ANALYSIS OF AMINES FROM ANIMAL AGRICULTURE

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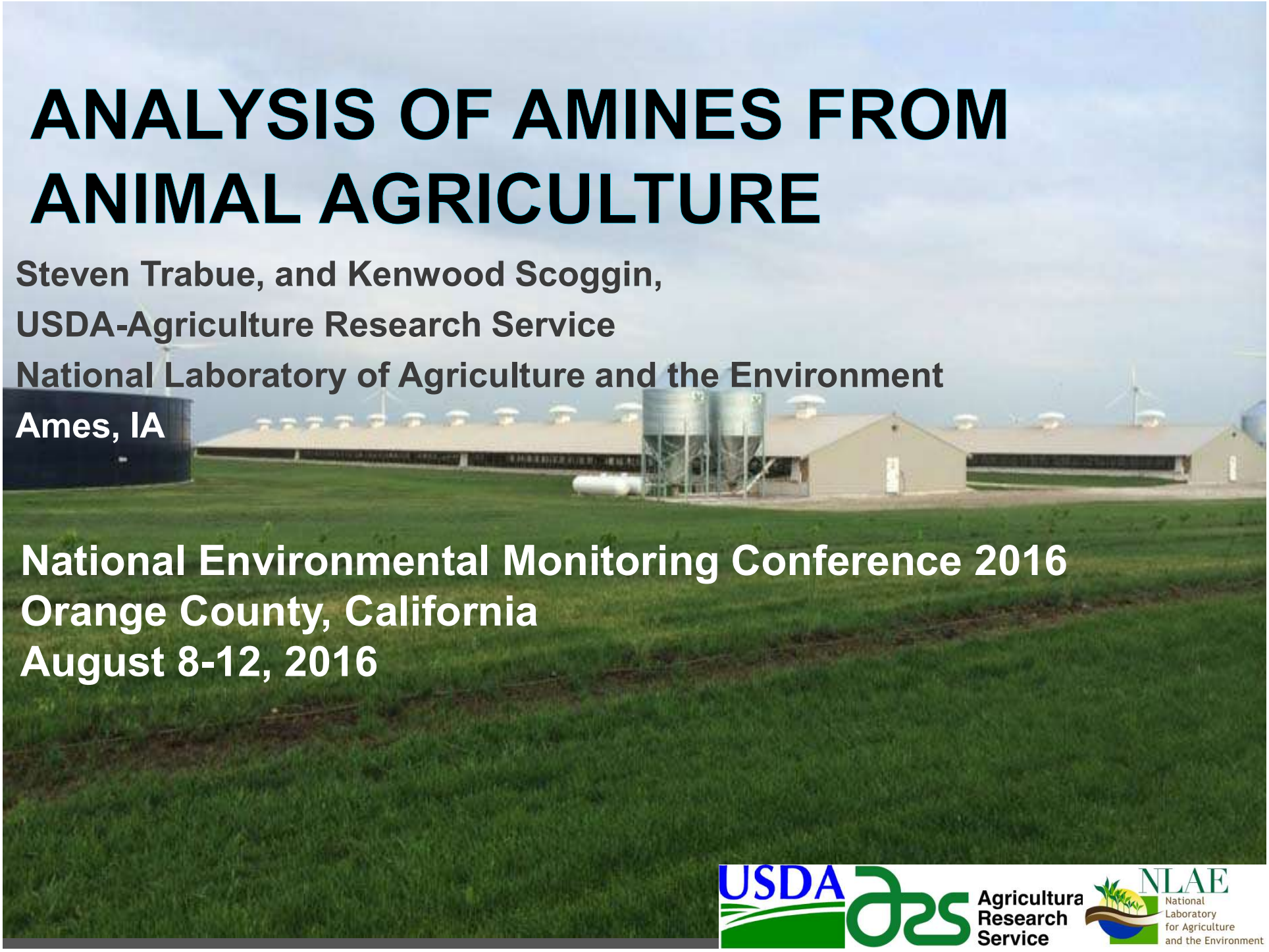

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Amines in Agricultural Production

1. Odorants (animal production)
   a. Swine (Hansen et al. Atmos. Environ. 2016)
   b. Poultry (Burnett ES&T 1968)
   c. Beef Cattle (Wright et al. JFAC 2005)
2. Particulate Formation
3. Food Spoilage

Analytical Challenges

1. Volatile in Nature
   - Limits sampling apparatus
2. Sorptive (sticky)
   - Limit surface contact
3. Reactive
4. High Ammonia Environments

Target Volatile Amines

Compound	Molecular Weight	Boiling Point	Odor Threshold
	g mol^{-1}	^{o}C	ppbv
Methylamine	31	-6	35
Dimethylamine	45	7	33
Trimethylamine	59	3	0.032
Ethylamine	45	16-20	46
Diethylamine	73	55	48
Triethylamine	101	85	5.4
Propylamine	59	47-50	25
Butylamine	73	77-79	1.5

Ammonia Concentrations

Poultry (Broilers & Layers)
10-25 ppmv

Swine (Sow & Grow-Finisher) 2-15 ppm

Open Feedlots (Beef & Dairy) 0.25-2 ppm

Current Reported Air Methods (Amines)

1. Discontinuous Monitoring
   a) Acid Traps (active and passive)
      1) GC Analysis: 80.0 ppbv (OSHA, 1992)
      2) IC Method: 3.49 ppbv (Cowen et. al. EPA ETV 2004)
      3) SPME: 660 ppbv (Chien et al. Anal. Chim . Acta 2000)
   b) Ion Exchange Resins 4.3 ppbv (Dawson et al. Atmos. Meas. Tech. 2014)
   c) Field SPME 2.38 ppbv (Kim et al. Anal. Chem. 2002)
2. Real Time Monitoring
   a) Ambient pressure Proton transfer Mass Spectrometer (Hansen et al. ES&T 2011)
   b) SIFT-MS 0.16 ppbv (Feilberg et al. Sensor 2015)

EPA Compendium Method IO-4.2

ChemComb Model 3500 Speciation Sampling Cartridge

- Partisol Model 2300 speciation samplers
- Leland Legacy Pumps

Sampling Rate: 10 L min^{-1}

Extracted Denuders with 10 mL DI Water

Breakthrough of ammonia

- Feedlot 2 hr (less than 10%)
- Swine 10 min (less than 5%)

Problem with IC Analysis

- Ammonia Peak interfered with most other peaks.
- Ammonia Concentration
  - Feedlot: 167 μg mL^{-1} (9.8 mM)
  - Dairy: 42 μg mL^{-1} (2.5 mM)
  - Swine: 69 μg mL^{-1} (4.1 mM)
  - Poultry: 174 μg mL^{-1} (10.2 mM)

Purpose of Method

1. Develop a robust high through-put analysis technique with minimal preparation time.

2. Independent of ammonia interferences.

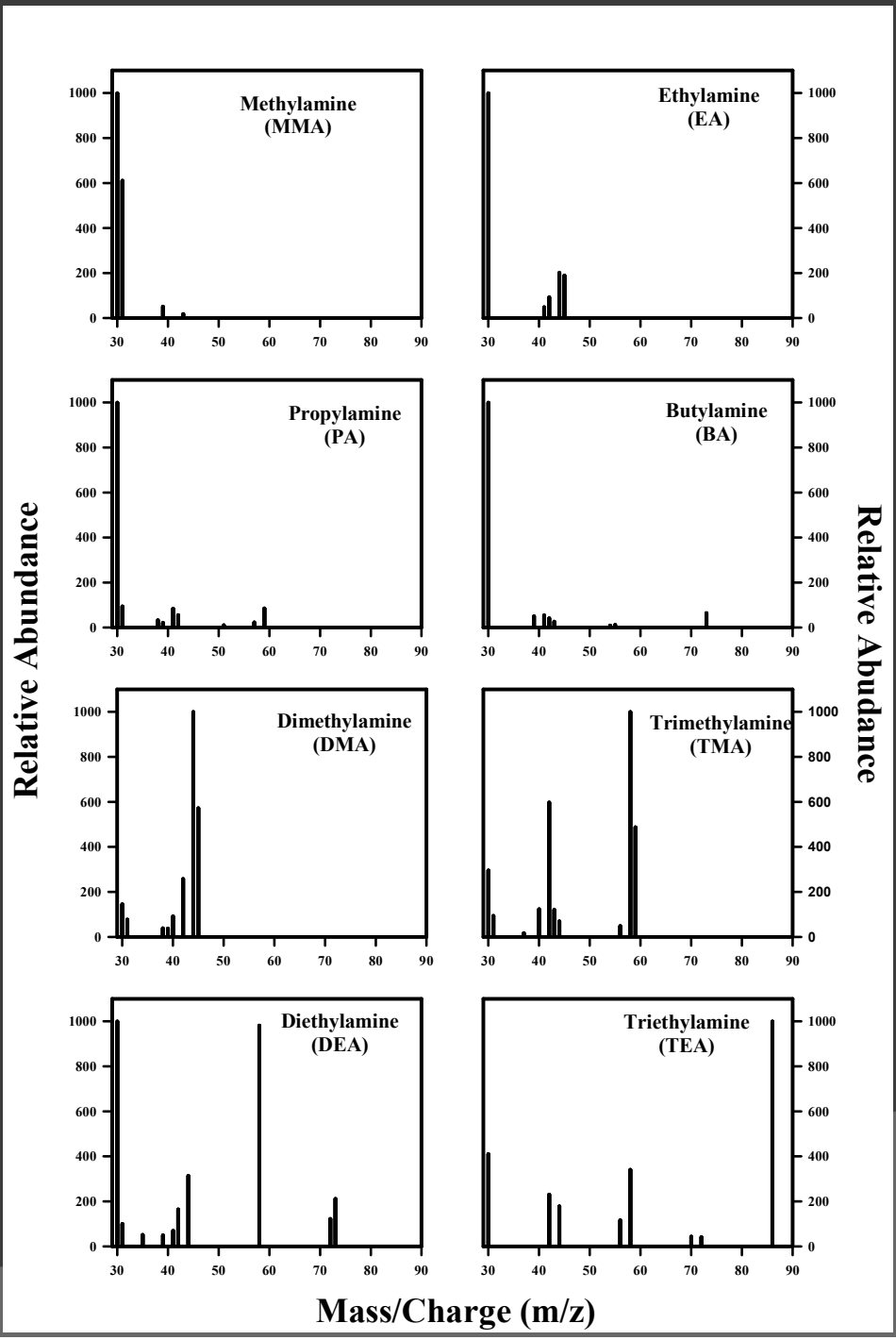
Analysis of Extracts Headspace SPME GC/MS

Optimizing Parameters

1. Fiber Choice
2. pH
   - A) 9; B) 12; C) 13 and D) 14
3. Extraction Temperature
   - A) 30; B) 50; C)70; and D) 100^{o}C
4. Extraction Time
   - A) 1 min; B) 2 min; C) 5 min; D) 10 min; and E) 20 min

Chemical Separation

METHOD DEVELOPMENT

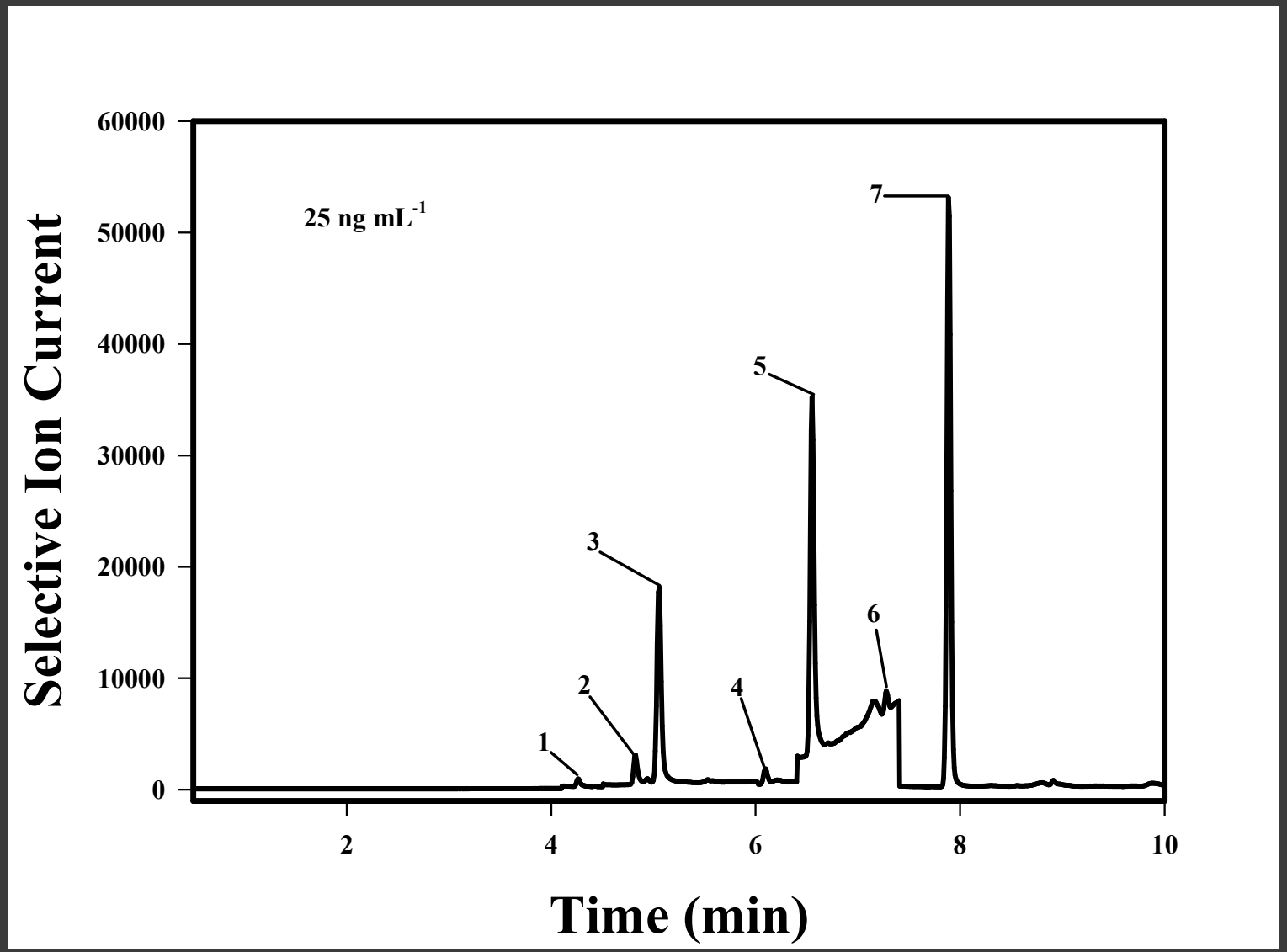

Methylamine
(MMA)
Ethylamine
(EA)
Propylamine
(PA)
Butylamine
(BA)
Dimethylamine
(DMA)
Trimethylamine
(TMA)
Diethylamine
(DEA)
Triethylamine
(TEA)
Relative Abundance
Relative Abudance
Mass/Charge (m/z)

Separation Technique

Agilent 6890 GC/MS

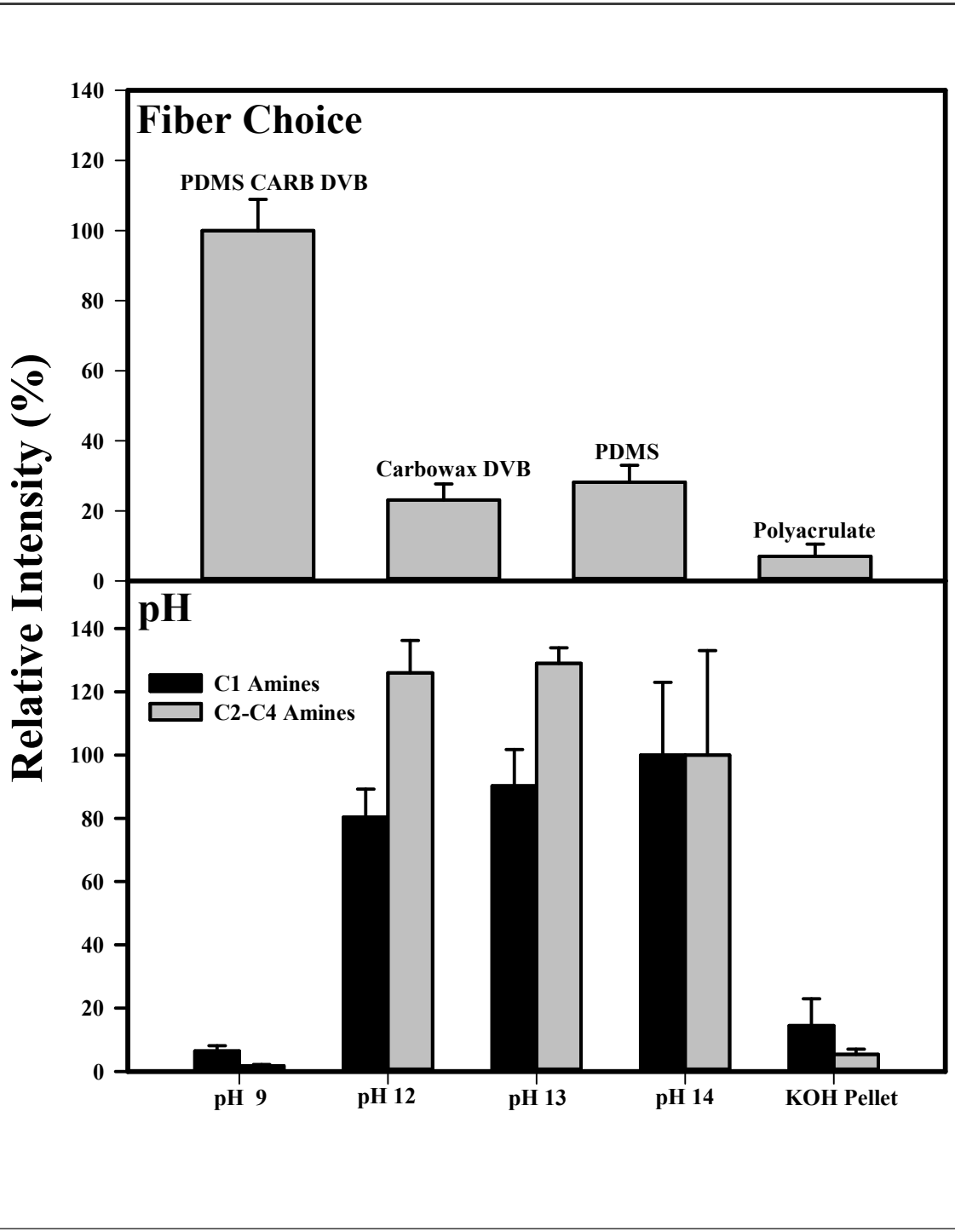
1. Gerstel, Inc MPS2 w/ SPME attachment
2. CP-Volamine 60 m, 0.32 µm, 5.0 µm
3. Oven
   - Initial 70°C, 2 min hold
   - 70 – 260°C @ 30° C/min
   - Hold at 260°C, 2 min
   - Cycle Time: 14 min

	Retention Time	Quant Ion
	min	m/z
Methylamine	4.2	30
Dimethylamine	4.8	45
Trimethylamine	5.1	58
Ethylamine	4.9	30
Diethylamine	6.6	58
Triethylamine	7.9	85
Propylamine	6.1	30
Butylamine	7.3	30

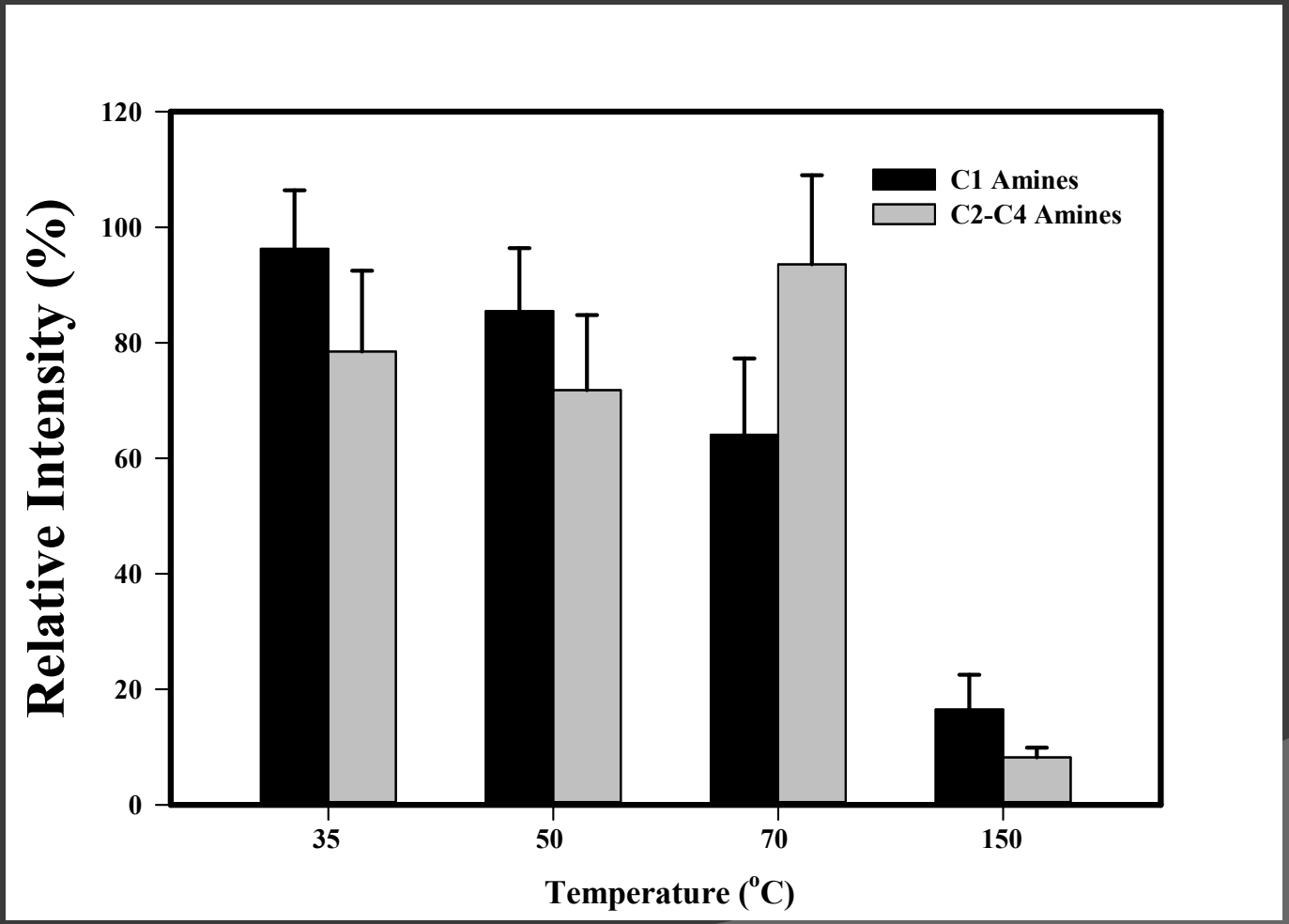

Selective Ion Current
60000
50000
40000
30000
20000
10000
0
25 ng mL-1
1
2
3
4
5
6
7
2
4
6
8
10
Time (min)

SPME Headspace

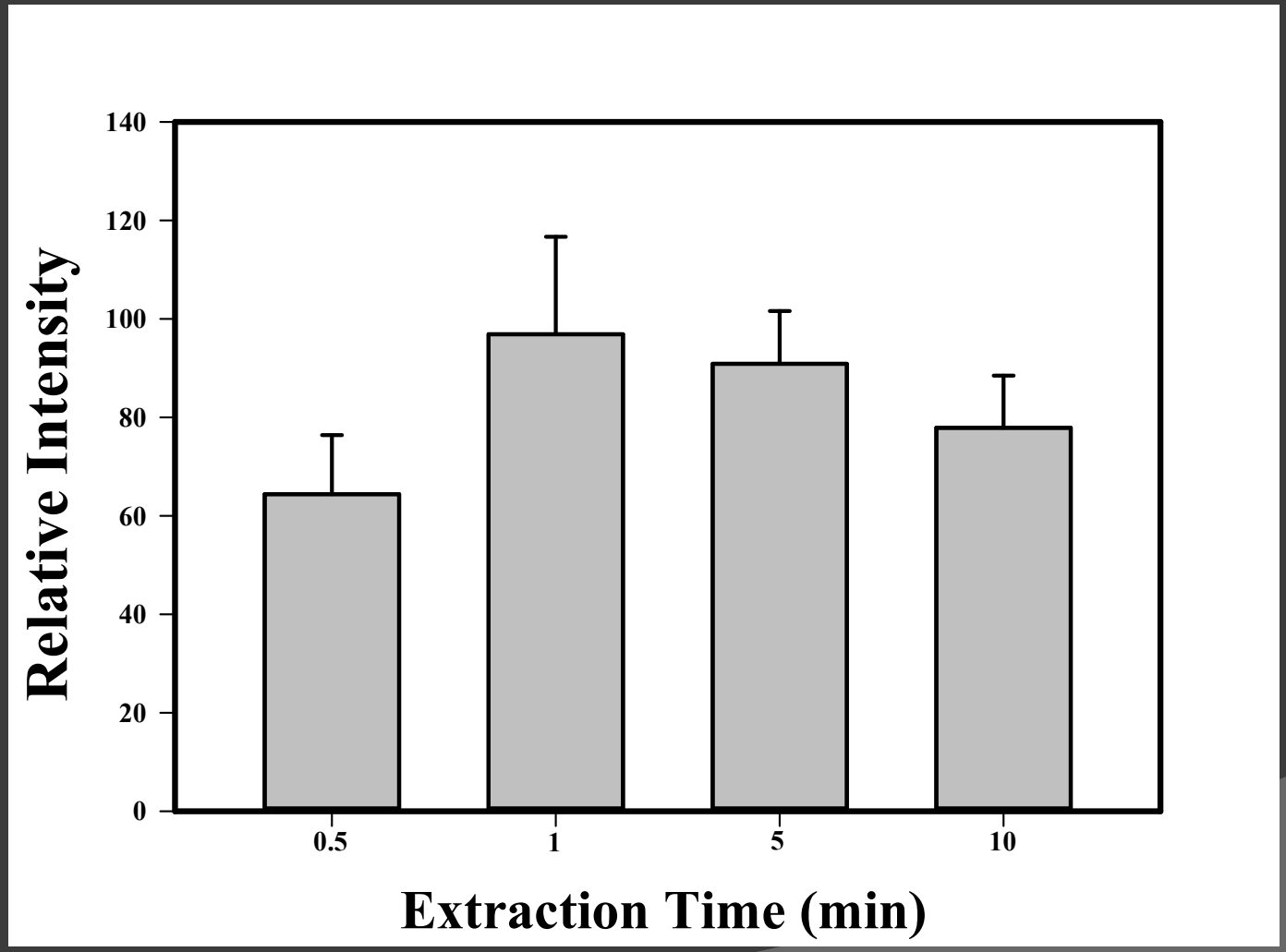
METHOD DEVELOPMENT


Fiber Choice
PDMS CARB DVB
Carbowax DVB
PDMS
Polyacrulate
pH
C1 Amines
C2-C4 Amines
Relative Intensity (%)
0
20
40
60
80
100
120
140
pH 9
pH 12
pH 13
pH 14
KOH Pellet

Extraction Temperature



Extraction Time



Sample Processing

Extraction of Denuder (10 mL HPLC Water)

Headspace Vial Preparation

1. Place two scopes of NaCl into 20 mL headspace vial (approx. 0.5 g).
2. Add 2 mL sample extract and seal.
3. Syringe in 100 μL 5 M KOH
4. Mix and add to autosampler.

Autosampler

1. Incubate headspace vial 5 min at 35°C
2. Extract headspace with SPME fiber (5 min)

METHOD PERFORMANCE

Volatile Amines

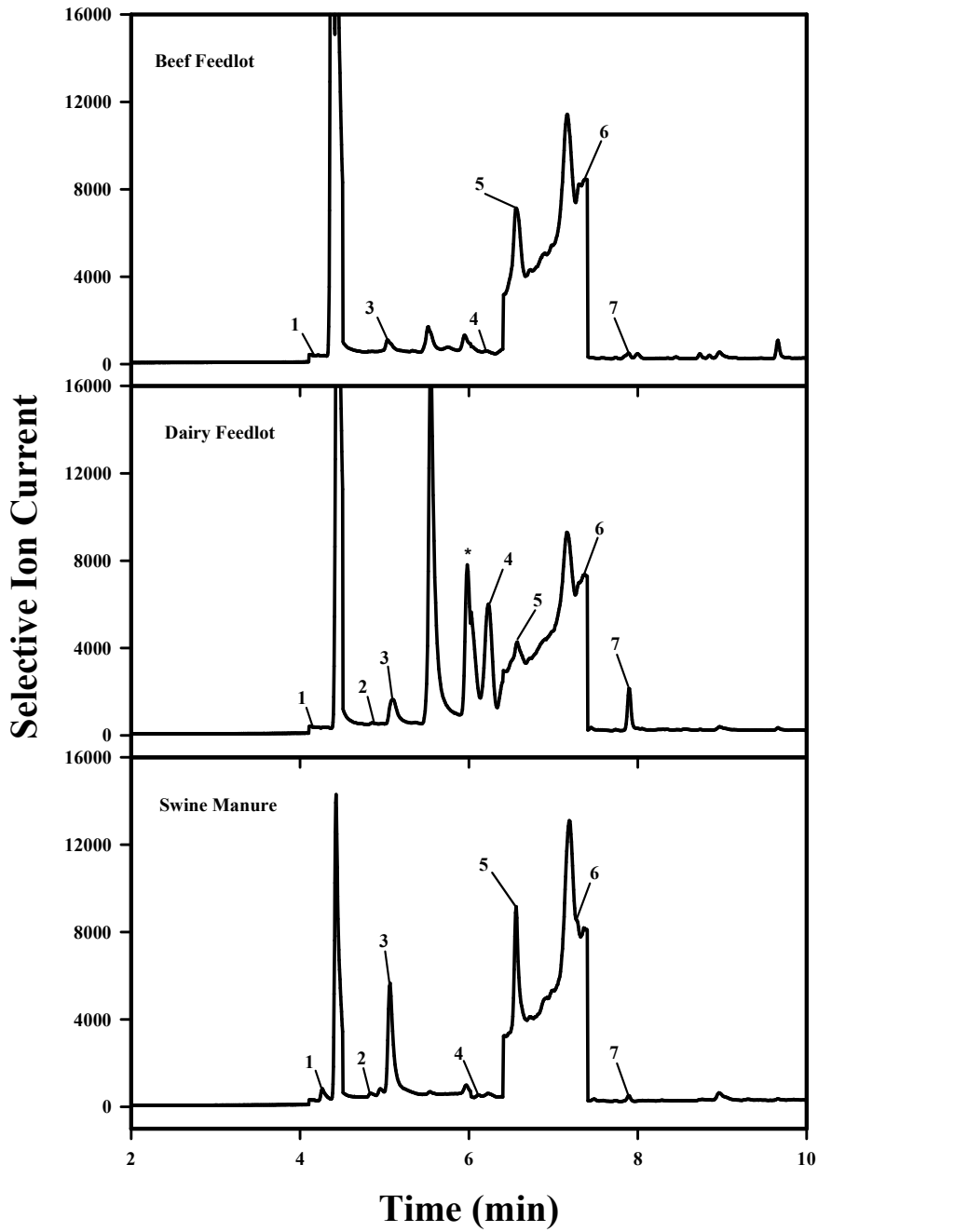
Compound	Range	r^2	Cal. LOD	Cal. LOQ	Accuracy	Repeatability
	ng mL^{-1}		—— ng mL^{-1} ——		%	%
Methylamine	10-333	0.960	10.2	42.9	11.7	12.1
Dimethylamine	10-333	0.974	2.4	6.3	9.4	11.1
Trimethylamine	10-333	0.905	1.6	3.7	18.7	11.2
Diethylamine	10-333	0.965	2.8	6.5	11.4	5.6
Triethylamine	10-333	0.980	0.5	1.5	7.2	7.6
Propylamine	10-333	0.968	6.8	13.7	10.3	9.2
Butylamine	10-333	0.981	3.9	7.9	8.4	5.7

Volatile Amines

Compound	Air LOD				Sample	
	Low Volume		High Volume		Concentration	CV
	ppbv	µg m^3	ppbv	µg m^3	µg m^3	%
Methylamine	0.800	1.02	0.085	0.085	2.78	33.1
Dimethylamine	0.130	0.24	0.011	0.020	0.47	61.4
Trimethylamine	0.066	0.16	0.005	0.013	3.86	22.5
Diethylamine	0.094	0.28	0.008	0.023	13.09	32.2
Triethylamine	0.012	0.05	0.001	0.004	0.06	33.9
Propylamine	0.280	0.68	0.023	0.057	BDL	NA
Butylamine	0.130	0.39	0.011	0.032	0.43	18.8

Ammonia Challenge

Compounds	Citrate Buffer	Ammonia Concentration (μg mL^{-1})					
	Blk	42	84	330	670	850	2100
	% Recovery						
Methylamine	100	93.5	115.4	90.3	92.8	18.0	10.6
Dimethylamine	100	109.1	107.2	96.8	94.4	7.1	3.7
Trimethylamine	100	92.5	88.6	82.0	70.4	28.6	6.3
Diethylamine	100	114.5	119.8	91.3	89.7	8.1	4.6
Triethylamine	100	123.7	127.8	91.3	84.4	12.1	2.2
Propylamine	100	119.6	108.8	97.4	95.7	24.8	11.0
Butylamine	100	120.4	103.0	94.4	78.1	25.5	12.3


Beef Feedlot
Dairy Feedlot
Swine Manure
Selective Ion Current
Time (min)
16000
12000
8000
4000
0
2
4
6
8
10
1
2
3
4
5
6
7
*

Compound	Swine		Dairy		Beef	
	Diet	Fan	Lagoon	Paddock	Central	10 m N
	μg m^3					
Methylamine	0.88	0.27	0.05	0.04	0.08	0.56
Dimethylamine	0.21	0.57	0.04	0.04	0.15	0.48
Trimethylamine	3.86	1.20	0.42	0.19	1.79	3.05
Diethylamine	13.09	0.80	0.35	0.24	0.05	0.10
Triethylamine	0.02	0.11	0.01	0.01	0.20	BDL
Propylamine	BDL	BDL	BDL	BDL	BDL	BDL
Butylamine	0.27	0.07	0.08	0.04	0.13	0.02

Chemical Class	Swine	Beef
	Odor Activity Value	Odor Activity Value
Reduced Sulfur	617	NA
Ammonia	55	1
Volatile Fatty Acids	122	25
Phenol Compounds	286	17
Indole Compounds	225	15
Amines	230	20

Conclusion

1. Headspace analysis with SPME is fast quantitative method for the analysis of volatile amines and organic nitrogen compounds. However, extraction and coating honeycomb denuders is still labor intensive.

2. Ammonia interferences were reduced compared to previous IC method. However, NH_3 levels above 700 ng mL^{-1} should be avoided.

3. Amine profiles for each livestock operations were unique and likely reflect dietary rations and animal type.

4. Trimethylamine was the key amine odorant and the most abundant amine. However, diet studies show that diethylamine is also significant amine compound in swine.