



# Collection & Analysis of Reduced Sulfur Compounds in Air

**Roy Smith** M.Sc., MBA, C.Chem.

Air Quality Manager, ALS Environmental – Waterloo Laboratory



# Reduced Sulfur Compounds (RSCs)



- Offensive low odour thresholds make RSCs of concern to regulatory authorities & the general public
- RSCs can cause headaches & nausea in many individuals
- Air regulations have been established based on odour & toxicity of individual compounds
- Approximately 60% of the total reduced sulfur (TRS) released is comprised of hydrogen sulfide
- In Ontario, approximately 74% of TRS is from the **Pulp & Paper Sector & the rest primarily from Iron & Steel, Petroleum Refineries, Municipal Sewage Treatment Plants & Landfills**

# Common Sources of Reduced Sulfur Compounds



Source	Common Reduced Sulfur Compounds
Landfills	Hydrogen sulfide
Sewers & wastewater treatment facilities	Hydrogen sulfide, mercaptans, dimethyl sulfide
Petrochemical refineries	Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, 2-methylthiophene
Pulp & paper mills	Hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide
Composting facilities	Hydrogen sulfide, carbon disulfide, methyl mercaptan, ethyl mercaptan, propyl mercaptan, dimethyl sulfide, dimethyl disulfide
Livestock activities	Hydrogen sulfide, carbonyl sulfide, dimethyl disulfide
Odorants in natural gas	Tert-butyl mercaptan, isopropyl mercaptan, n-propyl mercaptan, ethyl methyl sulfide

# Other Sources of RSCs and Significance



- The presence of reduced sulfur compounds as by-products in many industrial or energy processes make them of concern
- Low ppm amounts of sulfur odorants are added to natural gas & LP gases for safety purposes. Some odorants are unstable & react to form compounds having lower odour thresholds.
- Various fuel gases are used in energy production or converted to new products using catalysts that are poisoned by excess amounts of sulfur in the feedstock.
- Analysis of RSCs is required by industry to protect catalysts
- Methane & other gas fractions of landfill gases are often burnt or sold to natural gas distributors requiring analysis of RSCs for regulatory, production or distribution purposes

- Total reduced sulfur (TRS) is incorporated into Ontario Regulation 419/05: Air Pollution – Local Air Quality
- Based on its pattern of use & toxicology, TRS is composed of four compounds:

Hydrogen Sulfide	Methyl Mercaptan
Dimethyl Sulfide	Dimethyl Disulfide

- Hydrogen sulfide is used as the surrogate for TRS health-based standards due to its' extensive toxicological data base of information

# Ontario Ambient Air Quality & Standard Criteria



Contaminant	Criteria	Value (ug/m <sup>3</sup> )	Averaging Time	Limiting Effect	
Hydrogen Sulfide	AAQC	7	24-hour	Health	
	AAQC	13	10-minute	Odour	
	Standard	10	30-minute	Health & Odour	
Total Reduced Sulfur	AAQC	14*/7 <sup>+</sup>	24-hour	Health	
	<i>* Pulp &amp; Paper sector</i>	AAQC	13	10-minute	Odour
	<i>+ All other sectors</i>	Standard	10	30-minute	Health & Odour
Methyl Mercaptan	AAQC	13	10-minute	Odour	
	Standard	10	30-minute	Odour	
Dimethyl Sulfide	AAQC	30	10-minute	Odour	
Dimethyl Disulfide	AAQC	56	10-minute	Odour	

- In 2007, Environment & Climate Change Canada added Total Reduced Sulfur (TRS) to the Part 1A National Pollution Release Inventory (NPRI) substance list
- For purpose of reporting to NPRI, TRS is composed of six compounds reported as hydrogen sulfide:

<b>Hydrogen Sulfide</b>	<b>Methyl Mercaptan</b>
<b>Dimethyl Sulfide</b>	<b>Dimethyl Disulfide</b>
<b>Carbon Disulfide</b>	<b>Carbonyl Sulfide</b>

- In 2014, TRS reporting was required only for releases to air
- Hydrogen sulfide, carbon disulfide & carbonyl sulfide must be reported separately if the target emission limit is met for an individual substance

- Stability and reactivity of sulfur compounds makes them a challenge to collect & analyze within recommended hold times
- Option 1 - Inert silica (glass) coated canisters, valves & flow controllers
- Option 2 - Tedlar bags with polypropylene fittings, protected from light & heat
- Samples should be collected & shipped the same day overnight to arrive 9am the following morning to enable enough time for analysis
- To ensure hold times are met, the laboratory should be contact before sampling



# Recommended Hold Times for RSCs



- **24 hours** in Tedlar or foil bags
- **48 hours** in silica coated canisters
  - 6L canisters are used for ambient or indoor air 30 minute to 24hr time weighted average (TWA) samples
  - 1.4L canisters are used for landfill, treatment plants or other short-term grab samples
  - 1L glass BottleVacs are used for high ppm or % level tank-head, stack, or other short-term grab samples

- **ASTM D5504:** Standard Test Method for Determination of Sulfur Compounds in Natural Gas & Gaseous Fuels by Gas Chromatography & Chemiluminescence Detector
  - ✓ **Specific:** Equimolar detector for sulfur compounds allows detection of individual target analytes, unidentified compounds & total reduced sulfur (sum of individual compounds as hydrogen sulfide)
  - ✓ **Sensitive:** Low ppb<sub>v</sub> detection limits
  - ✓ **Wide Range:** Linear response over calibration range
  - ✓ **Accurate:** Applicable to wide range of gaseous samples including air, digester tanks, landfill, refinery gas, etc.

- Individual reduced sulfur compounds
  - 10 common compounds
  - 22 extended list of compounds
- Total Reduced Sulfur (as hydrogen sulfide)
- Reduced & Total Reduced Sulfur Packages
  - **Ontario:** hydrogen sulfide, methyl mercaptans, dimethyl sulfide, dimethyl disulfide & total reduced sulfur
  - **NPRI:** hydrogen sulfide, methyl mercaptans, dimethyl sulfide, dimethyl disulfide, carbon disulfide, carbonyl sulfide & total reduced sulfur

# Reduced Sulfur Compounds & Reporting Limits



22 compound list - reporting limits for **bolded compounds** are less than Ontario Reg. 419/05 ambient air quality criteria

Compound	RL (ppb <sub>v</sub> )	Compound	RL (ppb <sub>v</sub> )
ISOBUTYL MERCAPTAN	4	ETHYL MERCAPTAN	4
N-BUTYL MERCAPTAN	4	ETHYL METHYL SULFIDE	4
SEC-BUTYL MERCAPTAN	4	2-ETHYLTHIOPHENE	4
TERT-BUTYL MERCAPTAN	4	<b>HYDROGEN SULFIDE</b>	<b>4</b>
<b>CARBON DISULFIDE</b>	<b>2</b>	<b>METHYL MERCAPTAN</b>	<b>4</b>
<b>CARBONYL SULFIDE</b>	<b>4</b>	2-METHYLTHIOPHENE	4
DIETHYL DISULFIDE	2	3-METHYLTHIOPHENE	4
DIETHYL SULFIDE	4	ISOPROPYL MERCAPTAN	4
<b>DIMETHYL DISULFIDE</b>	<b>2</b>	N-PROPYL MERCAPTAN	4
<b>DIMETHYL SULFIDE</b>	<b>4</b>	TETRAHYDROTHIOPHENE	4
2,5-DIMETHYLTHIOPHENE	4	THIOPHENE	4

# Analysis of Air Samples for RSCs



Compounds found in the headspace of petrochemical tanks can vary widely

Compound	mg/m <sup>3</sup>	Compound	mg/m <sup>3</sup>
ISOBUTYL MERCAPTAN	-	ETHYL MERCAPTAN	1.3
N-BUTYL MERCAPTAN	-	ETHYL METHYL SULFIDE	-
SEC-BUTYL MERCAPTAN+THIOPHENE	-	2-ETHYLTHIOPHENE	-
TERT-BUTYL MERCAPTAN	-	<b>HYDROGEN SULFIDE</b>	<b>8.79</b>
CARBON DISULFIDE	-	<b>METHYL MERCAPTAN</b>	<b>1.75</b>
<b>CARBONYL SULFIDE</b>	<b>7.2</b>	2-METHYLTHIOPHENE	-
DIETHYL DISULFIDE	-	3-METHYLTHIOPHENE	-
DIETHYL SULFIDE	-	ISOPROPYL MERCAPTAN	-
DIMETHYL DISULFIDE	-	N-PROPYL MERCAPTAN	-
DIMETHYL SULFIDE	-	TETRAHYDROTHIOPHENE	-
2,5-DIMETHYLTHIOPHENE	-		

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Compound	mg/m <sup>3</sup>	Compound	mg/m <sup>3</sup>
ISOBUTYL MERCAPTAN	-	<b>ETHYL MERCAPTAN</b>	<b>10.9</b>
N-BUTYL MERCAPTAN	1.05	ETHYL METHYL SULFIDE	-
SEC-BUTYL MERCAPTAN+THIOPHENE	3.7	2-ETHYLTHIOPHENE	-
TERT-BUTYL MERCAPTAN	-	<b>HYDROGEN SULFIDE</b>	<b>1,580</b>
CARBON DISULFIDE	-	<b>METHYL MERCAPTAN</b>	<b>13.3</b>
CARBONYL SULFIDE	6.07	2-METHYLTHIOPHENE	2.99
DIETHYL DISULFIDE	-	3-METHYLTHIOPHENE	1.72
DIETHYL SULFIDE	-	ISOPROPYL MERCAPTAN	2.23
DIMETHYL DISULFIDE	0.56	N-PROPYL MERCAPTAN	5.01
DIMETHYL SULFIDE	-	TETRAHYDROTHIOPHENE	-
2,5-DIMETHYLTHIOPHENE	-		

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Compounds found in the headspace of petrochemical tanks can vary widely

Compound	mg/m <sup>3</sup>	Compound	mg/m <sup>3</sup>
ISOBUTYL MERCAPTAN	1.43	ETHYL MERCAPTAN	7.7
N-BUTYL MERCAPTAN	2.81	ETHYL METHYL SULFIDE	-
SEC-BUTYL MERCAPTAN+THIOPHENE	8.0	2-ETHYLTHIOPHENE	5.5
TERT-BUTYL MERCAPTAN	-	<b>HYDROGEN SULFIDE</b>	<b>38.0</b>
CARBON DISULFIDE	-	METHYL MERCAPTAN	8.1
<b>CARBONYL SULFIDE</b>	<b>10.6</b>	<b>2-METHYLTHIOPHENE</b>	<b>19.6</b>
DIETHYL DISULFIDE	-	3-METHYLTHIOPHENE	4.5
DIETHYL SULFIDE	-	ISOPROPYL MERCAPTAN	4.71
DIMETHYL DISULFIDE	-	N-PROPYL MERCAPTAN	6.88
DIMETHYL SULFIDE	-	TETRAHYDROTHIOPHENE	1.42
2,5-DIMETHYLTHIOPHENE	9.1		

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Compound	mg/m <sup>3</sup>	Compound	mg/m <sup>3</sup>
ISOBUTYL MERCAPTAN	-	ETHYL MERCAPTAN	3.8
N-BUTYL MERCAPTAN	1.19	ETHYL METHYL SULFIDE	-
SEC-BUTYL MERCAPTAN+THIOPHENE	2.8	2-ETHYLTHIOPHENE	1.9
TERT-BUTYL MERCAPTAN	-	<b>HYDROGEN SULFIDE</b>	<b>6.48</b>
CARBON DISULFIDE	-	METHYL MERCAPTAN	1.54
<b>CARBONYL SULFIDE</b>	<b>8.24</b>	<b>2-METHYLTHIOPHENE</b>	<b>7.1</b>
DIETHYL DISULFIDE	1.6	3-METHYLTHIOPHENE	1.6
DIETHYL SULFIDE	-	ISOPROPYL MERCAPTAN	2.11
DIMETHYL DISULFIDE	0.58	N-PROPYL MERCAPTAN	2.67
DIMETHYL SULFIDE	-	TETRAHYDROTHIOPHENE	1.42
2,5-DIMETHYLTHIOPHENE	3.0		



**Thank You!**  
**Questions?**

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