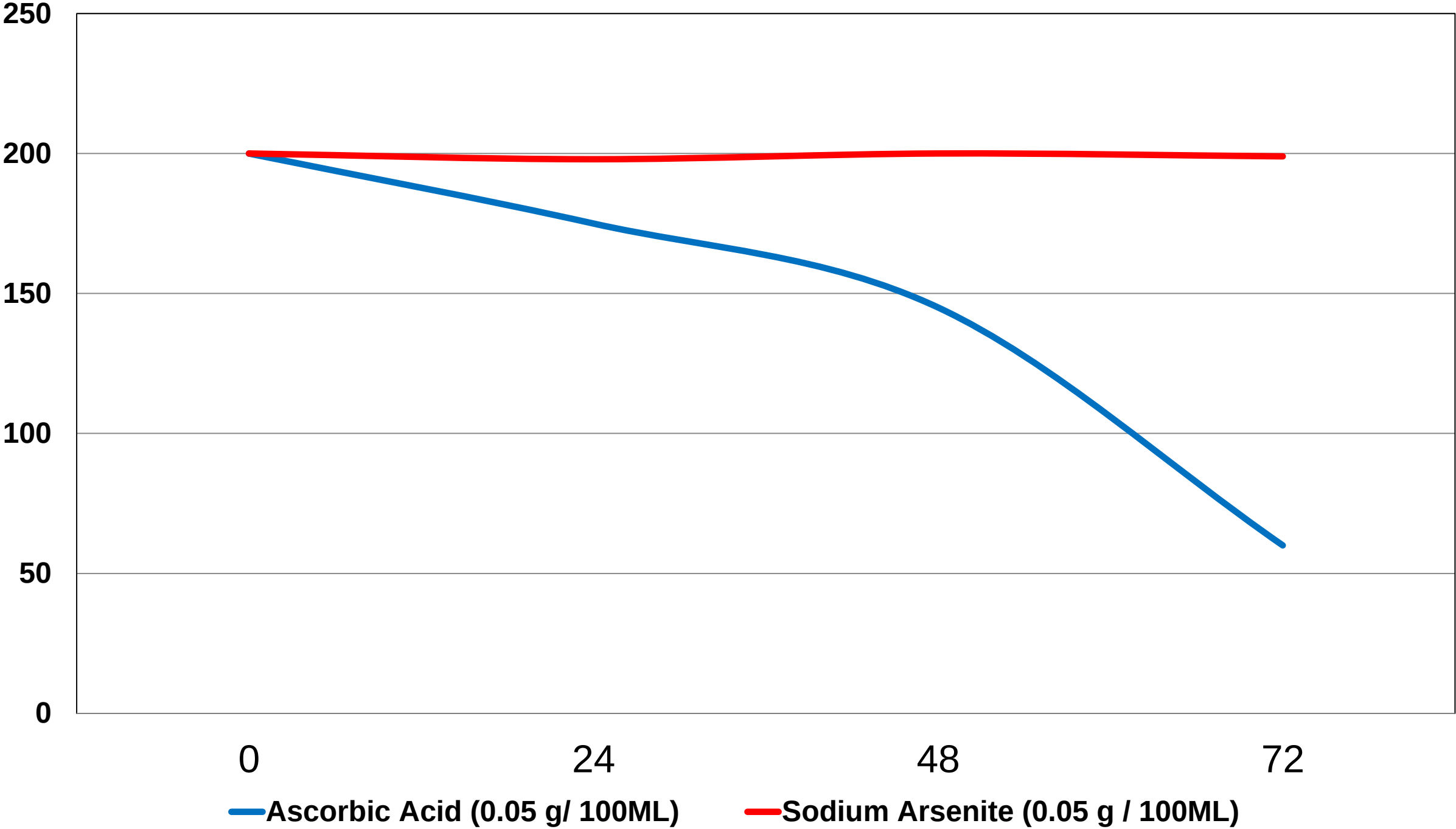
Recovery



Oxidizers react with free cyanide lowering its concentration



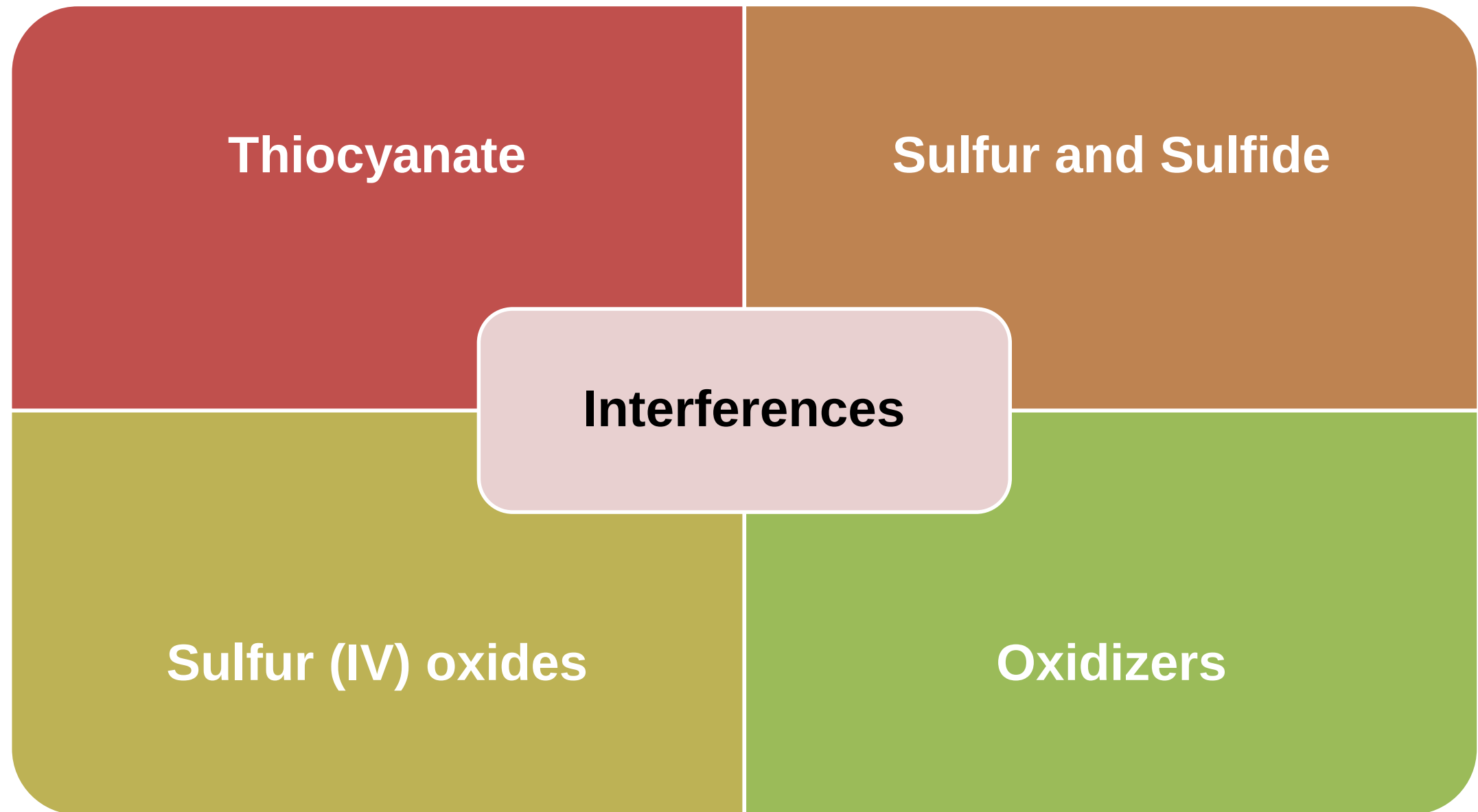
Loss of 200 ppb CN due to ascorbic acid addition



Contents

Methods and Interferences

These compounds are in almost every sample and interfere significantly

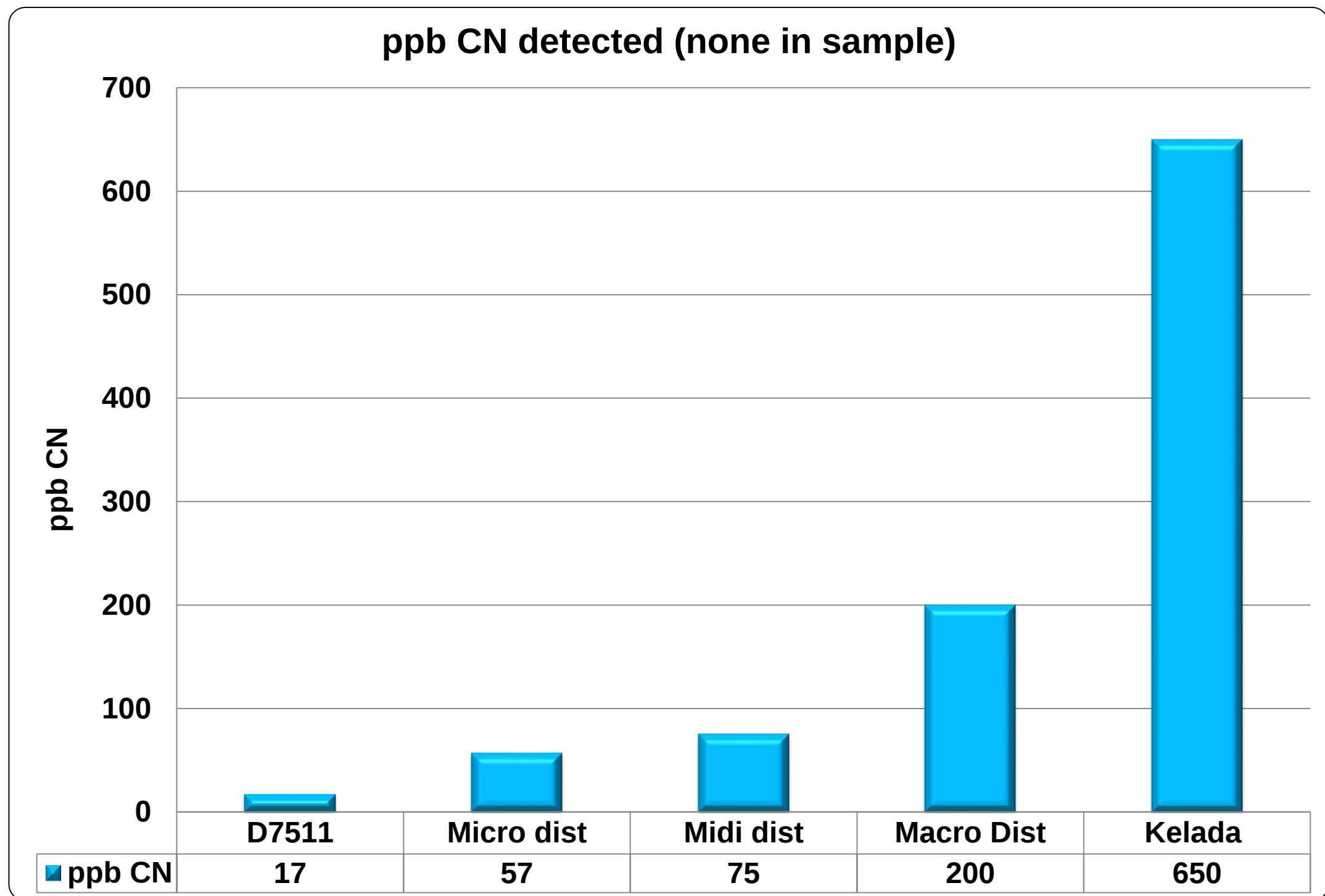


Thiocyanate

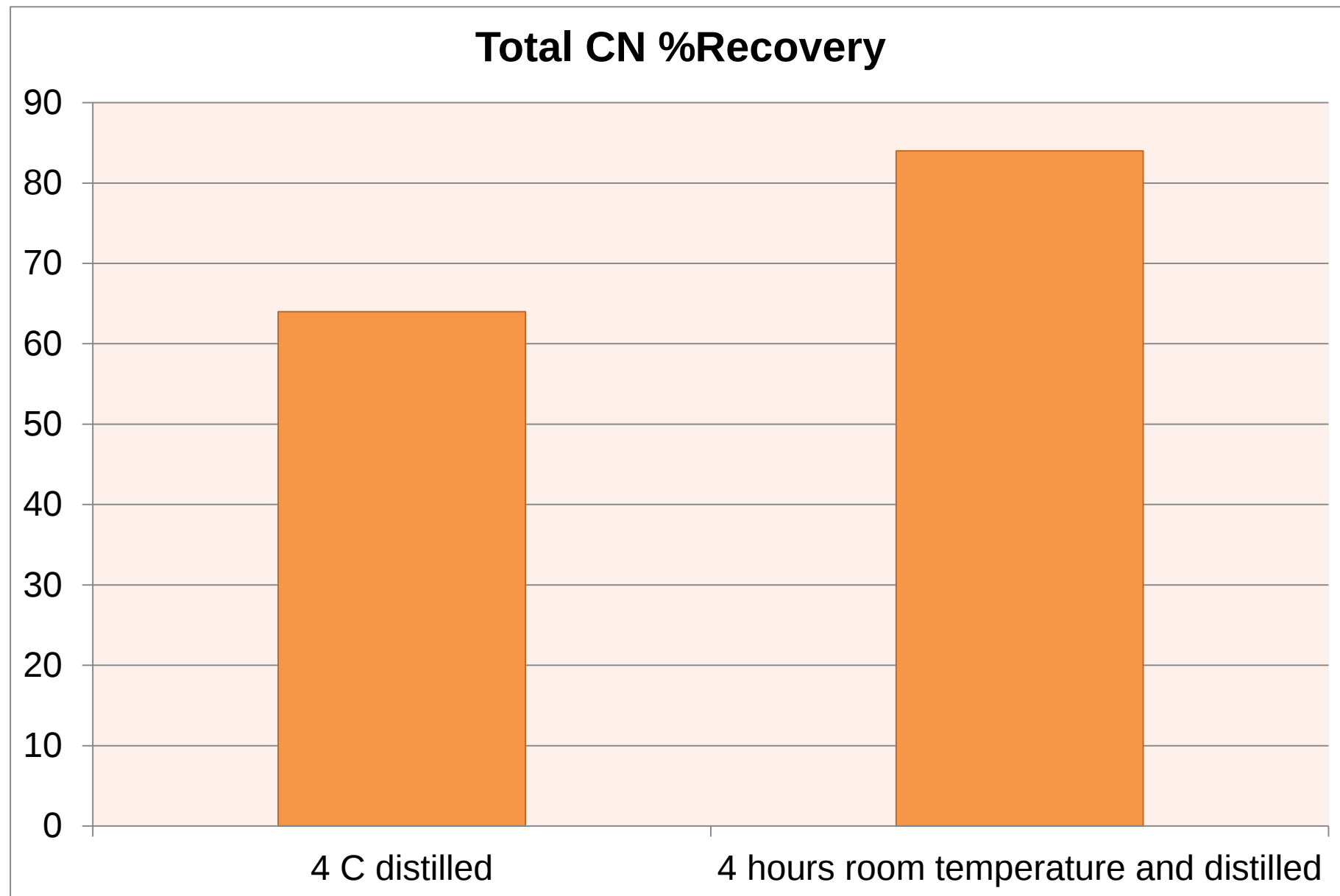
Destroy CN

Create CN

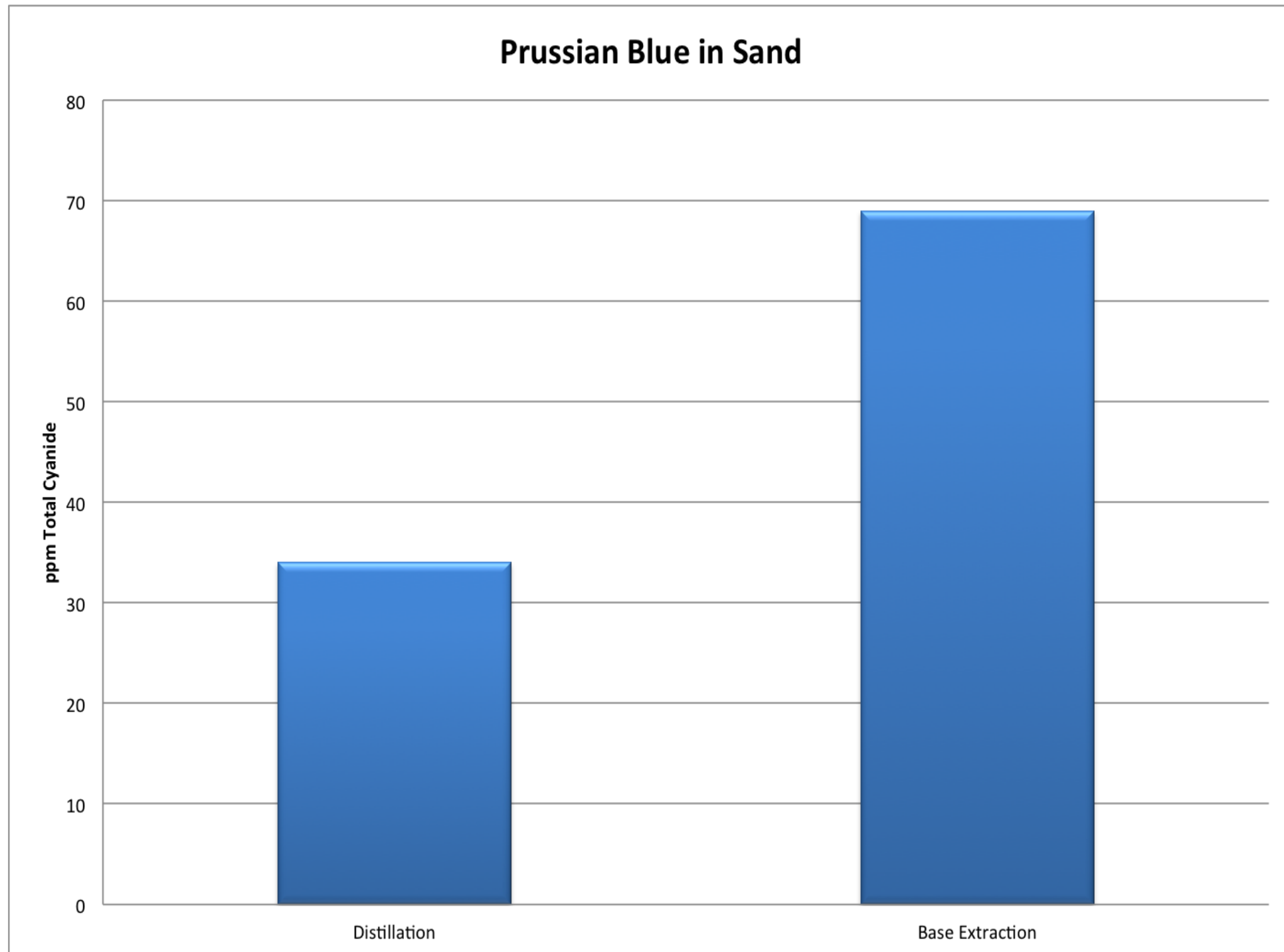
Recovery of CN from the ASTM “challenge matrix”



Recovery of Prussian Blue (particulate) Cyanide by distillation



Recovery of Prussian Blue from sand - distilled or extracted

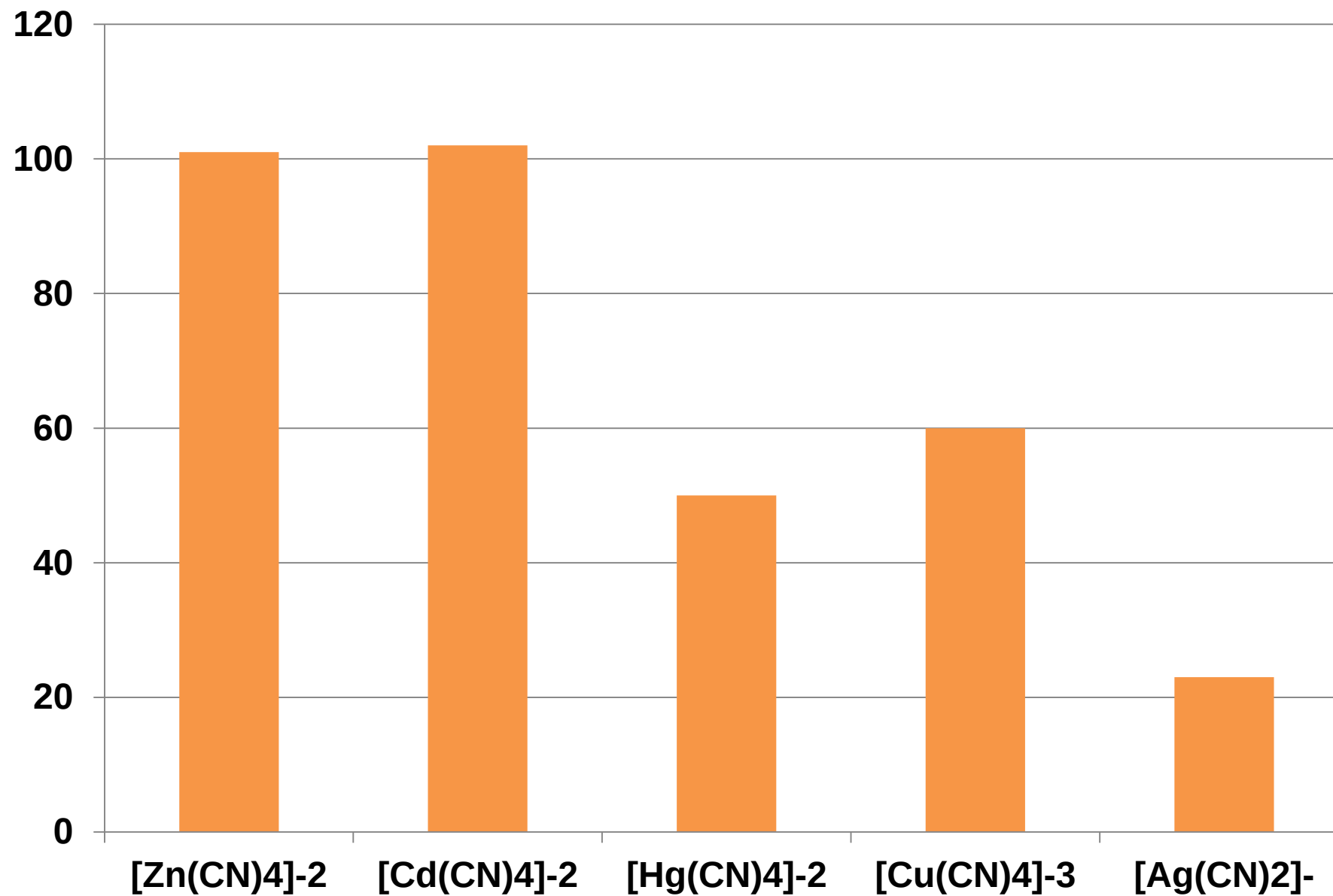


Free Cyanide Analysis

Method Number	Description	Measurement
ASTM D 4282	Micro-diffusion at pH 6	Colorimetry
ASTM D 7237	Auto-diffusion at pH 6	Amperometry
OIA-1677-09*	Auto-diffusion at pH < 2	Amperometry

*** Use if sulfide is present**

Recovery of metal-cyanide complexes by ASTM D7237



Available Cyanide Analysis

Amenable Cyanide—CATC methods measure “available cyanide”

Method Number	Description	Measurement
SM 4500-CN G	Alkaline Chlorination/ Manual Distillation	Colorimetry
ASTM D 2036	Alkaline Chlorination/ Manual distillation	Colorimetry, Gas Diffusion - Amperometry

ASTM D7365 recommends using D6888

WAD Cyanide methods measure “available cyanide”

Method Number	Description	Measurement
SM 4500-CN I	Buffered pH 4.5 manual Distillation	Colorimetry
ASTM D 2036	Buffered pH 4.5 manual distillation	Colorimetry, Gas Diffusion - Amperometry

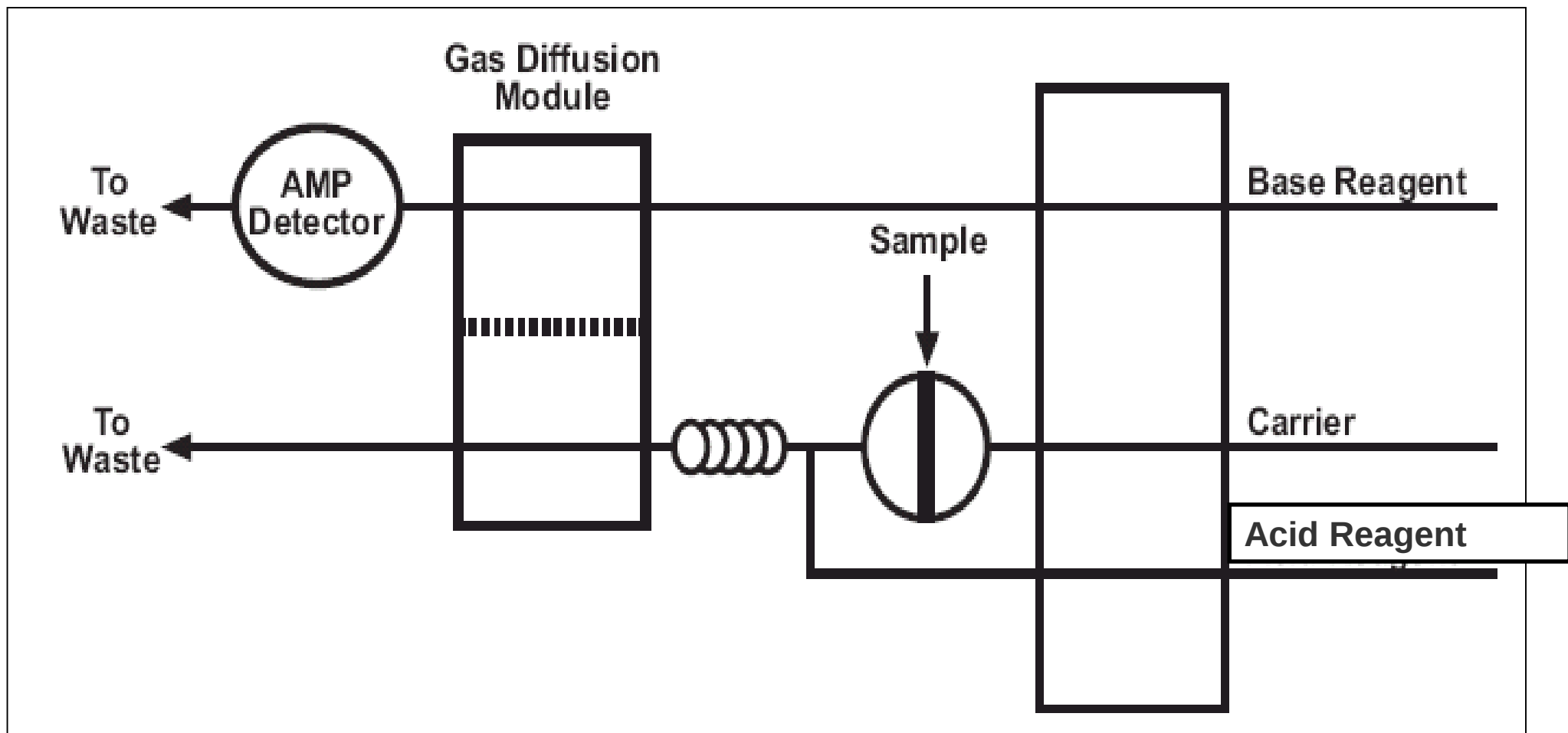
ASTM D7365 recommends using D6888

Ligand Exchange methods measure available cyanide

Method Number	Description	Measurement
OIA 1677	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry
ASTM D 6888	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry

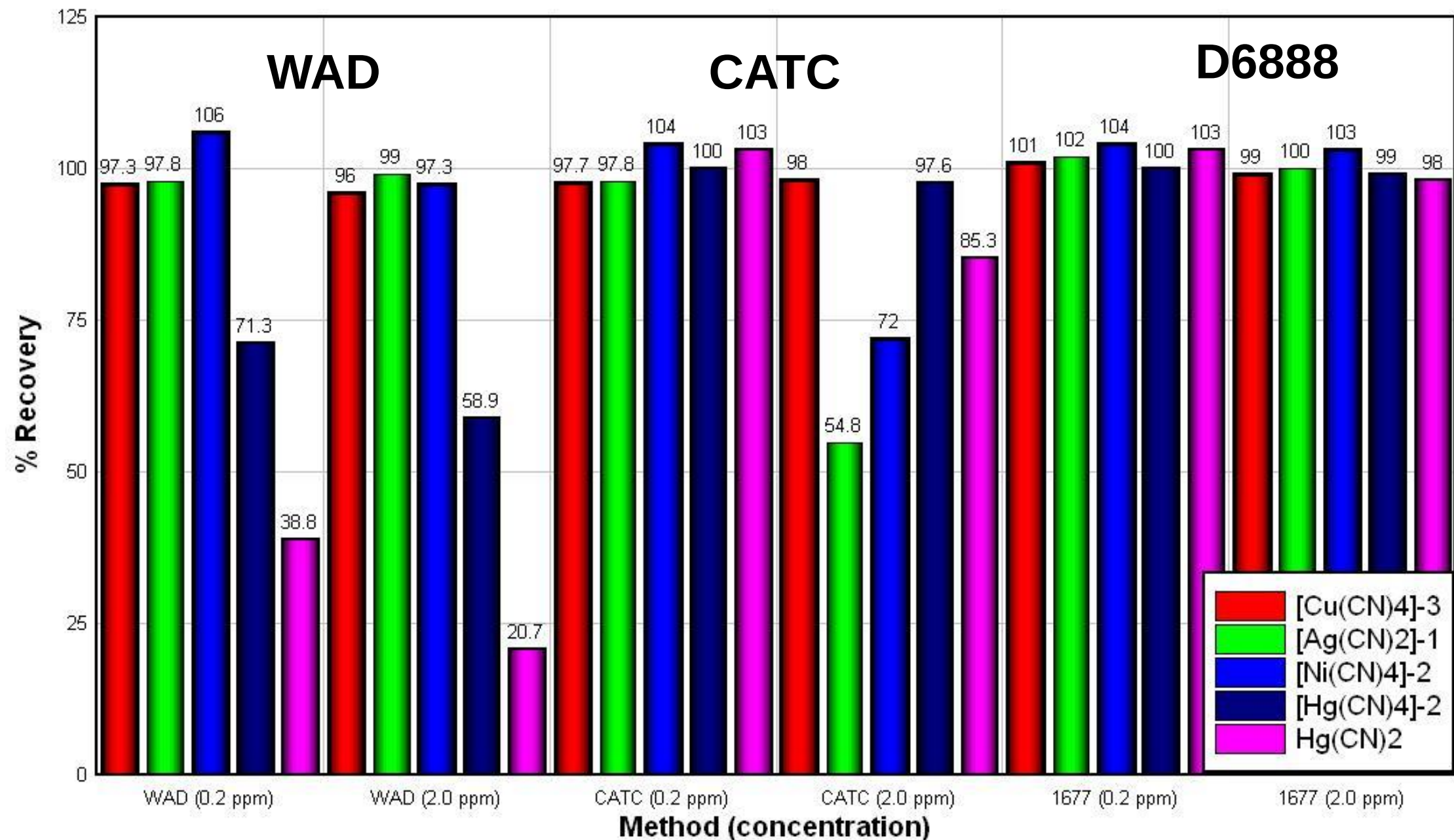
GD-amperometry methods do not require distillation

ASTM D6888 flow diagram

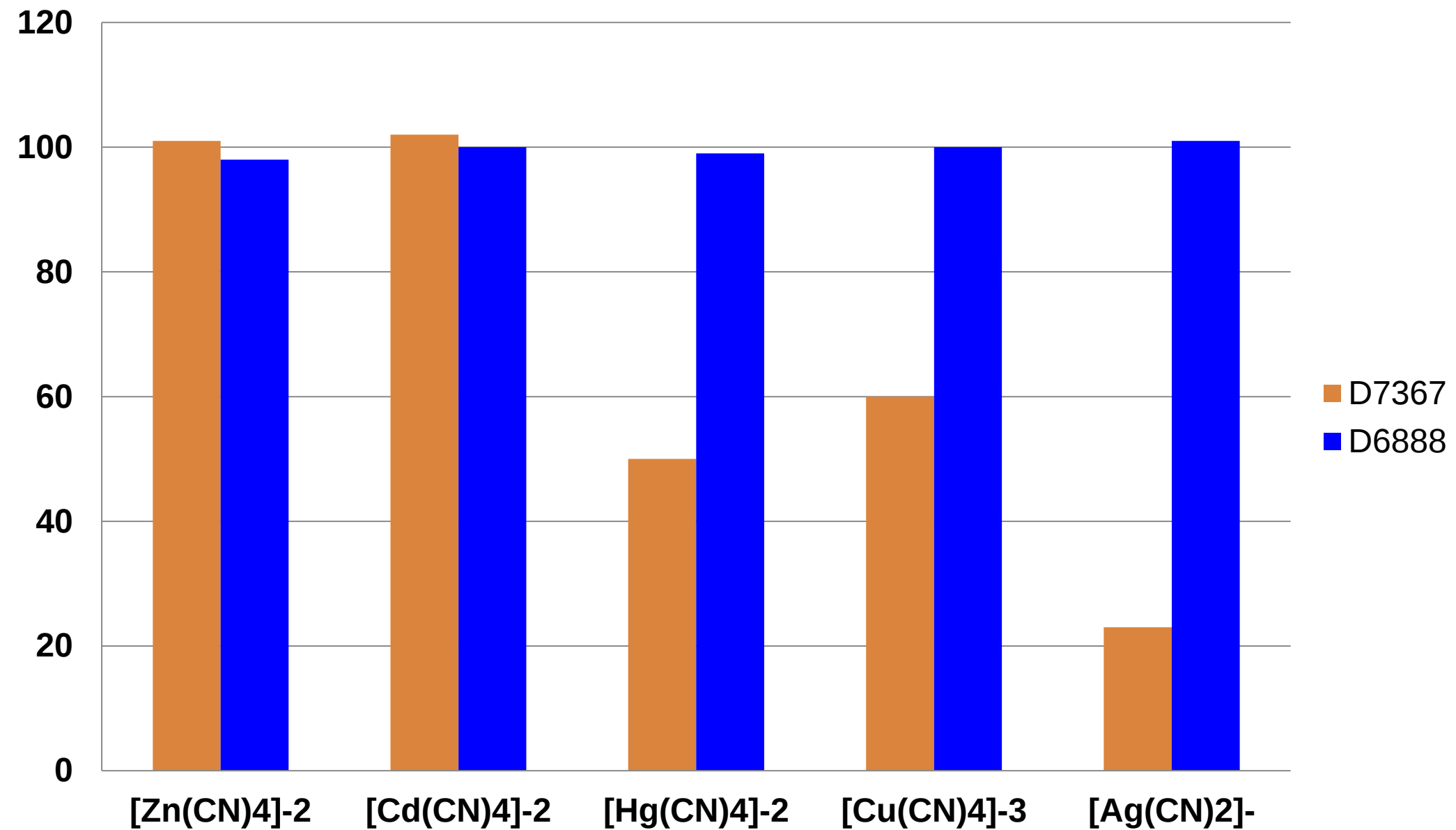


Ligand Exchange GD-amperometry methods get better recovery

Comparison of Recoveries by Available Cyanide Methods
Concentration Dependent Recovery by Cyanide Species



Recovery of metal-cyanide complexes by ASTM D7237 and D6888



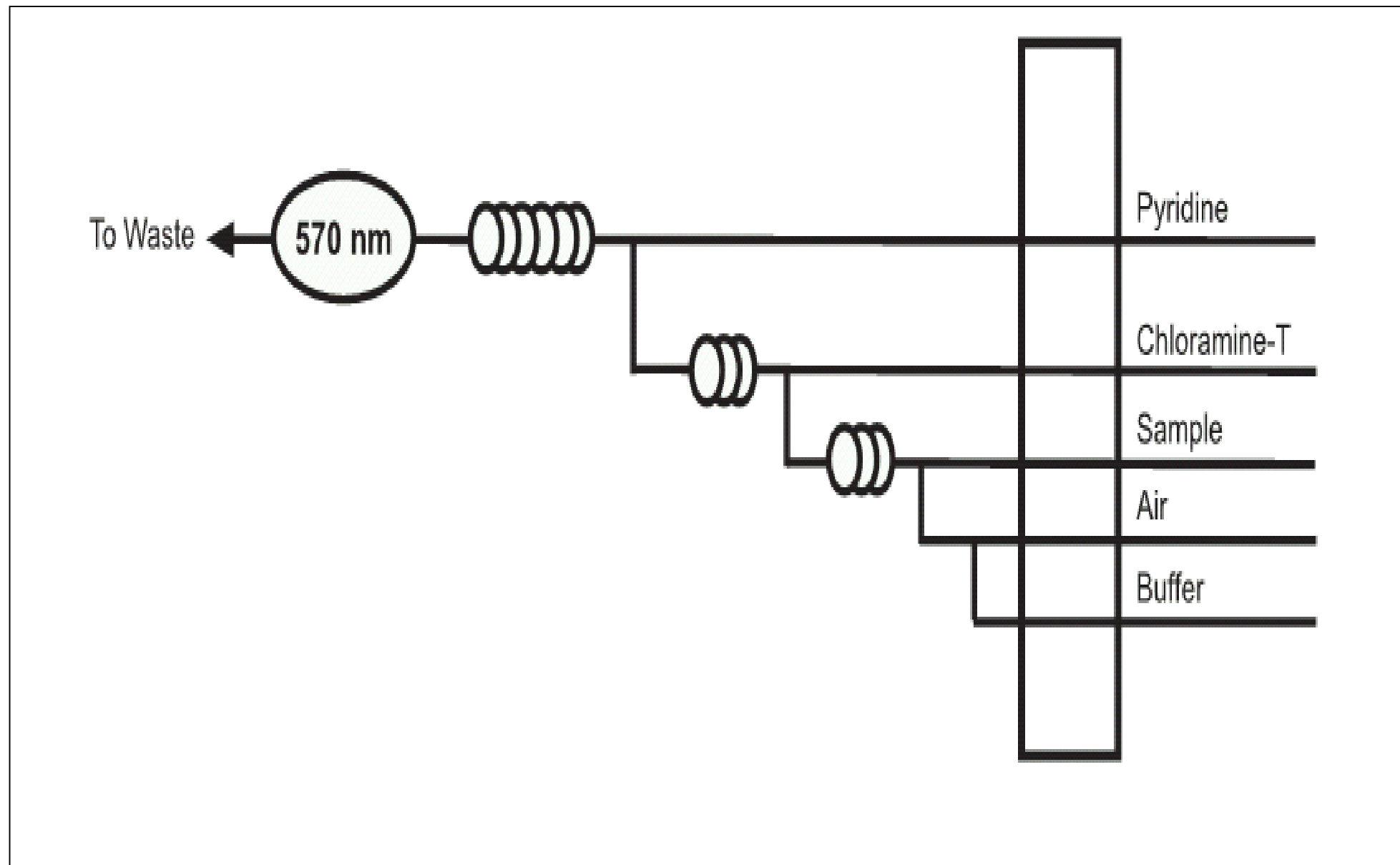
Total Cyanide Analysis

Manual Distillation Methods

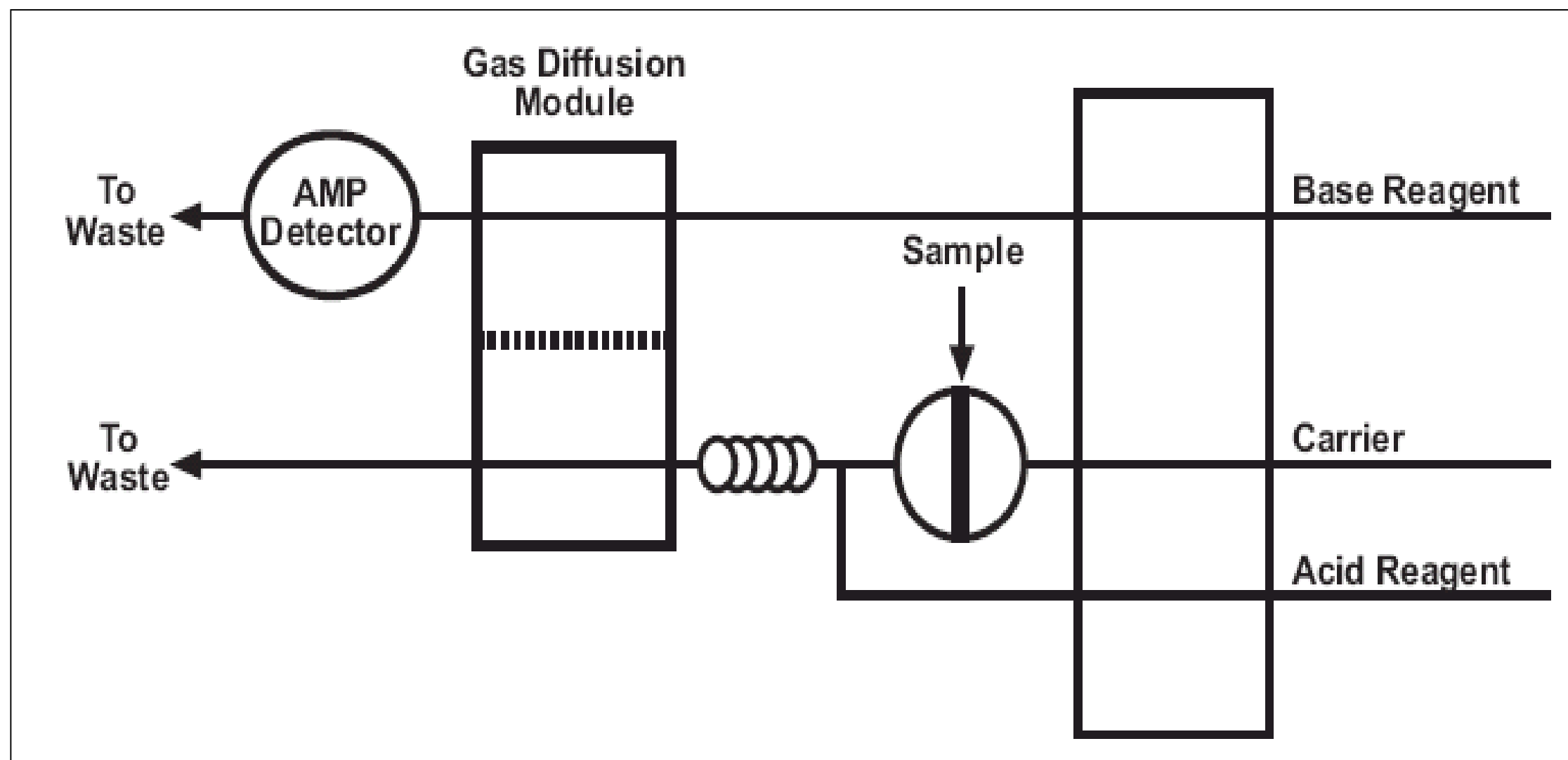
Total cyanide methods using manual distillation

Descriptive Name	Method Number	Description	Measurement
Total Cyanide	EPA 335.4	Midi Distillation – MgCl_2	Automated Colorimetry
	ASTM D2036	Midi / Micro/macro Distillation – MgCl_2	Colorimetry/ISE/amperometry/IC
	ASTM D 7284	Midi / Micro Distillation – MgCl_2	Gas Diffusion - Amperometry

Semi-automated colorimetric cyanide analysis flow diagram

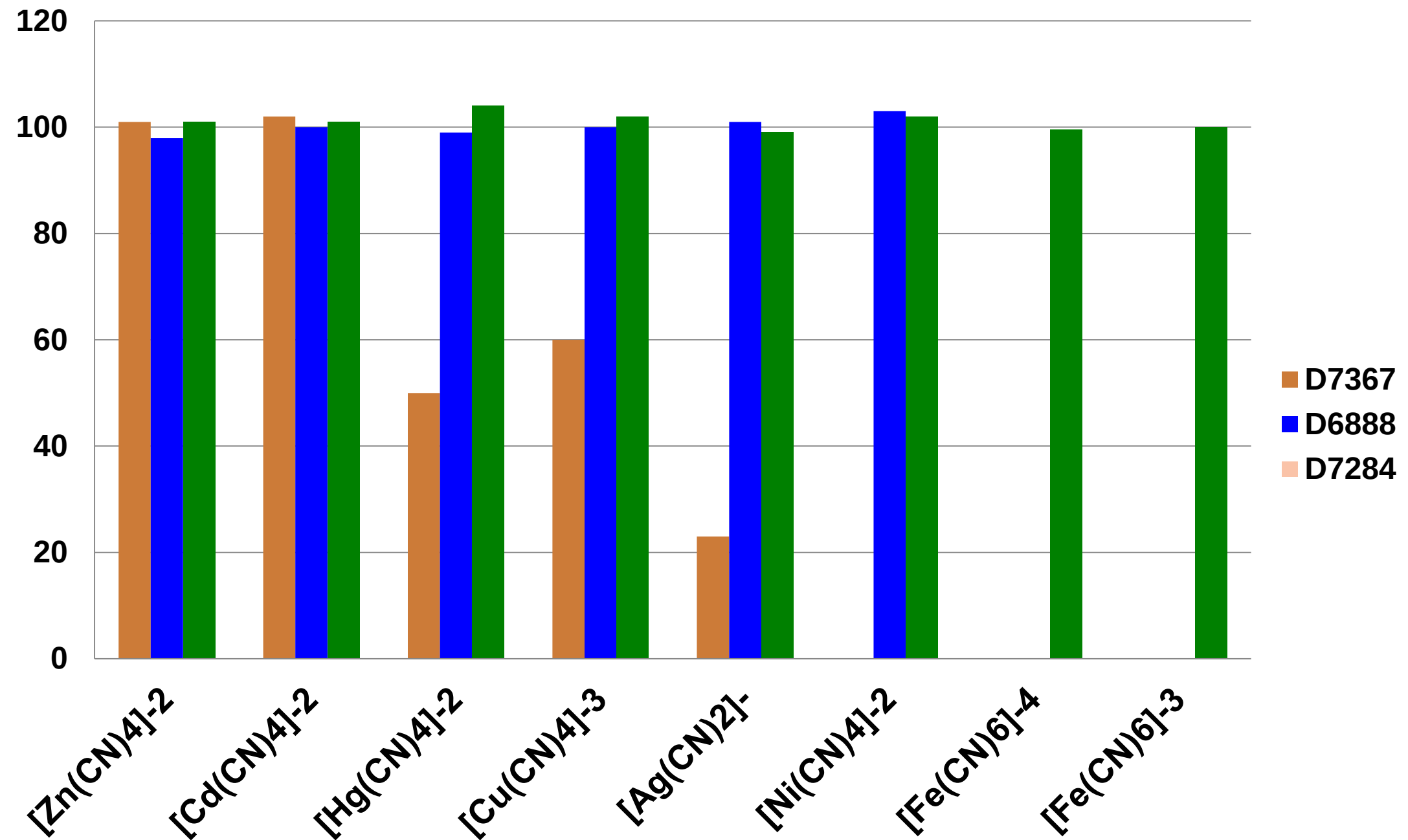


Semi-Automated GD-amperometric by ASTM D7284

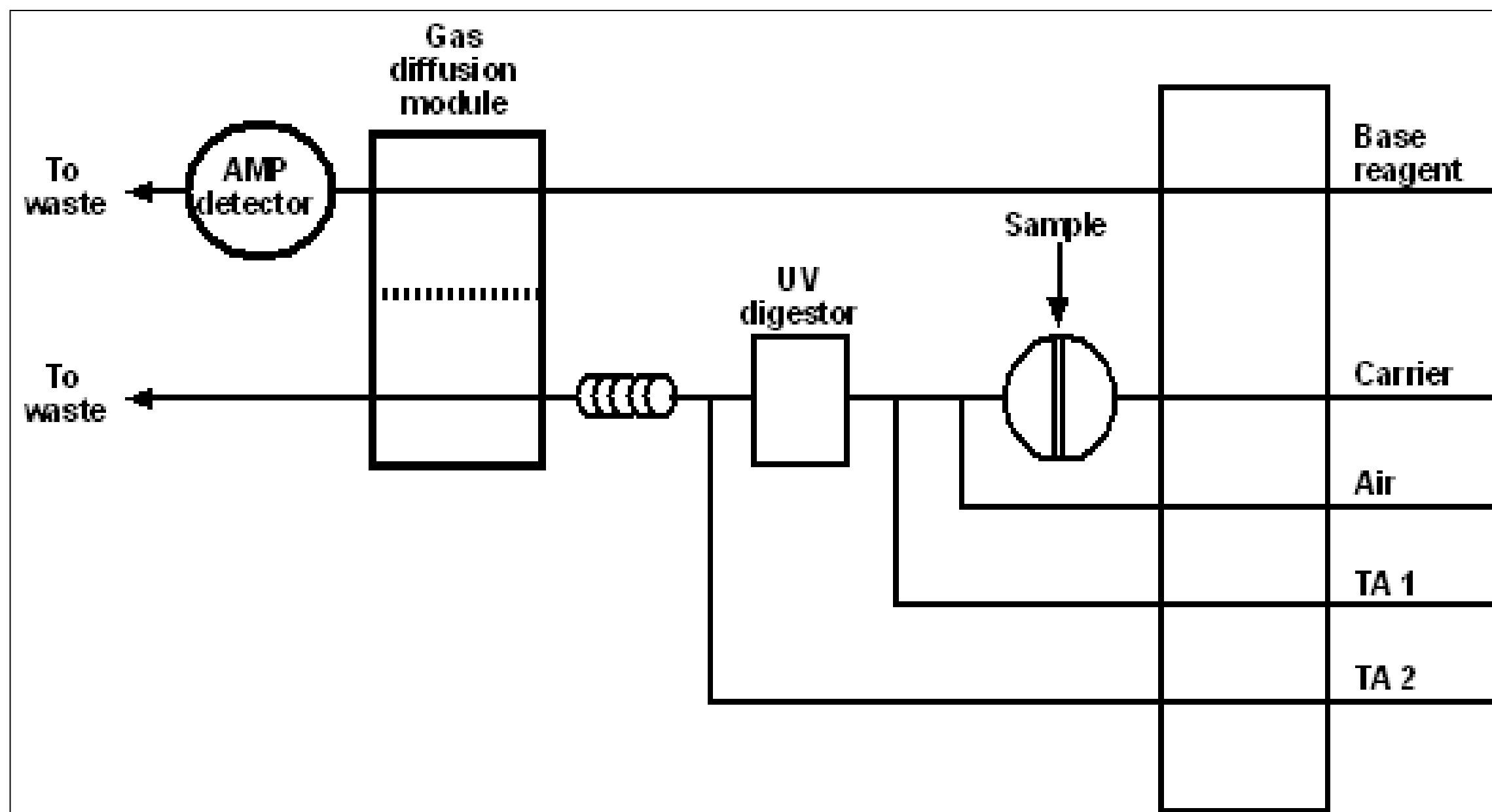


Same reagents as D6888 but no ligands

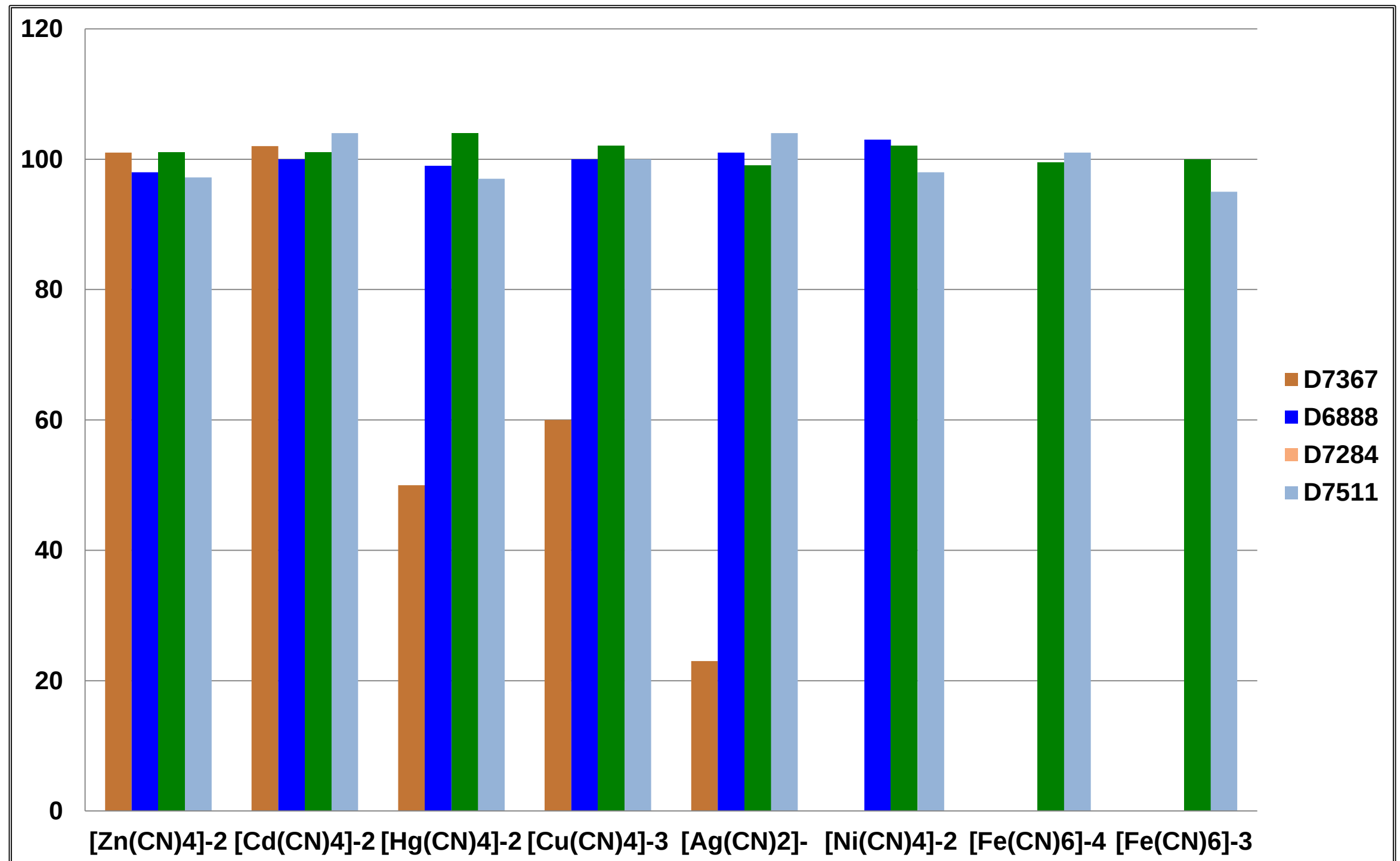
Recovery of metal-cyanide complexes by ASTM D7237, D6888 and D7284



FIA diagram of ASTM D7511



Recovery of metal-cyanide complexes by ASTM D7237, D6888, D7284 and D7511





Thank You

wclipps@shimadzu.com