Sampling and Analyzing Odorous Chemicals

BAAQMD Odor Evaluation Technical Conference
August 2, 2010

Alyson Fortune
Columbia Analytical Services

Presentation Overview

- Complexity of Odor
- Techniques to Measure Odorous Compound Concentrations
  - Amines
  - Carboxylic (Volatile Fatty) Acids
  - Reduced Sulfur Compounds
  - Volatile Organic Compounds (VOCs)
  - Aldehydes
- Field Case Study/Method Validation
- Summary

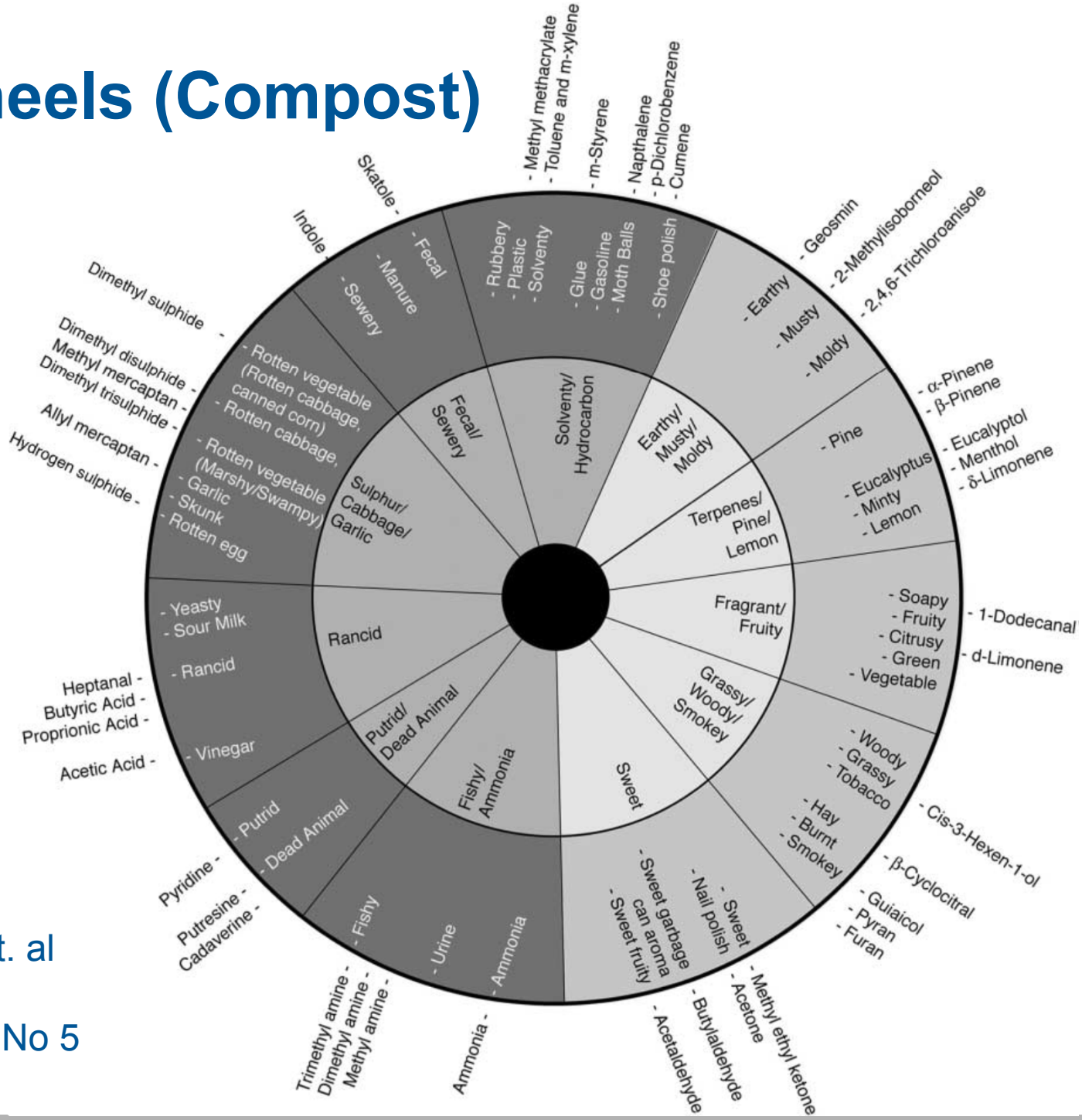
Odor Investigations: Complexity of Odors

Example: Wastewater Rx Plant

- No control over what comes into the plant
- Results in a complex mixture of compounds
- Organic processes further complicate odors
- Hydrogen sulfide (H_2S) used to be the main concern

Need to quantify a *whole range* of odorous compounds

Odor Wheels (Compost)

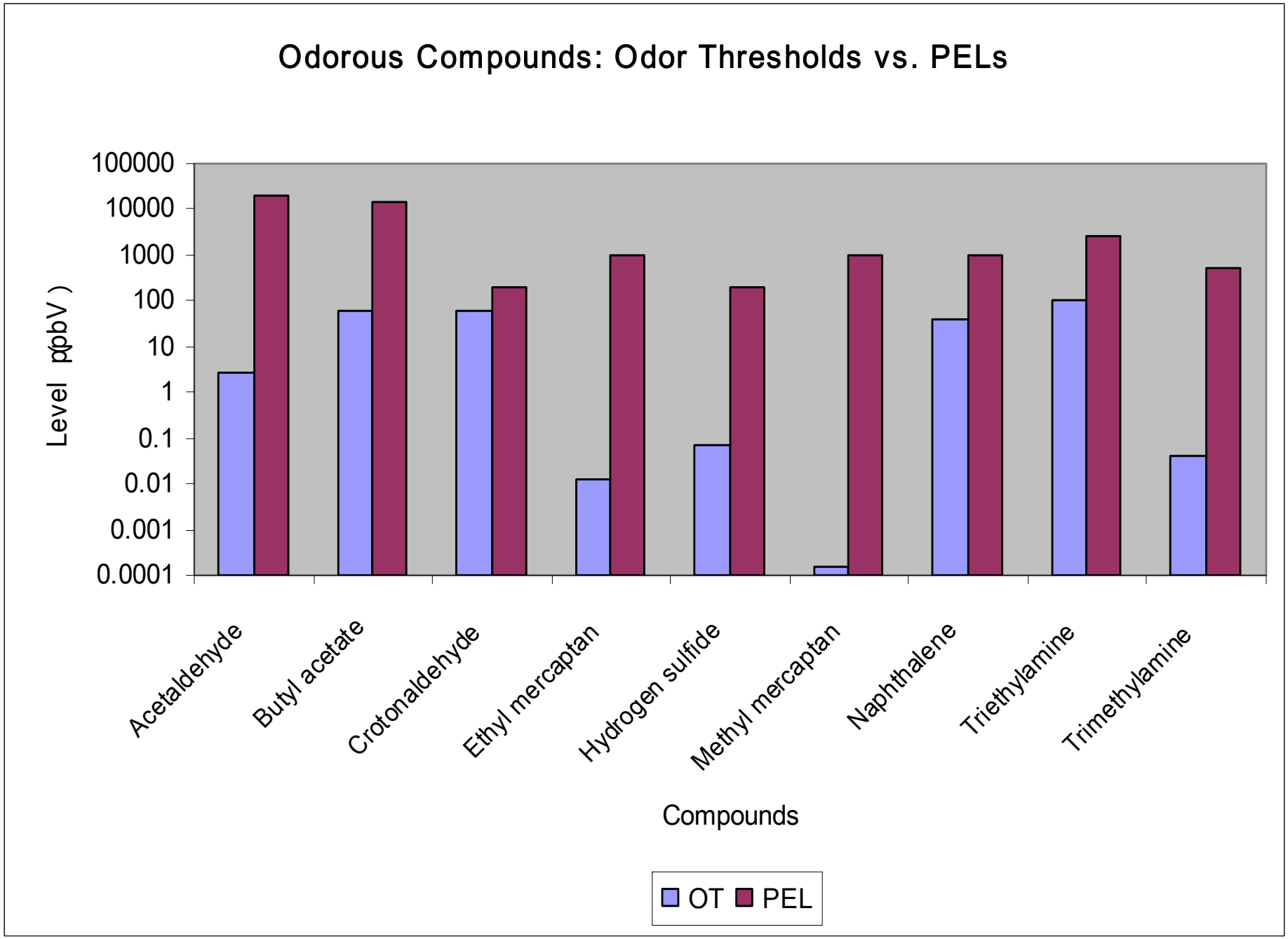


From Rosenfeld, et. al
Water Science &
Technology Vol 55 No 5
pp 345–357

Choose Wisely…

- The sampling and analytical method should be able to identify and quantify odorous compounds to the low ppbV levels

- Many existing methods were developed to address occupational exposures, not odor thresholds (e.g. OSHA methods, Dräger tubes)


Odorous Compounds: Odor Thresholds vs. PELs
100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Level (ppbV)
Acetaldehyde
Butyl acetate
Crotonaldehyde
Ethyl mercaptan
Hydrogen sulfide
Methyl mercaptan
Naphthalene
Triethylamine
Trimethylamine
Compounds
OT
PEL

Odor Wheels (Compost)

Earthy/Musty/Moldy	Earthy	Geosmin	In-House method: Anasorb 747, solvent desorb GC/MS *
	Musty	2-Methylisoborneol	In-House method: Anasorb 747, solvent desorb GC/MS *
	Moldy	2,4,6-trichloroanisole	In-House method: OVS tube, GC/ECD *
Terpenes/Pine/Lemon	Pine	a-pinene, b-pinene	EPA TO-15
	Eucalyptus	Eucalyptol	EPA TO-15/TO-17 (TIC)
	Minty	menthol	EPA TO-15/TO-17 (TIC)
	Lemon	d-limonene	EPA TO-15
Fragrant/Fruity	Soapy	1-dodecanal	EPA TO-15/TO-17 (TIC)
	Fruity		
	Citrusy	d-limonene	EPA TO-15
	Green		
	Vegetable		
Grassy/Woody/Smokey	Woody		
	Grassy	cis-3-henen-1-ol	TO-17 (TIC)
	Tobacco		
	Hay	β-cyclocitral	TO-17 (TIC)
	Burnt		
	Smokey	guiaicol, pyran, furan	EPA TO-15/TO-17 (TIC)

Odor Wheels (Compost)

Sweet	Sweet Nail polish Sweet garbage can aroma Sweet fruity	Methyl ethyl Ketone Acetone Butyraldehyde Acetaldehyde	EPA TO-15 EPA TO-15 EPA TO-11A EPA TO-11A
Solventy/Hydrocarbon	Gasoline Rubbery Plastic Solventy Moth balls Shoe polish Glue	 methyl methacrylate toluene, xylenes naphthalene, p-dichlorobenzene cumene styrene	 EPA TO-15 EPA TO-15 EPA TO-15 EPA TO-15 EPA TO-15
Fecal/Sewery	Fecal Manure Sewery	Skatole Indole	EPA TO-17 (Tenax) EPA TO-17 (Tenax)

Odor Wheels (Compost)

Sulfur/Cabbage /Garlic	Rotten vegetables (rotten cabbage, canned corn)	Dimethyl sulfide	ASTM D5504
	Rotten cabbage	Dimethyl disulfide, methyl mercaptan	ASTM D5504
	Rotten vegetable (Marshy/Swampy)	Dimethyl trisulfide	ASTM D5504 *
	Garlic	allyl mercaptan	ASTM D5504 *
	skunk		
	Rotten Egg	hydrogen sulfide	ASTM D5504, passive radiello
Rancid	Sour milk, yeasty		
	Rancid	heptanal, butyric acid, propionic acid	EPA TO-11A, In-House method: sorbent tube GC/MS
	Vinegar	acetic acid	In-House method: sorbent tube GC/MS
Putrid/Dead Animal	Putrid	pyridine	EPA TO-15/TO-17 (TIC)
	Dead animal	putresine, cadaverine	TO-17 (TIC)
Fishy/Ammonia	Fishy	trimethyl amine, dimethyl amine, methyl amine	CAS101 (GC/NPD)
	Urine		
	Ammonia	ammonia	OSHA ID-164

Amines

- Decomposition of amino acids
- Odor Descriptors: fishy, putrid, pungent or sour, fertilizer smell
- Collected on specially treated alumina sorbent tube (proprietary preparation)
- Columbia Analytical In-House Method 101
  - Specially modified GC/NPD (Nitrogen Phosphorous Detector)
- MRLs down to ~5 $\mu g/m^3$
  - ≤ Odor threshold for most compounds

Amines

Assumes 100L volume sampled

Compound	CAS No.	MRL (µg/m³)	Odor Threshold Range (µg/m³)	Character
Dimethylamine	124-40-3	5.2	1.4 - 2949	Putrid, fishy, ammonical
Ethylamine	75-04-7	5.8	15 - 6450	Sharp, ammonical
Trimethylamine	75-50-3	4.6	0.24 - 2100	Fishy, pungent
Isopropylamine	75-31-0	4.9	2900	Ammoniacal/amine
t-Butylamine	75-64-9	4.8	-	
Propylamine	107-10-8	7.2	-	
Diethylamine	109-89-7	5.1	60 - 389	Musty, fishy, amine
s-Butylamine	13952-84-6	5.0	-	
Isobutylamine	78-81-9	5.1	-	
Butylamine	109-73-9	5.0	239 - 41600	Sour, ammonia, fishy
Diisopropylamine	108-18-9	4.8	538 - 627	Fishy/amine
Triethylamine	121-44-8	5.0	414 - 120000	Fishy, amine
Dipropylamine	142-84-7	4.7	-	

Carboxylic (Volatile Fatty) Acids

- Decomposition of proteins
- Odor descriptors: rancid, fecal, vomitous, sweaty, goat-like
- Collected on a NaOH-treated silica gel tube
- Columbia Analytical In-House Method 102
  Gas Chromatography/Mass Spectrometry
- MRLs down to ~2-10 $\mu g/m^3$

  $\leq$ Odor threshold for most compounds

Carboxylic Acids

Assumes 100L volume sampled

Compound	CAS No.	MRL ($\mu g/m^3$)	Odor Threshold Range ($\mu g/m^3$)	Character
Acetic Acid	64-19-7	11	15 - 250000	Sour, vinegar
Propionic Acid (Propanoic)	79-09-4	2.8	2.5 - 60000	Sour, unpleasant, fecal
2-Methylpropanoic Acid (Isobutyric)	79-31-2	2.9	0.72-29200	Fecal, rancid butter
Butanoic Acid (Butyric)	107-92-6	2.6	0.25 - 37800	Rancid, sour, fecal, stench
2-Methylbutanoic Acid	116-53-0	2.6	100	Sweaty, goaty
3-Methylbutanoic Acid (Isovaleric)	503-74-2	2.6	0.17-11	Rancid, moldy cheese, fecal, sweaty
Pentanoic Acid (Valeric)	109-52-4	2.6	0.3 - 20	Fecal, sweaty
2-Methylpentanoic Acid	97-61-0	2.6		
3-Methylpentanoic Acid	105-41-1	2.6		
4-Methylpentanoic Acid (Isocaproic)	646-07-1	2.7	2 - 76	Stench

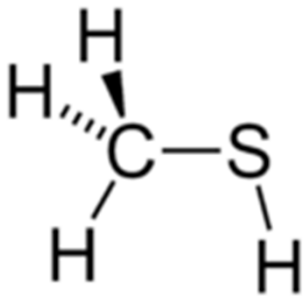
Carboxylic Acids, cont.

Assumes 100L volume sampled

Compound	CAS No.	MRL ($\mu g/m^3$)	Odor Threshold Range ($\mu g/m^3$)	Character
Hexanoic Acid (Caproic)	142-62-1	2.6	2 - 60	Fecal, sweaty
2-Ethylhexanoic Acid	149-57-5	2.7		
Heptanoic Acid (Enanthoic)	111-14-8	2.6	2.8 - 150	Pungent
Octanoic Acid (Caprylic)	124-07-2	2.6	0.29-24	Sweaty
Cyclohexanecarboxylic Acid	98-89-5	2.6		
Nonanoic Acid (Pelargonic)	112-05-0	2.7		
Benzoic Acid	65-85-0	3.0		

Reduced Sulfur Compounds: ASTM D5504

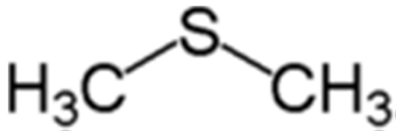
- Many sulfur compounds *are not stable* in stainless steel canisters (even “Silco” or FSL canisters)
  - Hydrogen Sulfide
  - Any compound with S-H bond
    - (e.g. H_2S, mercaptans)



Methyl Mercaptan

CH_4S

- Samples are best collected in Tedlar bags with Polypropylene fittings
  - 24 hour hold time (overnight shipping and laboratory notification required)



Dimethyl Sulfide

C_2H_6S

Reduced Sulfur Compounds: ASTM D5504

Picture courtesy of St. Croix Sensory

- Samples are best collected in Tedlar bags using “lung box” (a.k.a. “vacuum box”) technique
  - Pump draws vacuum on box to fill bag

Reduced Sulfur Compounds: ASTM D5504

- Odor descriptors: rotten egg, cabbage, vegetables, skunk, sulfur
- Laboratory analysis
  - Gas chromatography/ sulfur chemiluminescence detection (GC/SCD)
- No interference from other hydrocarbons
- Single digit ppbV sensitivity

Reduced Sulfur Compounds: ASTM D5504

Compound	CAS No.	MRL (ppbV)	Odor Threshold Range (ppbV)	Character
Hydrogen sulfide	7783-06-4	5.0	0.07-130	Rotten egg
Carbonyl sulfide	463-58-1	5.0	-	Pungent, Odorless
Methyl mercaptan	74-93-1	5.0	0.00015-42	Decayed cabbage, sulfide
Ethyl mercaptan	75-08-1	5.0	0.013-36	Decayed cabbage, sulfide
Dimethyl sulfide	75-18-3	5.0	0.1-20	Decayed/rotten cabbage (vegetables)
Carbon disulfide	75-15-0	2.5	7.7-74000	Disagreeable, vegetable sulfide
Isopropyl Mercaptan	75-33-2	5.0	-	
tert-Butyl mercaptan	75-66-1	5.0	0.5	Skunky, unpleasant
n-Propyl Mercaptan	107-03-9	5.0	0.0008-0.5	Unpleasant, cabbage
Ethyl Methyl Sulfide	624-89-5	5.0	-	sulfourous, garlic
Thiophene	110-02-1	5.0	-	Sweet

Reduced Sulfur Compounds: ASTM D5504

Compound	CAS No.	MRL (ppbV)	Odor Threshold Range (ppbV)	Character
Isobutyl Mercaptan	513-44-0	5.0	2000	skunk
Diethyl Sulfide	352-93-2	5.0	-	Sharp, garlic
n-Butyl mercaptan	109-79-5	5.0	0.02-1100	Skunk, unpleasant
Dimethyl disulfide	624-92-0	2.5	0.026-160	Sulfide, decayed vegetables
3-Methylthiophene	616-44-4	5.0	-	
Tetrahydrothiophene	110-01-0	5.0	-	Sharp, pungent
2,5-Dimethylthiophene	638-02-8	5.0	-	
2-Ethylthiophene	872-55-9	5.0	-	
Diethyl Disulfide	110-81-6	2.5	-	
Dimethyl trisulfide *	3658-80-8	2.0	1.2 - 4.5	Nauseating, rotten cabbage

* = compound available by special request

radiello® for Hydrogen Sulfide

- Passive/diffusive sampling
- Zinc acetate-treated polyethylene
- No holding time issues
- Reporting limit decreases with increased duration of exposure
  - Potential pptV level sensitivity
- Methylene blue: visible spectrometry

Picture courtesy of Sigma Aldrich

radiello® Reporting Limits

Sampling Duration	Reporting Limit (ppbV)
4 hours	15
8 hours	7.6
24 hours	2.5
72 hours	0.84
7 days	0.36

Assumes 0.35 µg MRL, sampling rate provided by manufacturer, collected at 25°C.

Volatile Organic Compounds

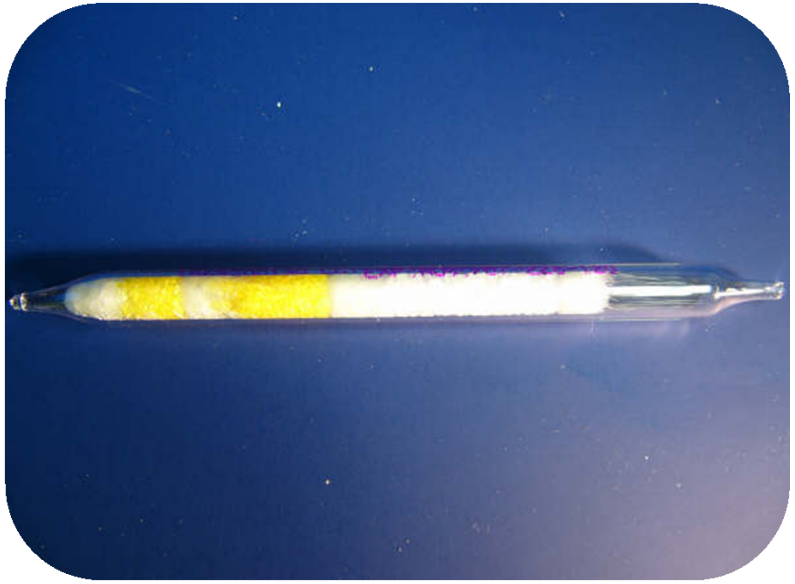
- VOCs: EPA TO-17 Screening
  - Thermal Desorption / Gas Chromatography / Mass Spectrometry (TD/GC/MS)
  - 15 most predominant or known odorous compounds in sample will be identified semi-quantitatively (TICs)
  - Tenax TA sorbent or Carbotrap 300 multi-sorbent
  - High pptV/low ppbV sensitivity

Volatile Organic Compounds

- VOCs: EPA TO-15
  - Gas Chromatography / Mass Spectrometry (GC/MS)
  - Standard list of 75 compounds, TICs also available
  - Grab sample or time-integrated into stainless steel (Summa or equivalent) canister
  - Low ppbV sensitivity

Aldehydes

- Aldehydes: EPA TO-11A
  - Odor descriptors: sweet, fruity, green, minty, pungent, unpleasant
  - DNPH treated silica gel
  - Must be kept cold prior to and after sample collection
  - High Performance Liquid Chromatography (HPLC/UV) analysis
  - Low ppbV sensitivity



Aldehydes

Assumes 100L volume sampled

Compound	CAS No.	MRL (ppbV)	Odor Threshold Range (ppbV)	Character
Formaldehyde	50-00-0	0.81	1197 - 59,867	unpleasant
Acetaldehyde	75-07-0	0.56	0.11 - 2299	green, sweet
Propionaldehyde	123-38-6	0.42	9.5 - 170	sweet, ester
Crotonaldehyde, Total	4170-30-3	0.35	37 - 1047	pungent, suffocating
Butyraldehyde	123-72-8	0.34	4.6 - 9007	sweet, rancid
Benzaldehyde	100-52-7	0.23	0.18 - 42	pleasant, bitter

Aldehydes, cont.

Assumes 100L volume sampled

Compound	CAS No.	MRL (ppbV)	Odor Threshold Range (ppbV)	Character
Isovaleraldehyde	590-86-3	0.28	0.45 - 2.3	forest green, moldy
Valeraldehyde	110-62-3	0.28	28	pungent
o-Tolualdehyde	529-20-4	0.20	-	
m,p-Tolualdehyde	620-23-5, 104-87-0	0.41	-	
n-Hexaldehyde	66-25-1	0.24	6.8 - 16	green leaves
2,5-Dimethylbenzaldehyde	5779-94-2	0.18	-	

Other aldehydes may be seen as TICs via EPA TO-17

Summary of Sampling Information

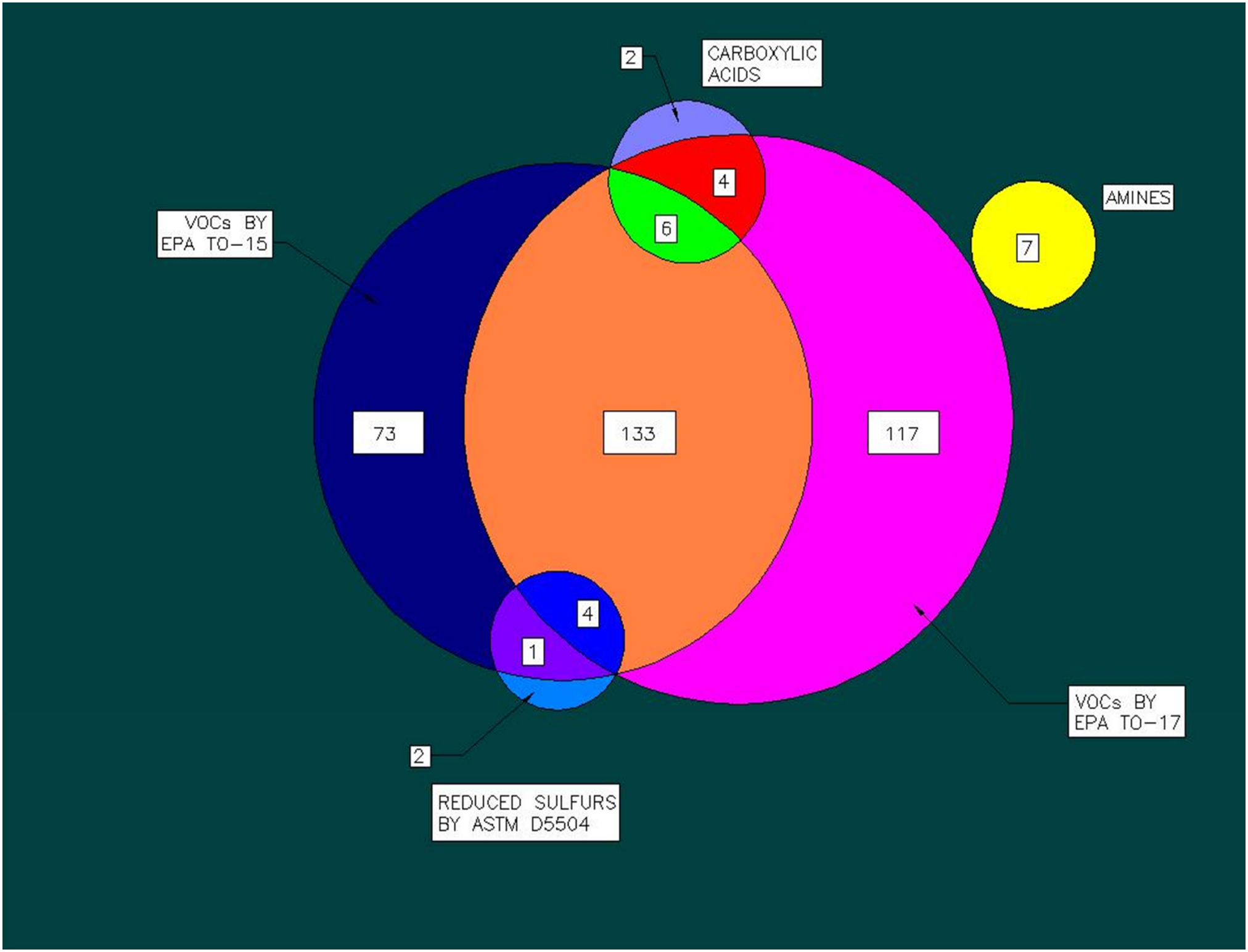
Target Compounds	Method	Media	Volume	Flow Rate	Sampling Interval	Reporting Limits
Amines	CAS AQL 101	In-House alumina tube	100 L (max)	1 L/min	100 minutes	4.6 – 7.2 $\mu g/m^3$
Carboxylic Acids	CAS AQL 102	NaOH Treated Silica Gel	100 L (max)	1 L/min	100 minutes	2.0 - 10 $\mu g/m^3$
Reduced Sulfurs	ASTM D5504-01	Tedlar bags	grab	grab	grab	2.5 - 5.0 ppbV
VOC Screen	EPA TO-17	Thermal desorption tube	4 L (max)	0.1 L/min	40 minutes	0.50 - 5.0 $\mu g/m^3$
Aldehydes	EPA TO-11A	DNPH treated silica gel	100L (min)	Varies	Varies	1.0 – 6.0 $\mu g/m^3$

Reporting limits subject to change based on instrument performance and may be dependent on volume sampled.

Field Study

- Samples collected at a composting facility containing:
  - yard debris
  - fish carcasses
  - chicken blood/fat
  - food waste
  - C&D (Gypsum)

- Results confirmed that no one method can be used to identify all compounds present


2
CARBOXYLIC ACIDS
4
6
AMINES
7
VOCs BY EPA TO-15
73
133
117
4
1
2
VOCs BY EPA TO-17
REDUCED SULFURS BY ASTM D5504

Summary

- No “One Size Fits All” sampling/analytical approach for odorous chemicals
- Large number of odors contribute to odor perception
- Additive, synergistic and antagonistic effects
- Multiple methods often required to address a single source
- Amines, carboxylic acids, reduced sulfurs, VOCs, and aldehydes are common analyses

Columbia Analytical Services INC

Questions?

Alyson Fortune
Air Quality Scientist
afortune@caslab.com
978-501-2735

www.caslab.com