So, a graduate student, huh?

How come you guys can go to the moon but you can't make my shoes smell good?

Homer Simpson (1994)

Introduction to Odor

Jacek Koziel

Dept. Agricultural & Biosystems Engineering

Dept. of Civil, Constr. & Environmental Engineering

Iowa State University

Ames, Iowa, USA

koziel@iastate.edu

PHYSIOLOGY NOBEL PRIZE

WINNING BY A NOSE

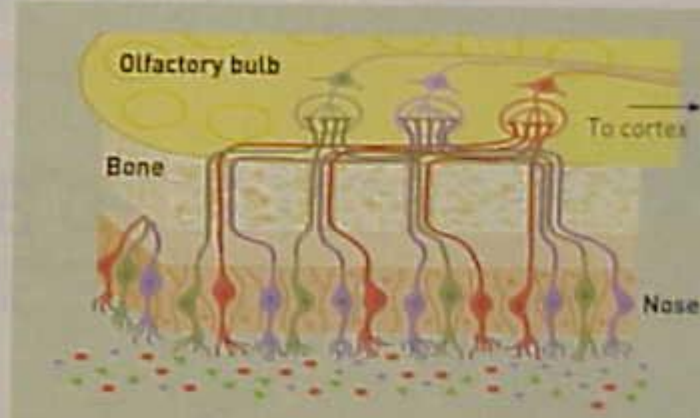
Laureates' research has demystified the sense of smell

TWO U.S. RESEARCHERS HAVE won this year's Nobel Prize in Physiology or Medicine for shedding light on the inner workings of the sense of smell.

Scientists had long wondered how the olfactory system recognizes and remembers more than 10,000 different odors. Richard Axel, 58, a Howard Hughes Medical Institute investigator and professor of biochemistry and mo-

lecular biophysics at Columbia University and Linda B. Buck, 57,

spanning receptor proteins found in a small patch of cells inside the nose. Mice make an astonishing 1,000 or so different kinds of these odorant receptor proteins. Humans, who don't rely as much as mice on their sense of smell, make about 350 different ones. Axel and Buck showed that these odorant receptor proteins belong to a family of proteins called G-protein-coupled receptors, a class that also includes the rhodopsin proteins that initiate vision.



HOW THE NOSE KNOWS Axel and Buck figured out how the binding of odorants (geometrical shapes at bottom) to protein receptors on the surface of cells in the nose causes electrical signals to be sent first to a region of the brain called the olfactory bulb and then on to the parts of the brain that control thought and emotion.

factory researcher Peter Mombaerts of Rockefeller University. "While the term 'breakthrough,' is all too often used, I believe this paper is one of the clearest examples," he adds.

Later, Axel and Buck—who started her own lab after her post-doc stint with Axel—independently showed that each cell in this region expresses only one type of odorant receptor protein. Each odorant molecule in a given scent activates several different types of odorant receptor proteins. As a result, a given scent gives rise to a unique signature of activated cells, allowing the brain to recognize and remember more than 10,000

National Geographic

September 2007 (Polish edition)

(by Magda Tilszer)

trafiają do kadzi z fermentującym miąższem.

Tajemnicą zepsutego wina zajął się dr Jacek Kozieł z Uniwersytetu Stanu Iowa w Ames. Zbadał on skład chemiczny substancji, jakie biedronki wydzielają pod wpływem stresu, np. gdy zbliża się drapieżnik. Stwierdził, że *Harmonia axyridis*,

BIEDRONKI 103

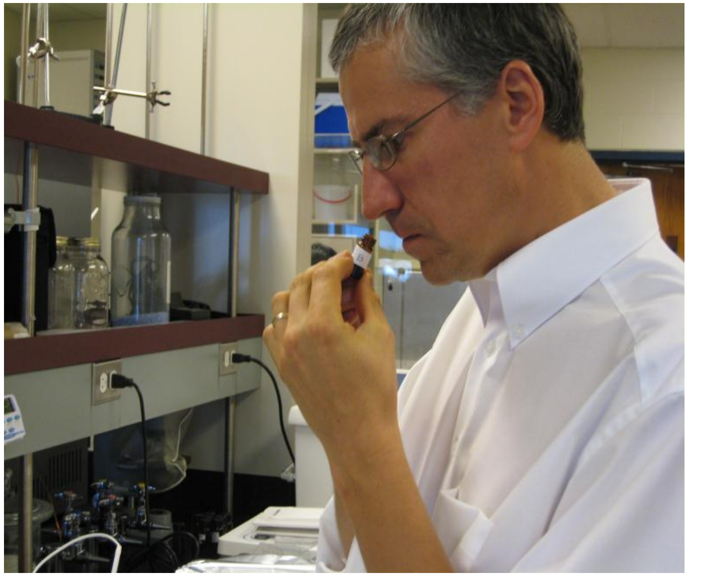
Heras Joel/Biosphoto/Photolink

My world of odors

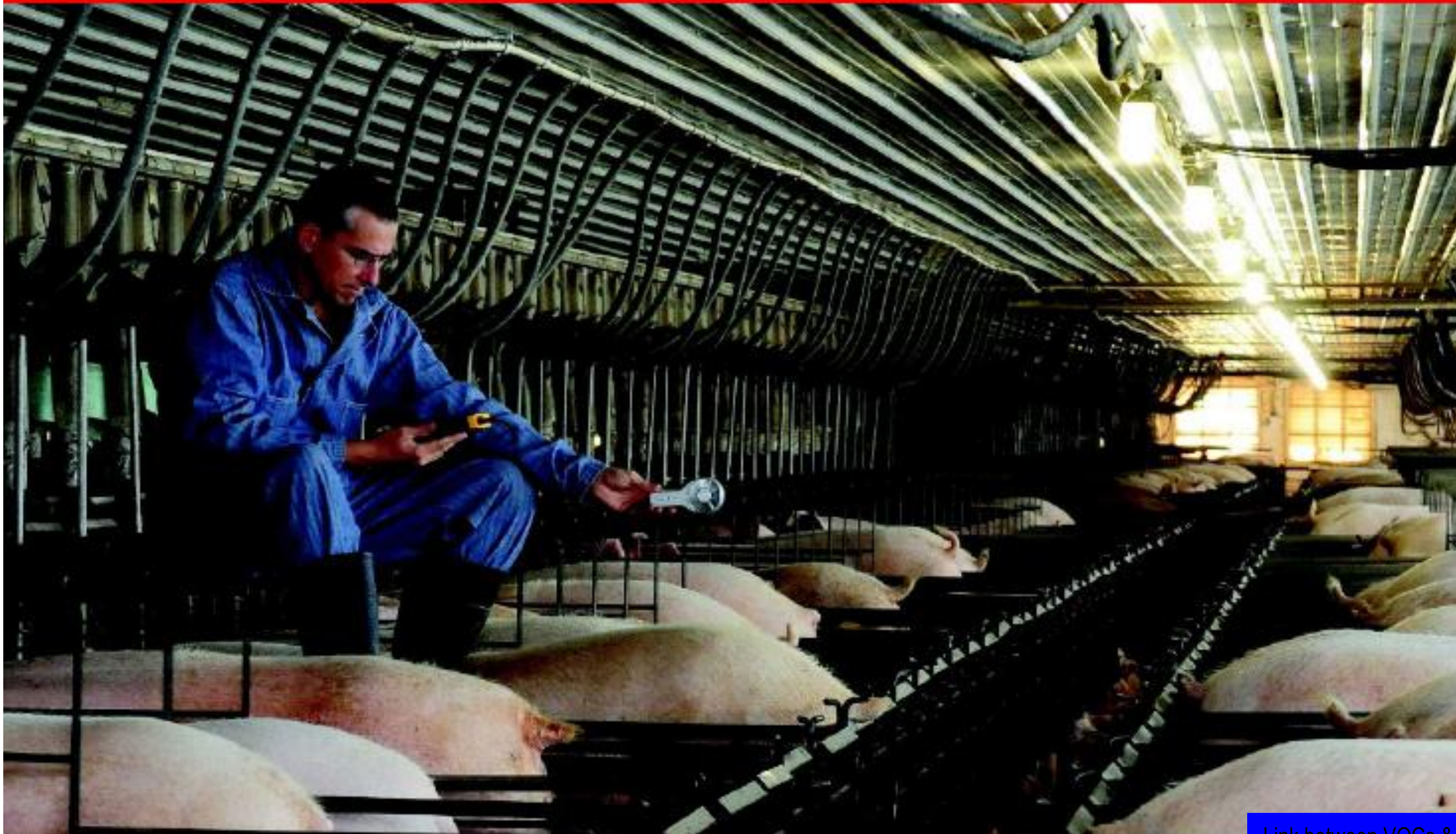
- Livestock and poultry odor
- Vodka
- Insects
- Biofuels
- Wine
- Human breath
- Animal mortalities
- Indoor air
- Spices
- Lion’s urine
- Particulate matter

World of odors

- Very complex mixtures of gases (beer?)
- Not all gases odorous
- Some are extremely odorous
- Very low concentrations
- ‘needle in the haystack’
- Link between concentration and perceived odor?
- What gases cause the characteristic odor?
- How to solve odor problems?
  - (advanced oxidation (ozone, UV))
- How to use this information?



NATURE|Vol 455|9 October 2008



WHAT IS THAT SMELL?

Jacek Koziel is a master of odours. On a pig farm in Iowa, he shows **Erik Vance** some of the peaks and troughs of life as a human detector.

Link between VOCs & odor with SPME-multidimensional GC-MS-Olfactometry

- *Wright et al., 2005*
- *Bulliner et al., 2006*
- *Cai et al., 2006*
- *Cai et al., 2007*
- *Koziel et al., 2007*
- *Lo et al., 2008*

So the key question is…☺

- …what causes the characteristic smell of concrete and steel? (materials are evidence of smells from environment)

Odor measurement with non-nose sensors

- Gas chromatography
  - separation of VOCs including odorants
  - MS, FID, PID, PFPD, …
  - ppq – ppt
  - gas concentrations
  - mature technology
- Real-time analyzers
  - Total VOCs or specific compounds (NH_3, H_2S)
  - ppb – ppm
  - gas concentrations
  - mature technology
- Sensor arrays (a.k.a. 'electronic noses')
  - ppb – ppm
  - evolving technology
  - principal component analysis (PCA)
  - PCA almost always "work"
- What compounds cause problems?
- Why odor mitigation works?

Long-term goals

- Solving livestock odor problem
- Solving odor problems
  - Bad breath
  - Ladybugs
  - Food (e.g., wine)
  - Consumer products
  - Nuisance and air quality

Approach

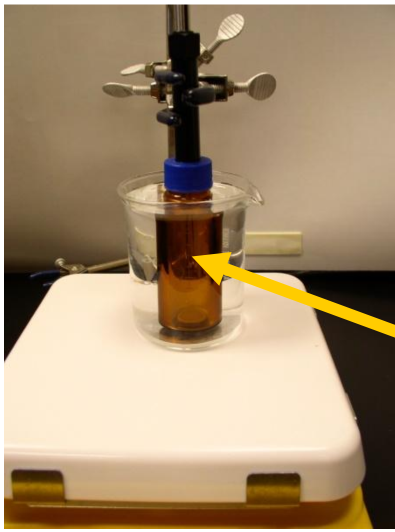
- Simultaneous chemical + olfactometry analysis
  - GC-Olfactometry approach
- Identification of key compounds responsible for odor
  "finding stinky 'needles' in the haystack of odor"
- Methods development for field measurements
- Development and evaluation of odor control technologies

Background

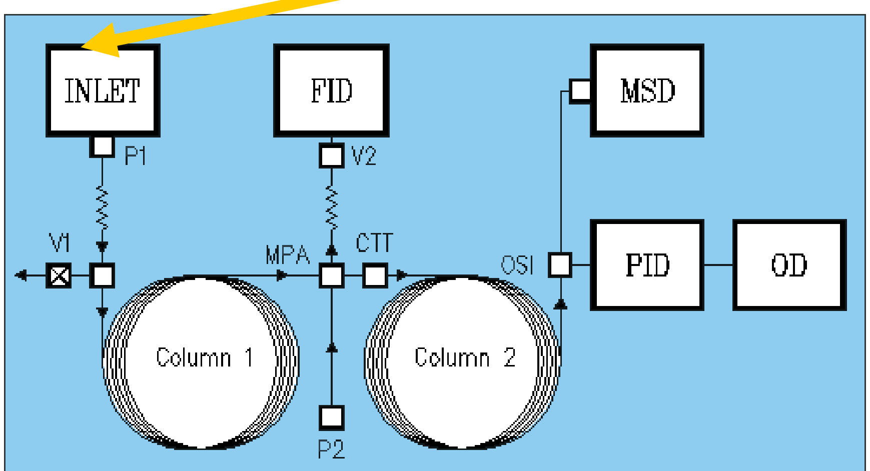
- Odor analysis is challenging
- Odor sources are complex (thousands of VOCs)
- Actual malodor is caused by small subset of high impact odorants
- Solving malodor problems involves isolation, identification, and reduction of high impact odorants

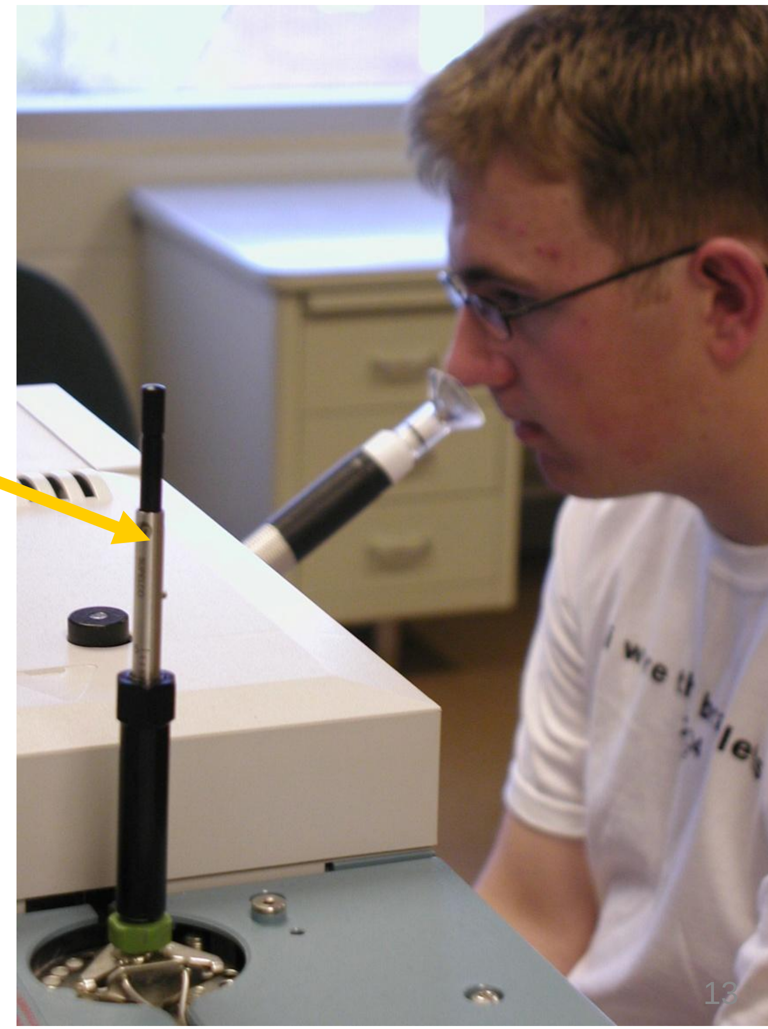
Simultaneous chemical and odor analysis

SPME-MDGC-MS-Olfactometry system



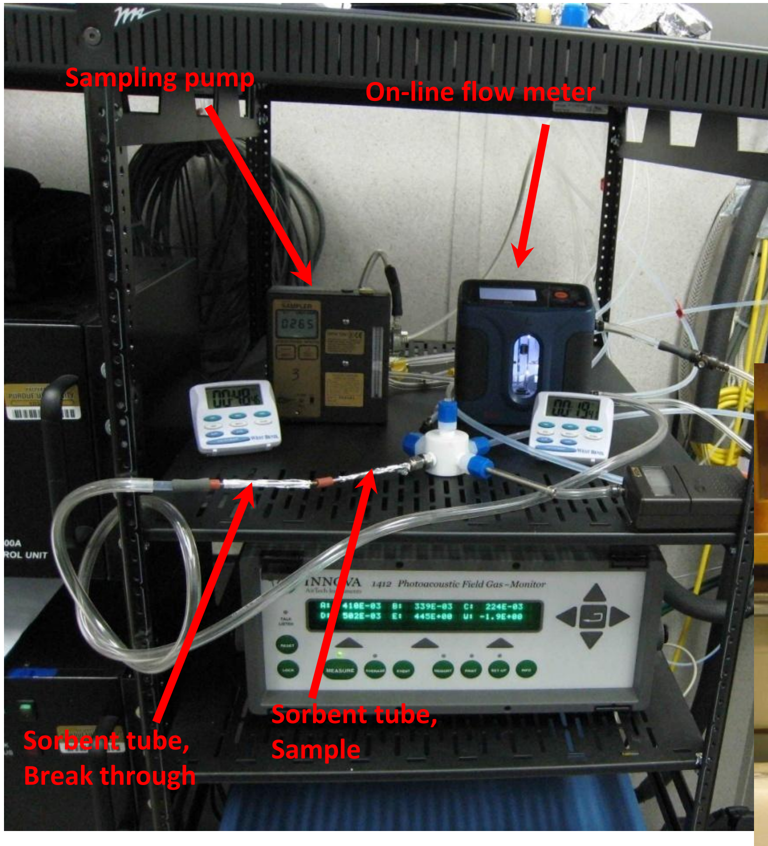
SPME

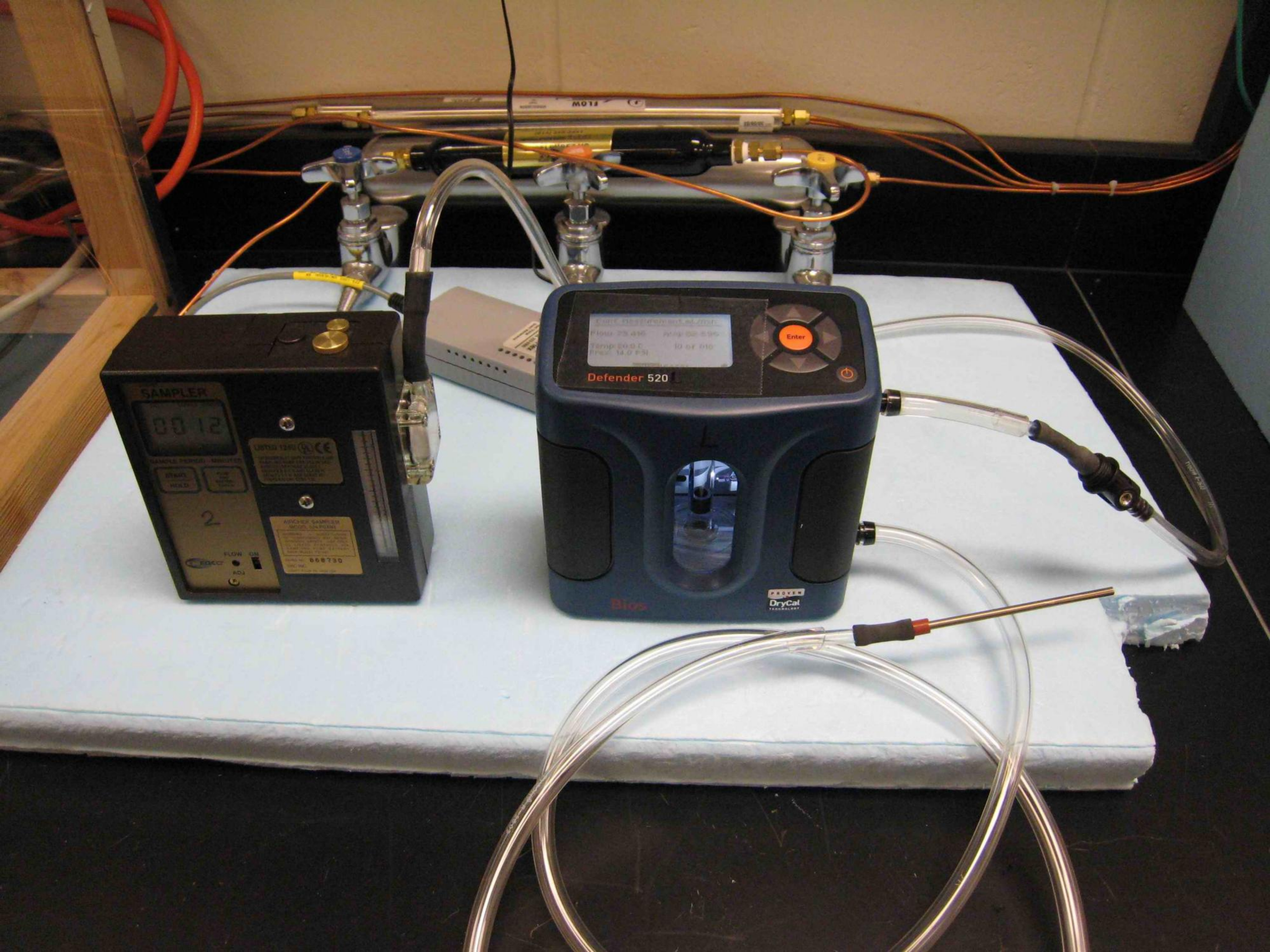




Simultaneous chemical and odor analysis

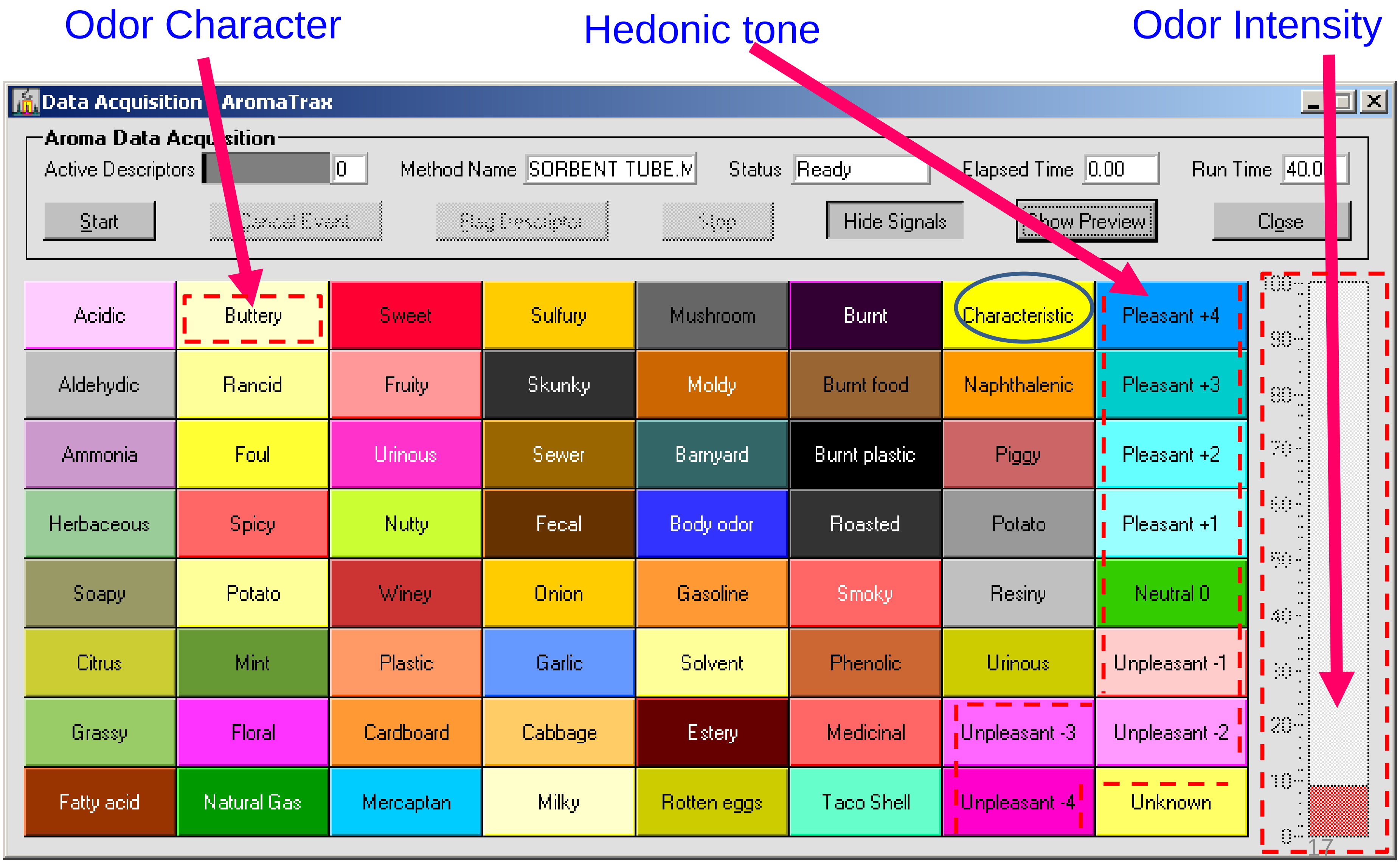
Sorbent tubes-MDGC-MS-Olfactometry system




SAMPLER
0012
2
FLOW
ON
ADJ
Defender 520
Enter
Bios
DryCal

Finding characteristic, odor-defining compounds

Characterizing odor caused by separated chemicals from one sample

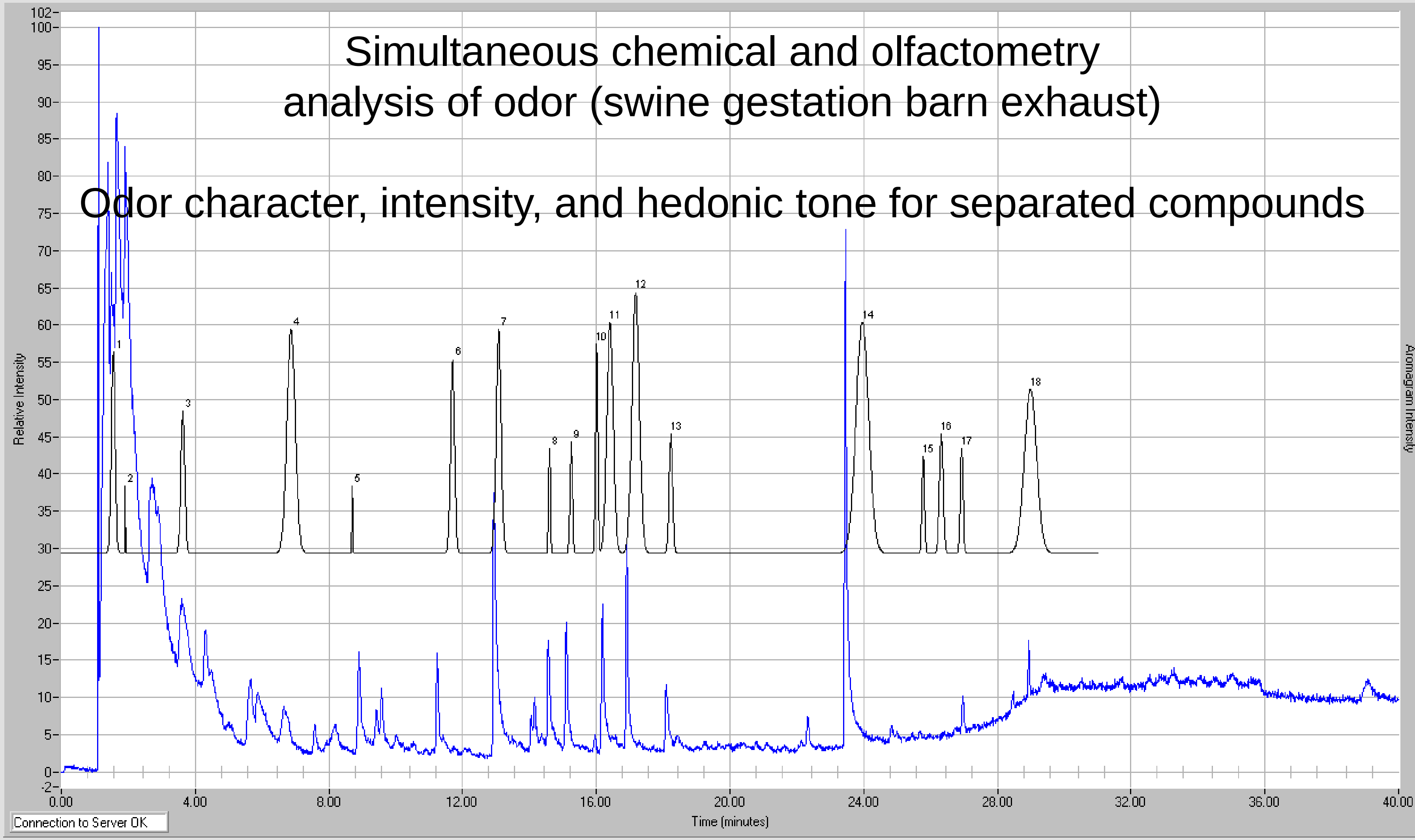


AromaTrax Aroma Characterization Software

File Data Acquisition Data Analysis Aroma Dilution Analysis Display Options Help

Simultaneous chemical and olfactometry analysis of odor (swine gestation barn exhaust)

Odor character, intensity, and hedonic tone for separated compounds



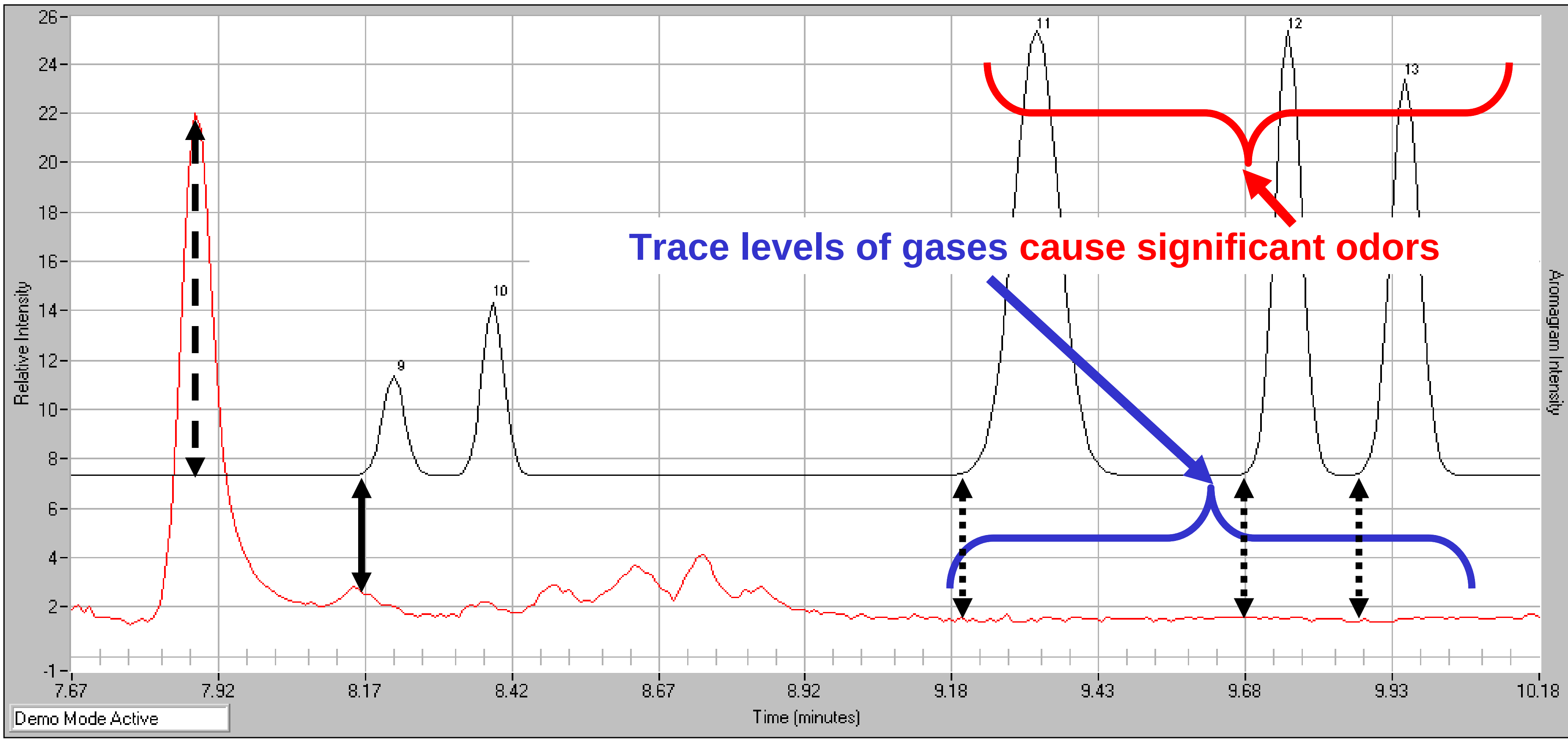
Raw Data File DATA.MS

Aroma Events 18

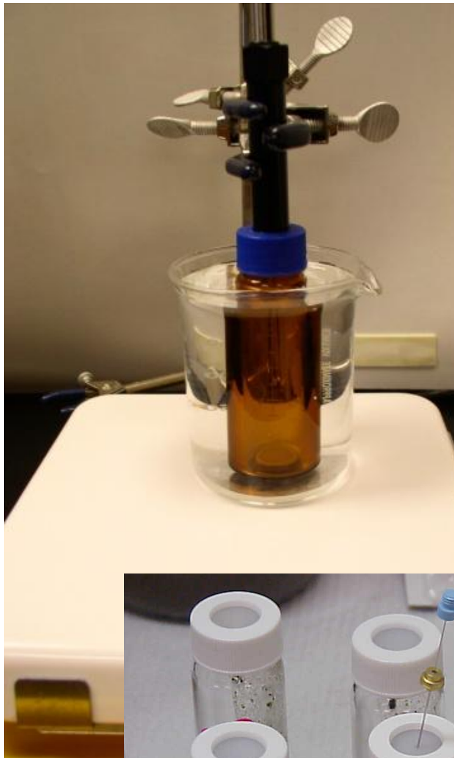
Results Data File OEP036.RS2

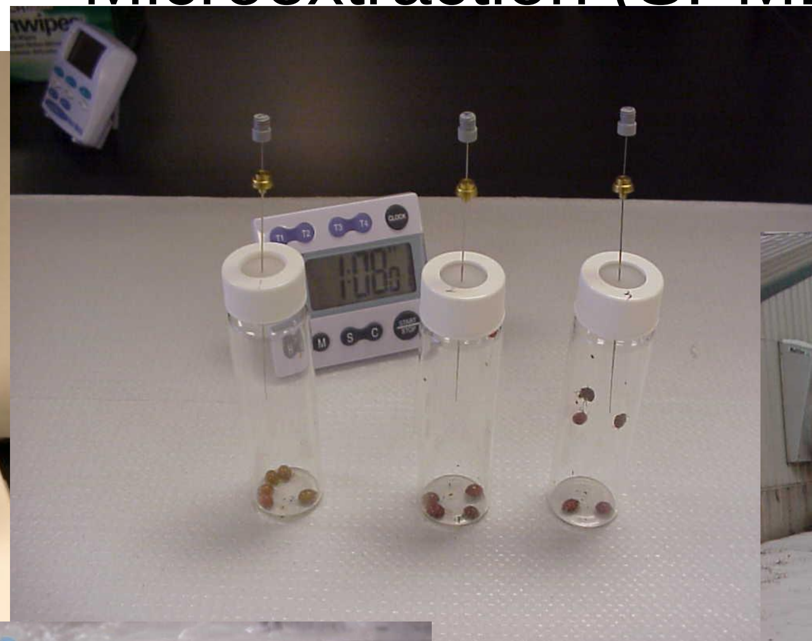
Event Number	Descriptor	Start Time (min)	Event Width	Intensity	Area
8	Acidic Fatty acid Body odor Unpleasant -1	14.54	0.14	14	195
9	Acidic Fatty acid Unpleasant -1	15.15	0.21	15	314
10	Unknown	15.92	0.19	28	531

Simultaneous chemical and olfactometry analysis of odor

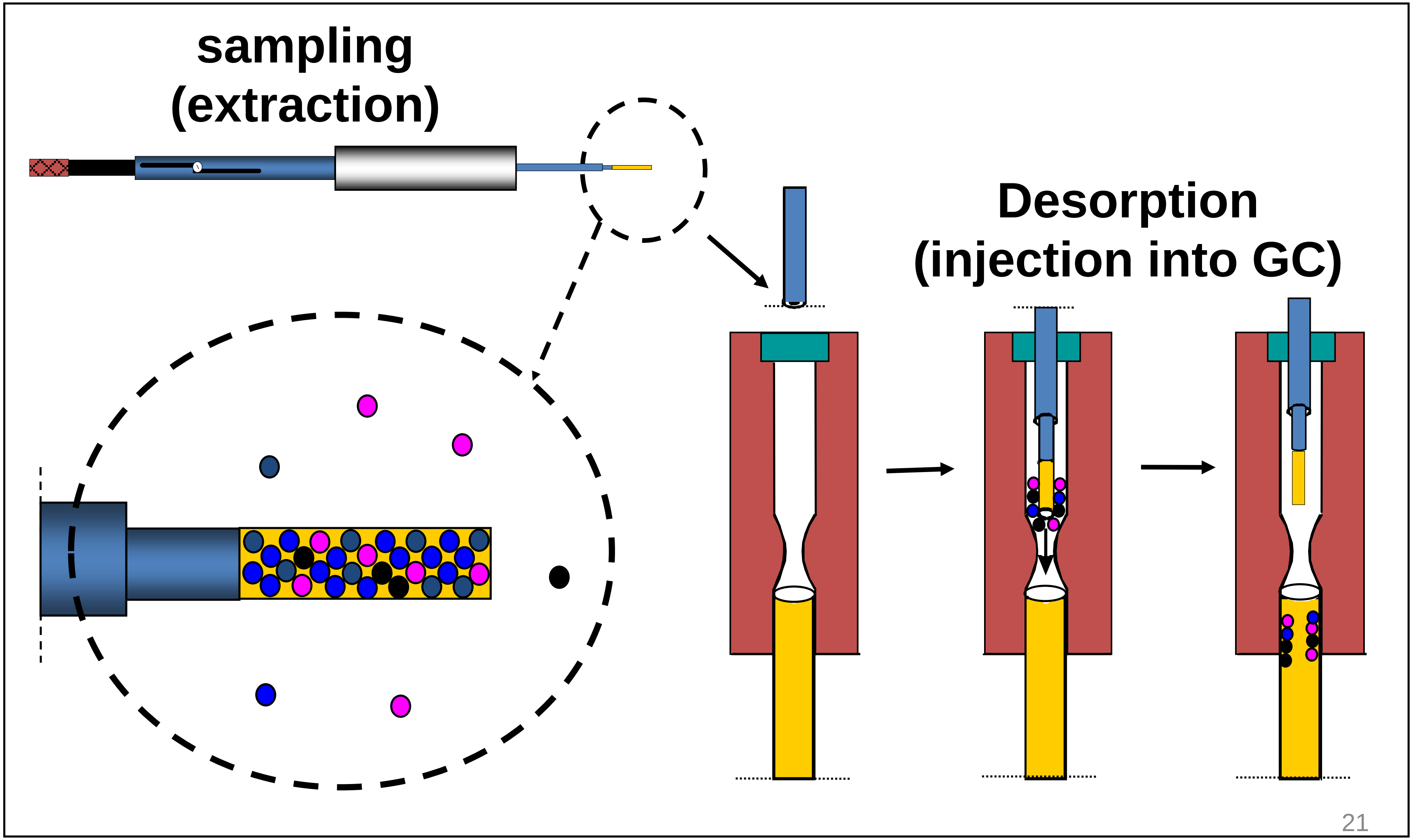


Sampling of odorants with Solid Phase Microextraction (SPME)

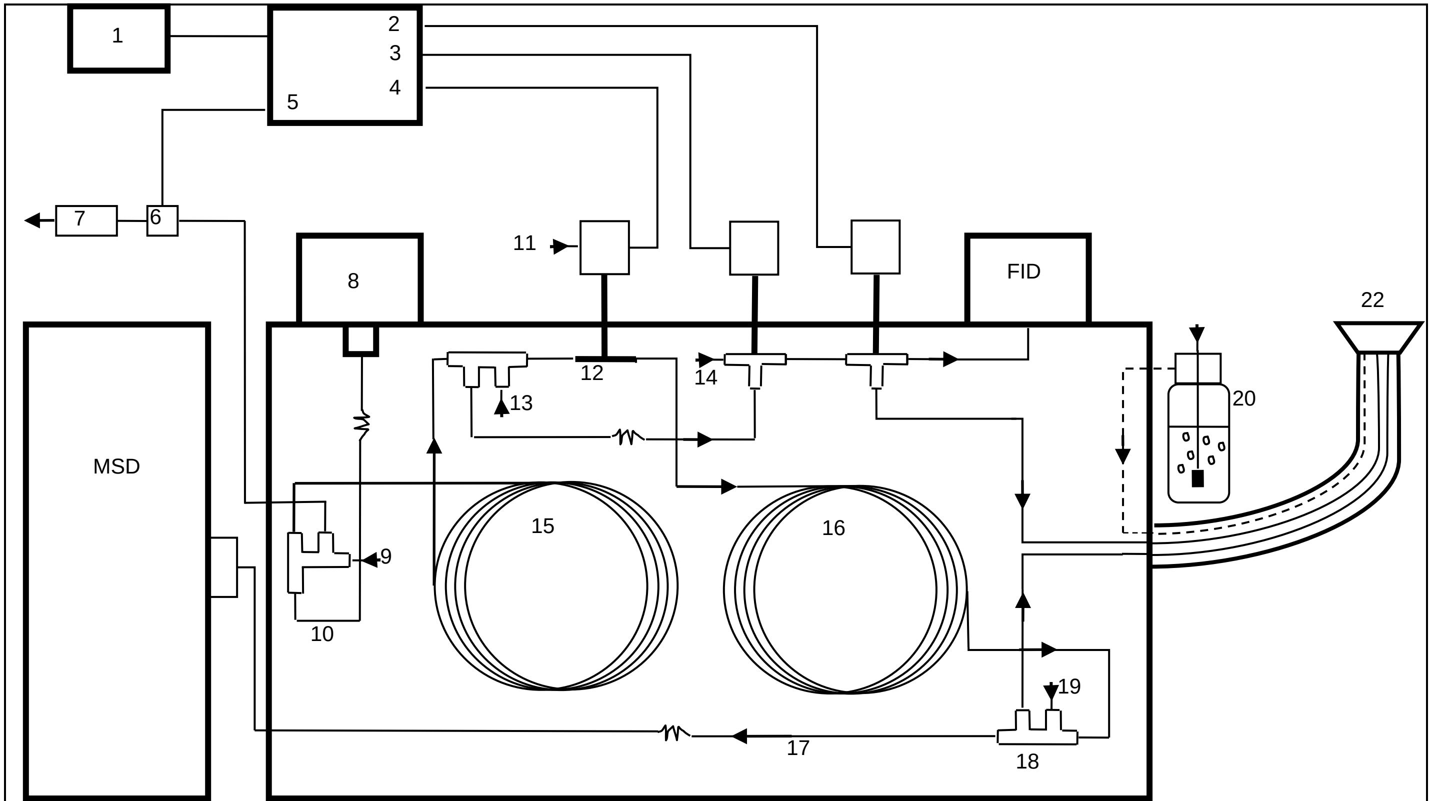




Sampling with Solid Phase Microextraction (SPME)



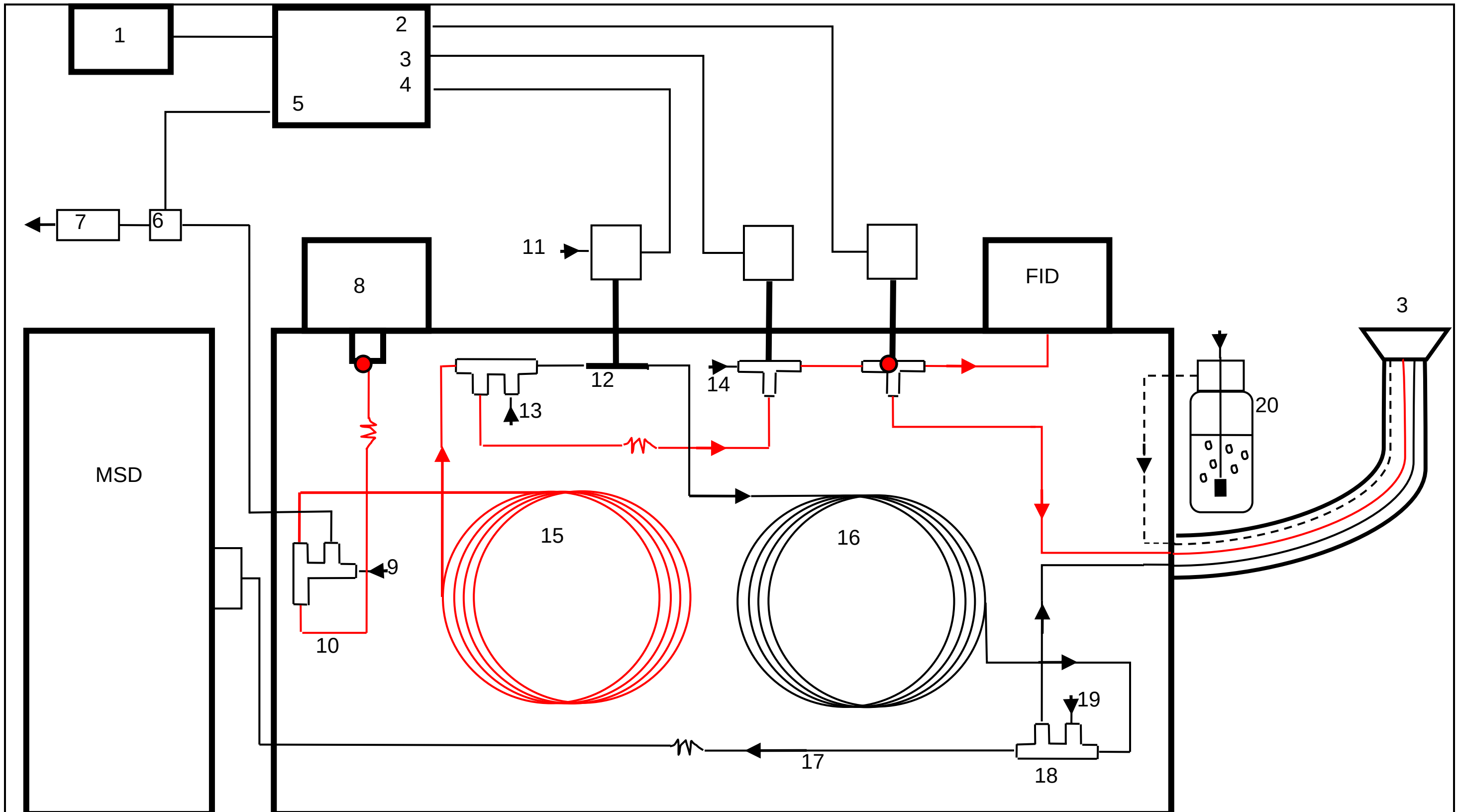
Methodology – Sample Analysis



Notes:

1: MultiTrax Controller
2: Precolumn Sniff Port Selector
3: Heartcut Valve
4: CO_2 Cryotrap
5: Precolumn Backflush
6: Solenoid
7: Filter
8: Injector
9: Backflush Sweep
10: Fixed Restrictor to Inlet
11: Liquid CO_2 Feed
12: CO_2 Cryotrap
13: Midpoint Pressure
14: Heartcut Sweep
15: Non-Polar Pre-column
(12 m × 0.53 mm ×1.00 μm)
16: Polar Column
(25 m × 0.53 mm × 1.00 μm)
17: Fixed Restrictor to MSD
18: Open Split Interface (OSI)
19: OSI Sweep
20: Humidifier
21: Air in
22: Sniff Port

GC-FID-O
No Heartcut Flow Schematic

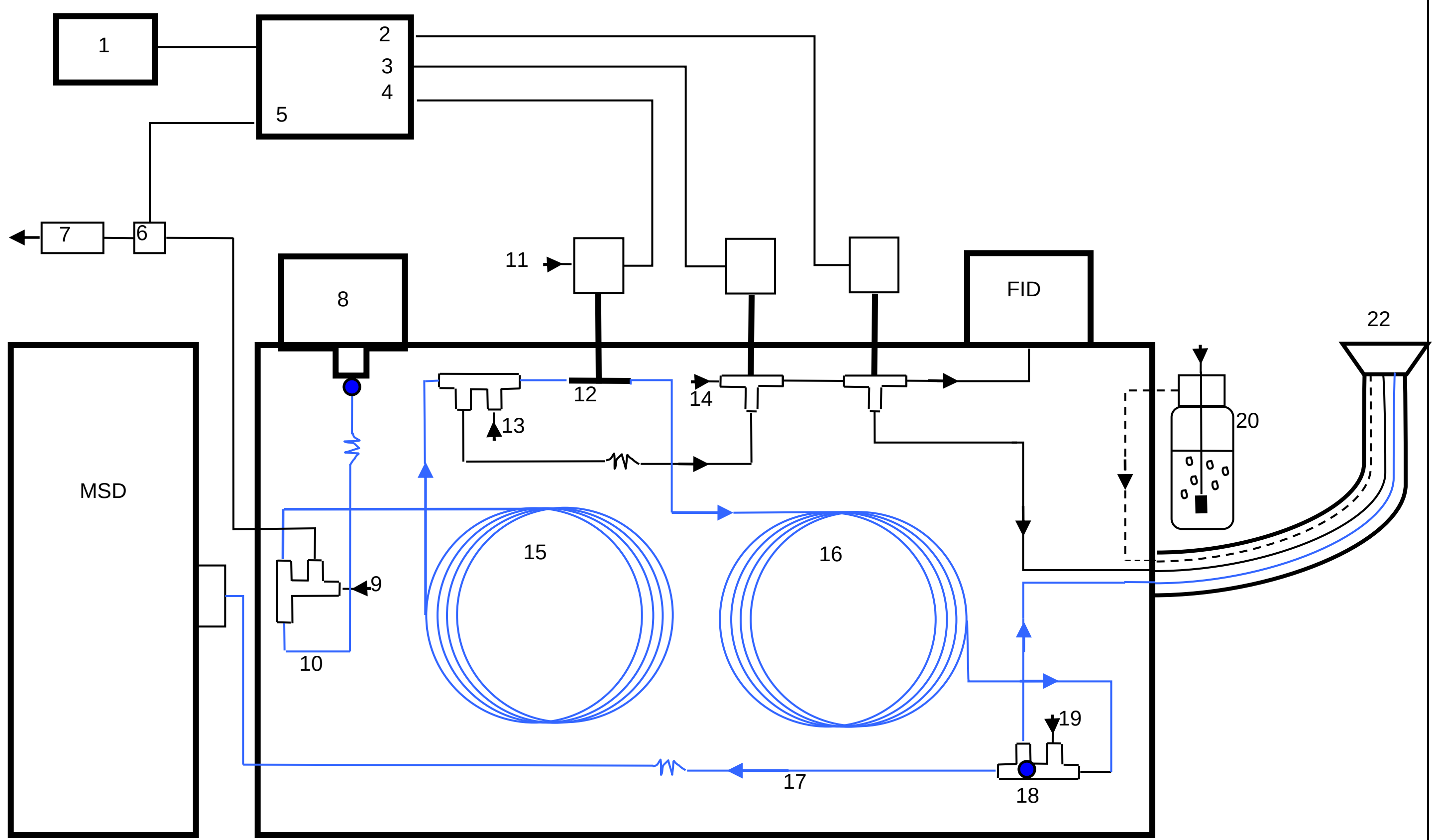


Notes:
1: MultiTrax Controller
2: Precolumn Sniff Port Selector
3: Heartcut Valve
4: CO_2 Cryotrap
5: Precolumn Backflush
6: Solenoid
7: Filter
8: Injector

9: Backflush Sweep
10: Fixed Restrictor to Inlet
11: Liquid CO_2 Feed
12: CO_2 Cryotrap
13: Midpoint Pressure
14: Heartcut Sweep
15: Non-Polar Pre-column
(12 m × 0.53 mm ×1.00 µm)

16: Polar Column
(25 m × 0.53 mm × 1.00 µm)
17: Fixed Restrictor to MSD
18: Open Split Interface (OSI)
19: OSI Seep
20: Humidifier
21: Air in
22: Sniff Port

MDGC-MS-O
Heartcut Flow Schematic



Notes:

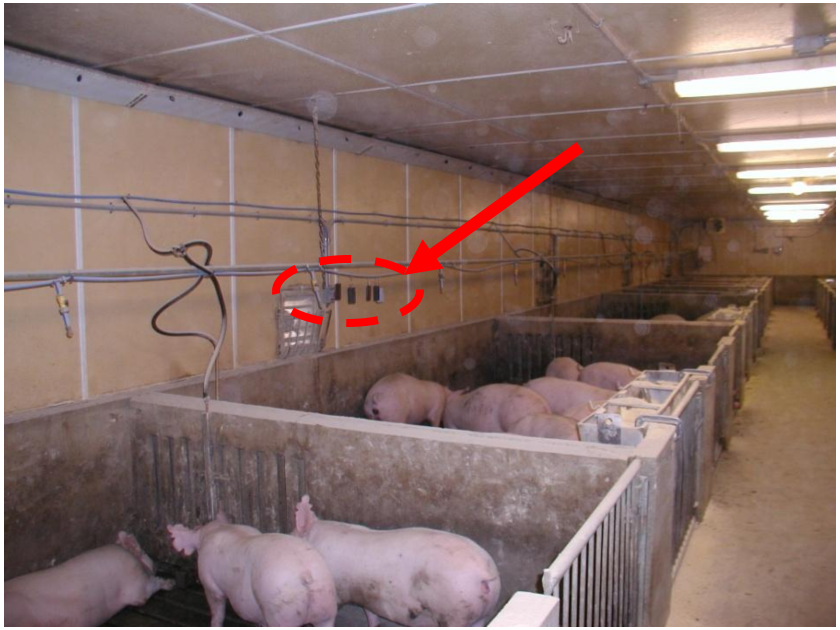
1: MultiTrax Controller
2: Precolumn Sniff Port Selector
3: Heartcut Valve
4: CO_2 Cryotrap
5: Precolumn Backflush
6: Solenoid
7: Filter
8: Injector

9: Backflush Sweep
10: Fixed Restrictor to Inlet
11: Liquid CO_2 Feed
12: CO_2 Cryotrap
13: Midpoint Pressure
14: Heartcut Sweep
15: Non-Polar Pre-column
(12 m × 0.53 mm ×1.00 µm)

16: Polar Column
(25 m × 0.53 mm × 1.00 µm)
17: Fixed Restrictor to MSD
18: Open Split Interface (OSI)
19: OSI Sweep
20: Humidifier
21: Air in
22: Sniff Port

Finding 'characteristic' swine odor

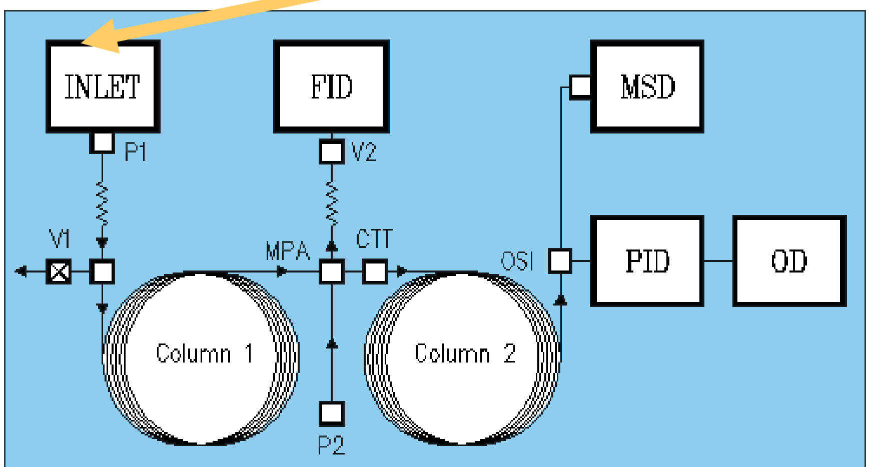
- Clean steel exposed for 1, 3, and 7 days
- Plates adsorb odor
- ISU swine research barn in Ames, Iowa
- Analysis at AAQ Laboratory
- Useful long-term storage of odor on plates



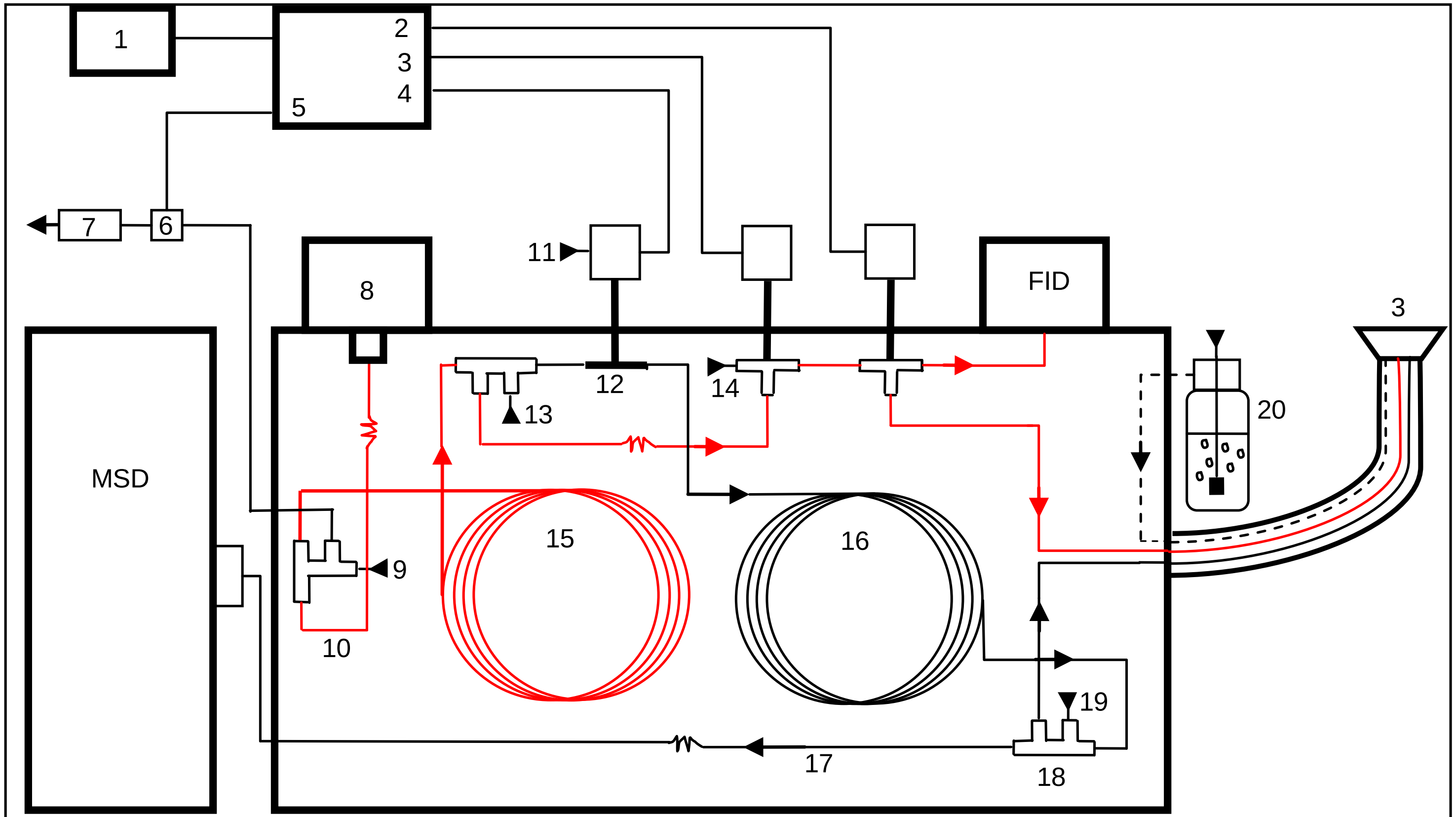
Simultaneous Chemical and Olfactometry Analysis

SPME-MDGC-MS-Olfactometry system

SPME



Multidimensional GC-MS-O: identification of characteristic odorants

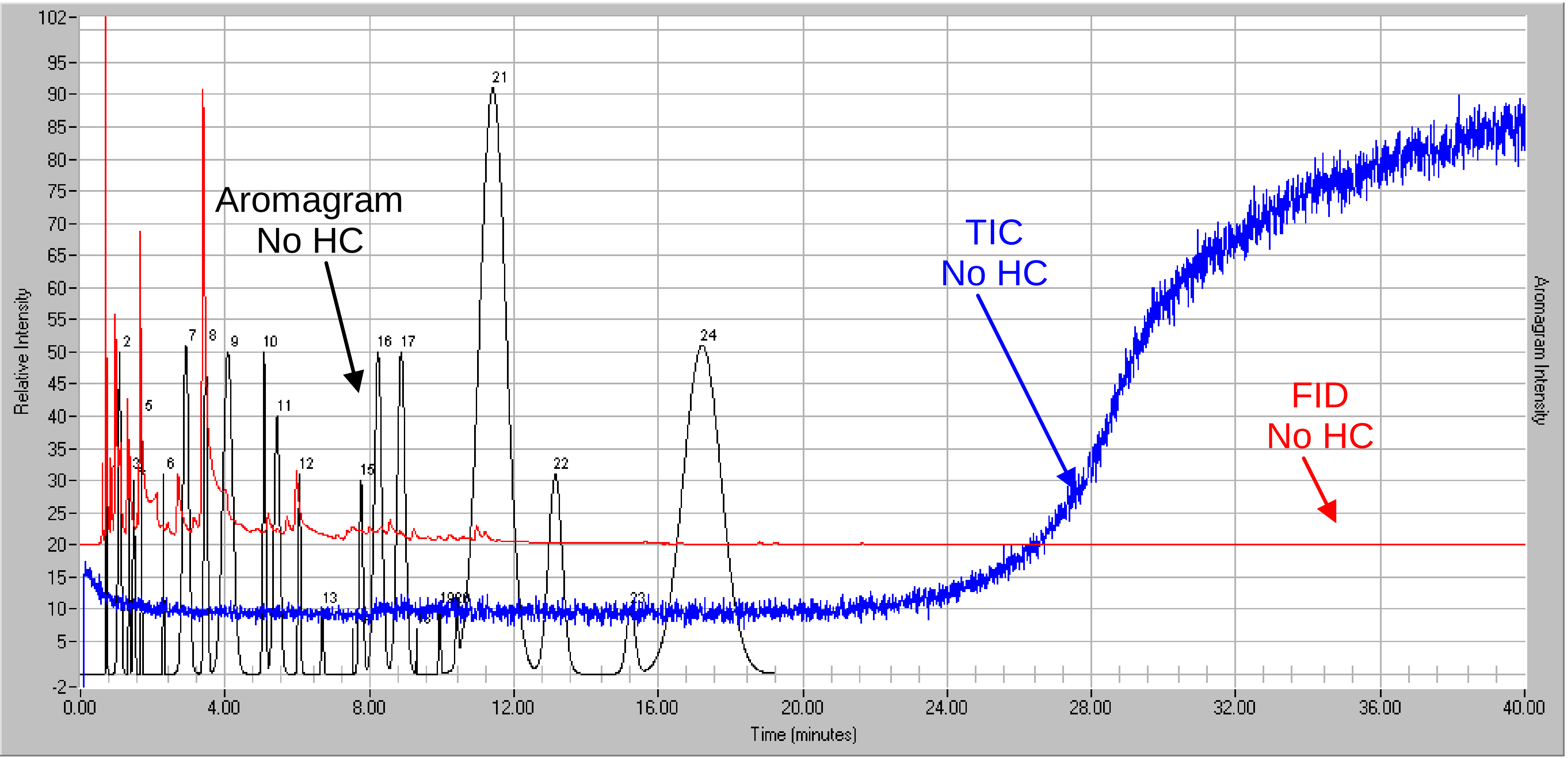


Notes:

1: MultiTrax Controller
2: Precolumn Sniff Port Selector
3: Heartcut Valve
4: CO_2 Cryotrap
5: Precolumn Backflush
6: Solenoid
7: Filter
8: Injector
9: Backflush Sweep
10: Fixed Restrictor to Inlet
11: Liquid CO_2 Feed
12: CO_2 Cryotrap
13: Midpoint Pressure
14: Heartcut Sweep
15: Non-Polar Pre-column
(12 m $\times$ 0.53 mm $\times$1.00 μm)
16: Polar Column
(25 m $\times$ 0.53 mm $\times$ 1.00 μm)
17: Fixed Restrictor to MSD
18: Open Split Interface (OSI)
19: OSI Sweep
20: Humidifier
21: Air in
22: Sniff Port

GC-O mode: "screening" for characteristic odorants

Multidimensional GC-MS-O: identification of characteristic odorants

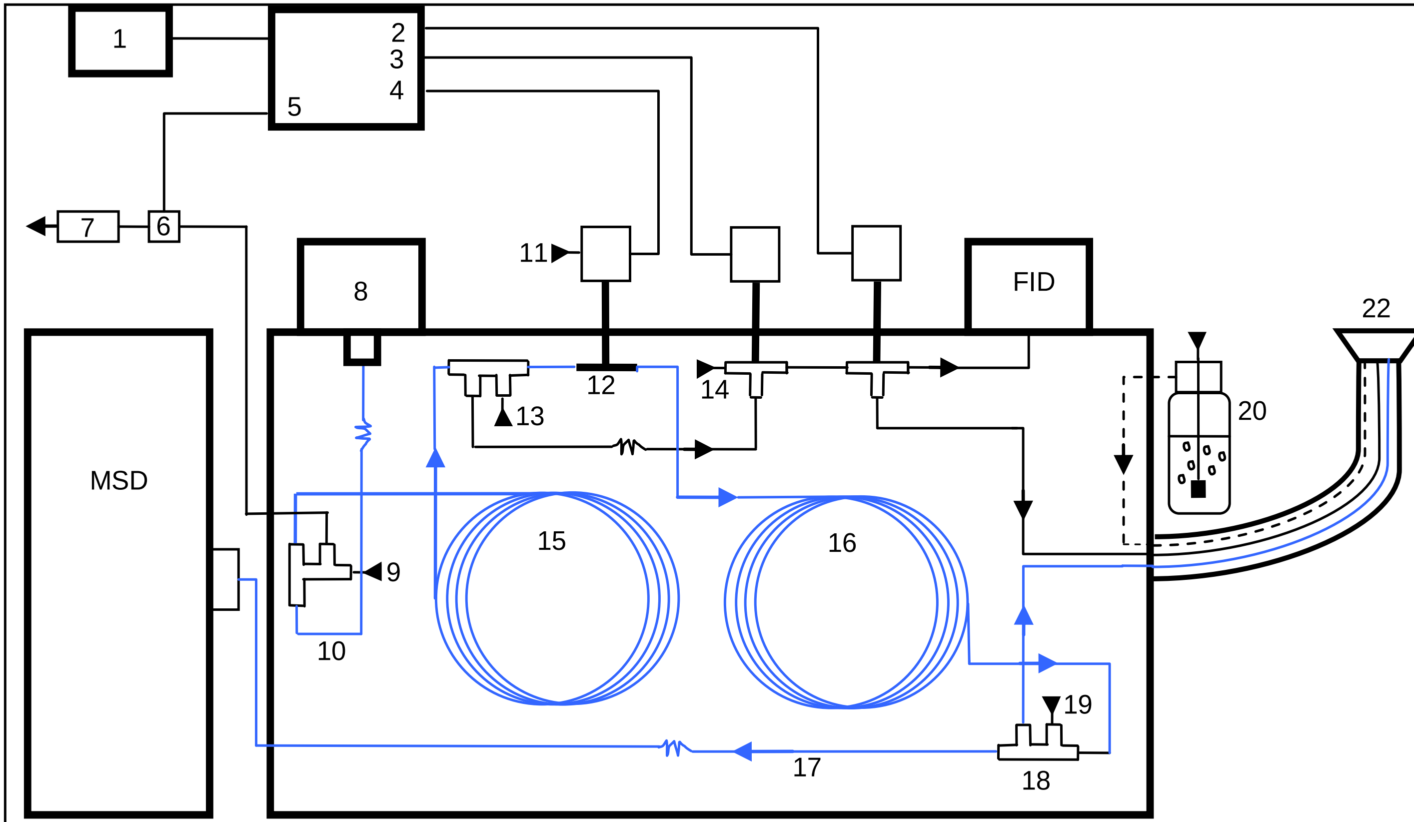


GC-O mode: “screening” for characteristic odorants

Selection of heart-cutting regions with characteristic swine odorants

HC	GC-O mode RT (min)	Odor Character
1	0.48 - 0.8	Fecal, sewer, foul
2	3.45 - 4.10	Skunky, buttery, body odor, fatty acid, foul
3	4.40 - 5.10	Body odor, fatty acid, buttery
4	9.90 - 13.55	Barnyard, medicinal, phenolic, **characteristic**, naphthalenic, piggy, taco shell, urinous, acidic
5	15.40 - 18.30	Barnyard, fecal, sewer, **characteristic**, piggy, naphthalenic

Multidimensional GC-MS-O: identification of characteristic odorants



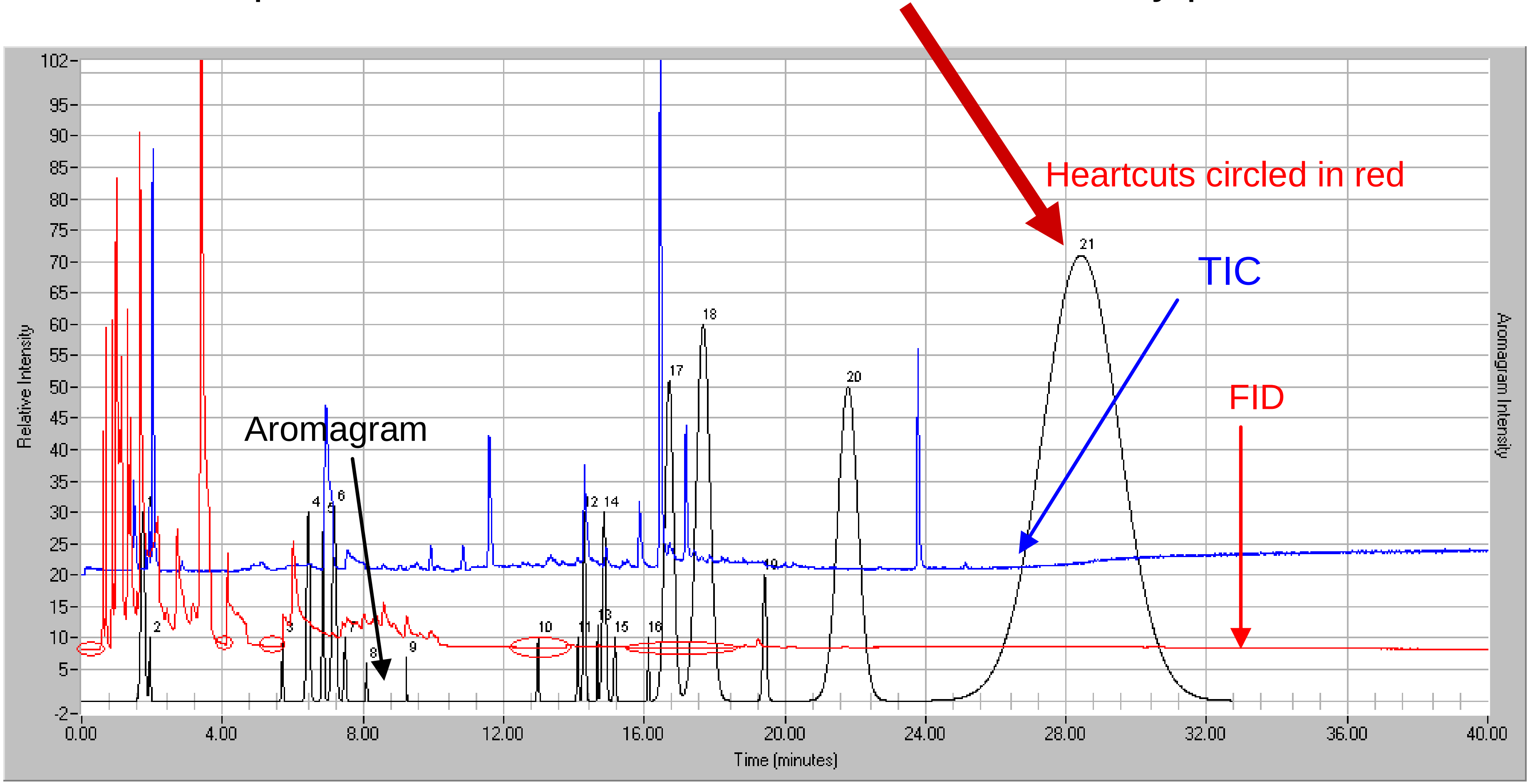
Notes:

1: MultiTrax Controller
2: Precolumn Sniff Port Selector
3: Heartcut Valve
4: CO_2 Cryotrap
5: Precolumn Backflush
6: Solenoid
7: Filter
8: Injector
9: Backflush Sweep
10: Fixed Restrictor to Inlet
11: Liquid CO_2 Feed
12: CO_2 Cryotrap
13: Midpoint Pressure
14: Heartcut Sweep
15: Non-Polar Pre-column
(12 m $\times$ 0.53 mm $\times$1.00 μm)
16: Polar Column
(25 m $\times$ 0.53 mm $\times$ 1.00 μm)
17: Fixed Restrictor to MSD
18: Open Split Interface (OSI)
19: OSI Sweep
20: Humidifier
21: Air in
22: Sniff Port

Multidimensional GC-MS-O mode: isolation and identification of characteristic odorants

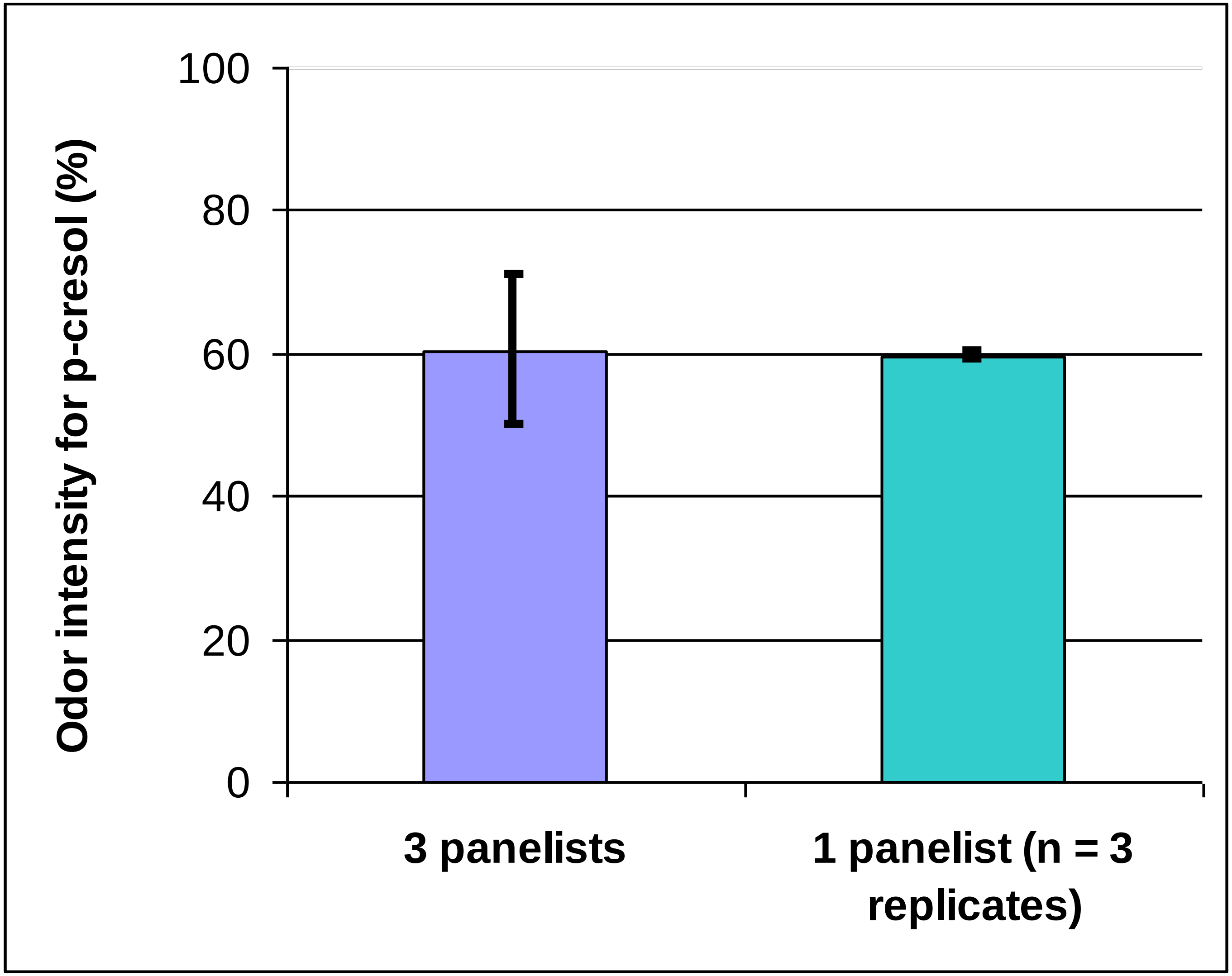
Multidimensional GC-MS-O: identification of characteristic odorants

Impact of the characteristic swine odor caused by p-cresol

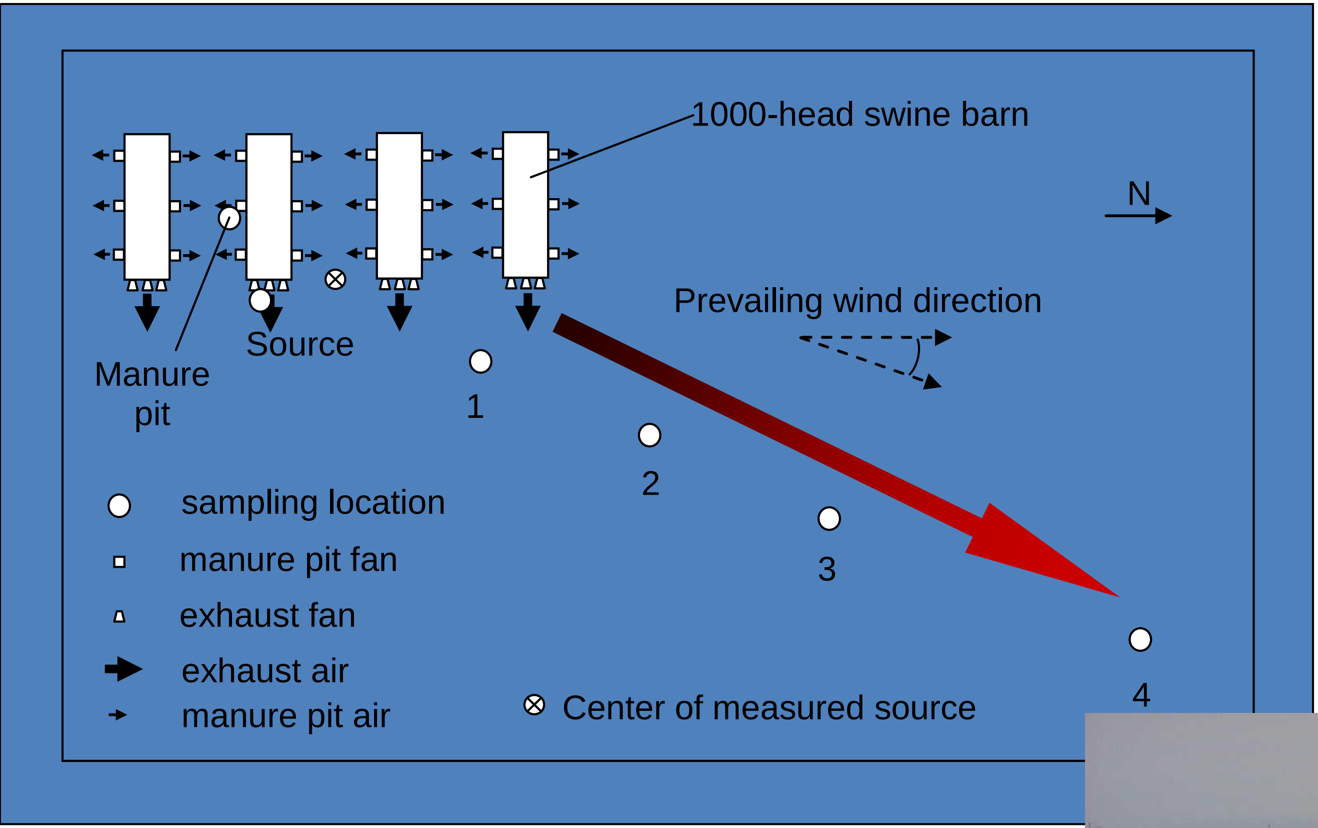


Multidimensional GC-MS-O mode: isolation and identification of characteristic odorants using "heart-cutting" from pre-column to the column

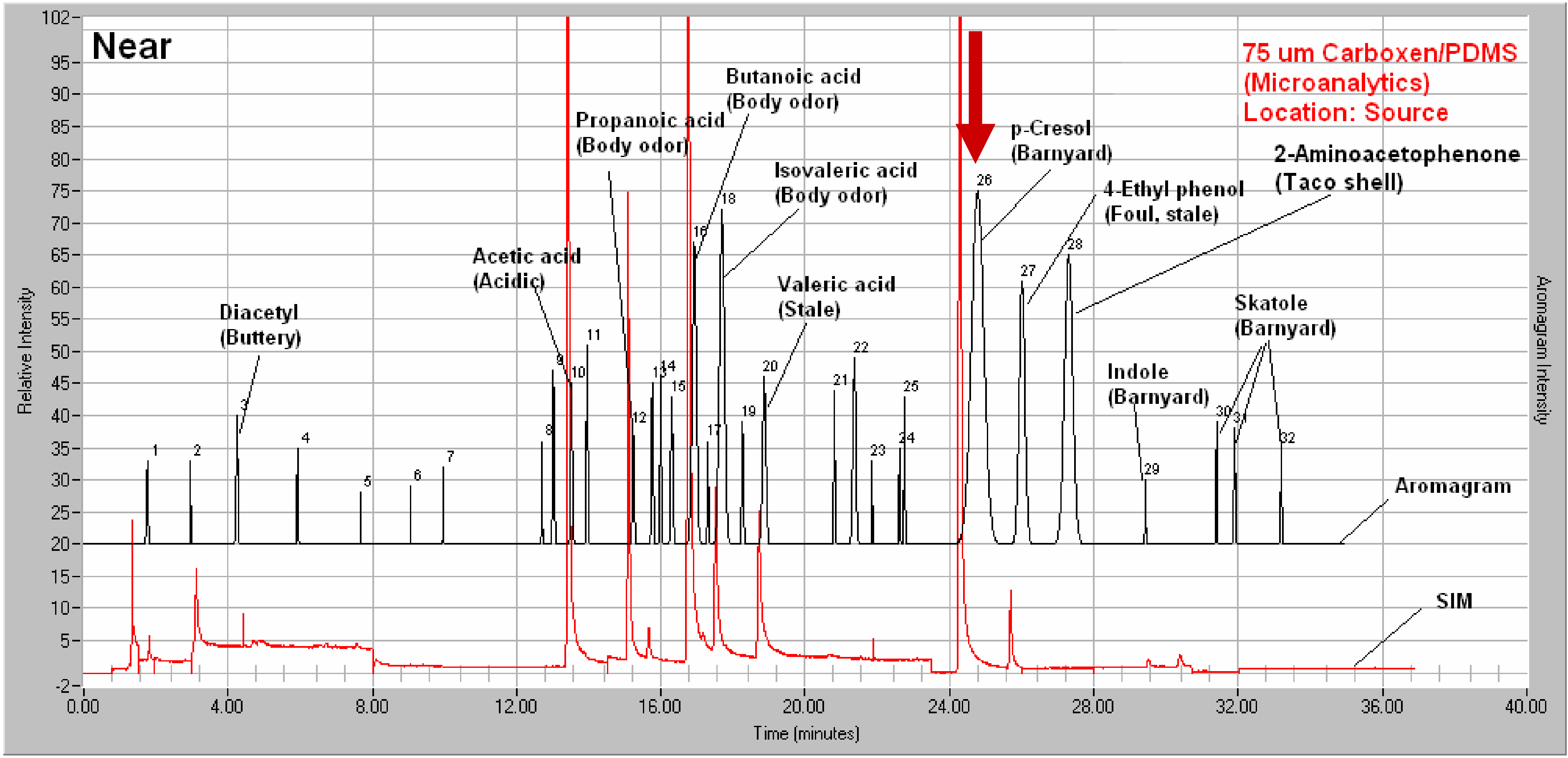
Impact of p-cresol (key characteristic swine odorant)



Identification of priority swine odorants of the highest impact downwind

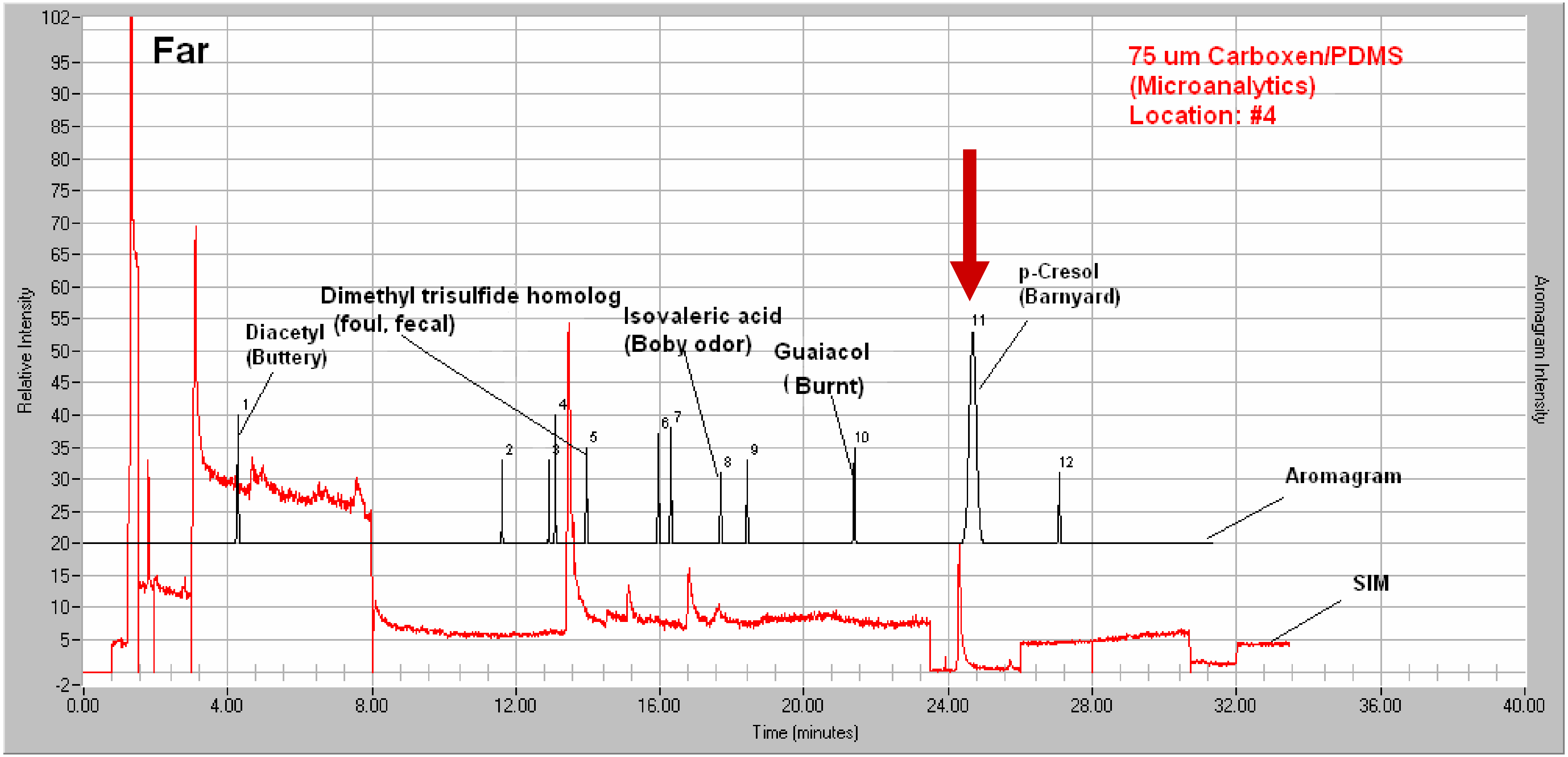


Identification of priority swine odorants of the highest impact downwind



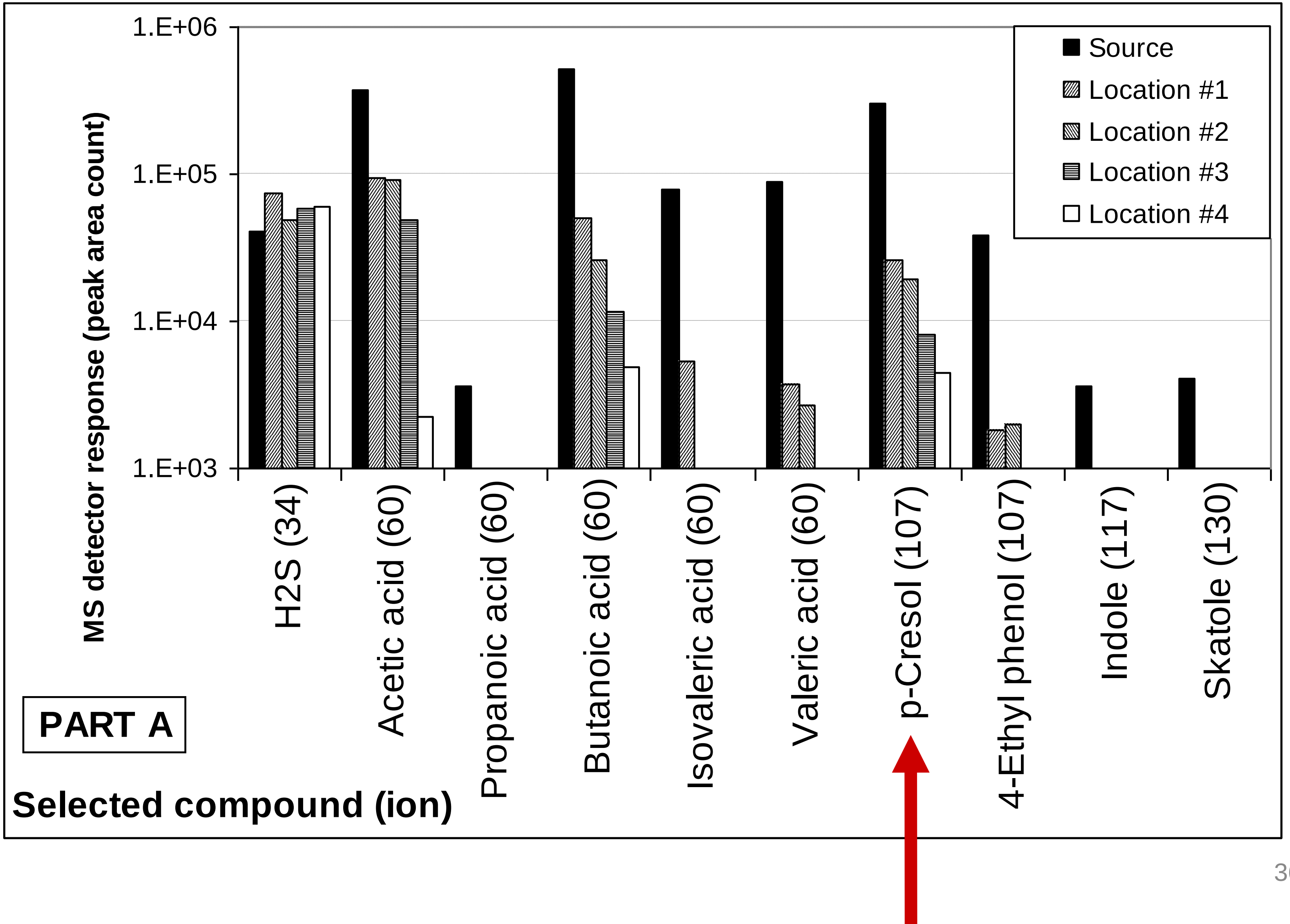
Near source:
20 min exposure of SPME fiber

Identification of priority swine odorants of the highest impact downwind

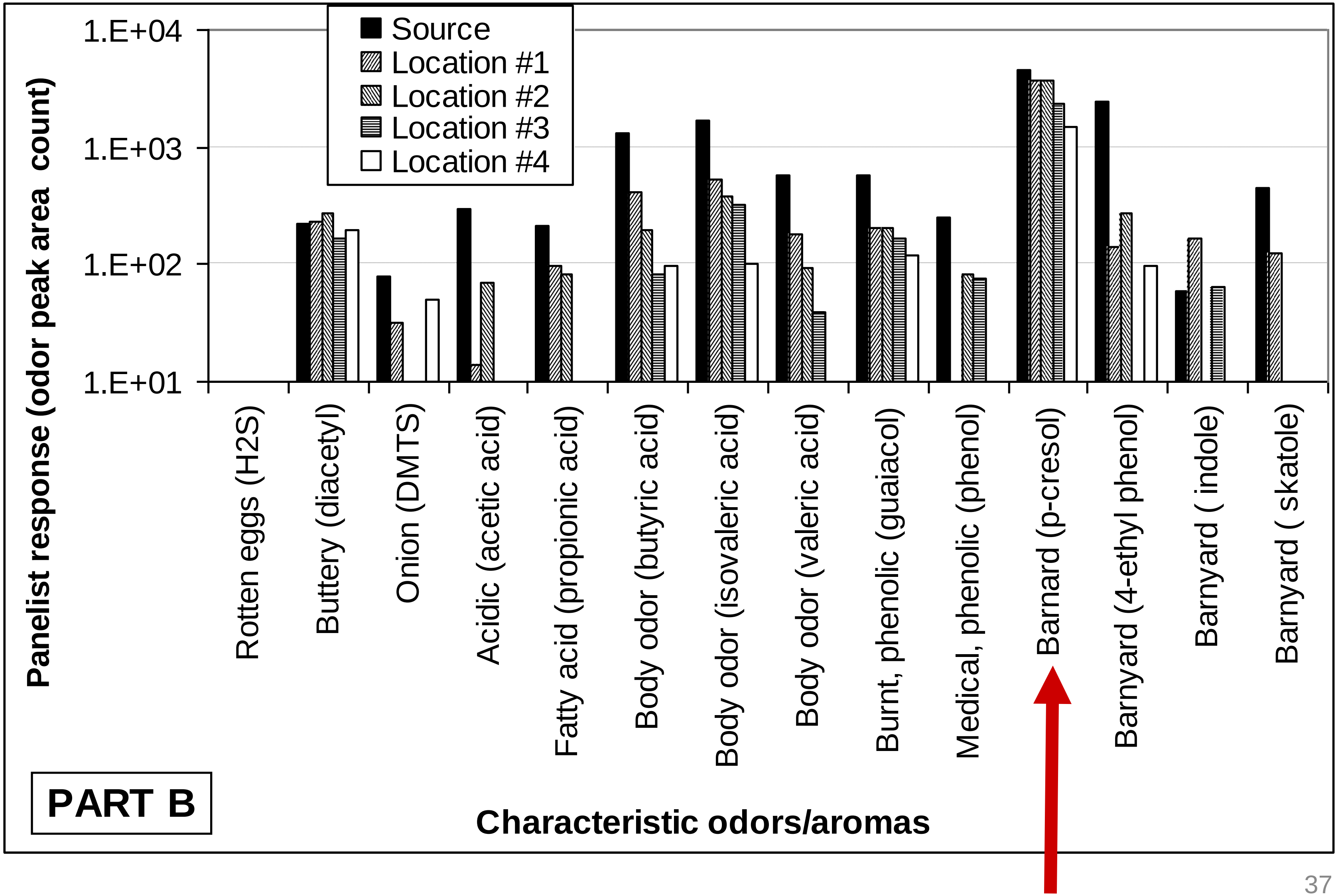


Far from the source:
20 min exposure of SPME fiber to ambient air

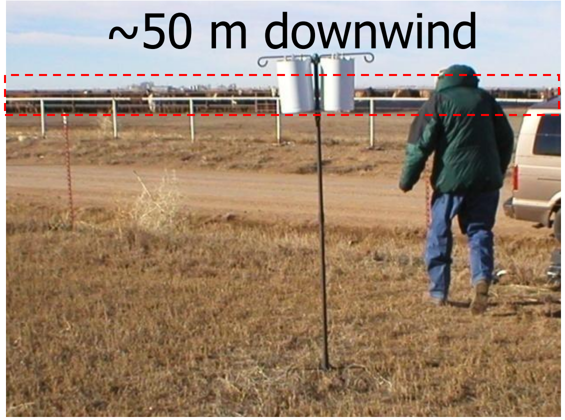
Identification of priority swine odorants of the highest impact downwind: chromatogram

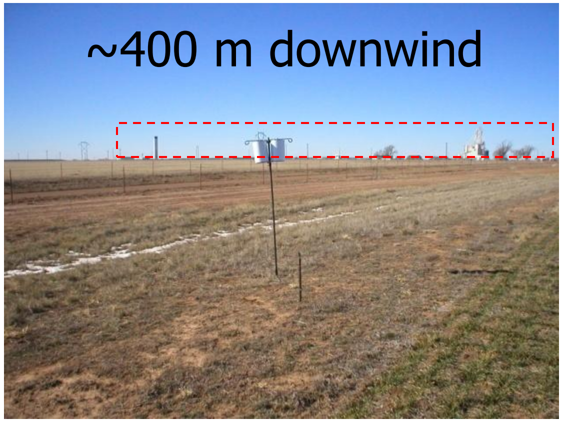


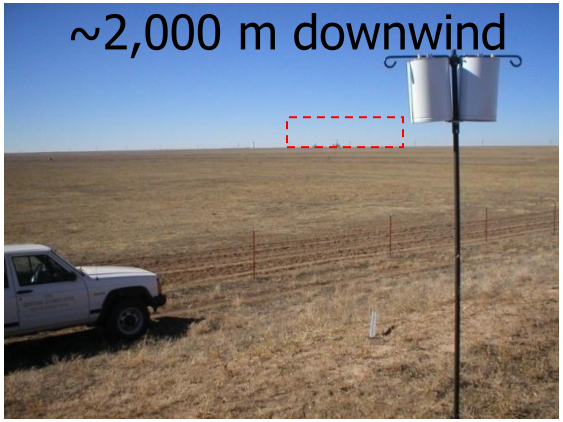
Identification of priority swine odorants of the highest impact downwind: aromagram

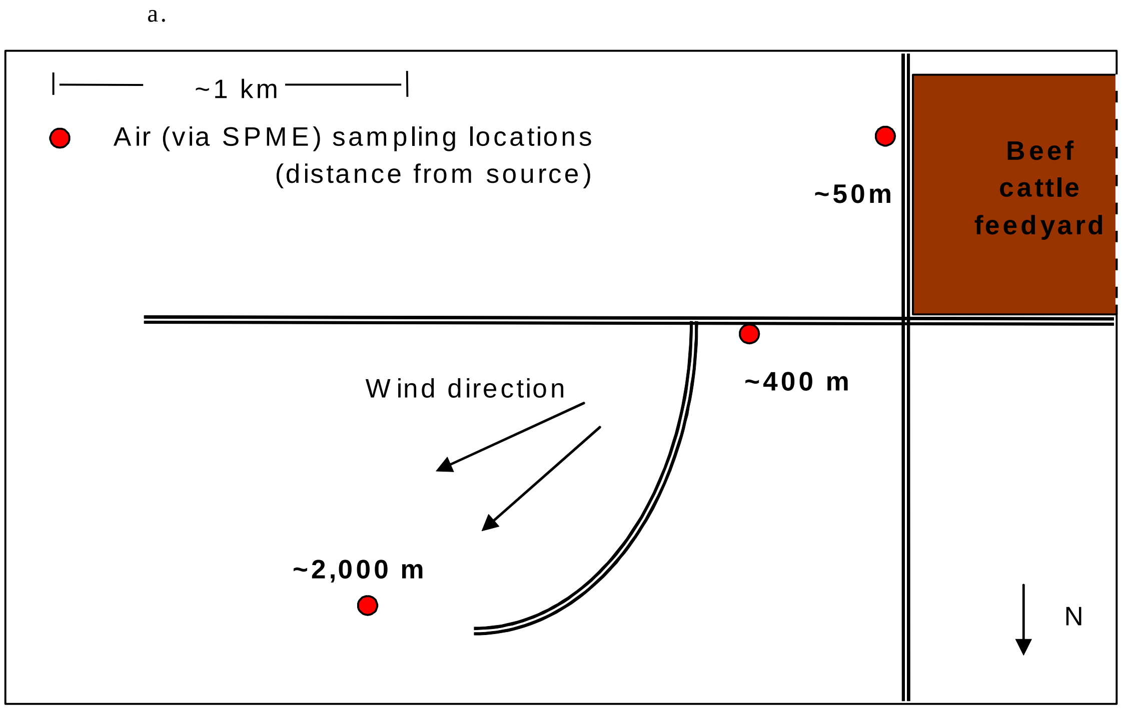


Identification of priority beef cattle odorants of highest impact downwind

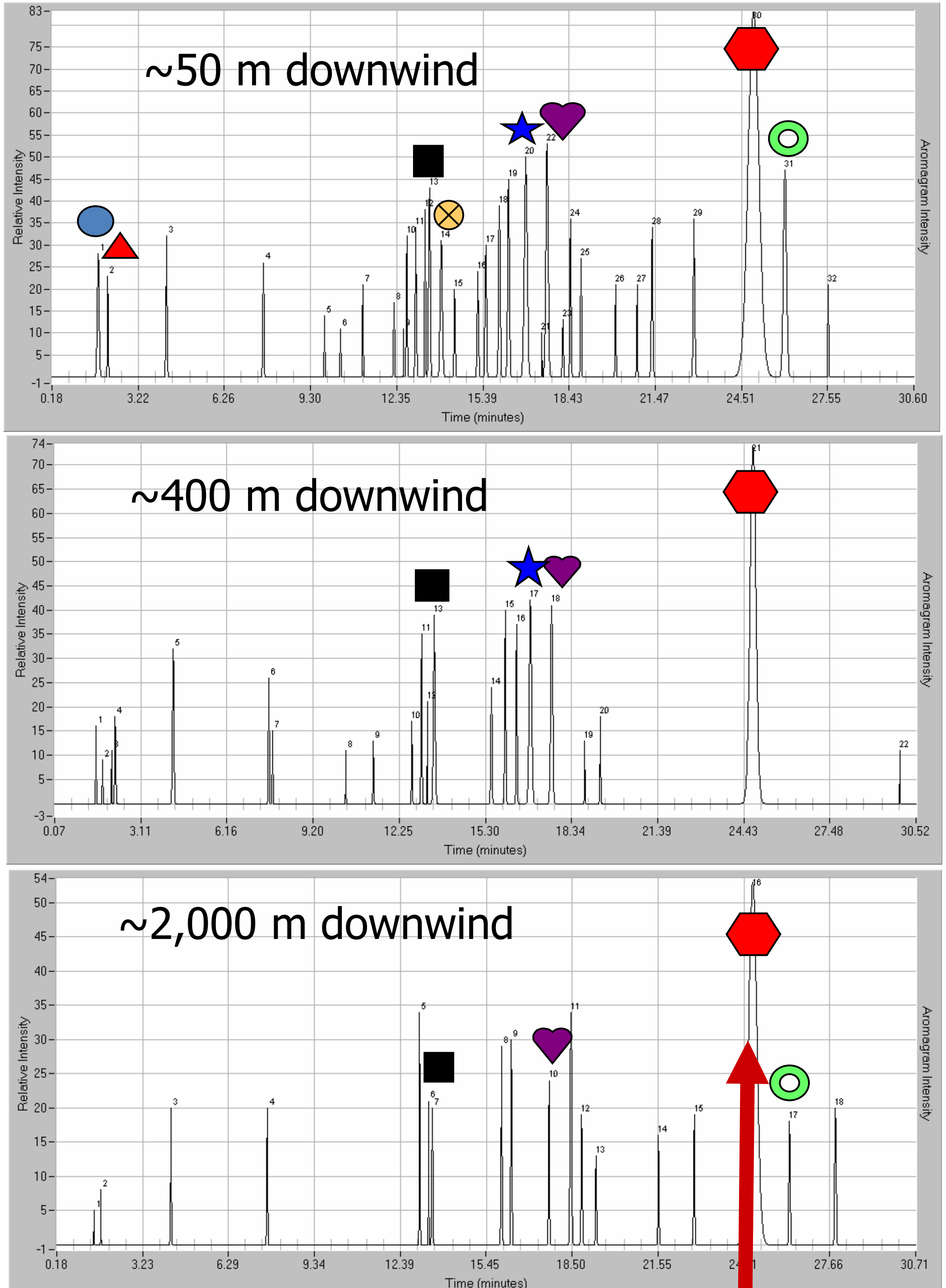








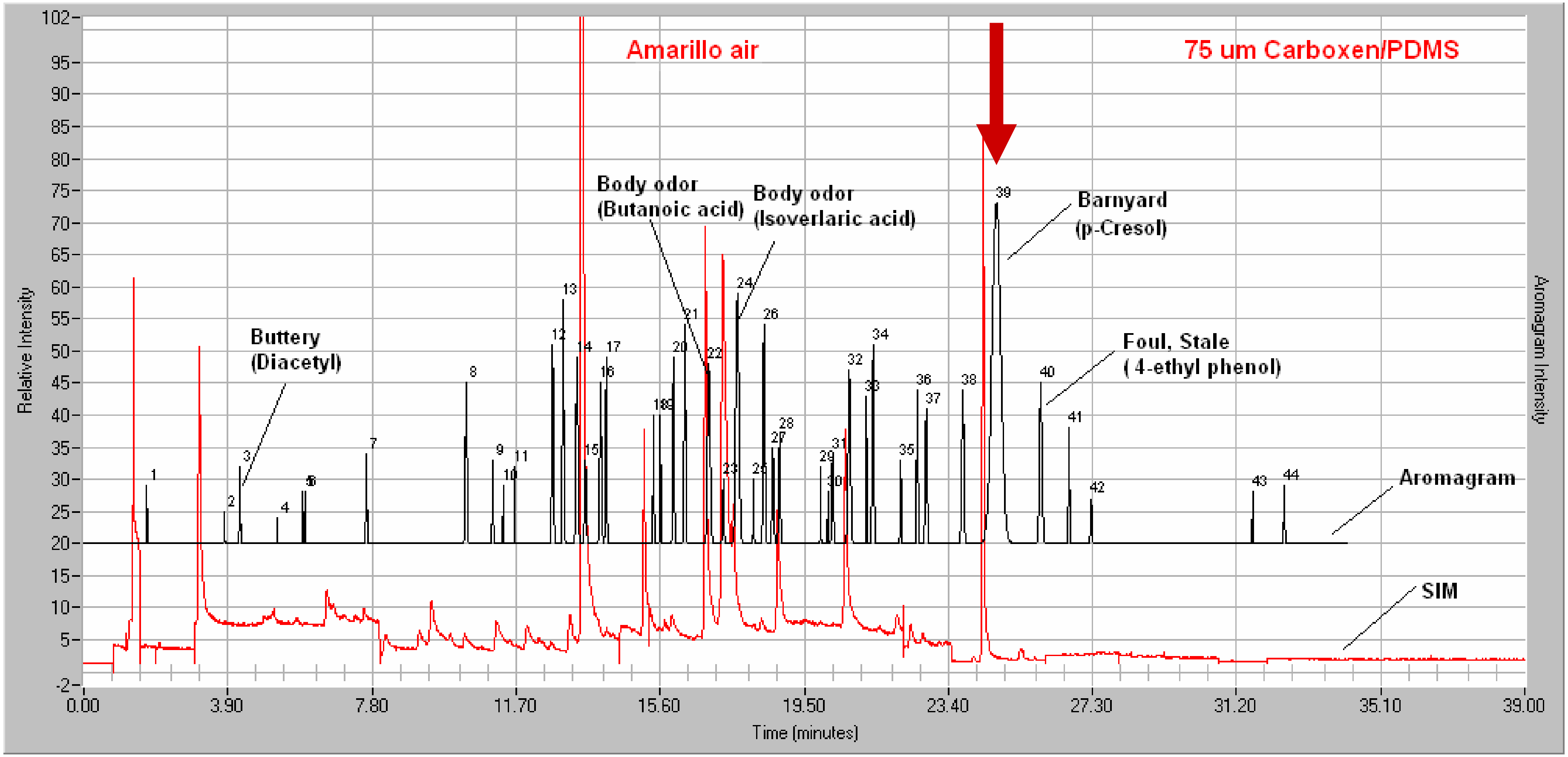
Analysis of beef cattle odor (aromagrams)



- p-ethyl-phenol
- p-cresol
- isovaleric acid
- butyric acid
- DMTS
- acetic acid
- methyl mercaptan
- trimethyl amine

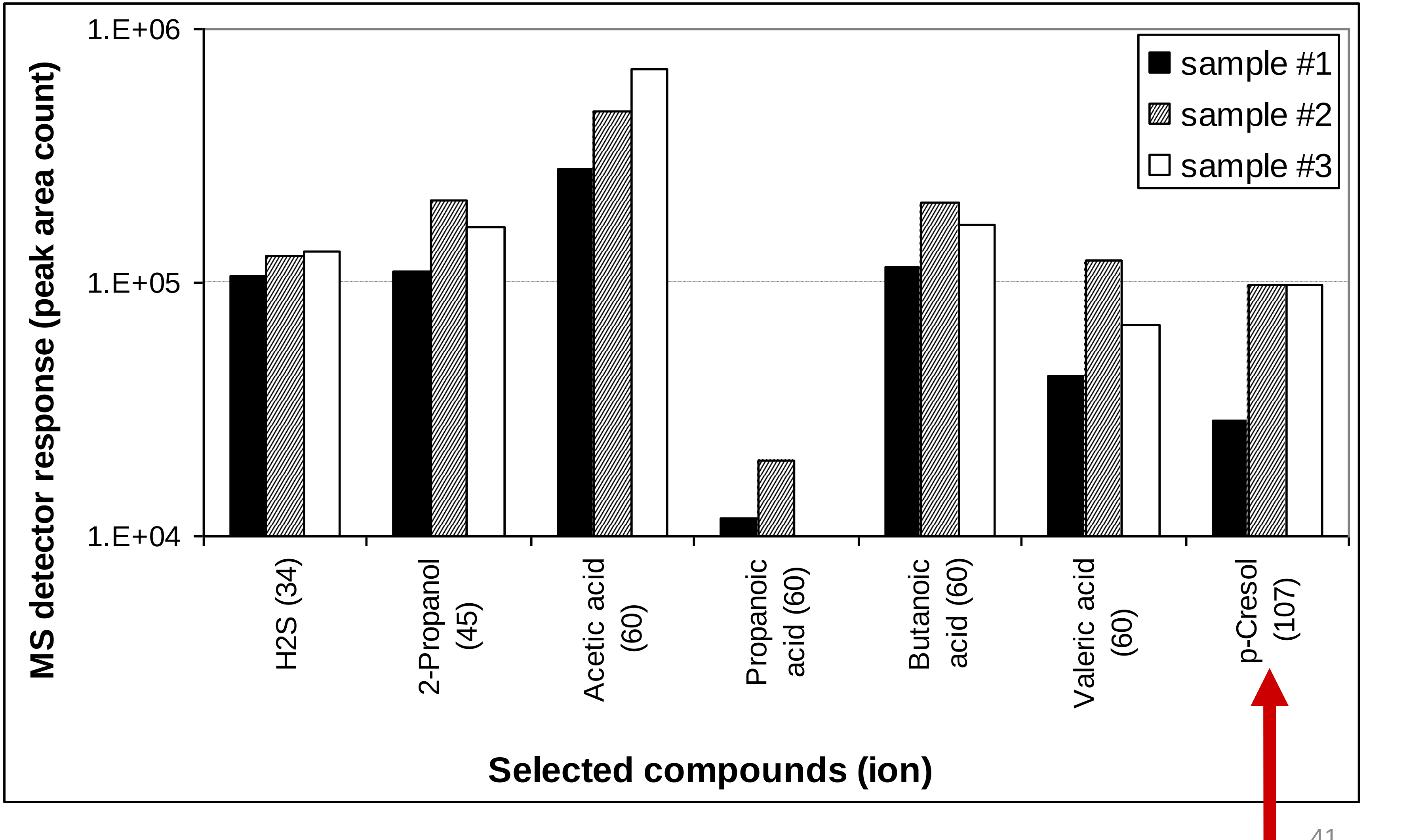
- Odorous VOCs and semi-VOCs undergo dispersion and chemical reactions
- Need to include chemical reactions with OH, NO_3, O_3 to model "odor"
- P-cresol is one of the most important odorants (and also a HAP)

Identification of priority beef cattle odorants of highest impact downwind



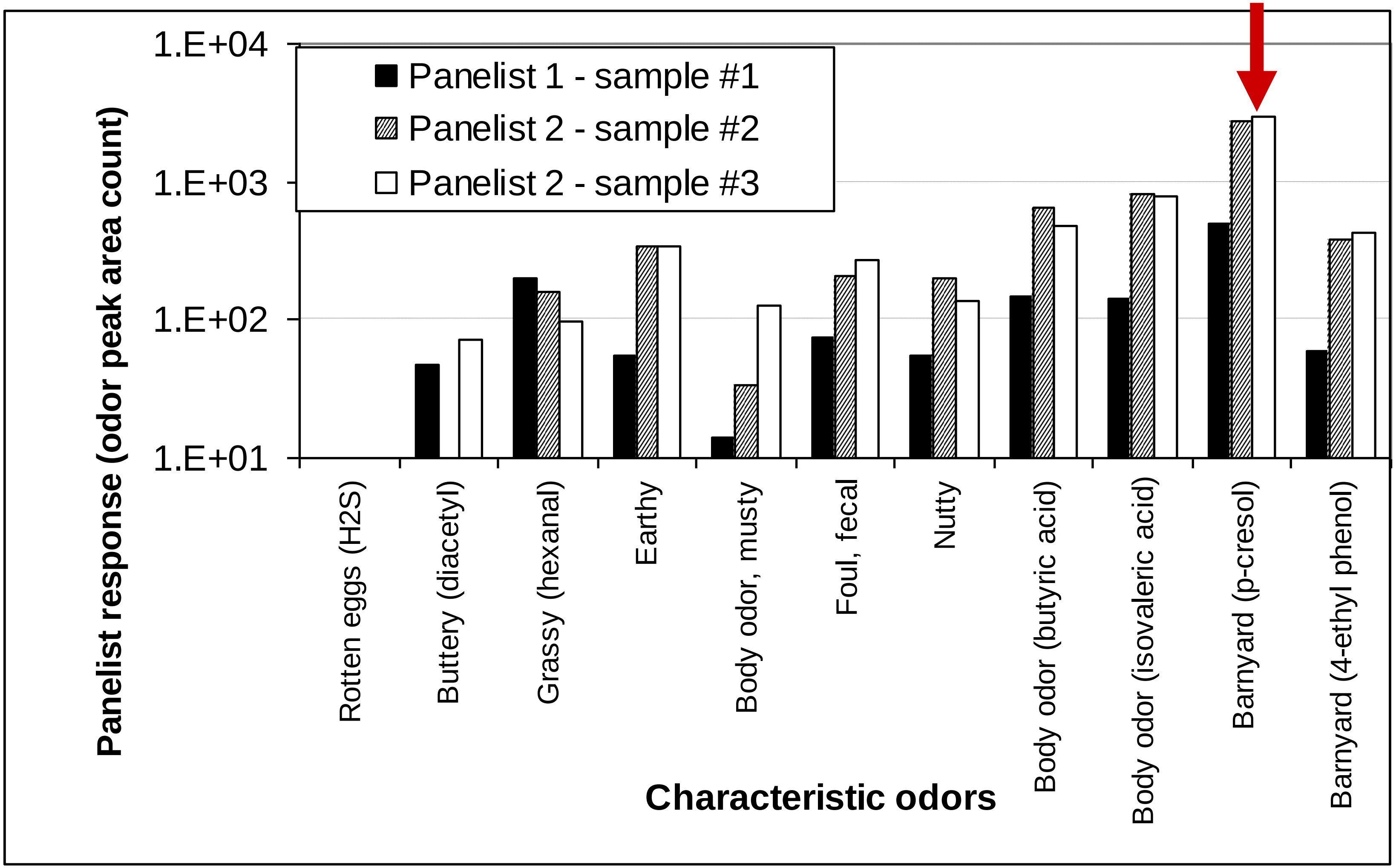
Samples collected with Carboxen/PDMS 85 micron SPME,
1 hr exposure to ambient air
16 km downwind from (50,000-head beef cattle feedlot in Texas

Identification of priority beef cattle odorants of highest impact downwind: chromatogram

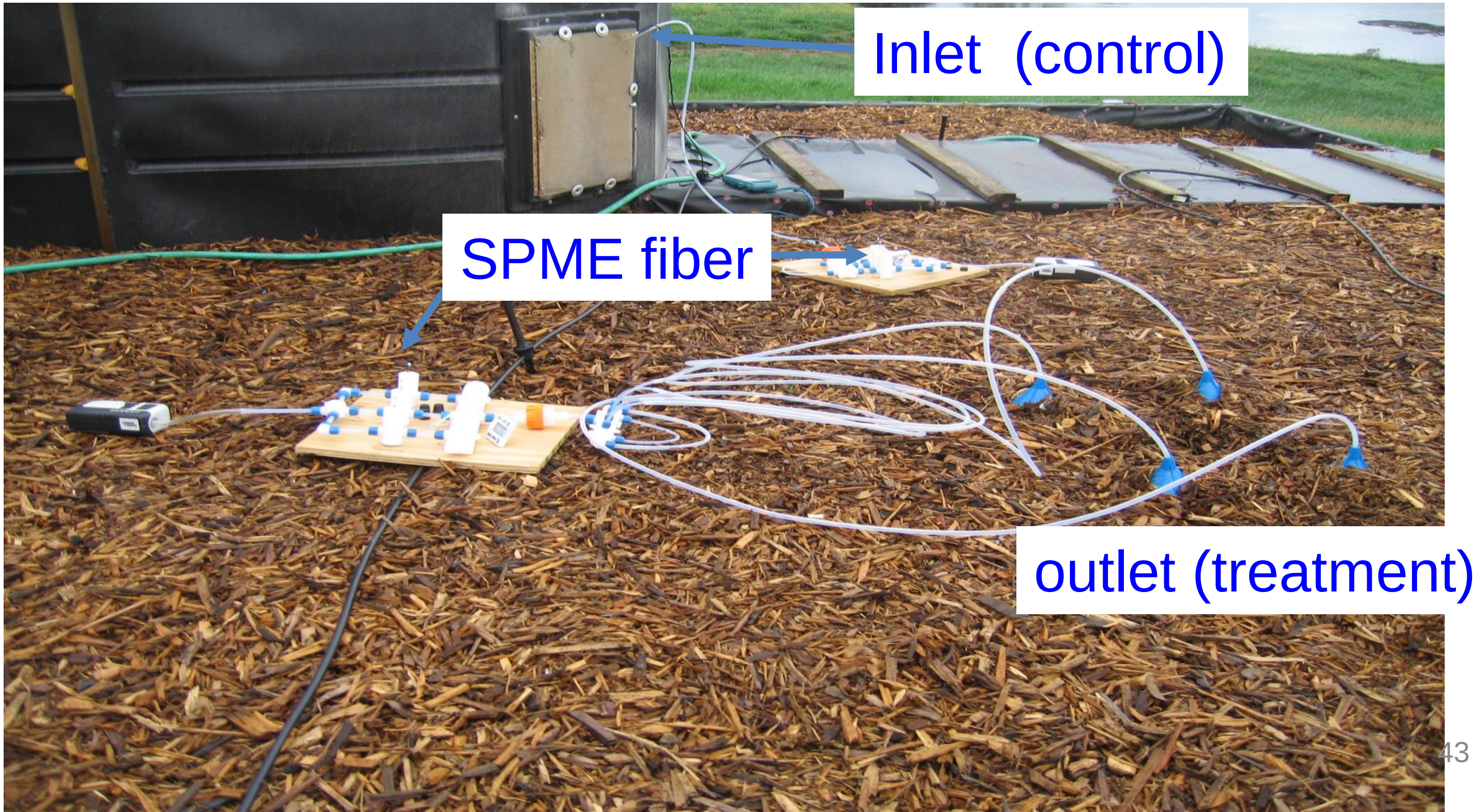


Identification of priority odorants of highest impact downwind: aromagram

Air samples collected 16 km downwind from a large beef cattle feedyard



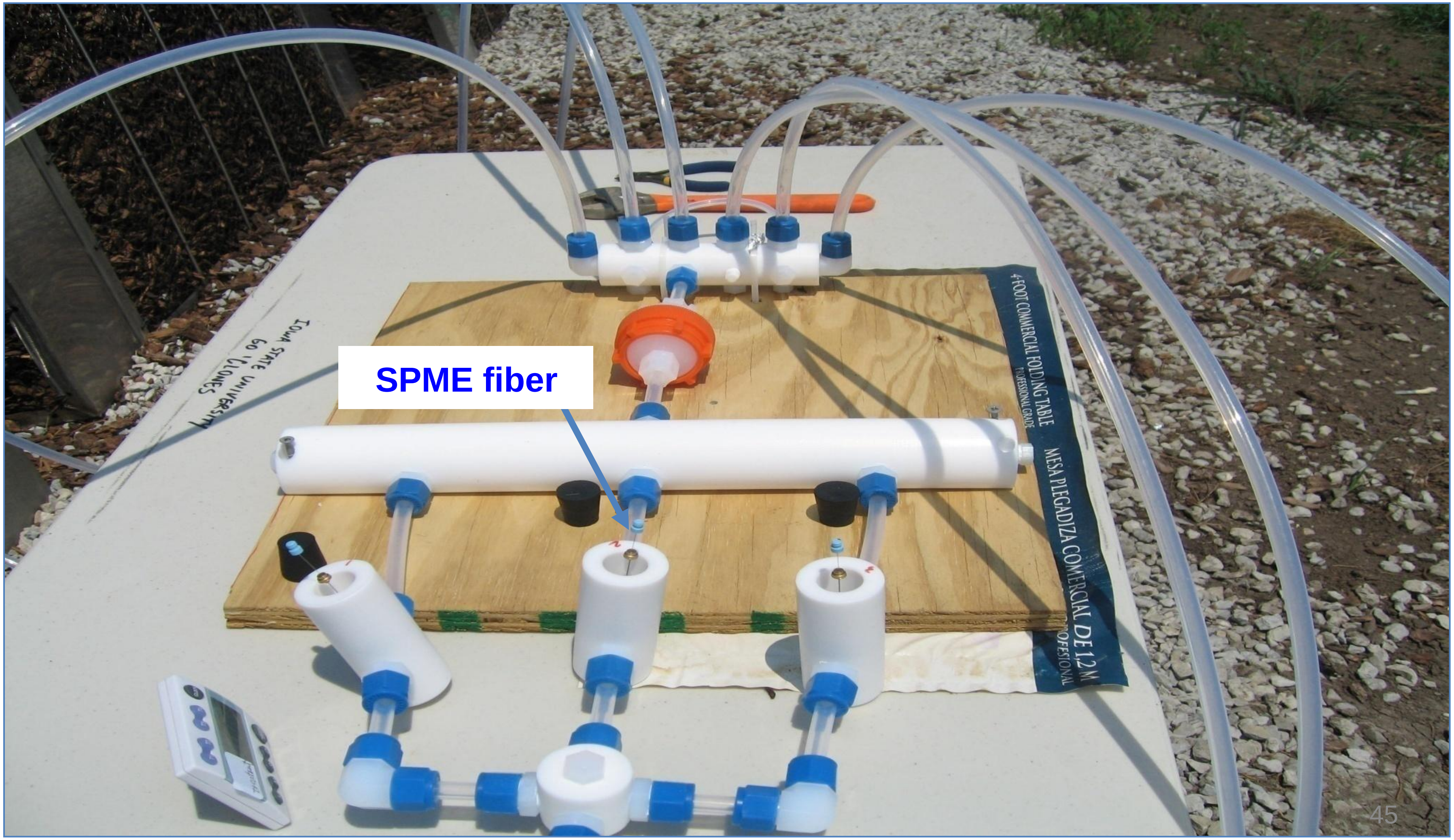
Evaluation of biofilter performance– swine finisher barn exhaust



Odor ‘cell’ biofilter

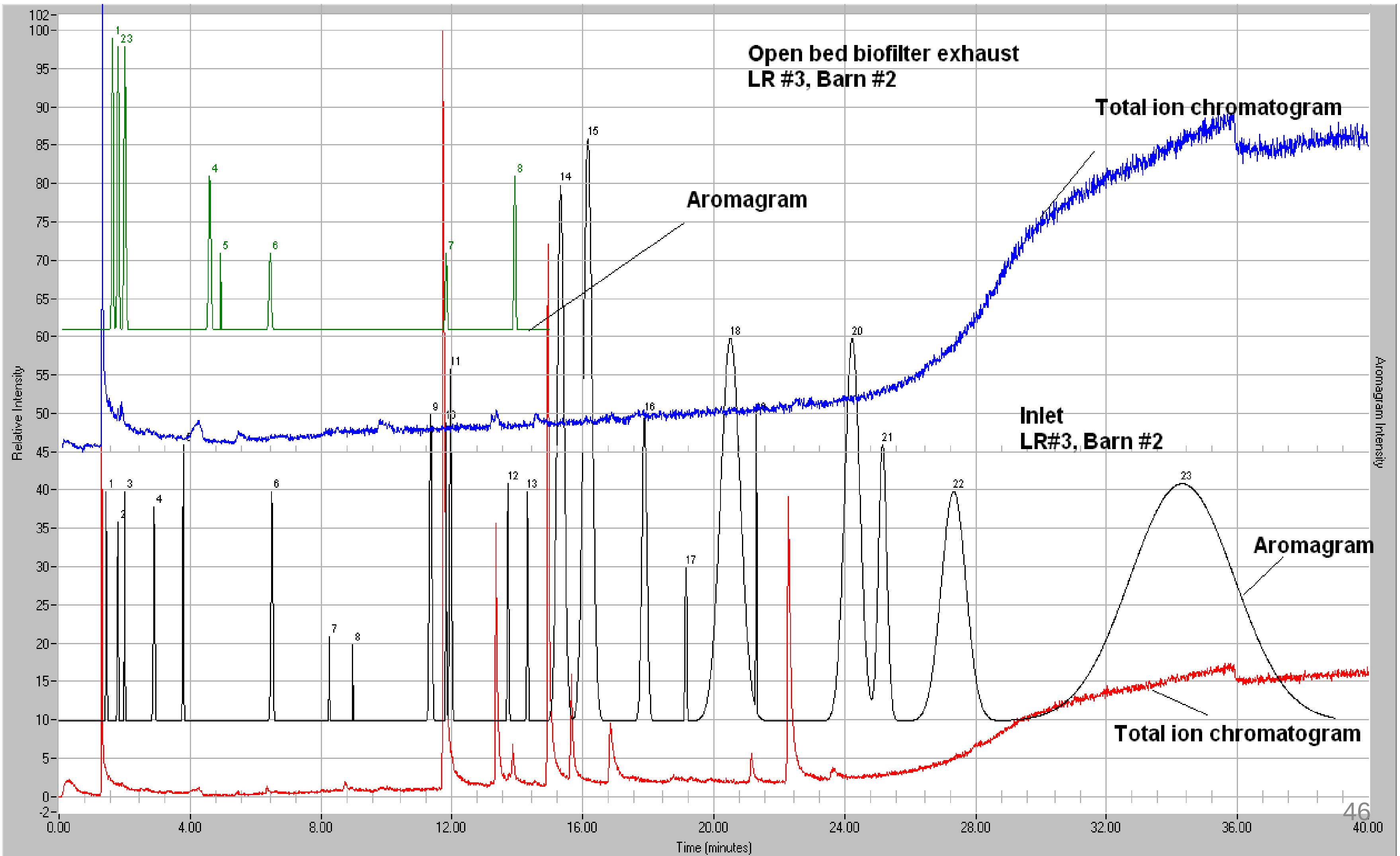
- Odor cell biofilter exhaust (treated air)

Sampling with SPME and odor bags



Evaluation of biofilter

- Comparison of aromagram and TIC between inlet and open bed BF exhaust air.



Effectiveness of biofilter treatment on swine odor

- Fifteen characteristic odorants responsible for swine odor selected for further evaluation including:

  Sulfides (3); Phenolics (3); Indolics (2); VFAs (7);

- The relative % reduction used to evaluate the effectiveness of different diet treatments.

$$\% \, Reduction = \frac{Ci - Ti}{Ci} \times 100 \, \%$$

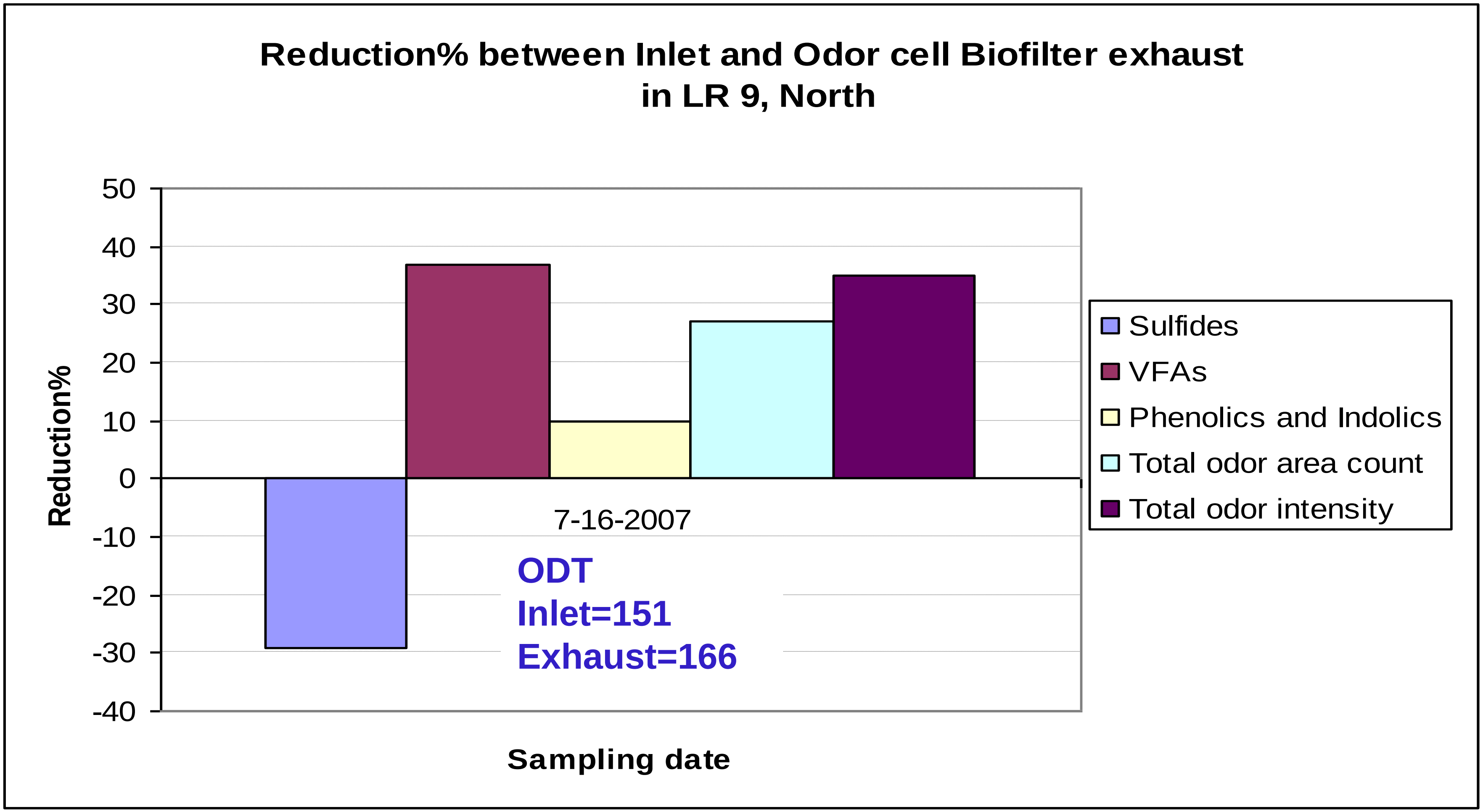
where:

Ci	=	peak area count of compound or odor “i” for the inlet gas, and
Ti	=	peak area count of compound or odor “i” for the biofilter exhaust gas.

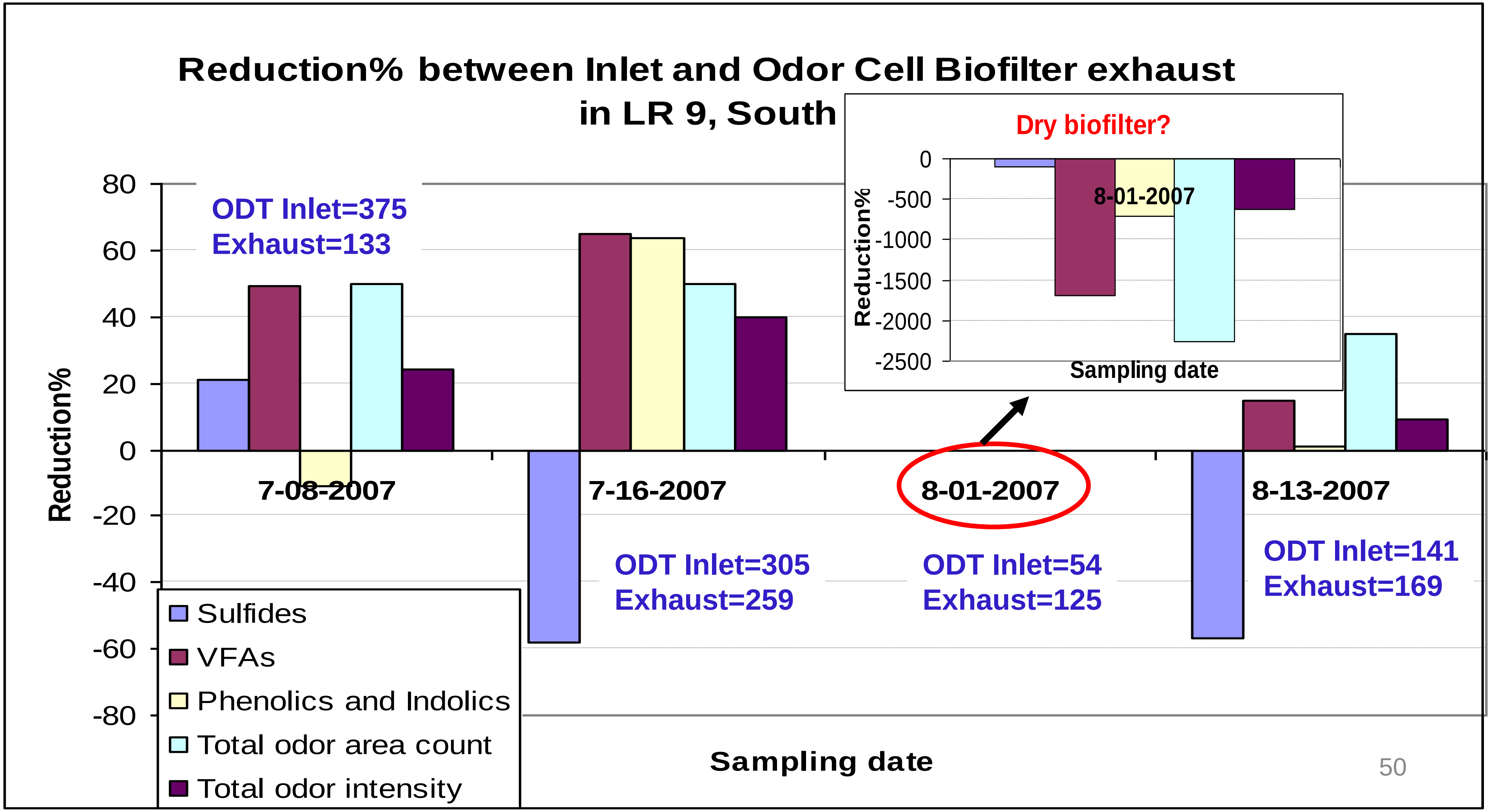
Example of chemical analysis and odorant % reduction

8-13-2007	Inlet, LR 3 South			BF exhaust, LR 3 South			
Compound	**Average**	**Stdev**	**RSD%**	**Average**	**Stdev**	**RSD%**	**Reduction %**
Dimethyl sulfide	3,486	217	6	3,684	1,069	29	**-6**
Dimethyl disulfide	4,308	1,921	45	5,516	1,076	20	**-28**
Dimethyl trisulfide	2,882	1,567	54	1,372	699	51	**52**
Acetic acid	5,157,131	476,728	9	100,094	46,234	46	**98**
Propanoic acid	1,729,513	108,229	6	42,374	11,395	27	**98**
Dimethyl propanedioic acid	347,178	6,891	2	43,498	2,107	5	**87**
Butanoic acid	6,560,819	368,405	6	164,784	47,724	29	**97**
Isovaleric acid	1,135,089	32,655	3	115,007	21,484	19	**90**
Valeric acid	2,298,297	67,572	3	0	0	0	**100**
Hexanoic acid	545,006	226,587	42	0	0	0	**100**
Phenol	528,587	37,970	7	111,670	23,427	21	**79**
p-Cresol	3,007,607	364,541	12	405,035	98,601	24	**87**
4-Ethyl-phenol	363,173	44,167	12	49,933	19,845	40	**86**
Indole	30,400	12,963	43	8,989	4,860	54	**70**
Skatole	26,602	9,738	37	9,469	3,167	33	**64**
Avg.			**19**			**27**	

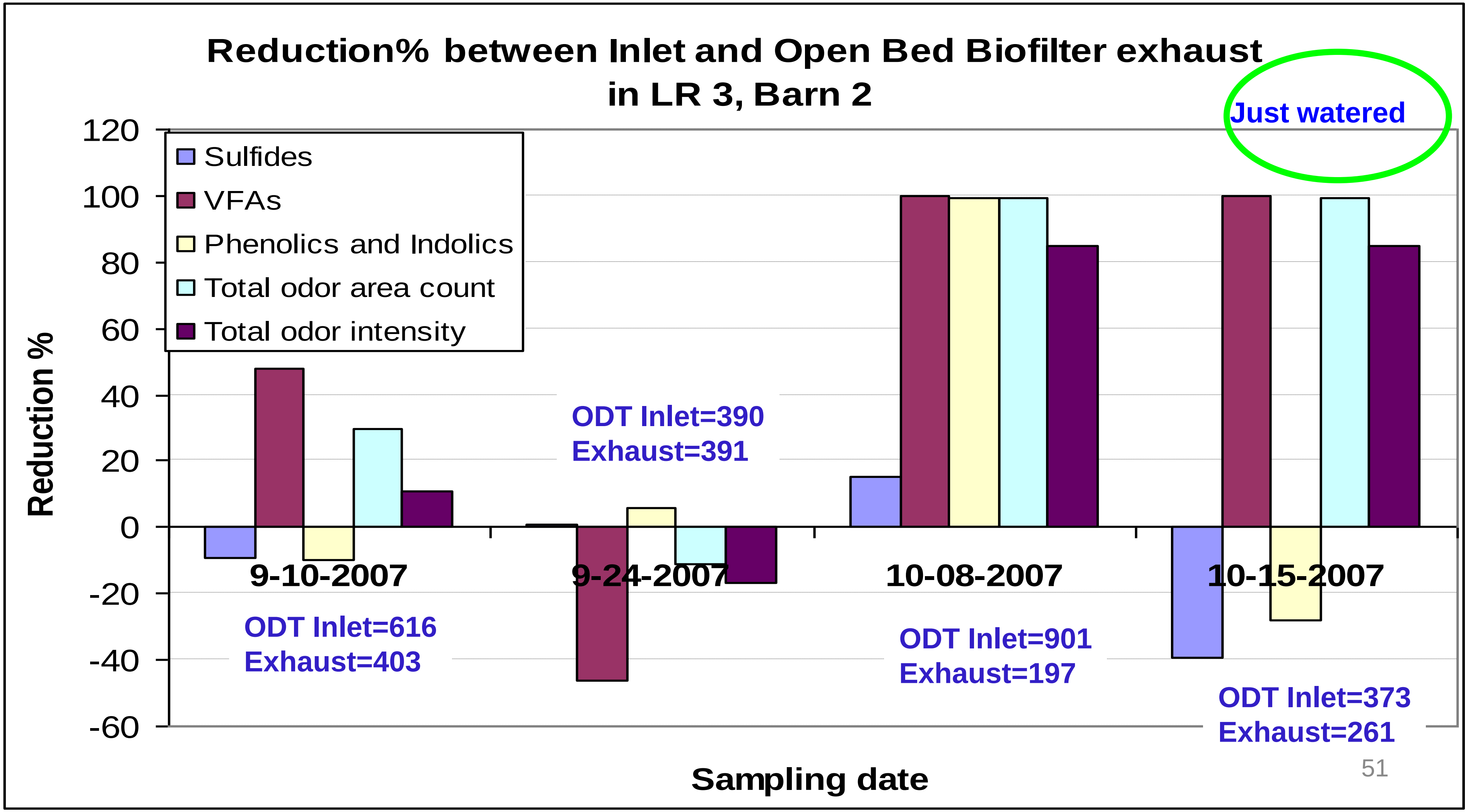
Odor Cell Biofilter



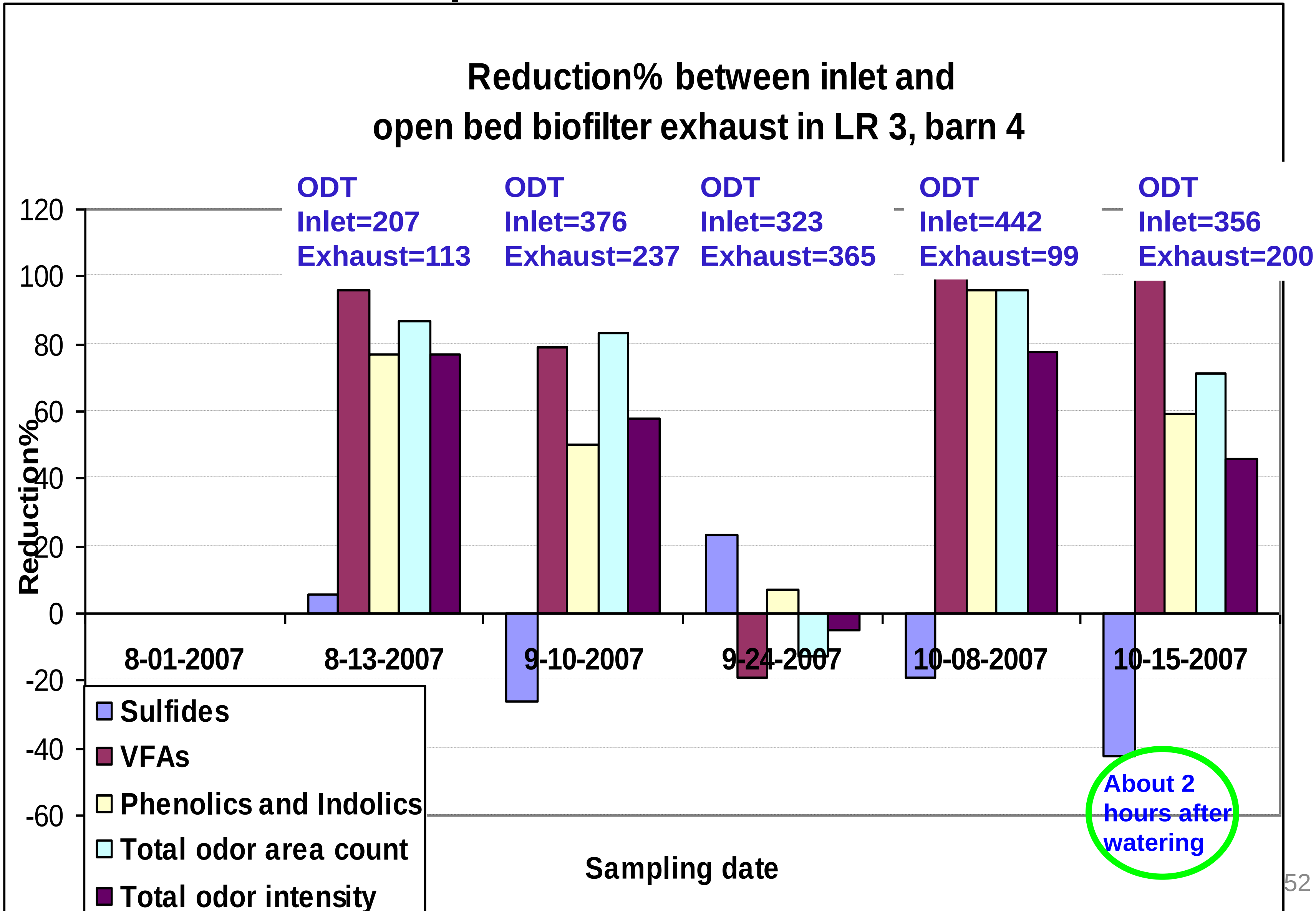
Odor Cell Biofilter



Open Bed Biofilter



Open Bed Biofilter

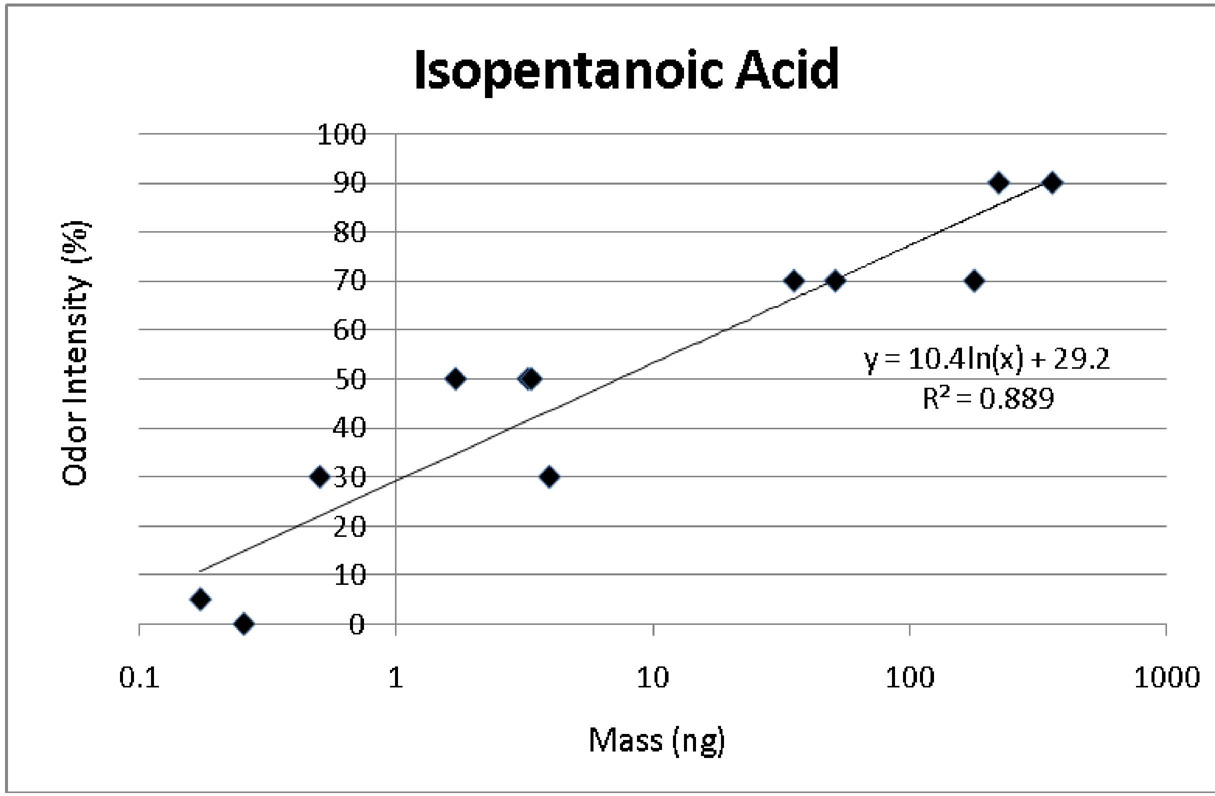


Correlation between odor intensity and gas concentration (mass on sorbent tube) (both swine and dairy sites – 1 month data)

Weber-Fechner Law

$$I = k_1 \log C + k_2$$

There is a linear relationship between odor intensity and the log concentration of the odorant.

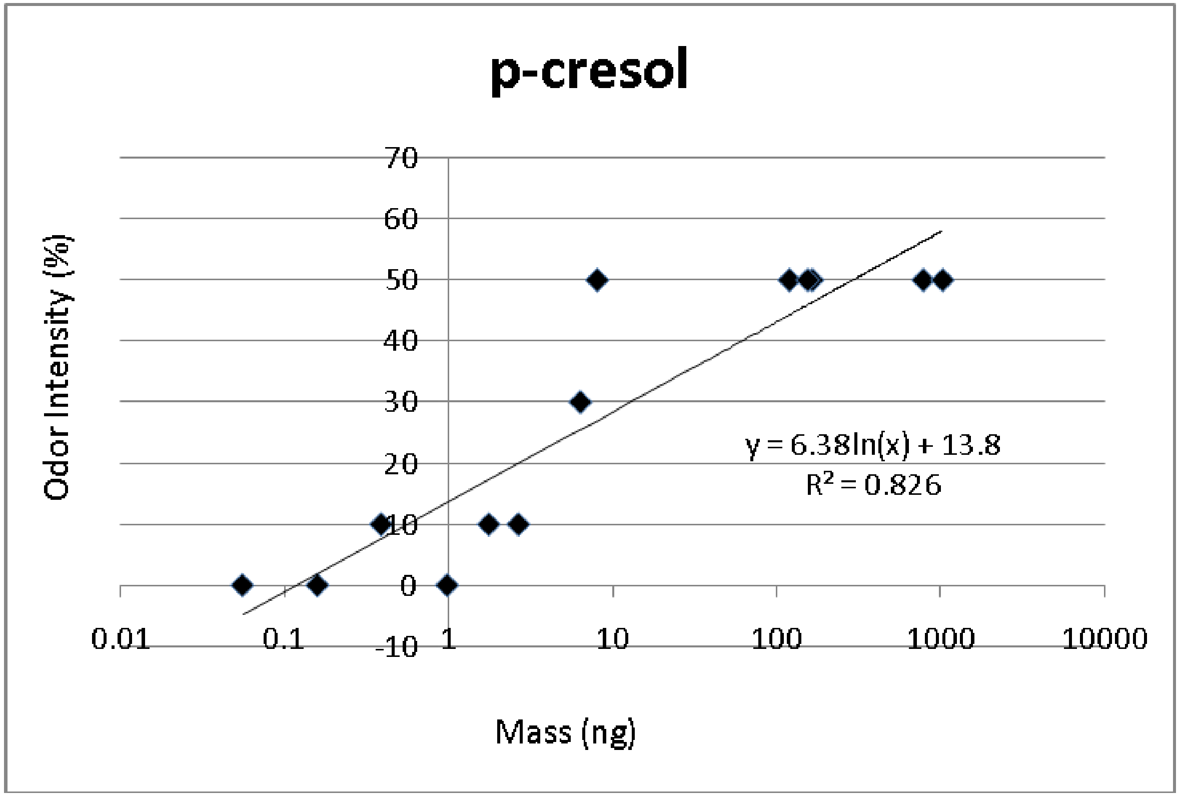


Typical VFA emitted from livestock facilities

Turk, A, et al. Human responses to environmental odors. Academic Press. 1974

Correlation between odor intensity and concentration
(mass on sorbent tube) (both swine and dairy sites – 1 month data)

Weber-Fechner Law



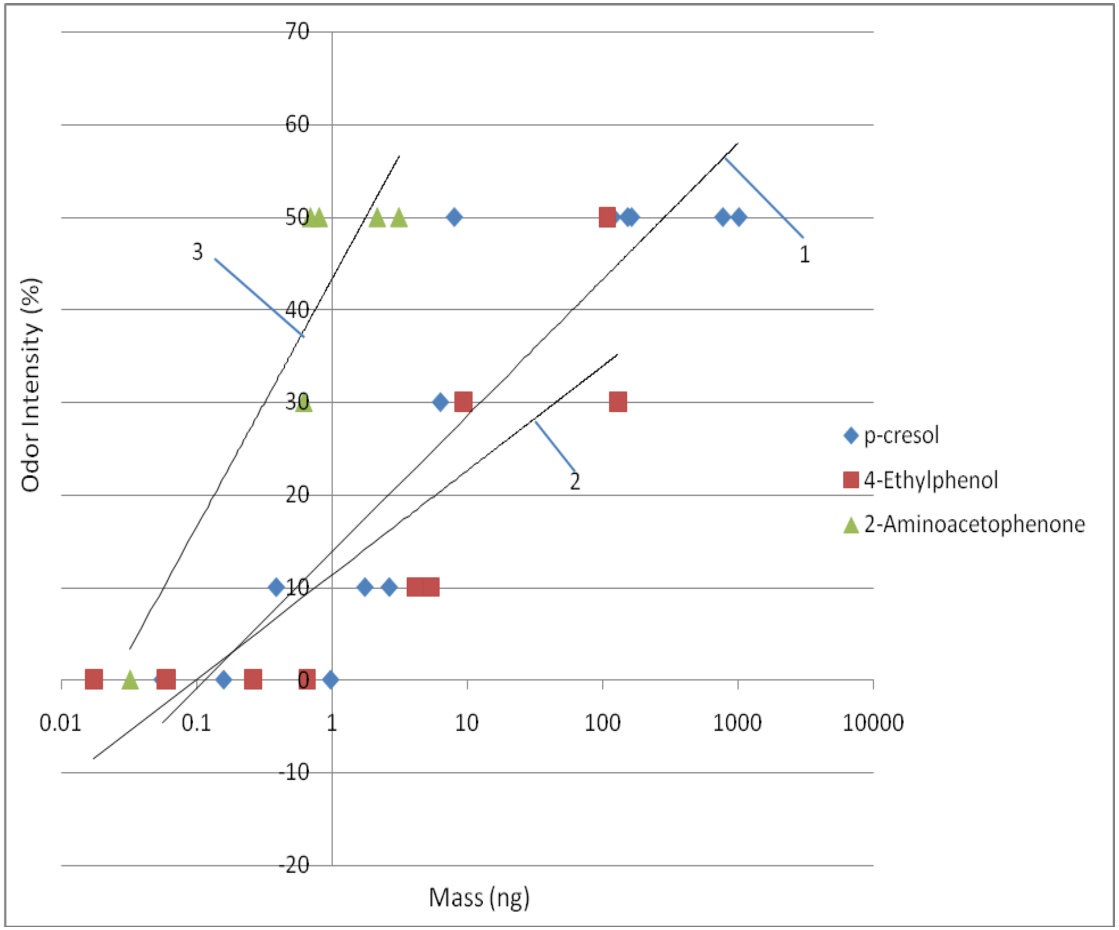
Typical phenolic emitted from livestock facilities

Correlation between odor intensity and gas concentration (mass on sorbent tube) (both the swine and dairy sites – 1 month data)

$R^2 > 0.750$

Weber-Fechner law

No.	Compound	Correlation equation	R^2
2	p-cresol	y = 6.38ln(x) + 13.8	**0.826**
3	4-Ethylphenol	y = 4.90ln(x) + 11.3	**0.756**
4	2-Aminoacetophenone	y = 11.6ln(x) + 43.4	**0.844**



Phenolics and other odors emitted from livestock facilities

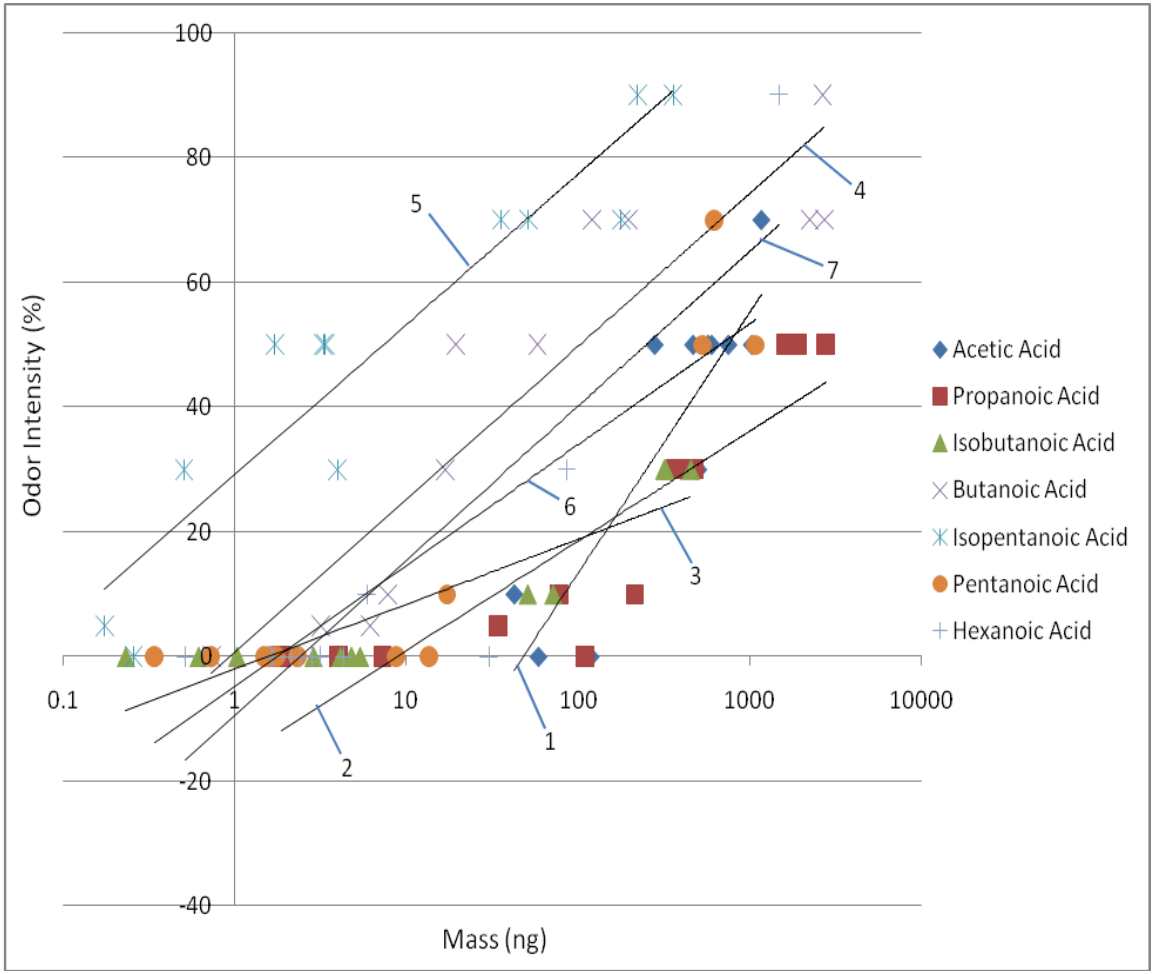
Correlation between odor intensity and gas concentration

(mass on sorbent tube) (both swine and dairy sites – 1 month data)

$R^2 > 0.750$

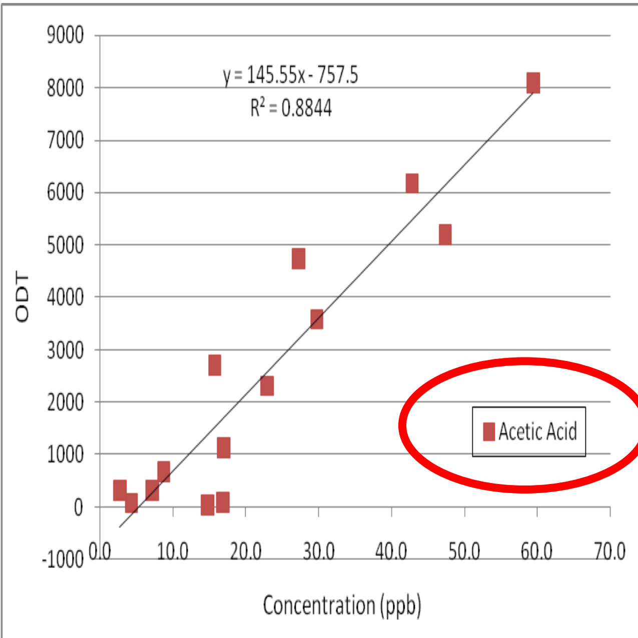
No.	Compound	Correlation equation	**R^2**
1	Acetic Acid	y = 18.2ln(x) - 70.3	**0.751**
2	Propanoic Acid	y = 7.64ln(x) – 16.7	**0.790**
3	Isobutanoic Acid	y = 4.53ln(x) - 2.00	**0.812**
4	Butanoic Acid	y = 10.6ln(x) + 0.757	**0.846**
5	Isopentanoic Acid	y = 10.41ln(x) + 29.2	**0.889**
6	Pentanoic Acid	y = 8.39ln(x) - 4.74	**0.827**
7	Hexanoic Acid	y = 10.8ln(x) - 9.37	**0.791**

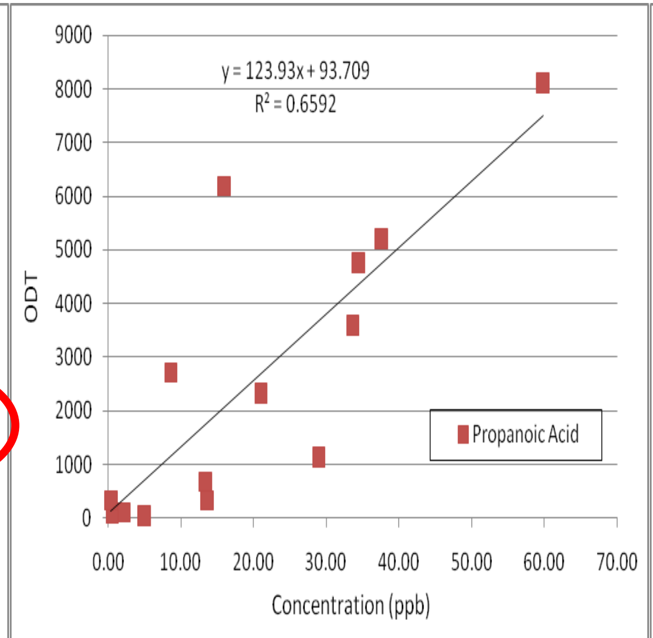
Weber-Fechner law

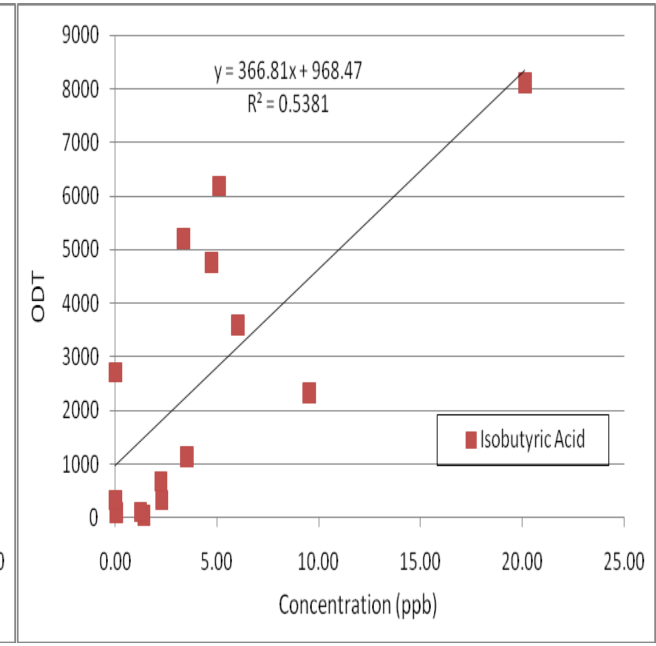


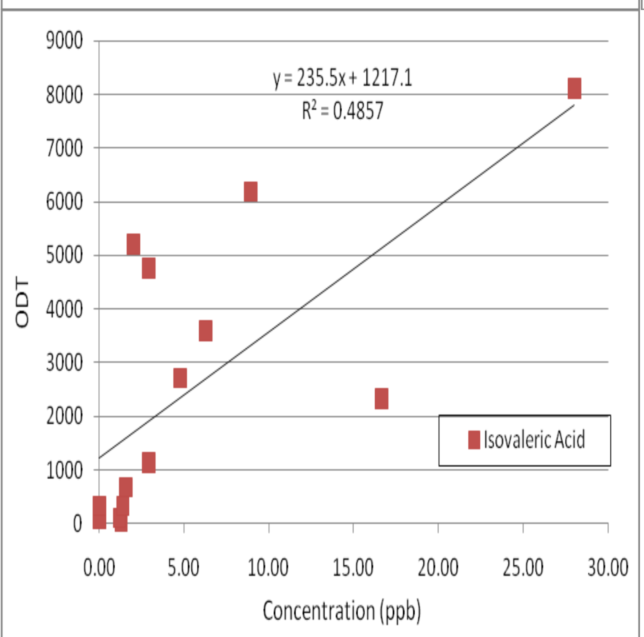
VFA emitted from livestock facilities

Correlations between ODT and concentrations – IA4B (swine barn)





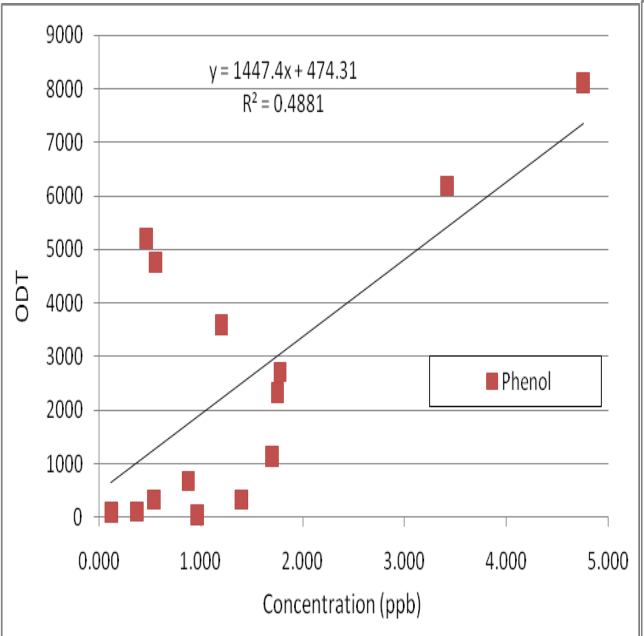


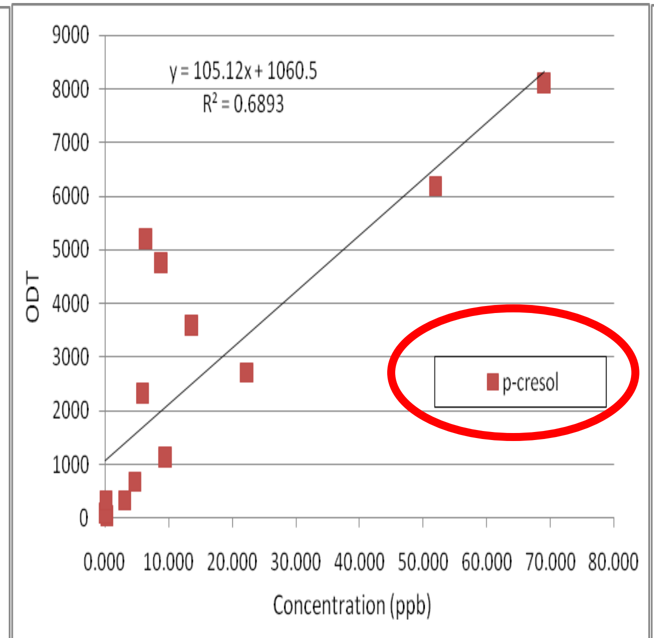


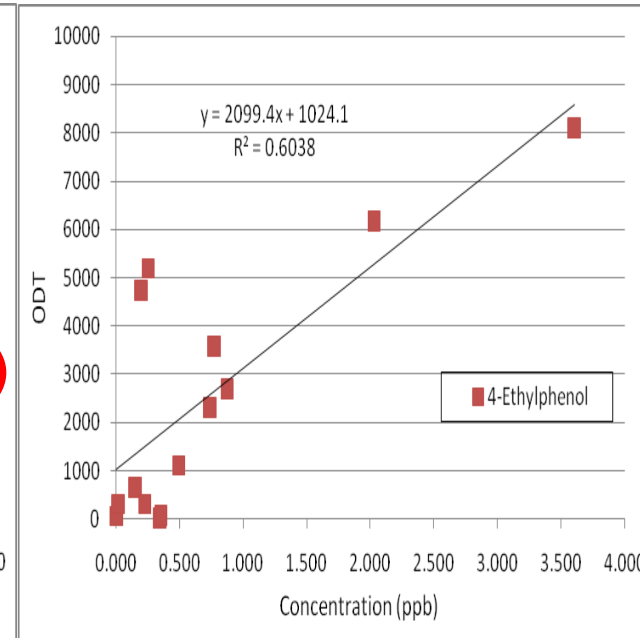
VFAs with significant R^2

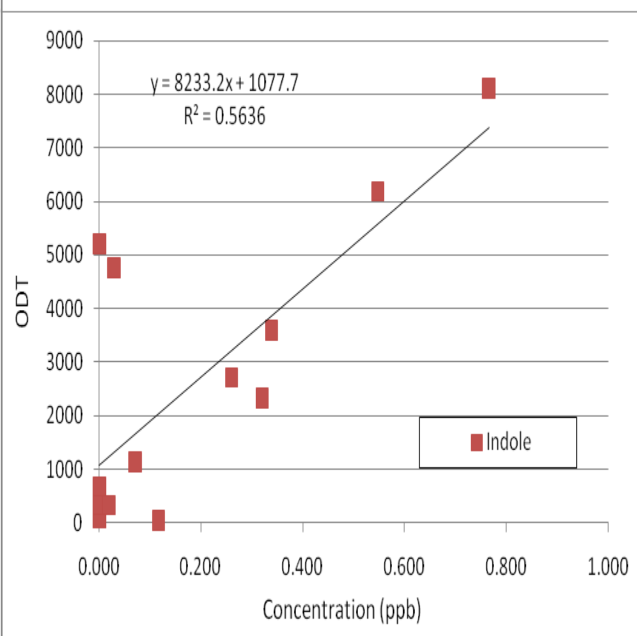
Acetic acid
Propanoic acid
Isobutyric acid
Isovaleric acid

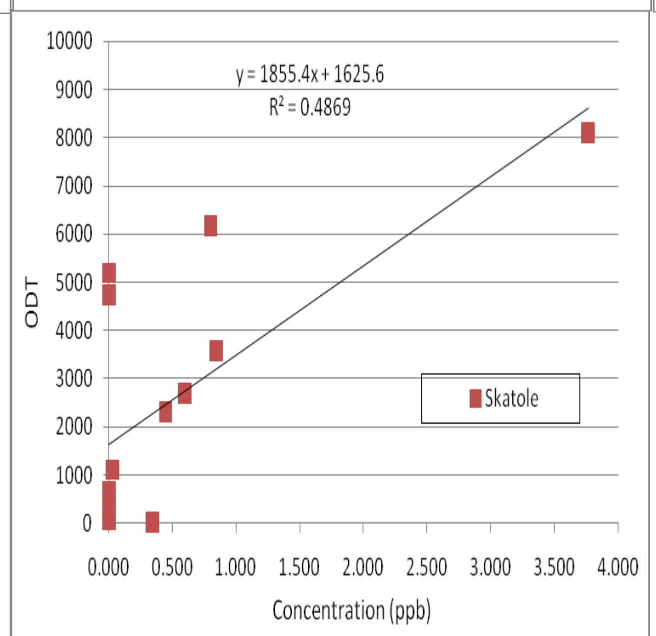
Correlations between ODT and concentrations – IA4B (Swine barn)











P-cresol, Indole and Skatole with significant R^2

Summary

- Combining chemical and olfactometry analysis is very useful in solving odor problems
- SPME-MDGC-MS-O approach is very useful well for sampling, separation, isolation and identification of characteristic odorants/aromas
- Only few analytes determine characteristic odors of any sample
- P-cresol appears to have the greatest characteristic swine odor
- GC-O approach and dilution olfactometry approach
- Measured odor concentration (ODT) appears to be correlated with the simultaneous chemical and sensory analysis
- Collection of large database of ODT, C_{gas}, hedonic tone, intensities for target VOCs, NH_3, and H_2S (Larry Jacobson – PI)