Evaluation of Procedures and Controls Used in Chemical Challenge Respirator Test Methods

Using ClO2, Tear Gas, and Other Difficult Species

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Some Aspects of Chemical Challenge Agent Testing

- Difficult & Highly Specialized
  - Methods not taught in Schools
- Non-Standard Test Equipment
  - Custom-made Equipment is Prevalent
- Few Labs & Few Forums for Idea-Sharing
  - No Journals or Technical Meetings

Service Life Testing

with Chemical Challenge Agents

- As part of a small community (cult) of expert labs ...

we seek a dialogue leading to increased ...

Standardization of Procedures

Test Method Evaluation

Scientific approach …

- Seeks to analyze methods rather than blame people for differences in test results.
- Control of Test Parameters within Test Methods lead to control of Test Results.

Chemical Challenge Tests

Basic Test Parameters …

- Challenge Agent Conc’n (ppm)
- Flow Rates (L/min)
- Time of Test (min)
- Break-Through Conc’n (ppm)
- Air Conditioning (Temp & RH)
- Pre-Conditioning (Temp, RH, & Flow Rate)

Challenge Test Parameters

Some are ... Dependent on Challenge Agent ...

- Challenge Agent Conc'n (ppm)
- Flow Rates (L/min)
- Time of Test (min)
- Break-Through Conc'n (ppm)
- Air Conditioning (Temp & RH)
- Pre-Conditioning (Temp, RH, and Flow Rate)

Others are ... Independent of Challenge Agent ...

Difficult-to-Control Agents lead to Difficult Tests

Basic Test Parameters …

- Challenge Agent Conc'n (ppm)
  - Measurement
  - Control
- Break-Through Conc'n (ppm)
  - Measurement
  - Control

Estimated Variation
in Generating Challenge Agents

Type of Challenge Agent	***Estimated Test Variation***
Agent Concentration Control & Measurement	± 5 - 50 %
Stable, Compressed Gas	± 5 %
Stable, Volatile Liquid	± 10 %
Reactive Liquid	10-50% or more
Non-Volatile Liquid or Solid	10-50% or more

Issues that Lead to Testing Difficulty

Agents & Issues …

Agent	*Property*	*Leads to …*
Chlorine Dioxide	**Unstable**	**Impurities in challenge mix**
Hydrogen Cyanide (HCN)	**Boils at 26ºC**	**Difficult to Store & Handle** (It doesn't know if it is gas or liquid)
Cyanogen Chloride (CNCl) ("CK")	**Boils at 14ºC**	**Difficult to Store & Handle**
Tear Gases **CN** **CS**	**Low Vapor Pressure** (hardly boils at all)	**Aerosol formation & condensation affect results**

Chlorine Dioxide

Issues ...

- Chlorine Dioxide **(ClO_2)** is unstable
- **ClO_2** generated by passing **Cl_2** through a column of **$NaClO_2$**

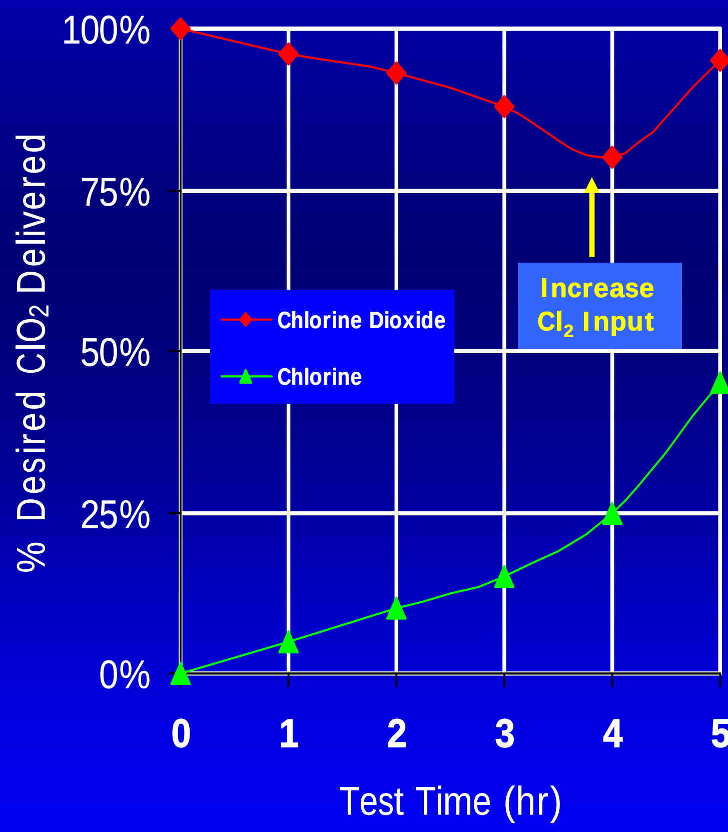
$$Cl_2 + 2ClO_2^- = 2\,ClO_2 + 2Cl^-$$

- **In Theory ...** **Cl_2** reacts completely in generating **100% ClO_2**
- **In Practice ...** % Yield to **ClO_2** decreases during test

Decrease in % Yield of ClO_2 As Test Progresses

- As Test progresses
  - ClO2 yield decreases
  - Replaced by un-reacted Cl2

- Current Test Instructions
  - Increase Cl2 addition
  - Bring ClO2 back to desired level
  - Increases un-desired Cl2 addition



Chlorine Dioxide Test

Suggestions …

- Re-charge column (fresh $NaClO_2$) before each test

OR

- Improve Chlorine Dioxide generation column
  - Include desiccant in the column
  - Change particle size or packing method

OR

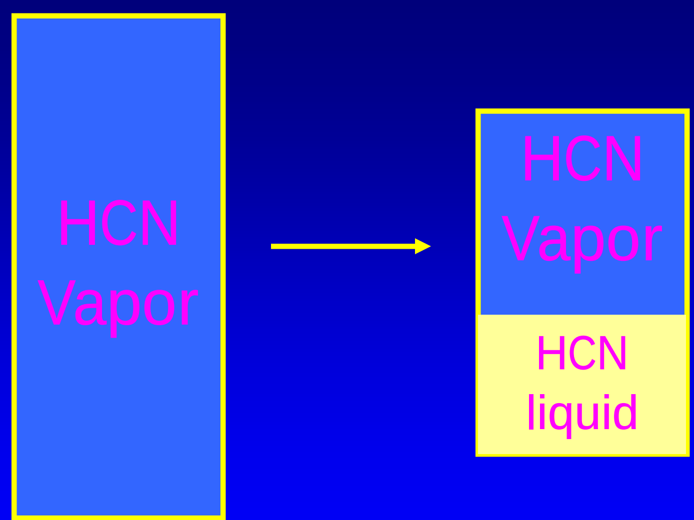
- Make a performance allowance in the test for excess **Cl2** inadvertently included in the Challenge due to the incomplete column reaction.

$$Cl_2 + 2ClO_2^- = 2\ ClO_2 + 2Cl^-$$

Hydrogen Cyanide Testing

A difficult issue with HCN Testing is obtaining and controlling HCN gas. *Due to its reactivity, you'd like to package HCN as a diluted material in an inert gas, but…*

Hydrogen Cyanide (HCN) condenses readily when compressed .



Hydrogen Cyanide Testing

Since it is impossible to package high levels of HCN with an inert gas, there are choices…

- Dilute HCN in Nitrogen
  - Safer, but it can take several cylinders (at \$700/cyl) to complete a set of tests
- 100% HCN liquid in metal container
  - Not so safe with \$10,000 transport fee
- Generate HCN in situ using NaCN + HCl
  - Messy, requires high technique, and not so safe

Hydrogen Cyanide Packaging

Possible solutions …

Purchase dilute Hydrogen Cyanide in nitrogen at low pressure in a VERY LARGE cylinder

- 10” x 57” cylinder --- 2,500 L of 5,000 ppm HCN
- approx. 40 hr of testing at 64 L/min

OR ...

Generate HCN by dropping acid into NaCN Solution

- Inexpensive procedure if you can develop the expertise

Cyanogen Chloride Testing
(CNCl) (CK)

Issues… (1) CK is difficult to obtain in any form.
(2) Instrumentation used in NIOSH STPs very expensive.

(1) 100% CK or diluted in Nitrogen
- Few sources of pure CK or mixtures

(2) Photoacoustic Spectrometer
- $42,000 per Instrument
- You need 2 Instruments
  - upstream & downstream

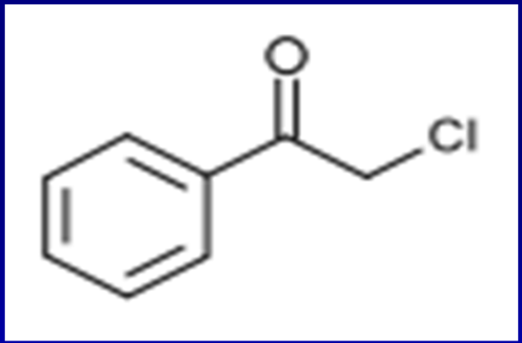
Cyanogen Chloride Testing

Possible solutions …

- Avoid $10,000 transportation fee by using diluted Cyanogen Chloride (at least 1 source)
- Avoid $42,000 by using 1 Photoacoustic Spectrometer (PAS) & 1 Flame Ionization Detector (FID)
  - FID Upstream
  - PAS Downstream

CN Tear Gas

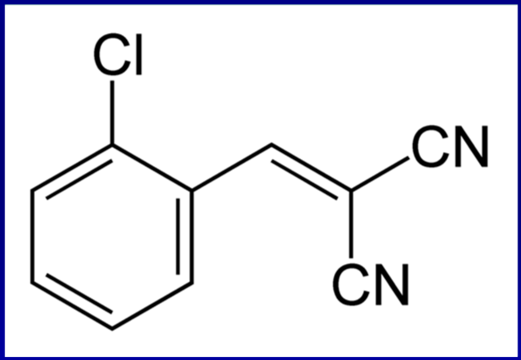
Phenacyl Chloride
Chloroacetophenone



m.p. 53°C
CAS 532-27-4

CS Tear Gas

2-Chlorobenzalmalononitrile
o-Chlorobenzylidene Malononitrile



m.p. 93°C
CAS 2698-41-1

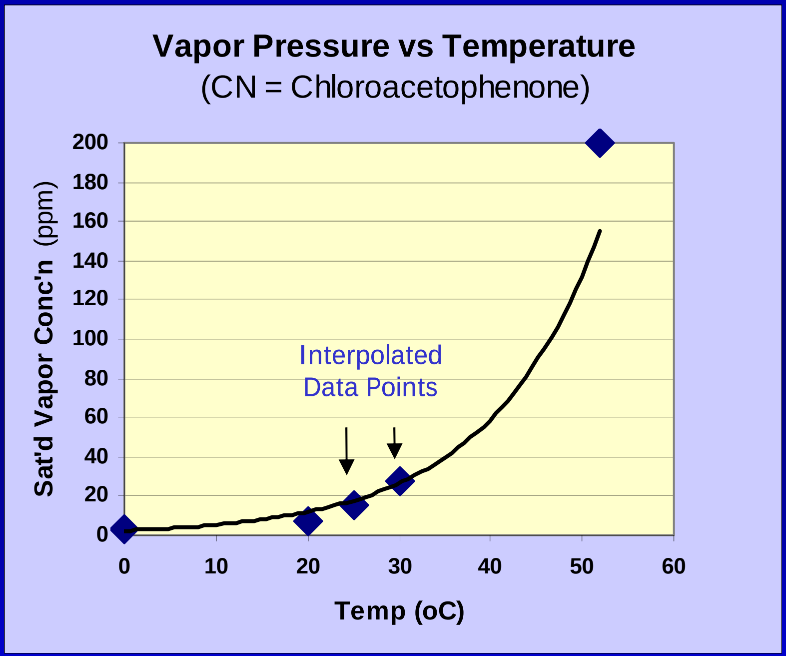
CN & CS Tear "Gas" Challenge Testing

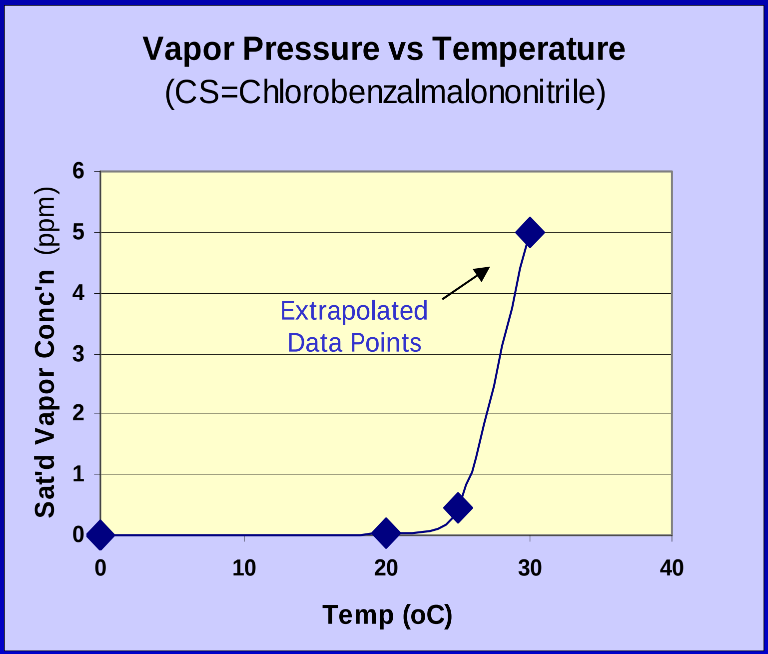
Issue … Low Vapor Pressure makes it difficult to vaporize 16 ppm CN required for Challenge

Issue … Low Vapor Pressure makes it difficult to vaporize 3 ppm CS required for Challenge

CN & CS Vapor Pressure vs Temperature

Is it actually possible to generate and maintain 16 ppm CN and/or 3 ppm CS?





It may be possible to maintain 16 ppm of CN at 25 ^{o}C, but $\geq$ 30 ^{o}C is probably required to stabilize 3 ppm of CS .

CN & CS Challenge Testing

Method Comparison ...

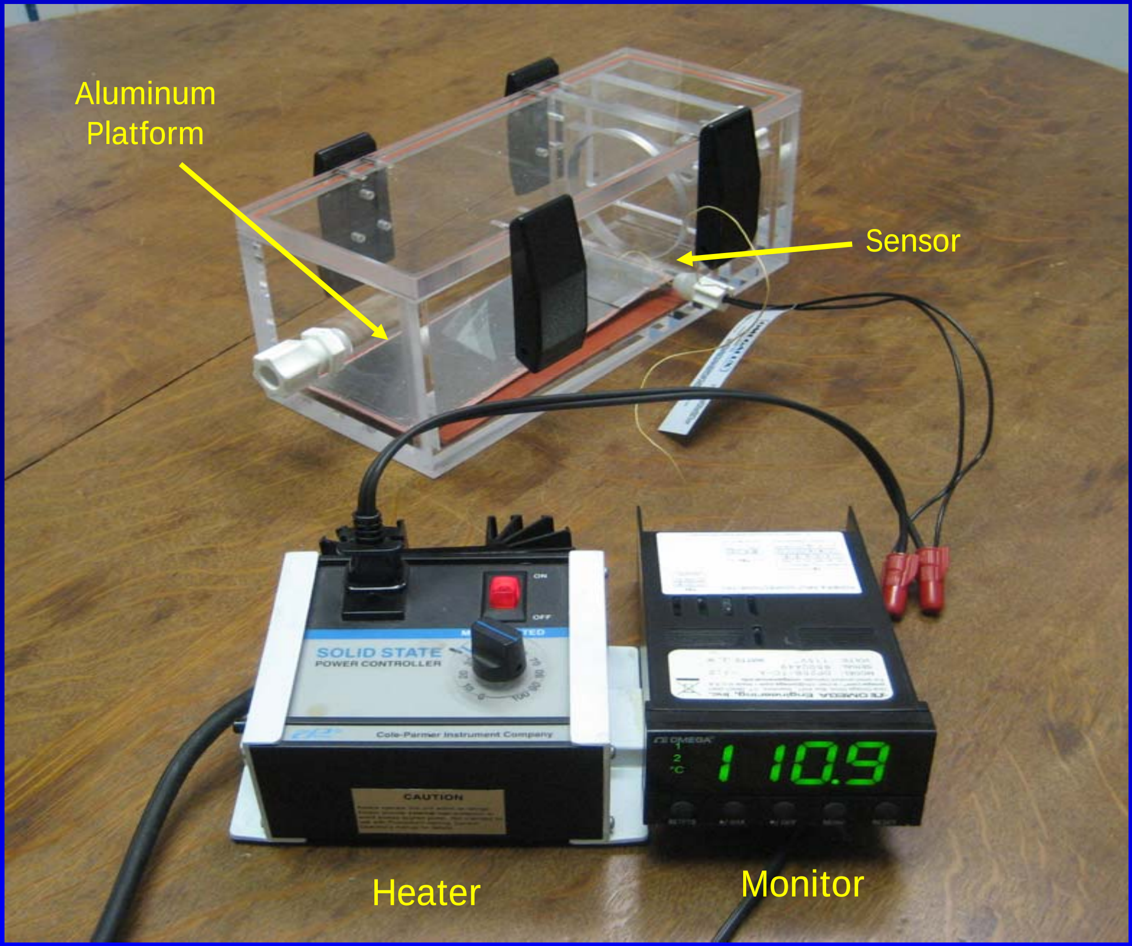
NIOSH NPPTL Lab	Aspect of Test	*Assay Tech MNR Lab*
Vaporization Chamber (5 gal drum)	**Generate Challenge Level**	**Vaporization Chamber** (with controlled flow across vaporization vessels)
30-min Sampling Tube With Lab Test (spectrophotometer)	**Monitor Challenge Level**	**Gravimetric Analysis** with FID and PID
30-min Sampling Tube With Lab Test (spectrophotometer)	**Monitor Break Through**	**Gravimetric Analysis** with FID and PID

Experimental Design
CN & CS Generation

In Vaporization Chamber …

- Input Air Flow
  - Controlled at 64 L/min
- Temperature
  - Heater w/ feedback from Chamber Sensor
- Tear Gas Concentration (ppm)
  - Wt Loss from Evaporation Dish
  - Calculate time–average Tear Gas Concentration
  - Observe Chamber for any crystal deposition

Tear Gas
Vaporization Chamber



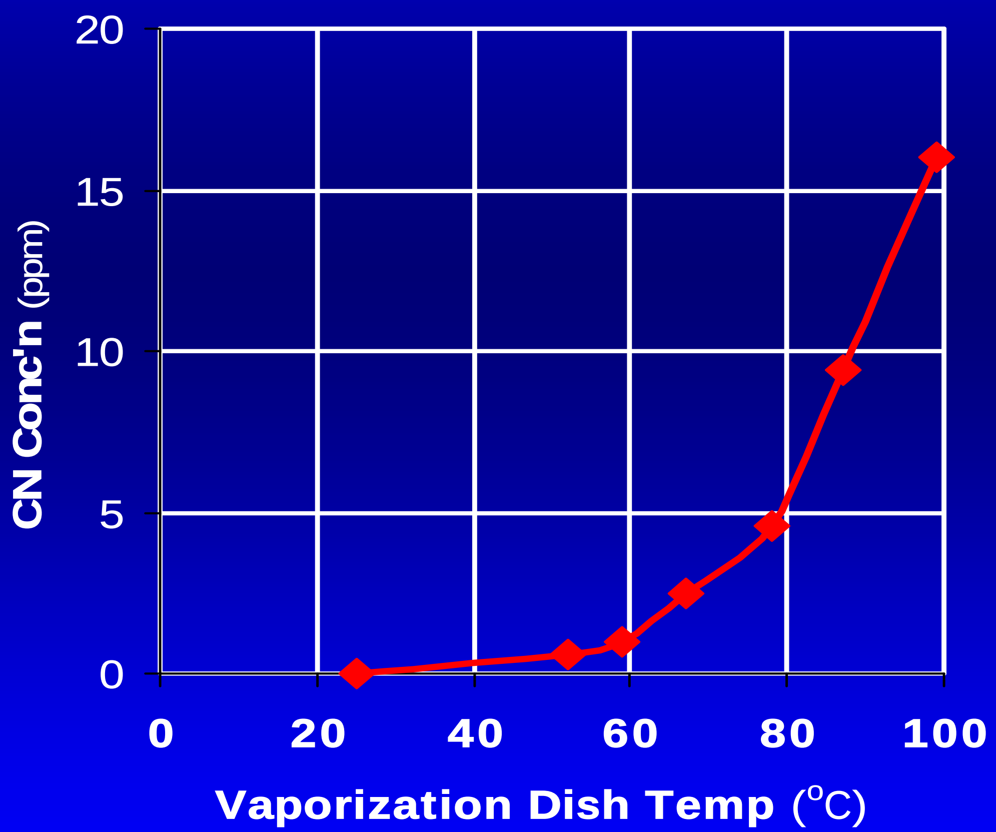
Experimental Results
CN Generation

In Vaporization Chamber …

- Input Air Flow
  - Controlled at 64 L/min
- Temperature
  - Measured and controlled on Aluminum Platform
- Tear Gas Concentration [CN], in ppm
  - Plot of [CN] versus Platform Temp
  - Plot of FID/PID response versus [CN]

CN Vaporization Concentration
vs Temp of Vaporization Dish

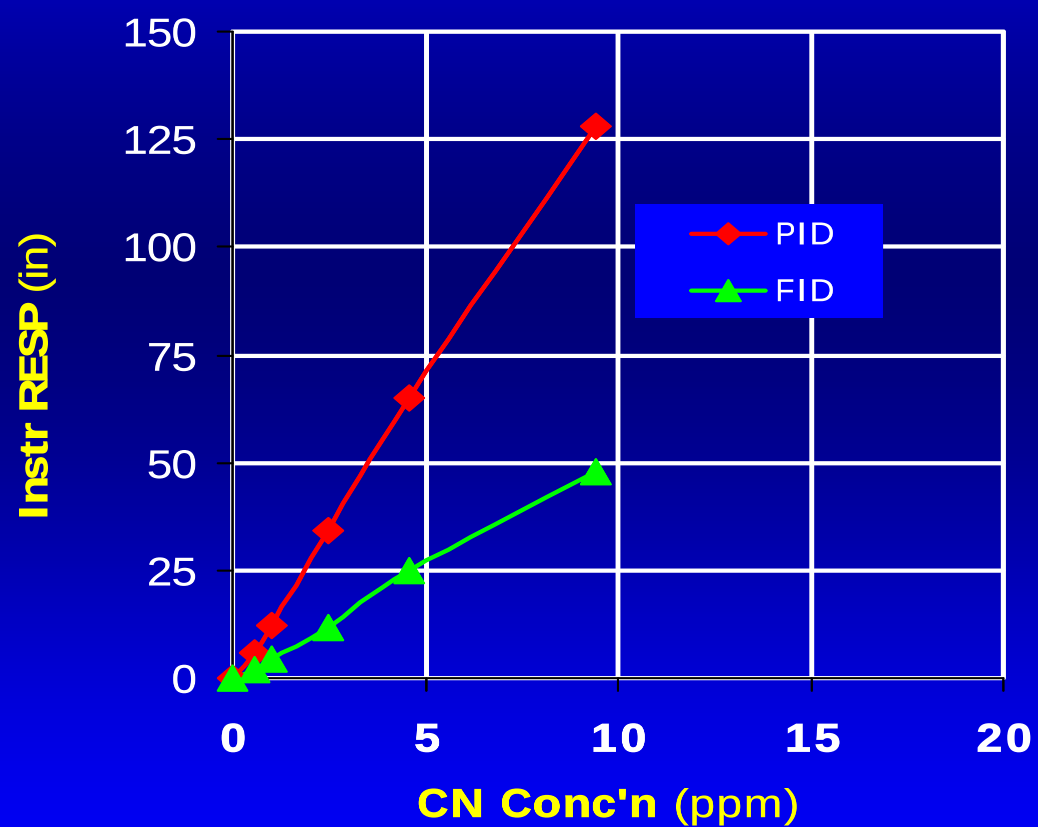
- Flow = 64 L/min
- CN Concentration
  - Determined by wt loss of CN
- Vapor Dish Temp
  - Measured Temp of Al Platform



PID & FID Response

Chloroacetophenone (CN)

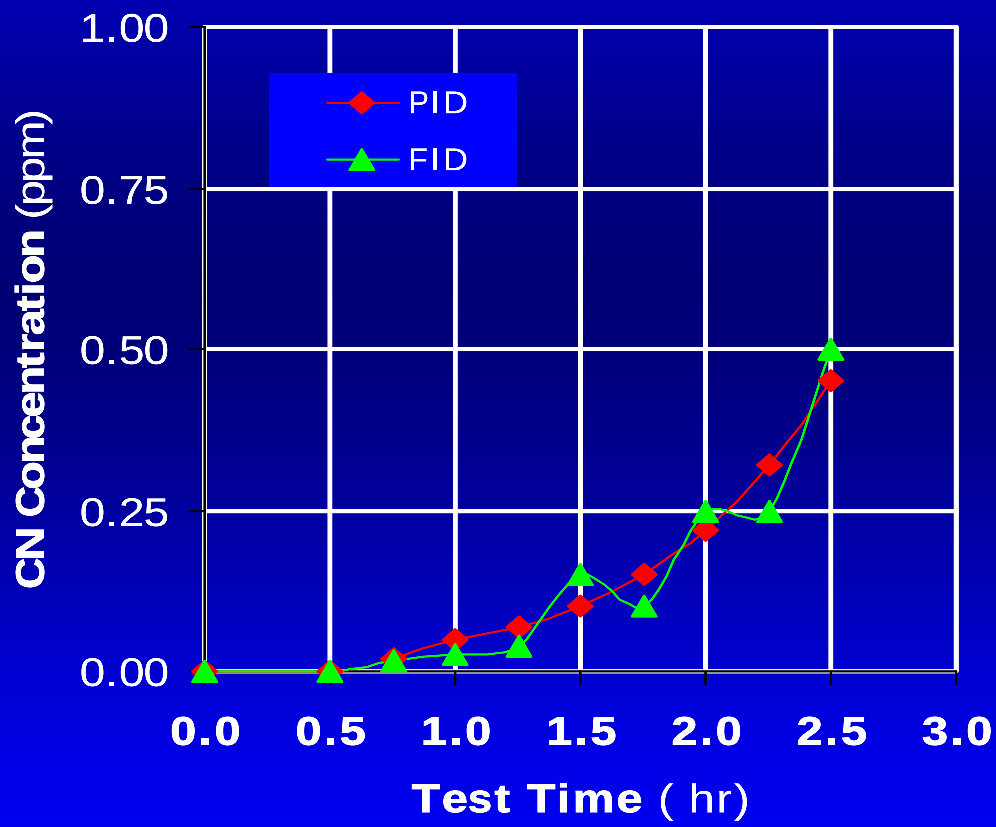
- CN Conc'n det'd by wt loss
- Instrument Response
  - Recorder Deflection (inches)



Gradual Breakthrough

at early time in test
more difficult to detect

- PID/FID response is instantaneous
- Chemical Tube Sampling Method requires 30 min
  - Not rapid enough to resolve differences between Service Lives when less than 2 hours



Results & Conclusions

- CN and CS may be vaporized from heated dish by passing controlled air flow over molten material in a Chamber
- It is possible to conduct challenge tests with 16 ppm of CN maintained at 25ºC without visible condensation.
  - Upstream & downstream CN can be monitored by FID & PID even though vapor saturation is near to 16 ppm at 25ºC
- It seems impossible to conduct challenge testing at 3 ppm of CS without visible condensation.
  - suggests CS is mostly aerosol and that saturated CS vapor concentration is << 3 ppm at 25ºC

Question

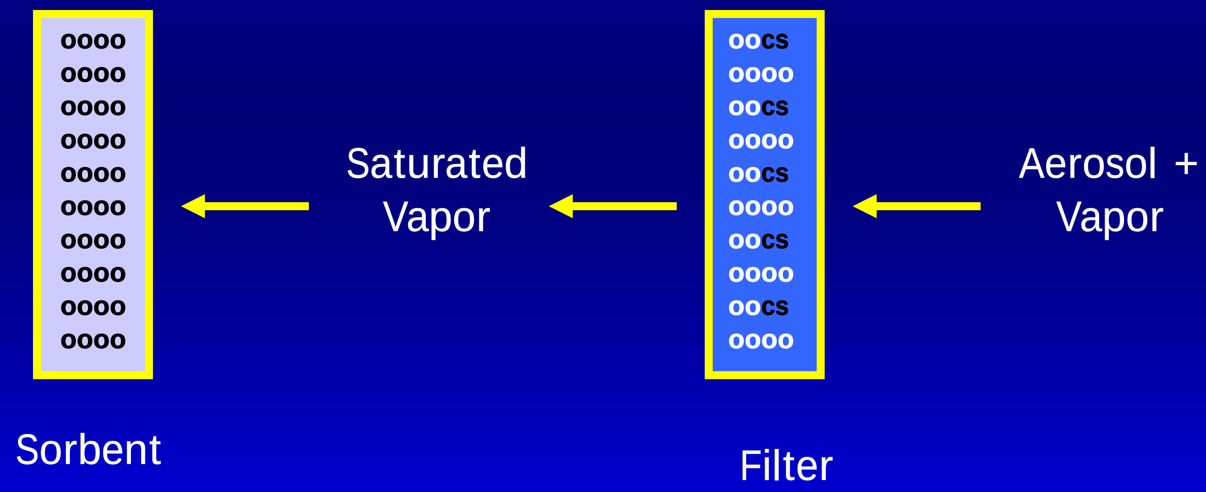
Are CN & CS (tear gas) Chemical Challenge tests meant to be …

Vapor Tests or Aerosol Tests ?

... OR ... Tests with mixed Vapor & Aerosol ?

Mixed Aerosol/Vapor

Issues



Final Comments

Suggestions for method improvement…

Tear Gas Challenge Tests may best be conducted using a continuous instrument for Upstream or Break Through monitoring (PID or FID).

Since tests with a mixed vapor/aerosol challenge can be expected to be non-reproducible ...

Tear Gas tests could be re-designed so the challenge would be 100% vapor.

Finis

Thanks for listening.