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The Application of Thermal Desorption GC/MS with Simultaneous Olfactory Evaluation for the Characterization and Quantification of Odor Compounds from a Dairy

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Few analytical methods exist that combine chemical and sensory analysis of odorous compounds in whole air. Volatile organic compounds were collected by sampling air downwind from a small dairy through sorbent tubes of Tenax TA and Carboxen 569. Samples were analyzed by thermal desorption into a cryotrap and subsequent gas chromatographic separation, followed by simultaneous olfactometry and mass spectrometry. Because compounds are concentrated during sampling, sensory analysis encountered compounds at a concentration 40 times that in air, making this a useful method for identifying trace compounds participating in odor. Twenty odorous and nonodorous compounds were identified and quantified, including straight-chain and aromatic hydrocarbons, chlorinated compounds, alcohols, ketones, aldehydes, and organic acids, at air concentrations of 0.55−320.20 μg/m^3. Compound peaks were characterized by odors ranging from offensive to pleasant, demonstrating the integrative nature of olfaction. This method could be useful in studying many kinds of odors in air.

KEYWORDS: Odor characterization; GC-olfactometry; thermal desorption; dairy; cattle waste

INTRODUCTION

California leads the nation in agricultural production, and animal husbandry constitutes a significant share of that production. In 1999, California's agricultural production was valued at a total of $25.0 billion, almost double that of second-place Texas at $13.2 billion (*1*). With a value of $4.09 billion, milk and cream together remain its top commodity; cattle and calves, its fourth largest commodity, is valued at $1.20 billion. The milk and beef cattle inventory numbers some 6.32 million head. Of this cattle population, 64.8% are housed in high-density operations of greater than 500 head/facility. California is also seeing rapid growth in its human population. In the past decade, the total population of California increased by 11.2% to its current estimated number of 33.1 million people (*2*). Coincidentally, the top five dairy counties of California (Tulare, Merced, San Bernardino, Stanislaus, and Riverside) all saw large population growth of 12.5−30.8% from 1990 to 1999. These trends have led to increased interest in addressing malodor associated with livestock waste.

More than 100 odorous compounds are present in animal operations (*3*); a recent study numbers the compounds from dairies at 70 (*4*). Most studies in the literature on livestock odor have focused on swine wastes, very few on dairies or cattle, and none on California dairies or outdoor dairies under arid climates. In the most recent and comprehensive study, conducted at indoor dairies in Sweden, concentrations of some 70 VOC's were measured ranging in concentration from 0.01 to 200 μg/m^3. Until recently, limitations in sampling and analytical methods severely hampered efforts to obtain a representative picture of the nature of odor under outdoor field conditions. Because of the bacterial nature of waste degradation, even minor changes in handling can create large biases in odors generated. This limits the usefulness of methods that attempt laboratory replication of field conditions, or when waste must be transported for extraction. Additionally, concentrations of malodors extracted from waste have been shown to be highly dependent on extraction procedure (*5*). The main challenge in pursuing the chemical analysis of environmental odors has been that these volatile organic compounds differ greatly in their various functionalities and physicochemical properties and exist in wide ranges of concentrations in ambient air. Many studies have therefore relied on the quantification of nontrace compounds such as ammonia and hydrogen sulfide, and occasionally on volatile fatty acids (VFAs), as "indicator compounds" for odor, irrespective of the far lower odor detection thresholds for compounds which may be found at far lower concentrations (*3*, *6*, *7*). Dynamic dilution olfactometry is an established method of measuring odor which has made it possible to bypass the various difficulties inherent in the chemical analysis of odors

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(*8*). In that method, panels of judges are exposed to dilutions of odorous whole air to define the degree of dilution necessary to achieve threshold. However, olfactometric data is subjective, expensive, and offers little information on the chemical basis of malodor, its generation, or its possible remediation (*9*).

By contrast, gas-chromatography/olfactometry offers the advantages of combining sensory data with the identification and quantification of compounds. The added benefits of using sorption followed by thermal desorption as a means of sample collection and analysis are that it concentrates airborne compounds to enhance sensitivity while also minimizing sample manipulation after collection. Clearly, incorporating mass-spectrometry provides yet another useful tool in chemical identification. One prior application of the method was recently reported, in which odors from plastics manufacturing were studied; however, in that application, sampling was conducted in flue gas train of the factory, rather than in outdoor air (*10*). The objective of this study was to demonstrate the capabilities of thermal desorption−GC−olfactometry/MS (TD−GC(O)−MS) as a novel method in identifying and quantifying malodors in whole air samples. A secondary objective was to identify and quantify compounds likely to play a role in malodor from dairy waste at a small California dairy.

MATERIALS AND METHODS

Preparation of Sampling Tubes. Glass-lined stainless steel sampling tubes, length 10.0 cm × 6.0 mm (o.d.) × 3.0 mm (i.d.), packed with 100 mg of either Tenax TA or Carboxen 569 adsorbents were obtained prepacked from the manufacturer (Scientific Instrument Services, Ringoes, NJ.) Tubes were thermally conditioned at 300 °C with 99.9999% helium flowing through at 20.0 mL/min for a minimum of 4 h. Caps equipped with Teflon seals were conditioned separately at 200 °C for a minimum of 2 h. Tubes were then sealed and kept refrigerated until use, but not for more than 2 weeks. Laboratory and field blanks from conditioned and unused tubes both left in the laboratory and returned from the field unused were analyzed to characterize background contamination. Care was taken to follow the recommendations for use established by previous researchers (*11*).

Site Description. The University of California Davis campus dairy was chosen as a trial site for sampling optimization. Air sampling was performed during the months of June to August 2001 on nine separate occasions. This small teaching facility, measuring 90 m × 93 m, houses 220 head of cattle (120 milking cows and 100 heifers) and is located on the University of California Davis campus. Samplers were located north of four concrete pens housing a total of 98 milking cows. These pens were scraped clean twice weekly, and air sampling was performed on days just prior to scraping. Prevailing daytime winds were from the south, and sampling was performed only during stable wind episodes when winds were between 3 and 8 mph, usually occurring during the hours of 12:00 to 3:00 pm.

Sampling Procedure. Air was sampled downwind from the area source using Tenax and Carboxen tubes in series, connected using tube unions, with Tenax tubes placed upstream from Carboxen tubes in the sampling train. Tube-to-hose connectors were used to connect them to sampling pumps (SKC Airchek 224-PCXR7; Eighty Four, PA). Gel ice-packs were wrapped around the Tenax tubes two inches below the mouth of the tube to protect them from intense sunlight and cool them as well as the sampled air. Care was taken to locate samplers away from structures that would create turbulence or obstruction to normal wind flow. A low-profile PVC frame was constructed to hold the samplers vertically 2 m above the ground, with the intake orifices held six inches above the frame. Sampling flow rate was monitored using a J&W ADM 3000 Gas Flowmeter (J&W Scientific, Folsom, CA) every 10 min and averaged over the length of the run to obtain final sampling volume. Flow rates remained generally steady for each station but varied from 20.0 to 65.0 mL/min between stations during independent testing episodes, depending on the pump and the sampling tube packing. Various sampling volumes were obtained, from 1 to 33 L, corresponding to sampling times from 30 min to 7 h. Local meteorological conditions were obtained from the UC Davis Meteorological Station. Sampling site temperature and relative humidity were monitored using a digital thermometer-hygrometer (RadioShack Digital Thermo-Hygro.)

Thermal Desorption. A short-path thermal desorption and cryotrap system was used to purge and desorb sampling tubes (Scientific Instrument Services Model TD-4). The cryotrap unit was installed around the analytical column just below the injection port and used pressurized carbon dioxide to cool a 1.5 cm section of the column to −60 °C. The thermal desorber tower assembly rested over the injection port and was controlled by means of a separate microprocessor also controlling the cryotrap. Tubes ready for analysis were attached to a syringe needle and then connected to the autoinjector. The system microprocessor program purged sampling tubes for 1 min with helium and then activated the lowering and insertion of the needle into the chromatograph injection port. During the 1 min injection phase, the desorption tube was maintained at ambient temperature while the carrier gas flow to the injection port was rerouted through the desorption tube, and the column head pressure was allowed to return to its setpoint. During the subsequent 5 min desorption phase, heating blocks were closed around the sorbent tube, gradually increasing the temperature from 100 to 250 °C, loading desorbed analytes onto the cryotrap just below the column head. Following desorption, the desorption tube was retracted, and an additional 30 s prerun delay preceded cryotrap shutoff and activation of the GC run. Percent recovery from thermal desorption for analyzed compounds was determined by loading standard compounds neat onto sorbent tubes using a GC syringe through a desorption tube injection head with concurrent purge gas (carrier gas) flow (Scientific Instrument Services, Ringoes, NJ.)

Gas Chromatography/Mass Spectrometry. The gas chromatograph (HP 6890) was equipped with a 1 m × 0.53 mm i.d., 1.5 μm, DB-5 guard column (J&W) followed by a 30 m × 0.25 mm i.d., 0.5 μm, DB-5MS analytical column (J&W, Folsom, CA). Carrier gas used was 99.9999% helium. Inlet split-ratio was set at 10:1. Column head pressure was set at 14 psi, the minimum necessary to ensure no backflow would occur through the olfactory outlet. Flow rate was held constant during the run at 1.6 mL/min. The oven temperature was held at 50 °C for 2 min and programmed to rise by 25 °C/min to 280 °C, where it was held for 1 min. The column effluent was split 2:1 between the olfactory port and the MSD via a three-way zero dead-volume splitter (Gerstel GP-3D/2 splitter; Mülheim an der Ruhr, Germany). This split ratio was achieved using a 1.4 m length of 0.10 i.d. deactivated silica tubing for the MS restrictor and a 1.1 m length of 0.15 i.d. deactivated silica tubing for the restrictor to the olfactory port. These dimensions created a 0.4 s holdup time between MS and olfactory detection. Both the gas chromatograph and mass spectrometer (HP 5972) were connected to and controlled by PC-driven HP ChemStation software, which was also used for analysis. The MS scan range was 20−200 amu for Carboxen samples and 35−350 amu for Tenax samples.

Olfactory Port. Deactivated silica tubing led from the splitter assembly to the glass sniffing funnel, which was equipped with a secondary entry through which filtered and humidified ambient air, was delivered at a rate of approximately 10 mL/min (Gerstel Olfactory Detector Port ODP-2). A trigger device enabled the sensory evaluator to record the time, duration, and intensity of smells perceived. The resulting graphical trace was collected using HP ChemStation, which overlayed it with the GC/MS data. In addition, the evaluator noted the character of the odor and gave a numerical measure of intensity, from 1 to 3, with 1 noting odors fleeting in nature that were difficult to define, 2 for those that were definite but not intense, and 3 for those that were intense and overwhelming to the nose. Only one evaluator was used throughout this study.

Characterization and Quantification. Compounds were initially characterized using the library search software of HP ChemStation (Wiley 138 and NIST 98 databases) and then confirmed using true standards, which were run both neat as well as loaded onto sorbent tubes and desorbed. Confirmation included matching both retention times and spectra. Quantification was performed by external standard. Standard solutions are listed in **Table 1**. From these stock sample solutions, serial dilutions were made to obtain solutions of 0.25×, 0.5×, and 0.74× in addition to the 1× stock solution concentration for the

Table 1. Summary of Standards Used in Identification and Quantification of Airborne Compounds from the UC Davis Dairy, with Recovery Data from Both Sorbents Used[a]

name	CAS No.	MW (g/mol)	*d*	mp (C)	bp (C)	vol (uL)	final vol (mL)	conc (ppm)	neat t_r (min)	des. t_r (min)	% recovery (tenax)	% recovery (carboxen)
Standard Solution 1: Organic Acids in Methanol												
formic acid	64-18-6	46.03	1.220	8.4	100.7	250	25	12.20	3.352	4.725	102%	99%
acetic acid	64-19-7	60.05	1.049	16.6	117.9	250	25	10.49	4.010	5.218	95%	95%
propionic acid	79-09-4	74.08	0.993	–20.8	141.0	250	25	9.93	4.990	5.954	99%	97%
vinylacetic acid	625-38-7	86.09	1.009	–35.0	169.0	250	25	10.13	5.793	6.879	95%	95%
valeric acid	109-52-4	102.13	0.939	–33.8	186.0	250	25	9.39	6.641	7.653	99%	99%
Standard Solution 2: Organic Compounds in Methanol												
acetaldehyde	75-07-0	44.05	0.788	–121.0	20.8	1000	50	15.76	5.798	6.606	103%	90%
ethanol	64-17-5	46.07	0.789	–117.3	78.5	1000	50	15.78	3.235	3.415	80%	100%
isobutyraldehyde	78-84-2	72.11	0.794	–65.0	64.2	1000	50	15.88	3.839	4.015	100%	102%
2-butanone	78-93-3	72.11	0.805	–86.3	79.6	1000	50	16.10	4.110	4.556	90%	100%
2-methyl-butane	78-78-4	72.15	0.620	–159.9	27.8	1000	50	12.40	3.346	3.675	82%	85%
pentane	109-66-0	72.15	0.626	–130.0	36.1	1000	50	12.53	3.461	3.857	84%	84%
pyridine	110-86-1	79.10	0.978	–42.0	115.5	250	50	4.89	5.523	6.322	75%	79%
2,3-butanedione	431-03-8	86.09	0.981	–2.4	88.0	1000	50	19.62	4.038	4.407	103%	99%
ethyl acetate	141-78-6	88.11	0.902	–83.6	77.1	250	50	4.51	4.239	5.000	102%	102%
1-nitropropane	108-03-2	89.09	0.993	–108.0	131.0	250	50	4.97	5.472	6.190	90%	98%
cycloheptatriene	544-25-2	92.14	0.888	–79.5	117.0	250	50	4.44	6.014	6.895	77%	85%
methylisobutyrate	547-63-7	102.13	0.891	–86.0	91.8	250	50	4.46	4.909	5.989	73%	100%
3-hexanol	623-37-0	102.18	0.819	NA	134.5	250	50	4.10	5.965	6.819	75%	80%
benzaldehyde	100-52-7	106.12	1.050	–26.0	178.0	250	50	5.25	7.412	8.605	79%	80%
o-xylene	95-47-6	106.17	0.870	–25.2	144.4	250	50	4.35	6.871	7.936	75%	83%
benzyl alcohol	100-51-6	108.14	1.045	–15.3	205.3	250	50	5.23	7.863	9.201	76%	80%
acetophenone	98-86-2	120.15	1.033	20.5	202.6	250	50	5.17	8.131	9.509	80%	84%
trichloroethane	71-55-6	133.40	1.339	–30.4	74.1	250	50	6.69	4.611	5.222	75%	90%
carbon tetrachloride	56-23-5	153.82	1.594	–23.0	76.8	250	50	7.97	4.780	5.448	80%	95%

[a] Retention times have been included for both the neat compounds injected by flash injection (neat t_r) and the compounds thermally desorbed and cryotrapped prior to separation (des. t_r).

solution of acids (Solution 1); and 0.05×, 0.1×, 0.25×, 0.5×, and 1× for the solution of organic compounds (Solution 2). Aliquots of 0.2 μL were direct-injected to obtain a linear curve of the response. These solutions were then injected onto the sorbent tubes for subsequent desorption to determine recovery. **Table 2** provides the airborne concentration ranges derived from quantification and corresponding odors and odor intensities. **Table 3** summarizes the peaks for which compounds could not be identified. To estimate the relative airborne concentrations those compounds might represent, we listed methyl isobutyrate and its response characteristics in lieu of an internal standard.

RESULTS AND DISCUSSION

Blanks. Peng and Batterman have exhaustively evaluated the performance and applicability to air sampling of the sorbent tubes used in this study (*11*). In this study, both laboratory and field blank unused Tenax and Carboxen tubes exhibited no background contamination. However, background peaks were encountered due to siloxane peaks from the column coating, typically at retention times of 5.369 and 6.705 min. These were no doubt due to repeated exposure of the column coatings to the acids sampled. Equally important, however, was that the olfactory evaluation of blank unused tubes during analysis showed that neither Tenax nor Carboxen tubes emitted any background odorous compounds that might have gone undetected by the mass spectrometer.

Sampling Optimization. A range of field sampling times and sampling volumes was tested to maximize collection efficiency for the wide variety of compounds expected, while paying special attention to odorous compounds. Sampling volumes were evaluated on the basis of the diversity and intensity of compounds yielded during analysis. In evaluating appropriate sampling times, four factors were taken into account: the duration of stable wind episodes, the change in temperature of the tubes during exposure, the accumulation of water on sorbent tubes, and the breakthrough volumes for the different compound classes.

Tenax and Carboxen sorbents were chosen as trap materials because they provided different affinities and different sorbent strengths. Tenax shows affinity for compounds with a wide range of boiling point, from 60 to 300 °C, and therefore makes a good choice for a general sorbent. Carboxen has a higher affinity for lower-boiling compounds, ranging in boiling point from 40 to 140 °C, and offers stronger sorption. Using the two traps in series offers the advantage of giving a wider range of affinities and sorbent strengths while also protecting the stronger sorbent from water using the weaker sorbent.

Wind patterns for the area alternate from prevailing North winds during the night to prevailing South winds during the day, with wind speeds cycling from calm conditions during the night to a peak of around 15 mph during mid-afternoon. In general, the ideal sampling time window occurred from noon to 3:00 pm. Sorbent tube heating due to ambient temperature and solar exposure was of concern in the way it might cause variations in, and lowering of, breakthrough volumes. Ice packs were used to keep tubes cool (around 4 °C) and hidden from direct sunlight, and they were effective for about 1 h, after which tube temperatures increased slowly to ambient temperature. On sampling days, air temperatures varied from 22 to 37 °C. Left uncovered, tubes reached temperatures around 10 °C higher than ambient temperature. Water accumulation also required consideration due to the possibility of icing during the cryo-focusing step of analysis. Fortunately, relative humidity was reliably low on sampling days, varying from 26% to 42%. For the large-volume samples attempted (20−33 L samples), chromatography problems such as loss of sensitivity, peak-broadening, and retention time variation were encountered and could be attributed to excessive water accumulation as described previously (*11*).

Most important was to achieve sufficient collection for a wide variety of compounds while minimizing breakthrough. Breakthrough volume data are readily available for a wide variety of compounds (*12*) and can be used to estimate a useful sampling

Table 2. Airborne Concentrations of Volatile Organic Compounds Observed at the UC Davis Dairy, with Accompanying Sensory Data[a]

compound	sorbent	odor	odor intensity (1–3)	low conc (ug/m^3 air)	high conc (ug/m^3 air)
		Acids			
acetic acid	carboxen	sweet/vinegar	2	3.98	86.94
propionic acid	carboxen	alcohol	2	62.40	89.63
vinylacetic acid	tenax	urine-like	2	87.52	254.64
		Esters			
ethyl acetate	tenax + carboxen	none-baked apple-perfumy	0	33.44	253.94
methyl isobutyrate	tenax + carboxen	none-cooked vegetables-molasses/sickly-plastic/smoke-sweet/caramel	2	80.28	347.18
		Alcohols			
ethanol	carboxen	none	0	213.17	320.20
3-hexanol	carboxen	sweat/rancid	2	7.38	41.76
		Aldehydes			
acetaldehyde	carboxen	dust/rot-smoke	1	82.73	248.78
isobutyraldehyde	carboxen	none	0	265.78	357.53
benzaldehyde	carboxen	plastic-bready	2	0.55	12.00
		Ketones			
2-butanone	carboxen	none	0	6.43	25.95
acetophenone	tenax	manure	3	2.86	3.87
		Hydrocarbons			
2-methyl-butane	carboxen	none	0	189.45	210.46
pentane	carboxen	none-soil-burning	0	167.62	273.97
1,3,5-cycloheptatriene	tenax	sickly sweet	3	12.84	80.70
o-xylene	carboxen	none-floral	0	3.42	40.69
		N and S Compounds			
pyridine	carboxen	buttery	2	8.94	26.60
1-nitropropane	carboxen	none	0	20.76	68.49
		Cl Compounds			
trichloroethane	carboxen	none	0	0.81	5.82
carbon tetrachloride	carboxen	manure	2	1.98	9.32

[a] All compound identities were confirmed by comparison of retention times and mass spectra with those of authentic standards.

Table 3. Summary of Olfactometric and Chromatographic Peaks from Airborne Sampling that Remain Unidentified

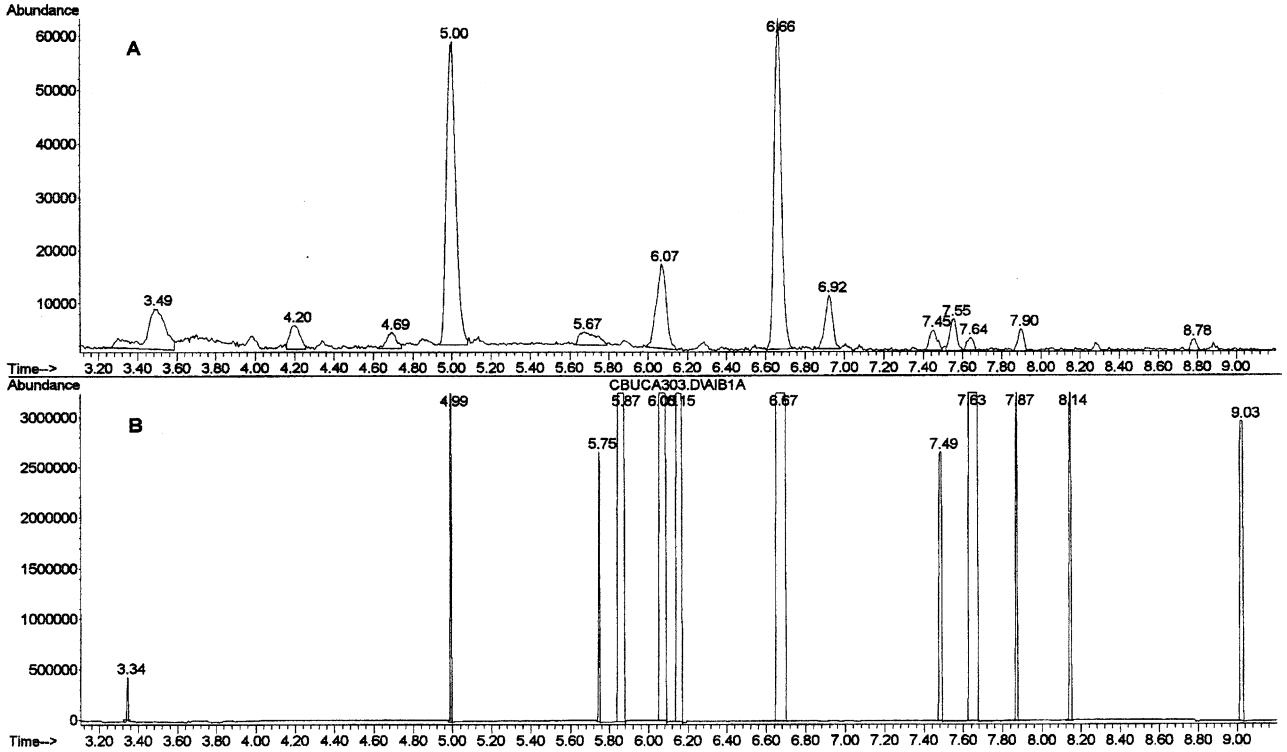
sorbent	t_r range (min)	peak	odor	odor intensity	relative conc[a] (ug/m^3)
carboxen	3.27–3.45	yes	smoke/roast cabbage	2	21.62
carboxen	4.00–4.14	no	sweat/compost	1	n/a
carboxen	4.51–4.61	yes	manure/compost	3	258.84
carboxen	5.81–5.92	no	melting plastic	3	n/a
carboxen	6.55–6.67	yes	perfume	3	43.14
carboxen	7.54–7.64	yes	rancid/coffee	3	11.14
carboxen	7.90–7.93	yes	none/rancid	0–1	5.94
carboxen	7.17–8.27	yes	none/fermented	0–1	2.61
carboxen	8.77–8.81	yes	none/oily	0–1	3.95
tenax	3.63–3.76	no	mud/silage	2	n/a
tenax	4.35–4.41	yes	sweet	3	14.12
tenax	7.51–8.04	no	dry grass/silage	3	57.38
tenax	8.22–8.33	yes	none	0	8.27

[a] Relative concentrations are calculated using methyl isobutyrate as a measure of concentration relative to peak area, and are intended solely for estimation of relative airborne concentrations.

volume. Low-volume samples (<2 L) resulted in low sensitivity. In addition, and perhaps surprisingly, high sampling volumes not only yielded poorer chromatographic results (likely due to the icing effects mentioned above), but also did not yield any new compounds in analysis, which might be attributed to the establishment of "steady-state" concentrations in the sorbent tube. The optimized sampling volume was 4.0 L, corresponding to a sampling time of 60−75 min.

Analytical Optimization. Analytical optimization was performed by adjusting the split ratio for the injection port, setting the temperature program for the chromatograph, and setting parameters for mass-spectrometry. In all of these regards, however, the most important factor was minimizing analysis time, not only for reasons of higher throughput, but also to minimize sensory fatigue during analysis.

The split ratio for the injection port was of some significance in adjusting to the higher inlet flow coming from the desorption system while maintaining sensitivity to the low concentrations of compounds sampled. With a desorption flow of 20 mL/min and a column flow of 1.6 mL/min, a split ratio of 10:1 was used. The temperature program was designed to accommodate short sensory periods no longer than 12 min while still allowing



Retention time (min)	Compound	Peak Area	Odor	Intensity
3.486	Butane	345500	Smoke	1
4.196	2-Butanone *	136091	None	0
4.693	Trichloroethane *	80392	None	0
4.995	Methylisobutyrate *	1876311	Sickly/fermented	2
5.674	Pyridine *	128148	Buttery	1
5.856	Unknown	0	Melting plastic	3
6.069	Acetic acid	523753	Sweet	3
6.149	Acetic acid	0	Vinegar	3
6.662	Isoamyl acetate *	1562880	Perfume	3
6.922	o-Xylene *	267213	None	0
7.450	Benzaldehyde *	107742	Plastic	2
7.553	Unknown	146705	None	0
7.641	Unknown	57378	Sickly/oily	2
7.898	Unknown	84021	Rancid	1
8.143	Unknown	0	Plastic	2
8.783	Unknown	41458	None	0
9.023	Unknown	0	Soil	2

Figure 1. Sample total-ion chromatogram (A) and olfactometric trace (B) from a 4.22 L sample collected on Carboxen at the UC Davis dairy on August 30, 2001. Asterisks denote compounds confirmed by matching retention times and mass spectra with those of authentic standards.

good separation of compounds and a final holding temperature designed to eliminate carryover from one run to the next. The latter was especially an issue because siloxane peaks had been found to be increasing from one run to the next, presumably due to the stripping of the GC column coating by acidic and other corrosive compounds present in the samples.

The difference in the amu range used for mass spectrometry for the two different sorbents reflect the differences in sorbent strength and sampling position. In effect, the higher amu range for Tenax is used to subtract water from analysis, while Carboxen is expected to have less water and also to adsorb more low-boiling compounds.

Standard Solutions. The standard solutions and the percent recoveries for the compounds are listed in Table 1. In general, Carboxen tubes yielded higher recoveries. The retention times for desorbed compounds often differed from those for standard compounds injected neat, which reflected the effect of cryofocusing on retention.

Sensory Evaluation. The sensory conditions were nonideal, since they had to be done in the laboratory setting. However, they yielded valuable information as to the character and strength of various odors. In addition to the mechanical device used for logging the occurrence and intensity/duration of odors, the evaluator noted a description of the smell, while avoiding such nondescriptors as "good" or "bad", using a scale from 1 to 3 to denote intensity of the sensation. As noted in prior studies (*10*), odor character can vary greatly depending on concentration. For example, the odors associated with the methyl isobutyrate peaks were found to have a variety of qualitative descriptors, increasing in intensity with concentration, from none to that of cooked vegetables, molasses, smoke, and at its most intense, to that of caramel. Also, certain peaks sometimes resulted in two distinct odor sensations due to the difference in concentration at the head of the band from that at its peak, especially for highly active compounds such as organic acids which have characteristically trailing peaks. Thus, acetic acid peaks often had an initial phase of smelling sweet before revealing its sharp vinegar

smell. Finally, the elution of intensely odorous compounds was found to lead to sensory overload and lower sensitivity to compounds eluting soon afterward, and the elution of subtly odorous compounds often led to a delay in sensory awareness. All of these issues inherent to sensory evaluations must be taken into account in giving proper weight to accompanying sensory data. This method differs significantly from previous work (*10*) in its application to whole air samples and its postcolumn rather than precolumn split, which allowed greater flexibility in setting split ratios.

Odorous and Nonodorous Compounds Observed. Figure 1 presents a sample chromatogram and olfactometry trace from a whole air sample taken downwind from the dairy studied. **Table 2** lists compounds sampled from whole air that were successfully identified and quantified, with accompanying sensory information. Most compounds were found on the carboxen sorbent tubes, which is not surprising given the volatile nature of these compounds and the stronger sorption offered by these tubes. Some compounds were sorbed onto both, in which case the air concentration was derived from the addition of the two samples. Highly volatile compounds that eluted first often exhibited "repeat" peaks in the early parts of the chromatograms, which appear to be related to the unevenness in rapid heating when the cryotrap first switches over from cooling to heating.

The compounds observed were quite varied in their chemical functionalities. Perhaps most surprising was the presence of two chlorinated compounds, carbon tetrachloride and trichloroethane. However, further investigation revealed that they likely originated from the common use of chlorinated disinfectants in dairy management. Several compounds that have been noted in previous studies seem conspicuously missing, notably phenols, cresols, indoles, and volatile fatty acids. These compounds may have been present at levels below the sensitivity of the instrumentation, but may also have been absent due to the atypical conditions at this dairy. Since manure was thinly distributed on concrete pads, climatic conditions were hot and dry, and the manure was scraped and taken offsite for disposal, very little anaerobic decomposition was likely to occur, and it is quite likely that these compounds were not generated at detectable levels.

In general, of those compounds that were correlated with odorous sensation, few had offensive characteristics at the concentration present in the olfactometer. When taking into the account the concentration that takes place during sorbent sampling and the various subsequent splitting steps during analysis, one finds that the concentration of the compounds at the nose port would be the equivalent to 40 times that of ambient air. Therefore, those individual compounds that did participate in odor in whole air would probably be recognized using this method. Compounds with the most intense odor sensation (such as acetophenone and cycloheptatriene) were found at relatively low air concentrations, while most compounds were found to have moderate to subtle odor. These results suggest that the overall sensation of malodors from a dairy results from some integrative effect of each constituent compound that takes place in the complex organoleptic response.

Perhaps most notable was the absence of amines and mercaptans, which is likely the result of the inherent bias in the method. Such highly active low-boiling compounds are known to have very low breakthrough volumes and could only be analyzed using megabore columns able to accommodate a high desorption volume without splitting the sample. However, such a technique would sacrifice mass spectrometric analysis (due to the difficulty in introducing a high flow into the instrument vacuum) as well as olfactometric analysis (to achieve greater sensitivity).

Table 3 summarizes the cluster of both olfactometric and chromatographic peaks that were observed and remain unidentified due to low concentration and inability to obtain mass spectrometric confirmation. Some of those compounds include highly odorous properties. The dairy used in this study is not representative of industrial-scale dairies because of its small size, its fully cemented floor, and its semiweekly cleaning. Therefore, results from this dairy are likely to be different both in character and in the amount of emissions relative to commercial facilities. The next step will therefore be to apply this method to a large-scale commercial dairy.

The use of thermal desorption−gas chromatography−olfactometry−mass spectrometry (TD−GC(O)−MS) provides a unique tool to study nuisance odors in whole air by incorporating sensory measurement and analytical data. Diverse classes of compounds present at low concentrations in air were successfully identified and quantified, and their accompanying sensory data show that trace compounds play a significant role in malodor. While demonstrated here for the purpose of studying odors from an agricultural operation, this method has a wide range of applications for all types of odors, such as those from industrial or biogenic sources.

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