



SANITATION DISTRICTS OF LOS ANGELES COUNTY

Odor Detection and Identification

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Preview

- Measuring odor strength
- Identifying odor components
- Air sampling

Sanitation Districts of Los Angeles County

- 5.3 million people
- 800 square miles service area
- 78 cities and unincorporated Los Angeles County
- www.lacsd.org

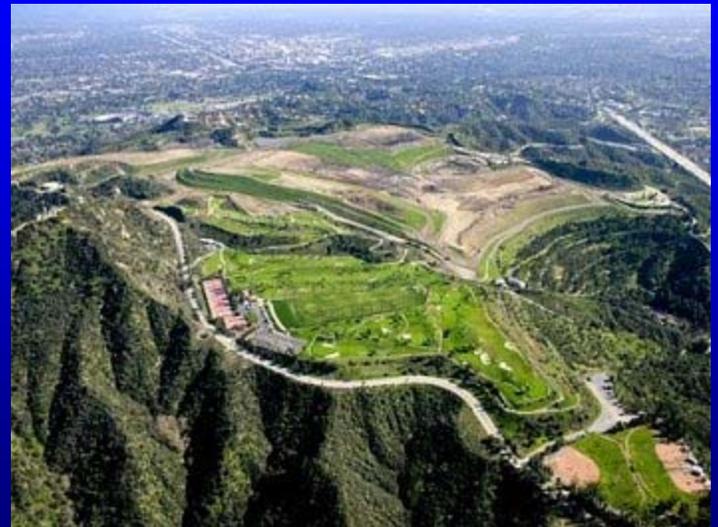
Sanitation Districts Service Area



Wastewater Treatment Plants



Sanitary Landfills



Odor Treatment

- To be a good neighbor and to comply with regulations the Los Angeles County Sanitation Districts have invested tens of millions of dollars in odor treatment facilities

Odor Treatment Processes

Biotrickling Filters



Activated Carbon



Odor Treatment Processes

- One Acre of Biofilters



- Loading Media into Biofilter



Monitoring Odors

- Instrumentation as “electronic nose”
 - For known odorants
- The human nose: Ultimate detector

Olfactometry

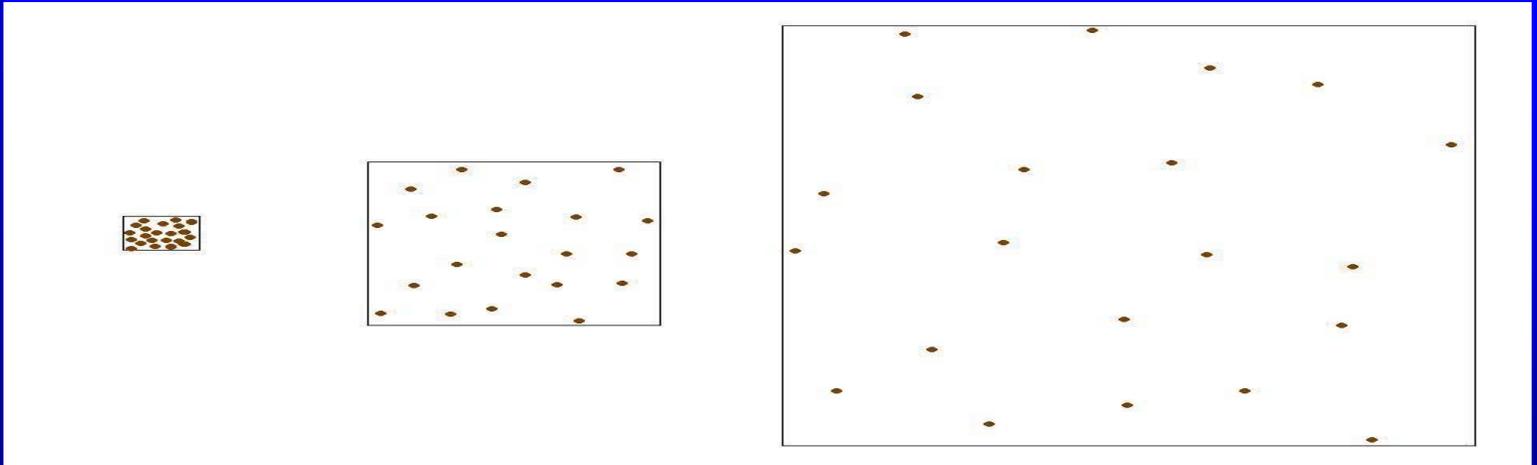
- Measuring an odor

Diluting an Odorous Air Sample

- Strong
- Weak
- Just Detectable
- If diluted enough, it cannot be smelled

Detection Threshold

- Odor:
- Strong Weak Just detectable
- Dilution Ratio:
- 1:1 1:20 1:100



Detection Threshold

- The dilution ratio needed to have the diluted sample be just barely detectable.
- Larger number = more powerful odor

Odor Panel

- People vary in odor sensitivity
- Use several people in Odor Panel
- Average their responses

Odor Analysts

- Abstain from eating spicy foods, garlic
- No perfumes, colognes, scented soaps

Olfactometer

- Presents diluted odorous sample to odor assessors
- Records their responses
- Sample dilutions range from 1:64,000 to 1:8

Ac'scent[®] Olfactometer



St Croix Sensory, Inc

Other commercial
olfactometers
available

Triangular Forced Choice Testing (ASTM E 679-91)

- Diluted samples are presented in a series of tests where the presented concentrations are increased stepwise from sub threshold levels
- An odor assessor is presented with 3 air streams, 2 with “blank” air and the 3rd containing the diluted sample. They must select one of the streams and assign a guess, detection or recognition
- The test is concluded when two consecutive correct recognitions are recorded

Olfactometry

- Begin with very dilute sample
 - Below detection threshold
- Three air streams, one has sample
- Which stream has sample?

Guess?? Detection... Recognition!!!

- GUESS - No distinction
- DETECTION - One port is different
- RECOGNITION - Definite odor

Odor Standards

- n-Butanol 40 ppb v/v
- Tetrahydrothiophene 0.5 ppb v/v

What Causes the Odor?

- Odor Panel analysis says a sample is odorous
- What compounds are causing the odor?
- Knowing what compounds cause the odor could help identify the source of the odor.

Hypothetical Sample Analysis: What Causes the Odor?

COMPOUND	CONCENTRATION PPM V/V
Propane	15
Acetone	5
Hexane	1
Toluene	0.2
Hydrogen sulfide	0.01
Methyl mercaptan	0.01

Odor Threshold Concentrations

- Chemical compounds vary greatly in how odorous they are.
- The concentration at which the odor from a chemical compound is barely detectable is its Odor Threshold.

Hypothetical Sample Analysis: What Causes the Odor?

COMPOUND	CONCENTRATION PPM V/V	ODOR?	ODOR THRESHOLD PPM V/V (1)
Propane	15	<	1500
Acetone	5	<	42
Hexane	1	<	1.5
Toluene	0.2	<	0.33
Hydrogen sulfide	0.01	>!	0.0004
Methyl mercaptan	0.01	>!!	0.00007

Are these all the Odor Compounds? Only the Nose Knows

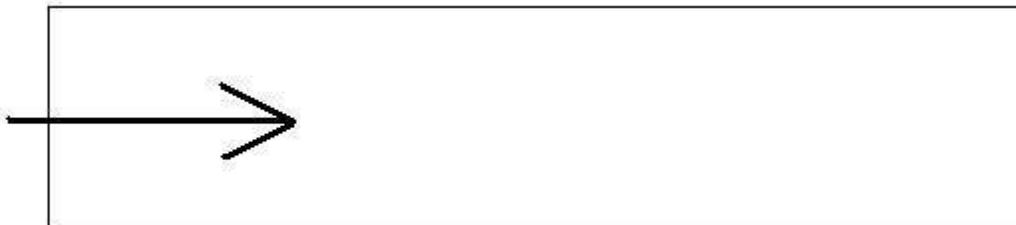
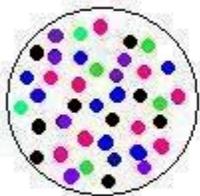
- Some odor compounds may not be detected
- Some identified compounds may not be listed in literature tables as odorous.

Gas Chromatography

Concept: Separation

- Sample is concentrated to a small volume, and injected into column inlet.
- The actual column is 60 meters long, 0.32mm ID.

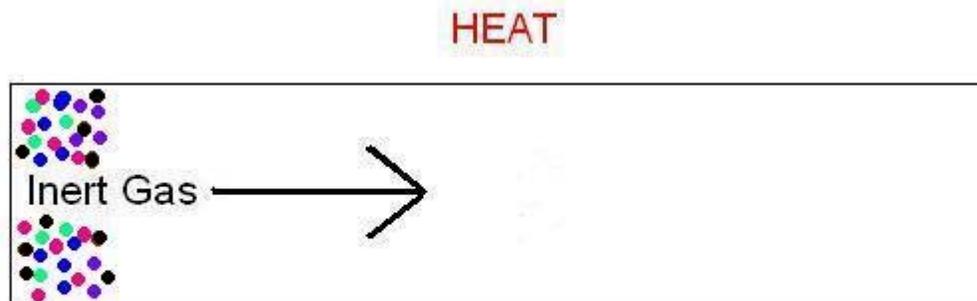
Sample



Gas Chromatography

Concept: Separation

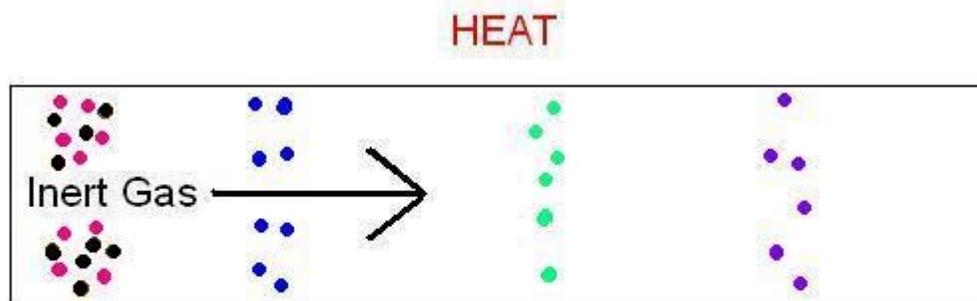
- Inert gas flows through column
- Column is heated gradually



Gas Chromatography

Concept: Separation

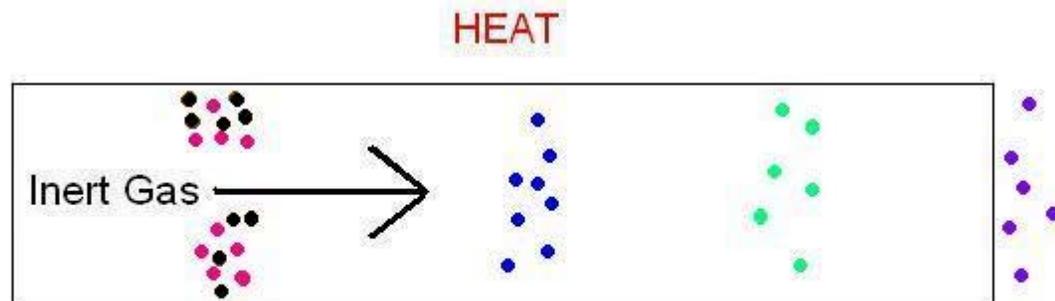
- Some compounds flow through column faster than others, so they come out sooner.



Gas Chromatography

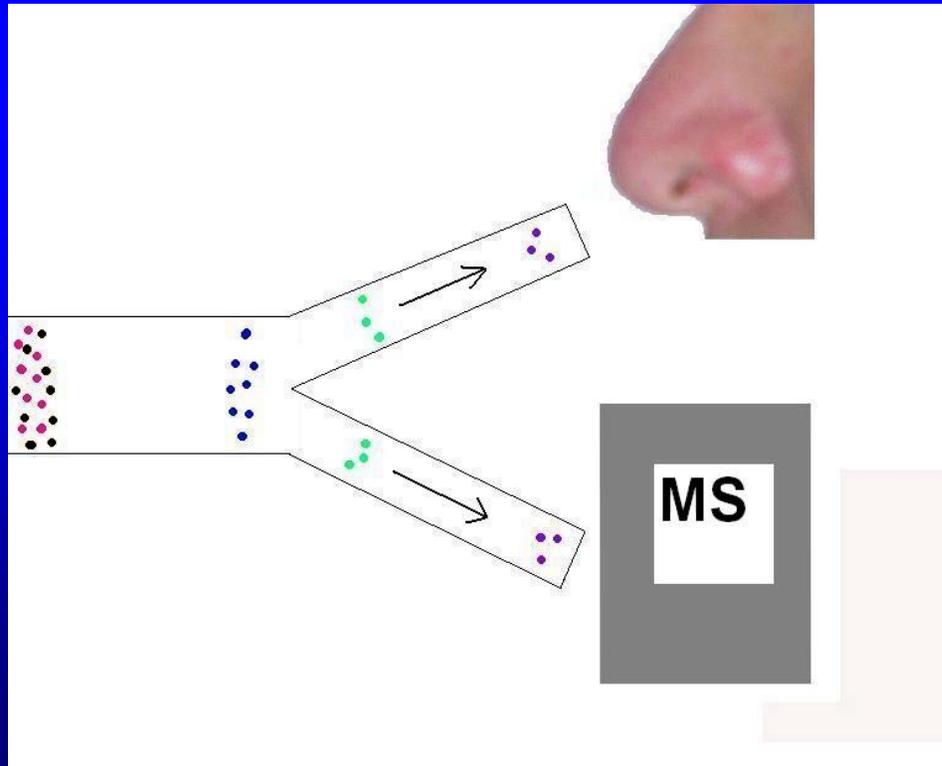
Concept: Separation

- Sometimes an odorous compound comes out at the same time as a non-odorous compound.



Gas Chromatography/Mass Spectrometry-Olfactometry

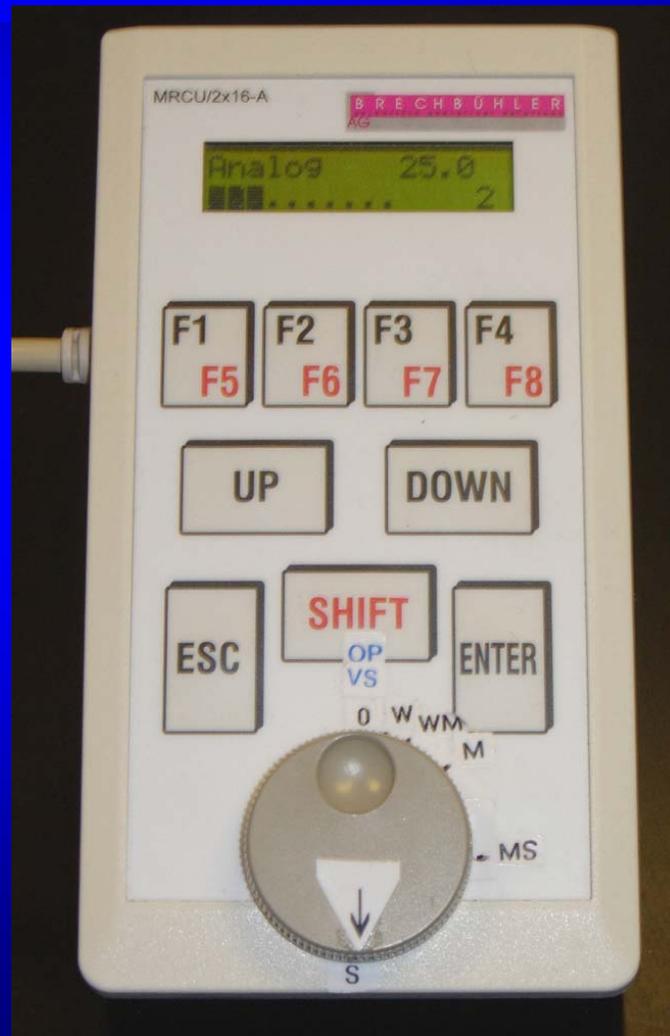
- Separated compounds to:
 - Nose
 - Mass Spectrometer (MS)
 - records a characteristic “fingerprint” for each chemical.



Sniffer



Brechbuhler Olfactory Signal Generator

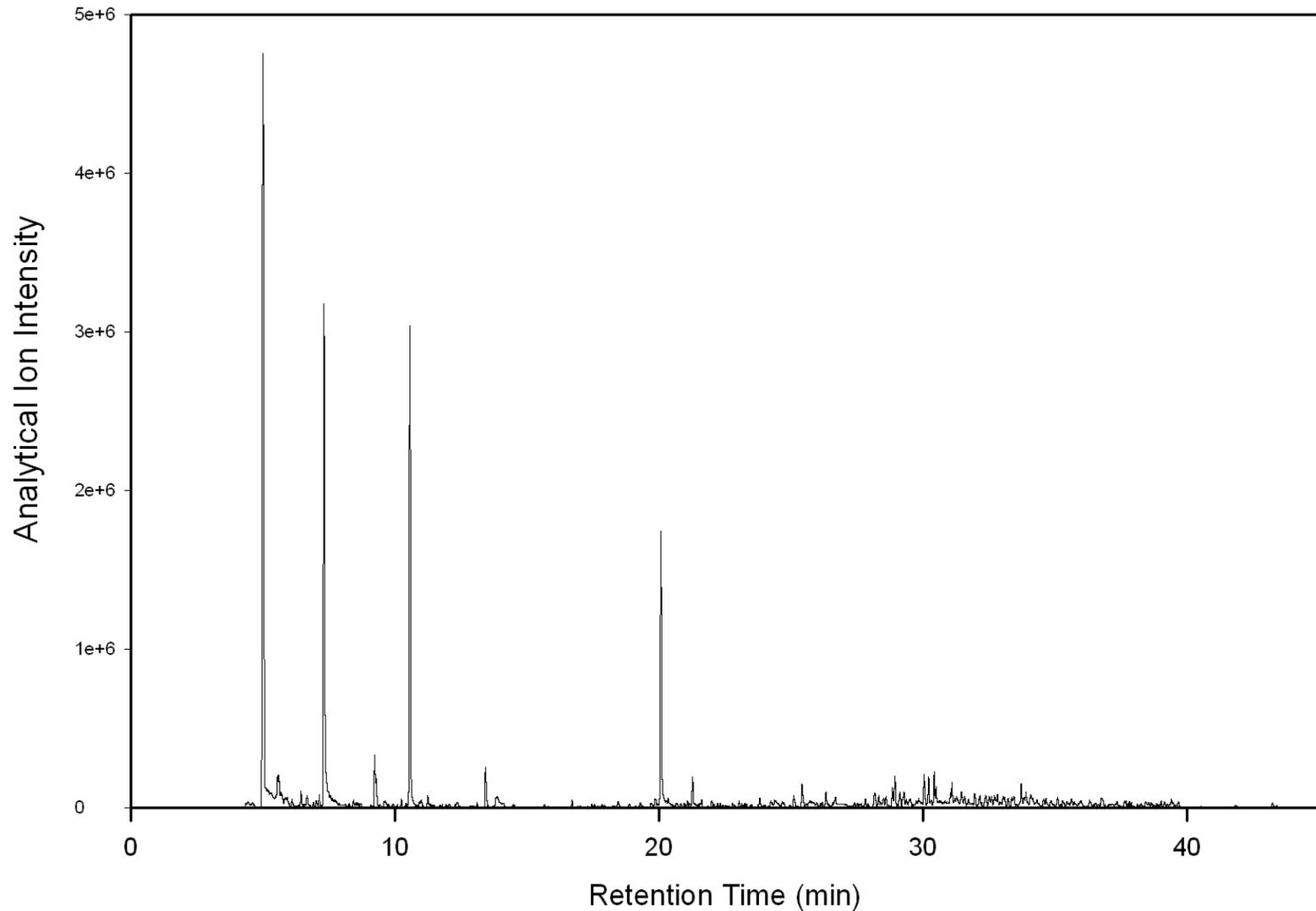


Measuring Odor Strength

<u>Odor Strength</u>	<u>% Fullscale</u>	<u># of Turns</u>	<u>Signal</u>
Overpowering	100	2	10.00 V
Very Strong	50	1	5.000 V
Strong	25	1/2	2.500 V
Moderate-Strong	12.5	1/4	1.250 V
Moderate	6	1/8	0.600 V
Weak-Moderate	3	1/16	0.300 V
Weak	1.5	1/32	0.150 V

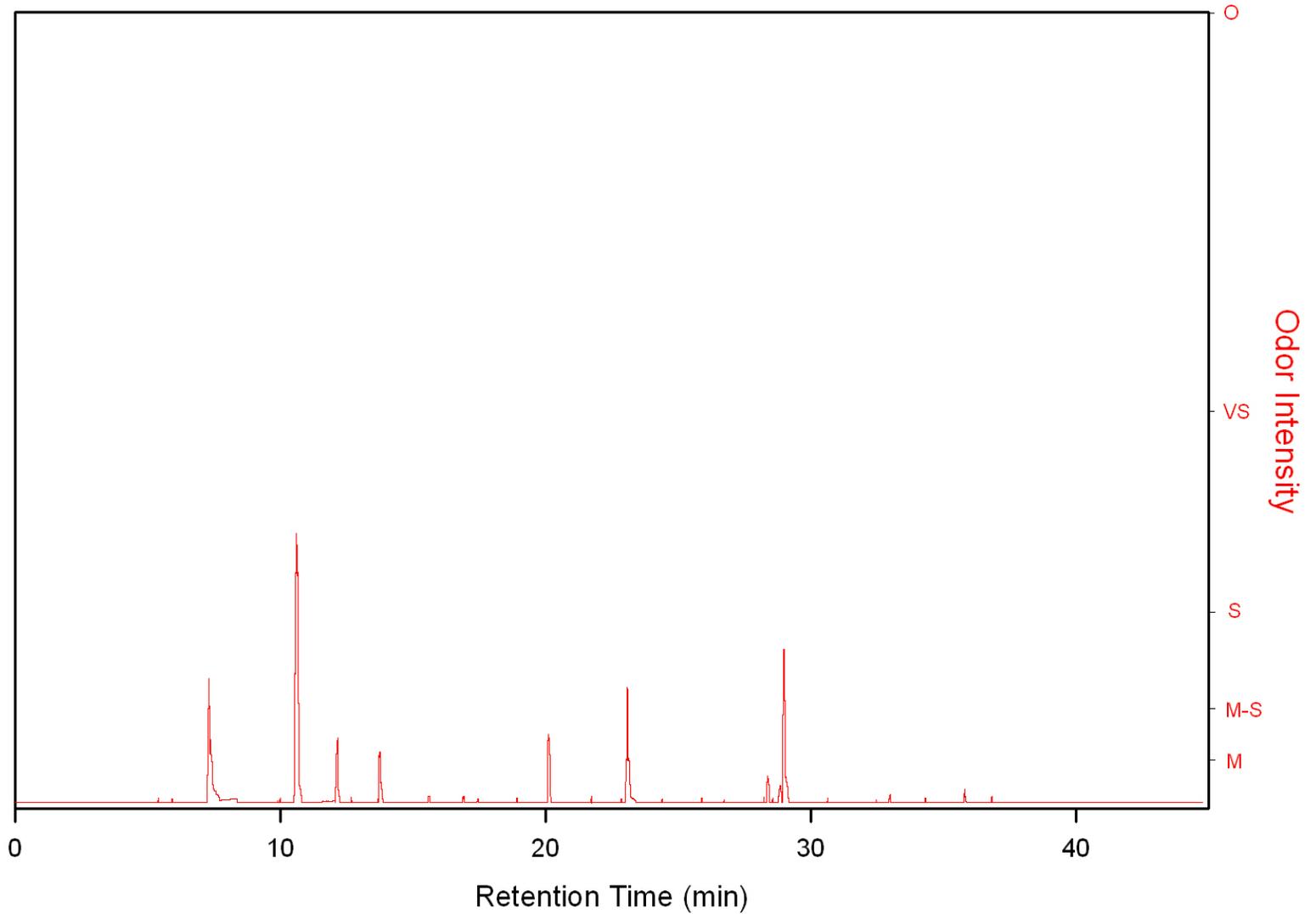
Mass Spectrometer Chromatogram: Compound identification

Pilot Scale Biofilter Inlet Mass Spectrometric Chromatogram



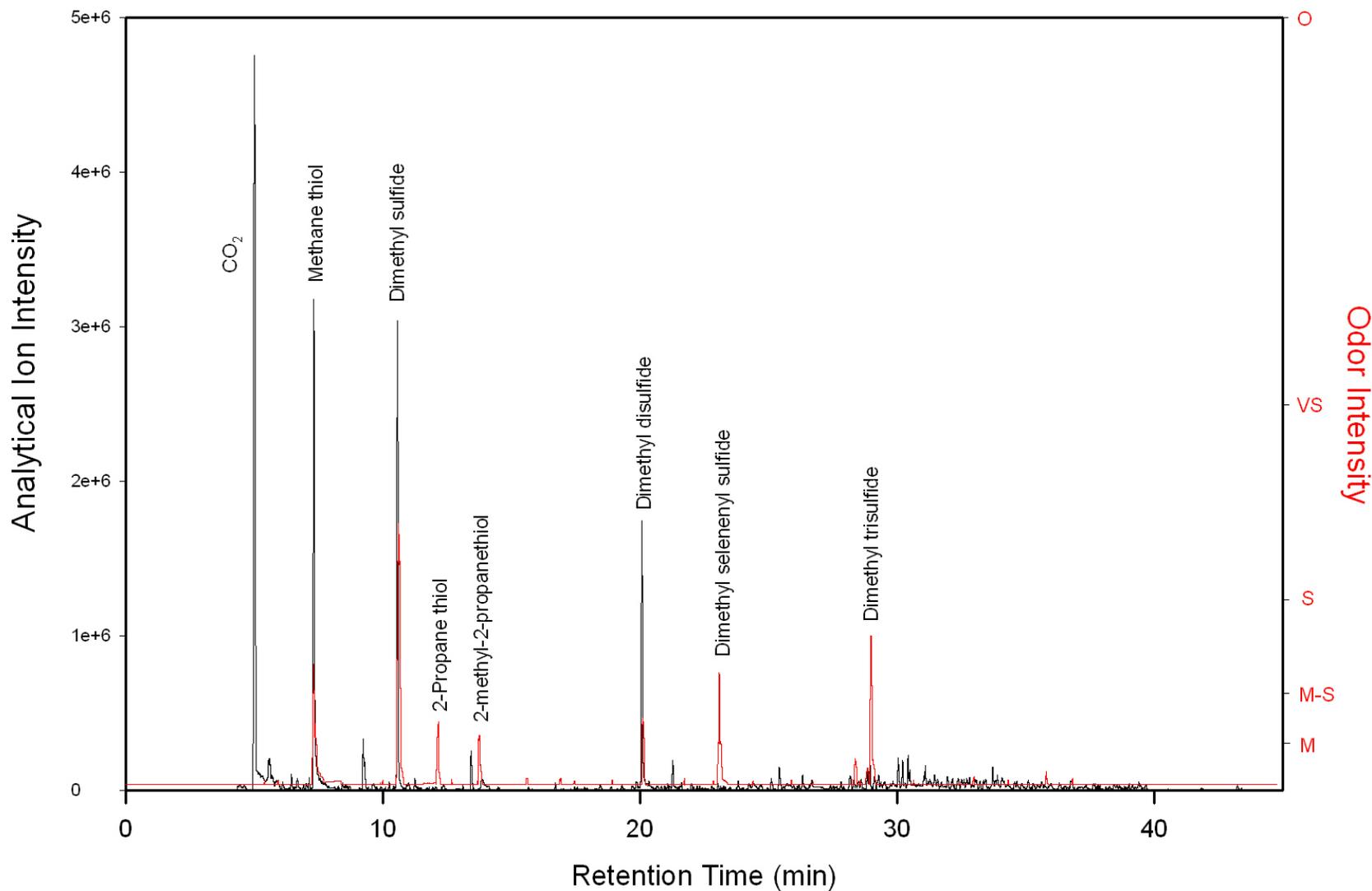
Odor Chromatogram: Odorant Detection

Pilot Scale Biofilter Inlet Odor Chromatogram



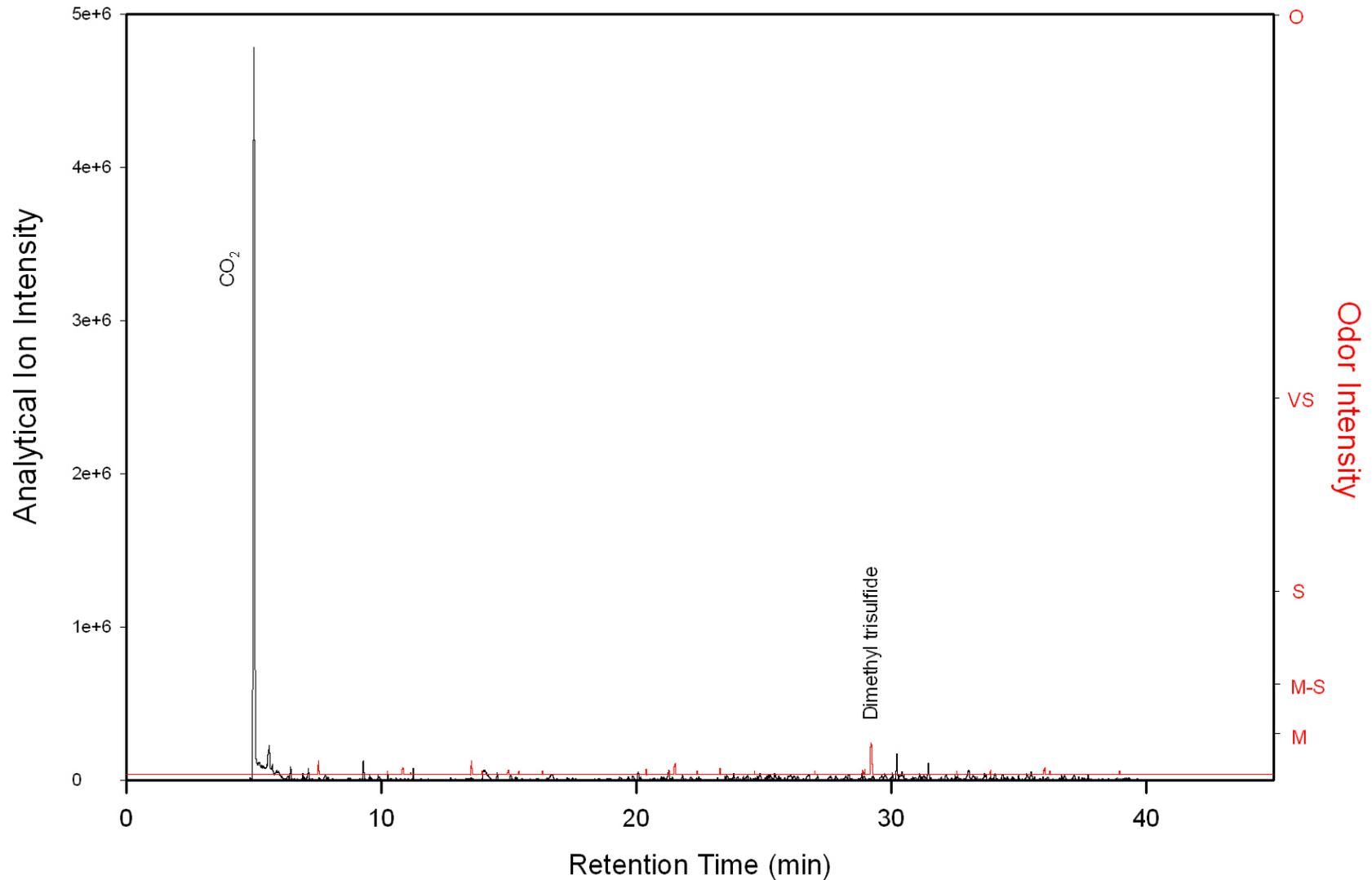
GC/MS and Odor Chromatogram to Identify Odorants

Pilot Scale Biofilter Inlet Combined Mass Spectrometric Chromatogram and Odor Chromatogram



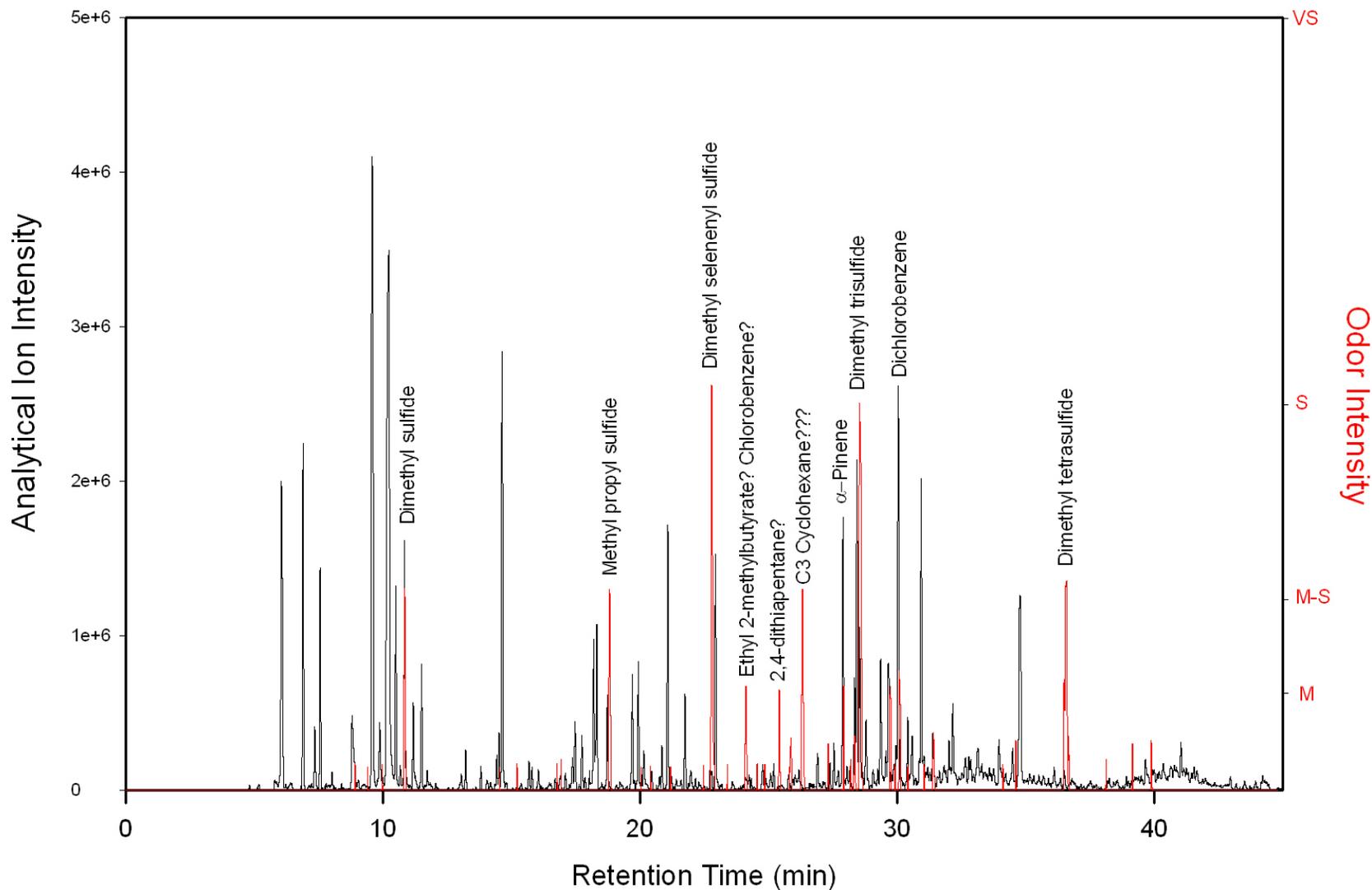
GC/MS and Odor Chromatogram to Identify Odorants

Pilot Scale Biofilter Exhaust Combined Mass Spectrometric Chromatogram and Odor Chromatogram



GC/MS and Odor Chromatogram to Identify Odorants: Some Samples are Quite Complex

Air inside Sewer Combined Mass Spectrometric Chromatogram and Odor Chromatogram



GC/MS-O Sample Screening

- Unfamiliar samples are pre-screened by GC-MS analysis first
- Safety precaution
- Avoid overwhelming odor analyst
- Avoid saturating instrument

Details of GC/MS-O Data Reduction

- A table is prepared listing time and intensity of odor response for each odor analyst.
- Raw GC/MS data is computer-processed using deconvolution, computer-searched against NIST MS library.
- For each odor, a corresponding retention time window in the GC/MS results table is examined for compounds to correlate with the odor.

Sampling

- Without good sampling technique, the sample is worthless.
- If the sample is worthless, the whole analysis is worthless.

Sampling

- Obtain samples from upwind and downwind of suspected odor source

Sampling

- Odor compounds:
 - Typically at very low concentrations
 - Frequently adsorptive (“sticky”) or reactive
- Only inert surfaces should contact the sample

Sample Containers

- Tedlar® bag or fused silica-coated stainless steel canister
- Some other labs use Nalophan® or Teflon bags



Sample Container Comparison

	Canisters	Tedlar Bags
Ease of Use Sampling	Easy	Moderate
Ease of Use Lab	Moderate	Easy
Inertness	Varies	Varies
Odor Residue	None	Slight
Cost	High	Moderate

Canister Sampling

- Open valve
- Close valve



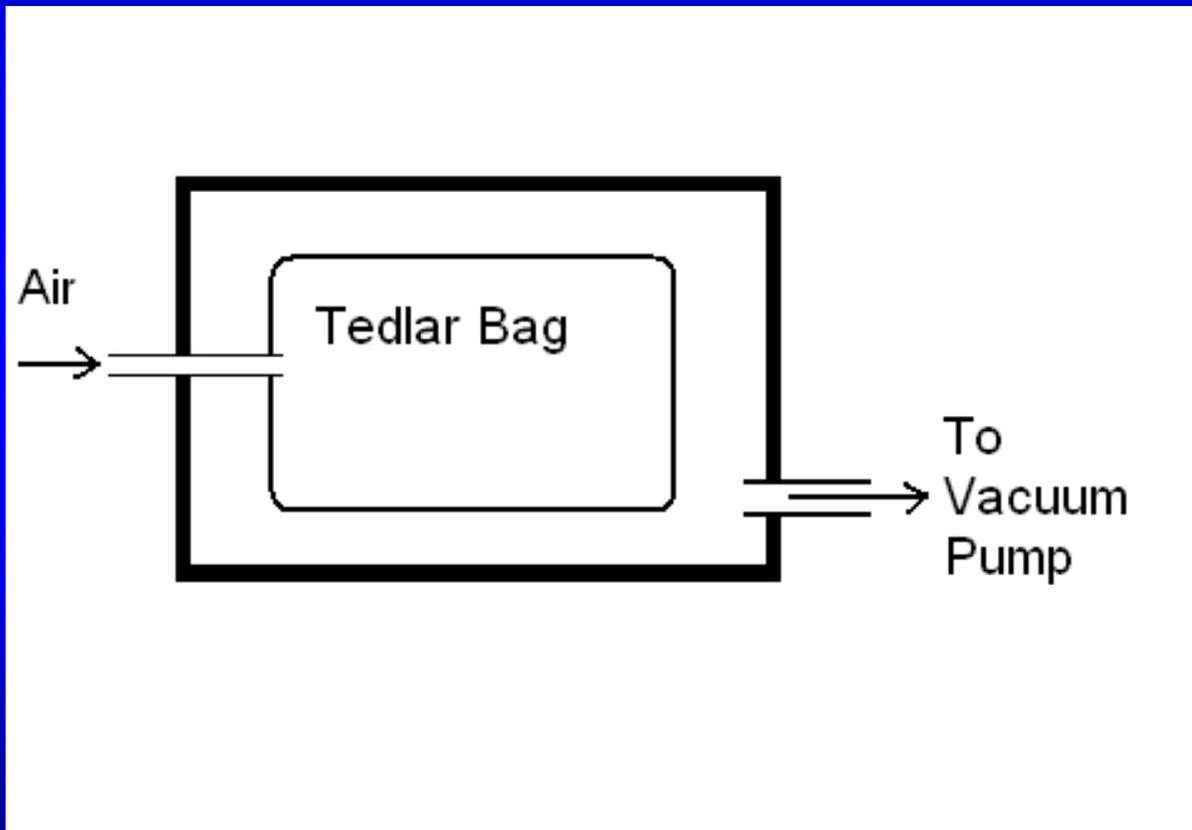
Canister Sampling

- Sampling a grab sample of air with a canister is easy.
- Start with a clean evacuated fused silica-lined stainless steel canister.
- Record the initial pressure.
- Open the canister valve.
- Close the canister valve when the canister pressure is still slightly less than atmospheric.
- Record the final pressure.

Bag Sampling

- Do NOT use pump to push the air sample into Tedlar bag
- Pump can alter the sample

Bag Sampler (“Lung” Sampler)



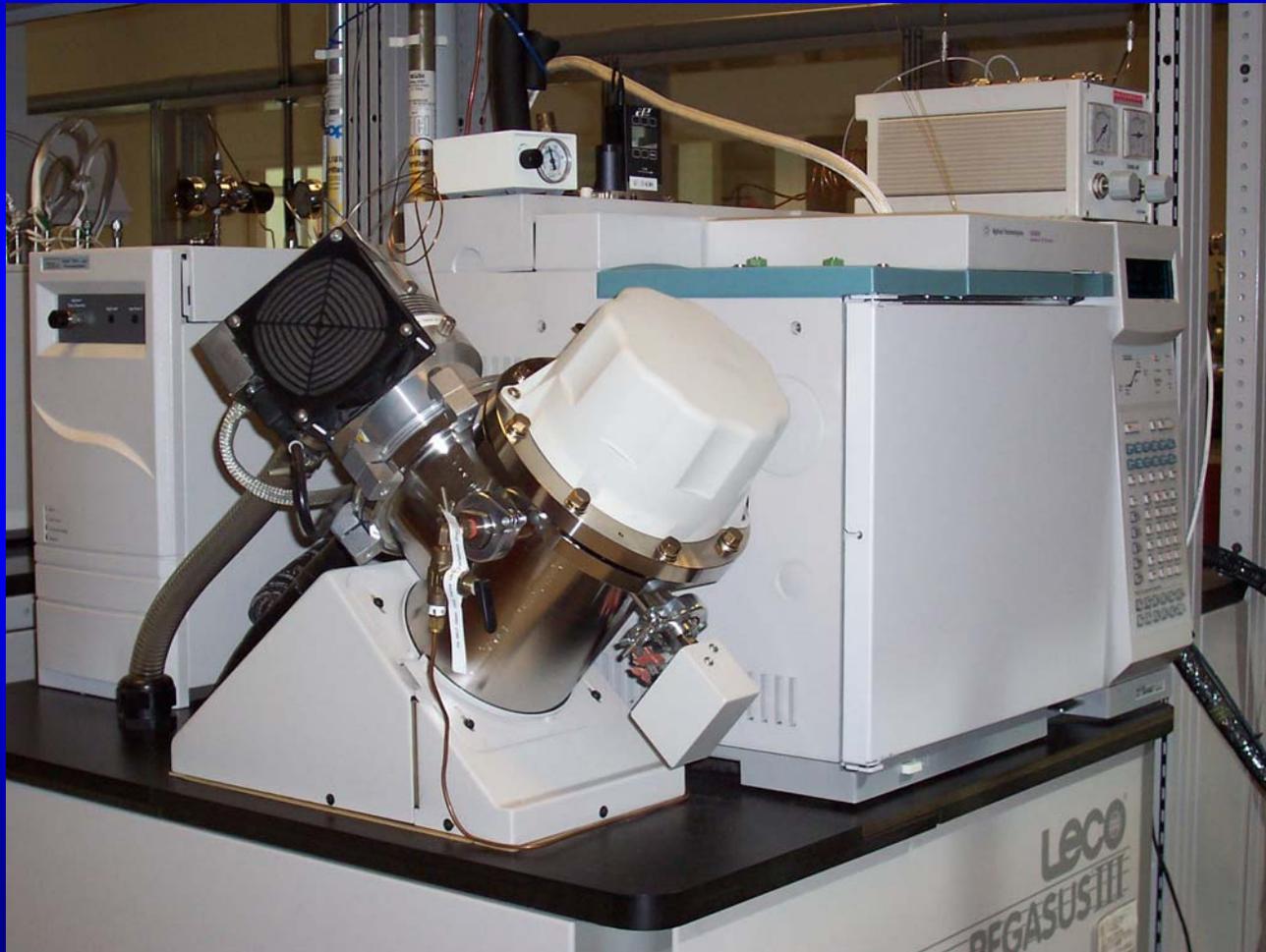
Bag Sampler (“Lung” Sampler): Converted watertight suitcase



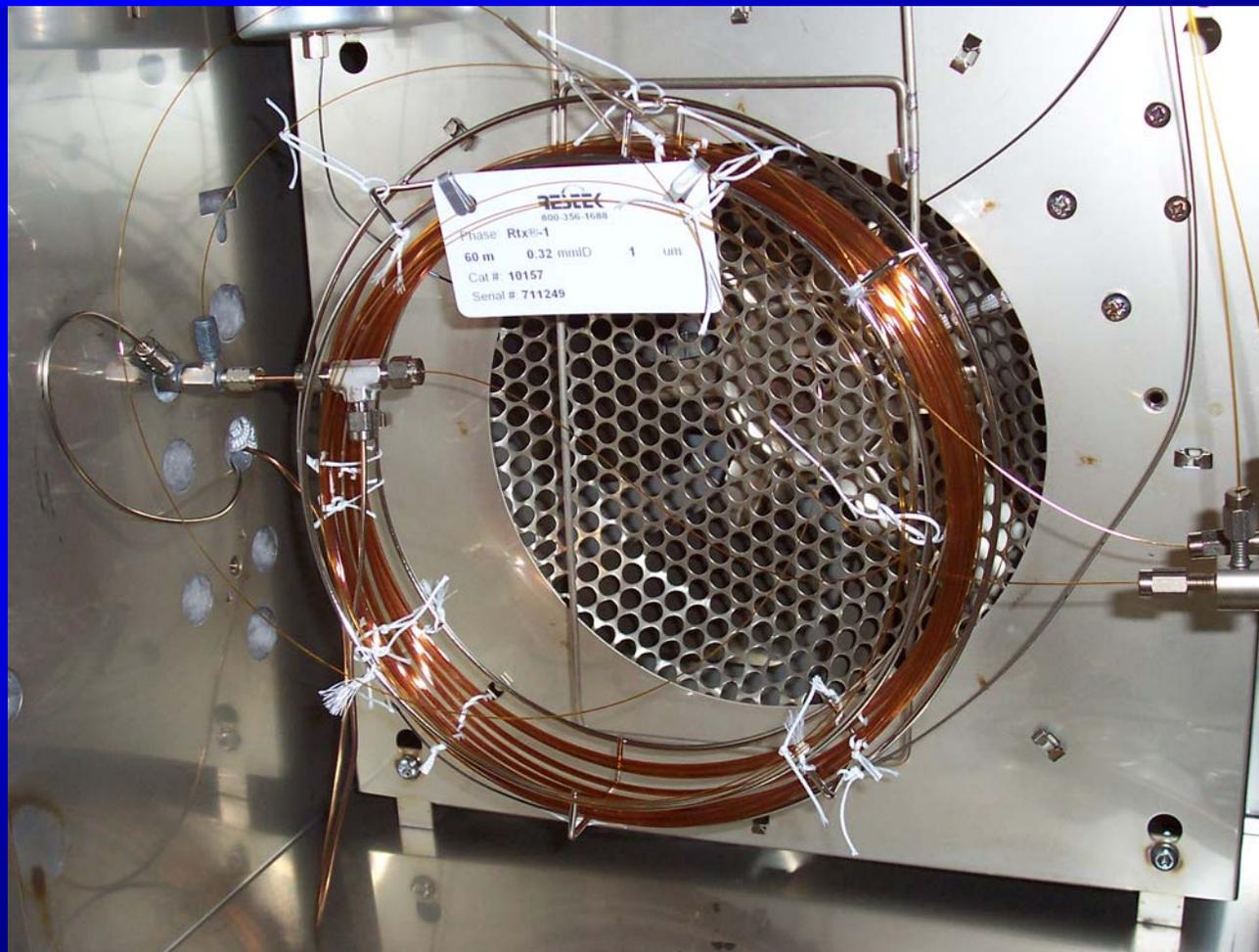
GC/MS-O Instrument Details

- Entech 7100 cryogenic concentrator
- Agilent 6890 GC
- LECO Pegasus® III time of flight mass spectrometer

LECO Pegasus GC-MS



GC Column, Open Split Interface, capillary lines to sniffers



Instrument Details

- Fused silica capillary tubing goes all the way to nose cones
- Heated transfer lines
- Humidified air in annular space around fused-silica transfer lines, mixes with sample at nose cones
- Capillary lines to odor analysts are longer than transfer line to mass spectrometer (12-15 second offset time)

Sniffer ports



Calculating the Combined Odor Response

THE GEOMETRIC MEAN IS USED

Combined response = $\text{SQRT}(\text{Odor1} * \text{Odor2})$

- Why not use the mathematical average?
 - Combined responses would not properly reflect the logarithmic nature of the intensities
- Non-detect responses from a sniffer
 - If zero is used in the calculation, the combined response would be zero
 - Use one-half the lowest detected intensity.

Measuring Odor Strength

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Moderate-Strong	12.5	1/4	1.250 V
Moderate	6	1/8	0.600 V
Weak-Moderate	3	1/16	0.300 V
Weak	1.5	1/32	0.150 V
Not Detected	0	0	0.075 V

Limitations of Method

- Present sampling and preconcentration method excludes organic acids and amines, and low-volatility compounds (Boiling Point >220 C).
- Can use other sampling and preconcentration methods:
 - Adsorbent tubes
 - Liquid impingers
 - SPME

Thank You!

References

- 1. Nagata, Yoshio: Measurement of Odor Threshold by Triangle Odor Bag Method, Japan Ministry of the Environment, at: http://www.env.go.jp/en/air/odor/measure/02_3_2.pdf
- 2. Verschueren, Karel: *Handbook of Environmental Data on Organic Chemicals*, 2nd Ed., 1983, Van Nostrand Reinhold, pp 42-59
- 3. Leland, J. V., Schieberle, P., Buettner, A., and Acree, T. E.: *Gas Chromatography-Olfactometry, The State of the Art*, 2001, ACS

References

- 4. European Committee for Standardization: Air Quality—Determination of odour concentration by dynamic olfactometry EN 13725:2003
- 5. American Society for Testing Methods: Standard Practice for Determination of Odor and Taste Thresholds By a Forced-Choice Ascending Concentration Series Method of Limits ASTM E 679 - 91
- 6. <http://www.lacsd.org/>
- 7. <http://www.fivesenses.com/>
- 8. <http://www.brechbuehler.com/>