

Measurement of Hydrogen Sulfide and Reduced Sulfur

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Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Measurement methods depend strongly on interpretation criteria
 - Medium (air, water, oil, waste solids)
 - Speciation (H_2S , mercaptans, TRS)
 - Characteristic (Odour, corrosiveness)
 - Sensitivity
 - ◆ Occupational, environmental or emergency response
 - Averaging time (urgency)

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Air as the medium
- ◆ Speciation or selectivity needed
- ◆ Time: 8 hours or more, 15 min, Ceiling
 - Ceiling has an ill-defined averaging time
 - OSHA and NIOSH state 10 minutes, ACGIH state a time
 - Alberta Govt. recommends direct reading method (60 seconds averaging time)

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Occupational measurements
- ◆ Unusually, 8 hour TWA values are very seldom measured for H₂S
 - ◆ Oil and Gas industry almost exclusively measures H₂S as a "Ceiling" OEL
 - ◆ If the 8 hour TWA is substantially reduced, TWA measurements could become much more common

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Long term TWA samples
 - Absorbents
 - Treated filters
 - ◆ Mercaptans
 - Length of stain indicators
 - Electrochemical sensors (data loggers)

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ NIOSH 6013 (4th Edition)
 - <http://www.cdc.gov/niosh/nmam/>
- ◆ Filter and 600 mg charcoal tube
- ◆ Flow rate 0.1 to 1.5 l/min
- ◆ 20 l recommended volume (40 l max)
 - 0.6 to 14 ppm for a 20 l sample

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Elute charcoal with alkaline hydrogen peroxide
 - Oxidizes H₂S to sulfate
- ◆ Measure sulfate by ion-chromatography
- ◆ Sulfur dioxide is a positive interference
- ◆ Mercaptans not measured
- ◆ Problems with high backgrounds

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Mercaptans NIOSH 2542 (4th Edition)
 - <http://www.cdc.gov/niosh/nmam/>
- ◆ Glass fibre Filter impregnated with mercuric acetate
- ◆ Protect samples from light
- ◆ Gas Chromatography with flame photometric detector
 - Speciates Methyl, Ethyl, propyl mercaptan
- ◆ Problem - it doesn't work !

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Commercial propane
 - 3 ppm H₂S, 12.3 ppm mercaptan
 - Pure propane, and diluted 1:6 with air
 - +22 C and -5 C
- ◆ At +22 C about 40% recovery
- ◆ At -5 C, about less than 20% recovery

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Length of stain indicator tubes
- ◆ Constructed to standard dimensions
- ◆ Hydrogen sulfide diffuses into the device and reacts with a color absorbent
- ◆ Length of colour stain is proportional to ppm-hours of exposure
- ◆ Sampling time 1 to 48 hours
 - 1 to 25 ppm for 8 h sample
- ◆ Sulfur dioxide and mercaptans don't interfere
- ◆ Unknown effect of low temperatures

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Electrochemical sensors (data loggers)
- ◆ Few manufacturers of sensors, many instruments
- ◆ Measure the electrical current needed to oxidize sulfur under controlled conditions
 - Build-up of sulfur reduces sensitivity of the cell, using detection severely reduces life
 - Example of calibration response with time

Gas plant Operator
TWA = 0.036 ppm

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Difficult to obtain long-term stability (varying temperature, battery voltage, vibration)
 - Improving with use of microprocessors
- ◆ Excellent for STEL (15 min samples)
- ◆ Resolution of units usually 1ppm, long-term accuracy be worse
- ◆ Reasonable selectivity for H₂S
- ◆ Hydrogen negative interference
- ◆ Mercaptans not measured

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Direct reading Instruments
 - Colorimetric Detector Tubes
 - H₂S and Mercaptan
 - ◆ Mercaptan Tubes scrub H₂S
 - ◆ Sensitivity not great, slow
 - ◆ Reliable and easy to use
 - ◆ Don't need cal gas
 - Great for emergency response

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Electrochemical meters
 - Averaging time is about 30 seconds for "Ceil measurements"
 - Require daily "Bump test"
 - Measure only H₂S
 - ◆ In mixtures with reduced sulfur, meters can be used. A sample can be taken to give ratio of H₂S to other species
 - ◆ May need to dilute sample with pure, dry nitrogen

Measurement of Hydrogen Sulfide and Reduced Sulfur



Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Electrochemical meters do have cross-sensitivity
- ◆ http://www.indsci.com/sup_gi_crossint.asp
 - 100 ppm of CO will read 2ppm
 - 100 ppm of SO₂ will read 10 ppm
 - 100 ppm of NO₂ will read -20 ppm
 - 100 ppm of H₂ will read 0.05 ppm

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Gold Film meter
- ◆ http://www.azic.com/products_631.aspx
- ◆ 1 min readings
- ◆ 0.003 to 50 ppm
 - Readings below the odour threshold
- ◆ 10 ppm mercaptan gives reading of 3 ppm
 - Use Drager mercaptan tube scrubber to remove H₂S mercaptan value

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Air Quality Trailers, usually H₂S only
- ◆ Photoluminescence of SO₂
 - Scrub hydrocarbons
 - Scrub SO₂
 - Oxidize H₂S to SO₂ (Molybdenum converter 350C)
 - Measure SO₂
- ◆ To measure TRS, Quartz converter at 900C

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Olfactometer
 - Use of a person to measure odour in air
- ◆ NOT a good idea for LPG stenching
 - Workers not usually selected for sense of smell
 - Olfactory fatigue (long-term?)
 - High concentrations of hydrocarbon present
- ◆ Recommend using detector tube on the undiluted

Measurement of Hydrogen Sulfide and Reduced Sulfur

- ◆ Summary
- ◆ Emergency response (1 to 100 ppm)
 - Fast, detector tubes, electrochemical meters
- ◆ Occupational (0.1 to 20 ppm)
 - Data logging electrochemical meters, passive colour
- ◆ Odour issues (0.001 ppm upwards)
 - Trailers, Gold Film, speciation vital