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This project was initiated to find a practical way of identifying the volatiles and monitoring their relative concentrations. Special attention was given to the identification of the organic acids.

Volatile compounds produced in a swine confinement building were trapped by porous polymers, Porapak Q and Tenax GC, and identified by combined gas-liquid chromatography and mass spectrometry. GLC outputs were used as the basis for estimating concentrations.

The odorous gases responsible for the nuisance are principally released during anaerobic and faculative decomposition of manure. The amines, mercaptans, sulfides, organic acids, and heterocyclic nitrogen compounds are generally regarded as being of greatest importance in odorous air.

About 30 compounds were positively identified by the trap method, including the organic acids acetic, propionic,

butyric, and valeric. The concentration of these acids was found to be in the 10^{-6} µg/l range.

Identification of Volatiles from a Swine Center using Porous Polymers and Cold Traps

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

IDENTIFICATION OF VOLATILES FROM A SWINE CENTER USING POROUS POLYMERS AND COLD TRAPS

INTRODUCTION

There is now a pressing need to control the pollution resulting from agriculture. The increase in population and the natural trend of higher meat consumption per capita has necessitated larger animal production units and the increased proximity between population centers and these livestock enterprises has increased the potential for pollution. Gases released by these large animal feeding facilities has created intense odor nuisances that people living in suburban areas will not tolerate. This concern has and will lead to more pressure on the farmer to control or minimize objectionable odor production.

Due to the intense odor resulting from present practices used in swine feeding facilities, the producers will be required to institute some form of odor monitoring and control. Three specific problems arise from the confinement feeding of animals: (a) odor control for the sake of the producer and surrounding areas; (b) possible toxic effects of the individual gases and their combinations on the animals and personnel; and (c) potential damage to the structural components of the confinement building (14).

Recently damage suits have been filed relating to odor control or lack of it, and more such litigations may be

filed in the future as populations centers move closer to agricultural land and feed lots increase in size and number. Animals have died and farm personnel effected where volatile chemicals have been allowed to build up to a dangerous level due to malfunctioning equipment (14). The long range future of present animal confinement rearing and feeding procedures may well depend upon drastic changes in all such facilities to control pollution including odor for man and animals sake.

Identification of the gases or compounds responsible for odor is essential before effective odor control can be accomplished. This study was initiated to identify and quantitate volatiles present in a swine feeding center and to devise practical methods for rapid monitoring of the obvious odors as well as those which cannot be detected readily by the nose but still have an impact on man, animals, or surrounding environment.

LITERATURE REVIEW

Methods of Odor Measurement

Most of the previous work on odor has been directed toward elucidating the function of the sense organ and identifying the nature of odor itself.

The human nose is still the most incomparable instrument for distinguishing between differences and intensities of odorous compounds and between pleasant and unpleasant odors. It can detect the presence of compounds in the sub-part-per-billion concentration range (25).

Schutz (22) devised a method of odor measurement requiring panelists to judge the odor of an unknown chemical to each of nine standards which is called the matching standards technique. Standard methods (23) states that an odor panel should consist of not less than five, and preferably more than ten, members.

Various means of odor measurement by chemical and physical methods have been studied, among the most widely used is chromatography.

Until recently, the measurement of odor at extremely low threshold levels by the usual analytical methods has not been possible. However, recent developments in gas chromatography and mass spectrometry and methods of concentration and trapping have enabled researchers to separate and identify volatile components with relative ease.

Direct Sampling

This method was used at Cornell University by Burnett and Sobel (2) for identifying odors from poultry manure. The manure was filtered and centrifuged and the supernatant was injected directly into the gas chromatographs.

The low concentrations of compounds and the difference in concentration of components from the liquid waste and the air make this method undesirable.

Salting Out

Merkel (13) used this technique with swine manure volatiles. Anhydrous inorganic salts are added to a solution of the material to be tested. The mixture is then shaken and heated to 60°C to release the dissolved gases. A sample of the headspace gas is then injected into the chromatograph.

This method is easily and quickly conducted. Heating, however, may alter the normal conditions of the waste and the efficiency of the salting out effect is questionable.

Selective Absorption

Selective absorption techniques involve contacting gases with specific reagents in which they are either soluble or form stable products. This concentration method was used to isolate alcohols, amines, carbonyls, and sulfur derivatives by Merkel *et al.* (14). Nitrogen was bubbled through a liquid

manure sample and through a series of tubes containing the selected absorbant. The absorbed compounds were regenerated by various means and the expelled gases or the distilled liquids were injected into the chromatograph. Some of the procedures are tedious and time consuming and here again may not be representative of those odors characteristic of the barn atmosphere.

Frus et al. (5) used a flask containing potassium dichromate-sulfuric acid solution to trap gases from a sample of manure. The gases from the manure were bubbled through the solution for COD (Chemical Oxygen Demand) analysis. The COD technique was sensitive to individual organic gases believed to contribute to manure odor, but whether air COD is an overall measure of the level of organic gases is unknown.

Atmospheric ammonia has been measured by an absorbing surface of dilute acid. Ammonia absorption rates measured near feedlots were as much as 20 times greater than near controls (10). Ammonia was measured in a swine building atmosphere by absorbing in a 2% boric acid solution and then using Nessler's reagent to form a typical color which can be measured on a Spec 20 at a wavelength of 420 mμ (17).

Absorption techniques have been tried in the detection of amines in the air from an animal chamber bubbled through 5% acetic acid. After 12-48 hours of aeration the liquid was subjected to chromatographic analysis (17). Several amines were

detected, however, the chromatographic results were questionable and it was not verified by another method. The dilute acid traps were also used to absorb basic compounds volatilized from a cattle feedlot. The collected trappings were returned to the laboratory, filtered and evaporated to dryness at 50°C under vacuum. The resultant residue was taken up in a few milliliters of the dilute acid and analyzed for amines by gas chromatography (19). Ten different amines were identified by this procedure.

The biggest drawback to direct sampling, salting out and some selective absorption is that the compounds identified may not be physiologically responsible for the odors detected by the nose, or those which occur naturally in the vicinity of the barn yard air, especially if the samples are taken under laboratory conditions. The dilute acid traps at the feedlots may, however, be detecting the same compounds as the nose. Further tests are needed to substantiate this.

Fractional Condensation

Vapors can be condensed at various temperatures. This method was used in identifying the volatile components of skim milk (4). The condensate from various traps may be injected into the chromatograph. Transfer of the condensate requires special handling methods and has been little used.

Cryogenic Collection

Air can be sampled by circulation through cold traps in dry ice or liquid gas, however this method is unsuitable unless the moisture can be removed. Dessicants may be used to remove moisture, but they often absorb odor as well.

The optimum system depends on the selection of an appropriate cryogen. For this purpose liquid oxygen has been found to be the best since it does not liquify the major component of air and efficiently freezes out low molecular weight compounds (20). Dry ice is readily available and the easiest to work with but doesn't retain H_2S efficiently. Cryogenics may prove to be the most efficient method for collecting volatiles, however, not the simplest.

Headspace Concentration

Zlatkis *et al.* (26) adsorbed headspace gas of volatile organic metabolities in human urine by heating and then letting the vapors pass through a short water condenser and then onto a porous polymer trap. The trap was then inserted into a modified injector port of a gas chromatograph. Fifty-one compounds were identified by this method.

Miller *et al.* identified methyl mercaptan, dimethyl disulfide, dimethyl trisulfide, 3 methyl-1-butanol, and a trimethylamine produced in fish muscle by certain bacteria (15). The volatiles were collected on Porapak Q traps for

subsequent condensation in a capillary column, and then volatilized for gas chromatographic-mass spectral analysis. Porapak Q was also used to entrain any organic volatiles emitted from female fir beetles as a sexual attractant (21).

A combination of selective absorption and headspace trapping was used by Hartung et al. to identify carbonyl compounds in a swine building (8). Sample air was pulled through a column packed with silica gel impregnated with aqueous acidic DNPH solution. Carbonyl compounds in the air samples were converted to DNPHs (2,4-dinitrophenylhydrazones) and eluted from the column with hexane. The elute from the reaction column was evaporated to a small volume and spotted on thin layer chromatography plates.

The combination of headspace trapping or absorption and cryogenics shows the greatest promise for detecting that which we breath and therefore smell.

Odor Production

Odors associated with livestock production are generally related to manure, however, other odors from the animals themselves, dead animals, feed, or cleaning compounds and medicines may also contribute to the total atmospheric load.

Manure is a mixture of carbohydrates, fats, proteins, and their products and as such is a natural growth substrate for microorganisms. When manure undergoes decomposition as a result of microbial growth, volatile metabolic end products

and their intermediates escape into the atmosphere. This is a prime source of odorous gases.

The odor of manure can also be assumed to be a function of the animals' condition, how the manure is handled, the feed, and the microbial population in the animal and the confinement area. This would allow for a considerable variation in the volatile compounds possible.

Under normal storage conditions of organic wastes, an anaerobic or facultative environment develops. In anaerobiosis, the terminal hydrogen acceptor is organic matter. The end products of complete anaerobiosis are methane, ammonia, hydrogen sulfide, nitrous oxide, nitrogen, ferrous ion, and carbon dioxide (1). Two of these end products, NH_4 and H_2S, are very odorous.

Many of the end products and their intermediates of fermentation constitute a major source of volatile odors. The main products in carbohydrate decomposition are acids, aldehydes, alcohols, ketones, carbon dioxide, methane, and water (1).

Lipids are degraded into fatty acids and glycerol, and the fatty acids into acetyl CoA plus any number of smaller chained fatty acids by beta-oxidation (12).

Proteins are hydrolyzed, cleaving the large molecules into amino acids. The amino acid decomposition can proceed in many ways depending on the organisms present and the environment. General reactions of amino acids include

transamination, decarboxylation, racemization, and deamination (12). Many end products and intermediates are possible from amino acid decomposition including ammonia, hydrogen sulfide, acids, amines, mercaptans, sulfides, alcohols, aldehydes, ketones, esters, and alkyl ring structures (1, 12).

The decomposition of manure is a stepwise process in which complex organic compounds are degraded into smaller molecules. Any combination of these are possible, and the observed odor represents the sum of the individual constituents. Research to identify the chemical compounds present has yielded about 45 compounds so far (16). This list is undoubtedly incomplete, but does indicate the complexity of the problem.

MATERIALS AND METHODS

Swine Center

Air samples were taken from inside the adult Oregon State University swine barn above the animals on a platform eight feet above the floor.

The 150-175 swine in the barn were being fed corn rations throughout the sampling period. The building was washed completely once a week with the manure and wash water going into an anaerobic lagoon about 150 feet from the confinement area. The water from this pond is pumped out and used for crop irrigation.

Traps

Volatile compounds were trapped on Porapak Q (Waters Assoc., Framingham, Mass., 80/100 mesh ethylvinylbenzene-divinylbenzene polymers) and Tenax GC (Applied Sci. Lab., State College, Penn., 35/60 mesh 2,6-diphenyl p-phenylene oxide polymers) packed inside stainless steel traps 103 mm by 6 mm O.D. by 3 mm I.D. (Fig. 1). The barn air was drawn through a glass manifold holding four traps for 24 hours using a small Dyna-Vac pump. The traps could then be run immediately or stored in refrigeration without any loss of volatiles. All sample traps were purged with nitrogen (30 ml/min) for one and a half hours. The traps were first heated to 55-60°C for one hour to remove traces of water and

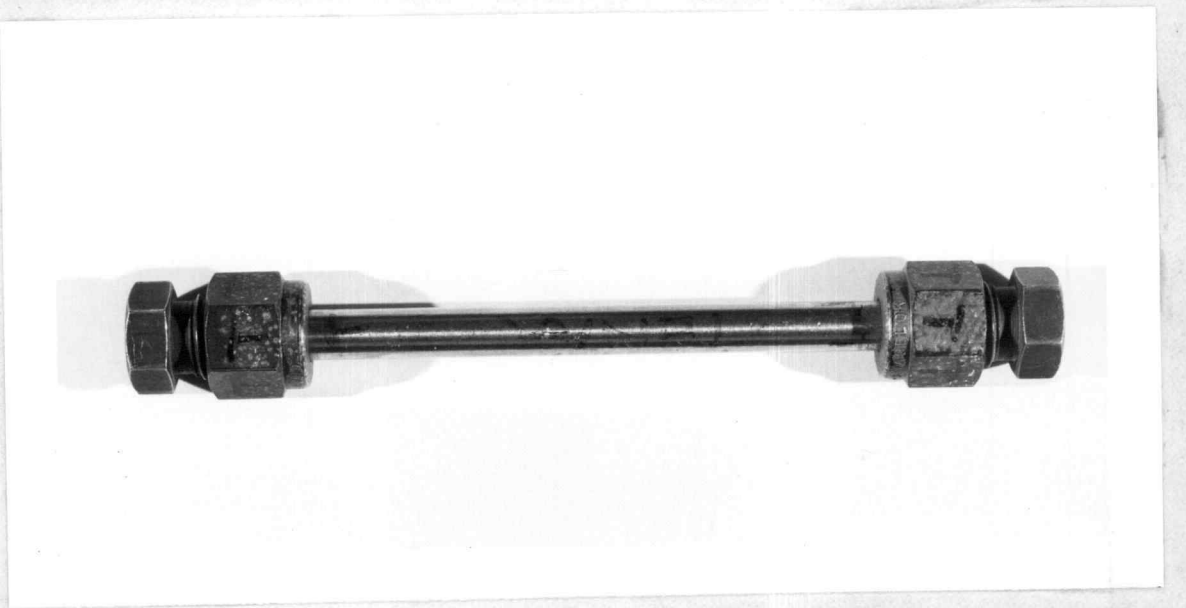


Figure 1. Stainless steel trap 103 mm x 6 mm O.D. x 3 mm I.D.

then reversed and reheated to remove the trapped volatiles. The traps were first heated to remove excess water because water interferes with the spectrum. It is harmful to the ionizing tube in the mass spectrometer and completely covers up the lower mass range. Excessive water in the gas chromatograph has a tendency to broaden the peaks and run them together. The Porapak Q traps were then heated to 150-160°C for thirty minutes, while being purged with nitrogen, to transfer the entrained volatiles to an open tubular stainless steel trap 150 mm by 1.25 mm I.D. immersed in dry ice (18). The Tenax traps were heated to 200°C. The small cold traps were connected to the gas chromatograph by a modified inlet system (Figures 2 and 3). The cold traps were transferred to the mass spectrometer in dry ice and connected by a modified inlet system. The cold traps in both instances were heated with a heat gun that reaches 500°C to volatilize the entrained odor constituents.

Chromatography

The analysis was made on a F & M Model 402 gas chromatograph fitted with a dual flame ionization detector, a Honeywell strip chart recorder, and a Hewlett-Packard 3370A integrator. A Beckman GC2A with a thermal detector was used to identify free gases. A Finnigan 1015C mass spectrometer in conjunction with a Varian Aerograph series 1440 GLC was used for mass spectral analysis.

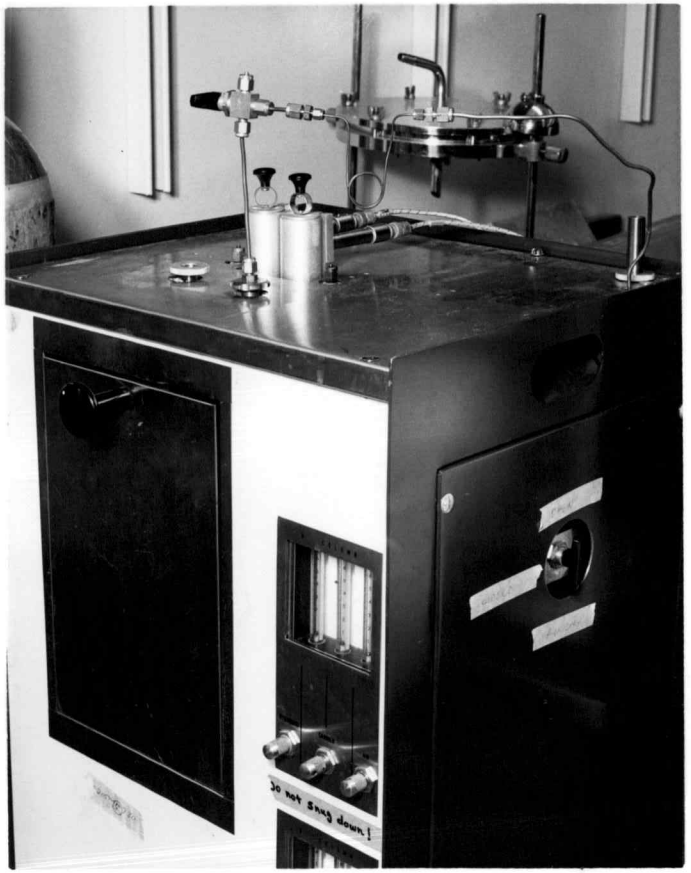


Figure 2. Modified inlet system F & M Model 402 chromatograph. Valve on right side of oven is to direct carrier gas flow through tubular stainless steel trap.

Figure 3. Close-up view of 150 mm cold trap connected to carrier gas flow of chromatograph. Valve at left allows trapped volatiles to enter the column in the oven.

Columns

The following columns were used including a 6' x 1/8" O.D. stainless steel tubing packed with 5% Triton X305 (Sigma Chemical Co., St. Louis, Mo.) coated on 100/120 mesh Chromosorb W (F & M Scientific, Avondale, Penn.); a 6' x 1/8" O.D. stainless steel tube packed with 4% Carbowax 20 M + 0.8% KOH on Carbopack B (Supelco, Inc., Bellefonte, Penn.); a capillary column 100' x 0.75 mm I.D. stainless steel coated with 5% Ethylene Glycol Succinate (F & M Scientific, Avondale, Penn.); a 200' x 0.75 mm I.D. capillary stainless steel column coated with 5% Triton X305; and a 153.8 m by 0.75 mm I.D. capillary stainless steel column coated with 8% Carbowax 20M (Supelco, Inc., Bellefonte, Penn.). Carrier gas flow rates were: 30 ml/min. of helium for the 1/8" columns and 12-15 ml/min. of helium for the capillary columns.

The columns used with the thermal detector were run isothermally at 40°C. The Carbopack B column was run isothermally at 90°C. The Carbowax capillary column was operated at 70°C for five minutes and then termpature programmed to 150°C at 2°C/min. The Triton X305 capillary column was programmed to operate at 60°C for five minutes and raised to 150°C at 4°C/min. and held. The EGS column was programmed to run at 110°C for four minutes and raised to 175°C at 4°C/min. and held.

The 1/8" Porapak Q and Triton X305 columns were used with the thermal detector for free gas identification. The Triton X305 and Carbowax 20M capillary columns were used for general identification, the EGS column was used for free acids and the Carbopack B column was used for amines with the FID system.

Selective Absorption

Selective absorption was used to identify alcohols and carbonyls. Nitrogen was bubbled through a manure slurry in a three liter flask and then into a collecting tube containing 25 ml of absorbant (14). A tube containing propylene glycol was used for absorbing alcohols. Any carbonyls absorbed were removed in carbon tetrachloride by successive steps of liquid extraction using the technique described by Suffis and Dean (24). The solutions were distilled and injected into the gas chromatographs.

RESULTS AND DISCUSSION

Over 30 Swine Center samples were studied. The technique involves a 24 hour sampling period and about four hours sample preparation and GLC separation. By using an adsorbant system several samples may be simultaneously taken and/or stored for later analysis. The traps were purged for 24 hours with helium or nitrogen at 200°C before using again.

Before running the cold traps on the chromatogram, they were checked in the labs for odor retention. After purging a 103 mm trap from both the Swine Barn and OSU campus into the open tubular stainless steel traps in dry ice, the cold traps were removed from the dry ice and heated to let the trapped volatiles escape into the atmosphere. The escaping volatiles were then smelled by several people in the lab to get a relative comparison of the two odors. The trap from the swine barn smelled like manure odors and the one from the campus had a slight musty smell.

Table 1 shows the compounds identified, the traps and columns used, and the compounds' retention times.
Many of the compounds were detected from more than one column, but for convenience only listed once. There were two xylene isomers and several alkyl benzene isomers seen and hence the variation in retention times. This is in agreement with the recent work done by Hammond *et al.* using a similar trapping method with Chromosorb 102 as the collecting

Table 1. Volatiles identified from the Swine Center atmosphere using the trap method and combined GLC mass spectral analysis.

COMPOUND	COLUMN	TRAP		RETENTION TIME
		Tenax	Porapak	Seconds
2 Butanol	Triton	+	+	75
sec-butanol	"	+	+	81
Hexanal	"	+	+	97.5
Dimethyl Disulfide (DMDS)	"	+	+	105
3 amino pyridine	"	+	-	120
n-butanol	"	+	+	140
Dimethyl Trisulfide (DMTS)	"	+	-	450
Toluene	"	+	+	130
Xylenes	"	+	+	varies
Alkyl benzenes	"	+	+	"
2,3 Butanediol	"	+	+	170
Acetoin	"	+	+	180
Indane	"	+	-	345
Benzaldehyde	"	+	+	540
Me-napthalene	"	+	-	1440
Diacetyl	Carbowax	+	+	240
2-octanone	"	+	-	210
Acetic acid	EGS	+	+	85
Propionic acid	"	+	+	115
N-butyric acid	"	+	+	150
Valeric acid	"	+	+	210
Acetophenone	"	+	-	240
Caproic acid	"	+	-	275
Enanthic acid	"	+	-	300
Phenol	"	+	+	455
P-cresol	"	+	+	515
2-ethoxy-1-propanol	"	-	+	195
Et-phenol	"	-	+	580
Benzoic acid	"	-	+	645
Trimethyl amine (TMA)	Carbopack B	+	+	75

agent (7). The major organic constituents they collected were a series of alkylated aromatic hydrocarbons. Junk and Svec, also found many alkylated aromatic compounds plus the aliphatic acids, hexanal and diacetal using macroreticular resins as trapping materials (11).

Table 2 shows the compounds detected by selective absorption. The alcohols of greatest concentration found were ethanol and butanol. The aldehyde concentrations were about

Table 2. Compounds detected by selective absorption and GLC.

COMPOUND	COLUMN	ABSORBANT
Methanol	Triton	Propylene glycol
Ethanol	"	"
N-propanol	"	"
Iso-propanol	"	"
N-butanol	"	"
Iso-butanol	"	"
Formaldehyde	Carbowax	Carbon Tetrachloride
Acetaldehyde	"	"
Propionaldehyde	"	"
Iso-butyraldehyde	"	"
Heptaldehyde	"	"
Valeraldehyde	"	"
Octaldehyde	"	"
Decaldehyde	"	"

the same as the alcohols with formaldehyde and acetaldehyde being most prevalent.

Table 3 shows the fixed gases found over a slurry of manure and water. Samples were taken in a gas tight syringe and injected directly into a column of a gas chromatography equipped with a thermal detector. The Triton X305 column was used for sulfides and Porapak Q column was used for methane, carbon dioxide, nitrous oxide, and nitrogen. No satisfactory

Table 3. Fixed gases found over a slurry of manure and water. Gas samples injected directly into chromatograph with a thermal detector.

GAS	COLUMN	RELATIVE RETENTION TIME
N_2	Porapak	30 seconds
CH_4	"	36 seconds
CO_2	"	85 seconds
H_2S	Triton	70 seconds
NH_3	Chemical absorption	

column was found for the identification of ammonia and consequently the Nessler's chemical test was used to confirm its presence. Carbon dioxide and methane were the most abundant gases found.

Traps were also set up outside Nash Hall on the OSU campus about one and a half miles from the Swine Center. The compounds identified on Triton X305 column were very similar between the swine barn and the OSU campus traps (Figures 4 and 5). The alkyl benzene isomers were common in both locations with the only difference being that the concentrations were slightly higher from the Swine Center. However, the chromatographic results on the EGS column in similar locations were very different (Figures 6 and 7). The acids and phenol compounds being absent in the traps from on campus. The chromatographic results from the Carbopack B column for amines were surprising. The campus chromatograph showed more peaks than the one of the Swine Center (Figures 8 and 9). The

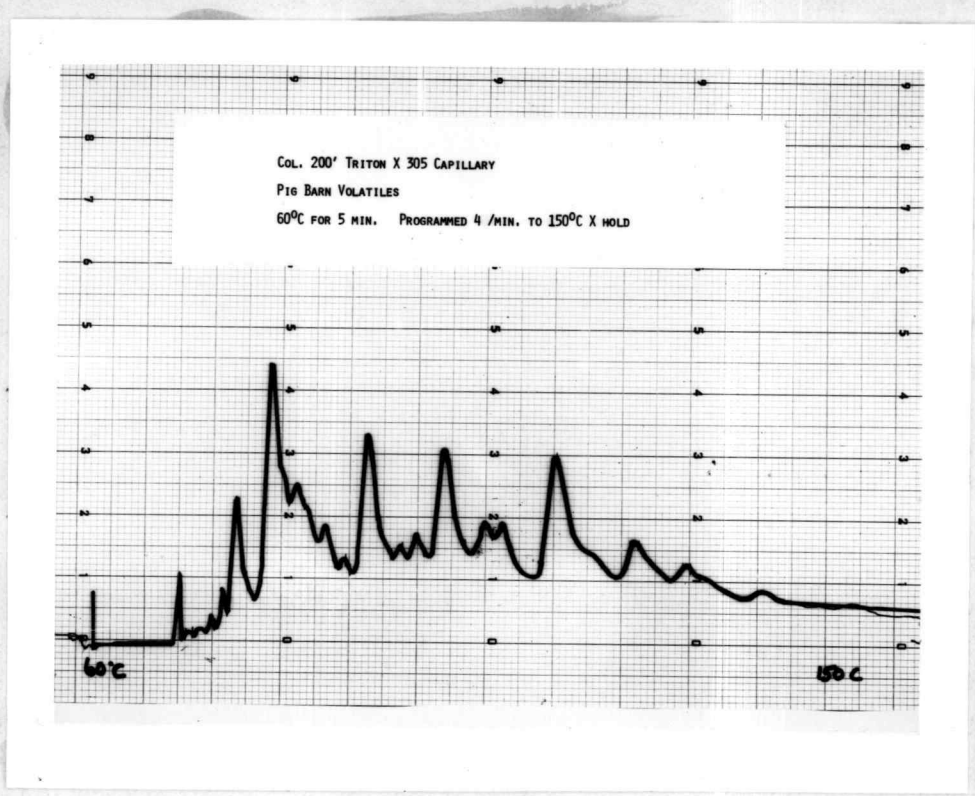


Figure 4. FID chromatogram of volatile compounds from the swine barn run on a 200' Triton X305 capillary column.

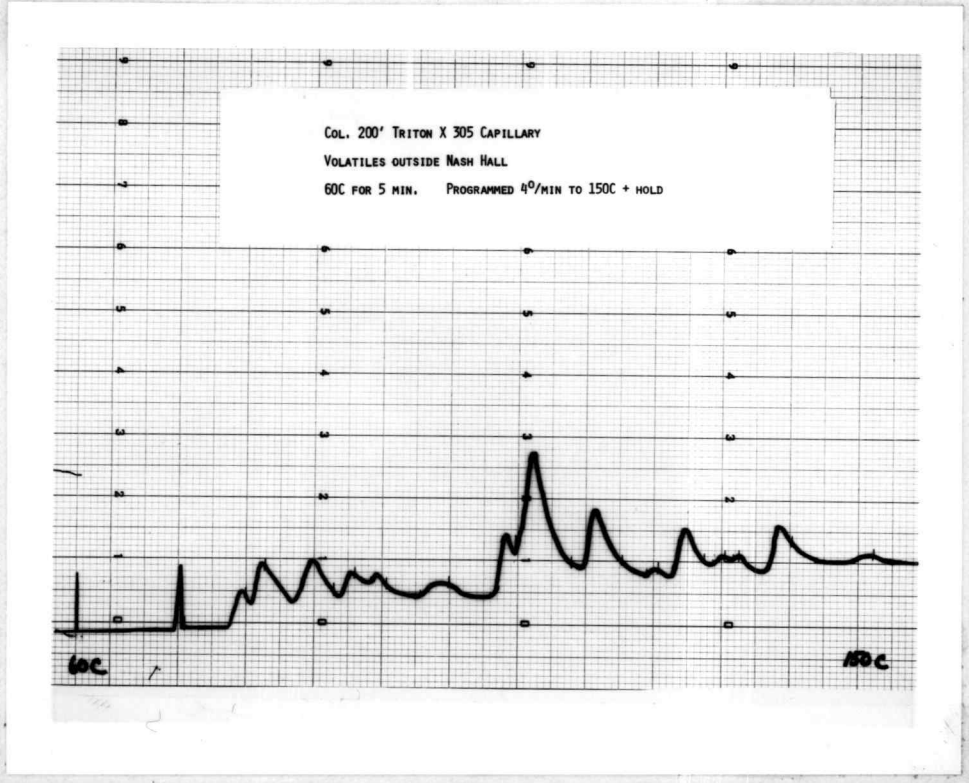


Figure 5. FID chromatograph of volatile compounds from OSU campus run on a 200' Triton X305 capillary column.

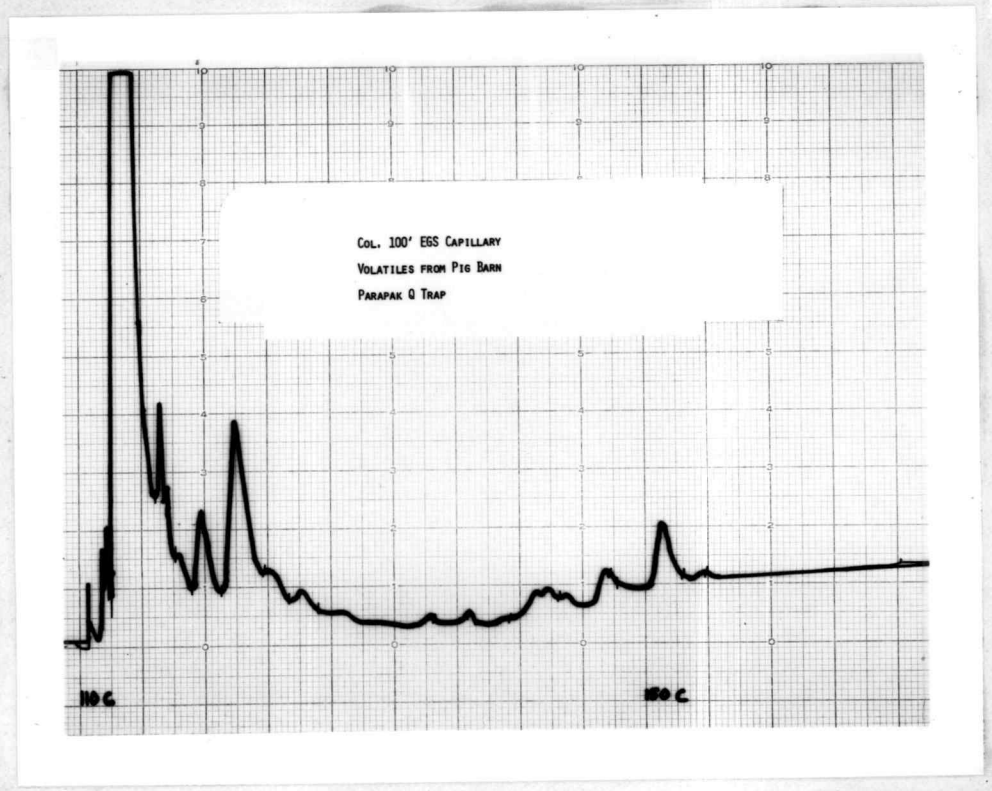


Figure 6. FID chromatogram of volatile compounds from the swine barn run on a 100' EGS capillary column.

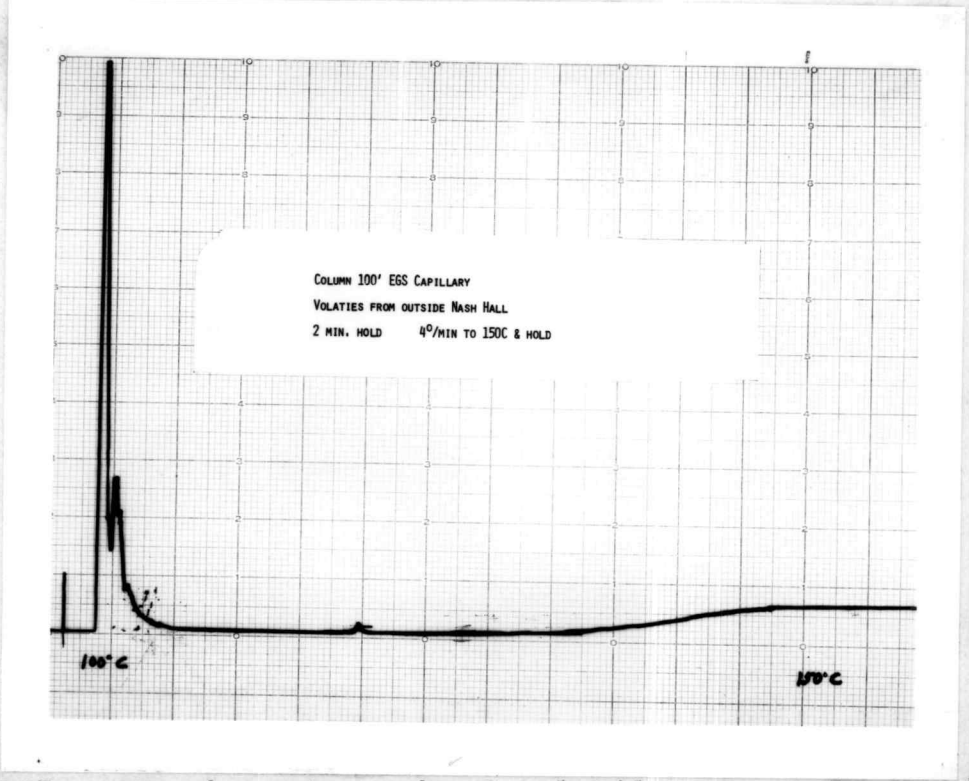


Figure 7. FID chromatograph of volatile compounds from OSU campus run on a 100' EGS capillary column.

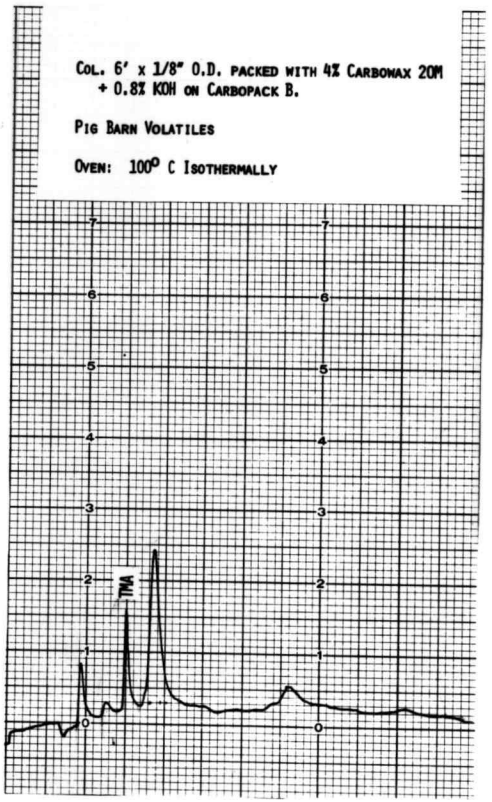


Figure 8. FID chromatogram of volatile compounds from the Swine Center run on Carbopack B column.

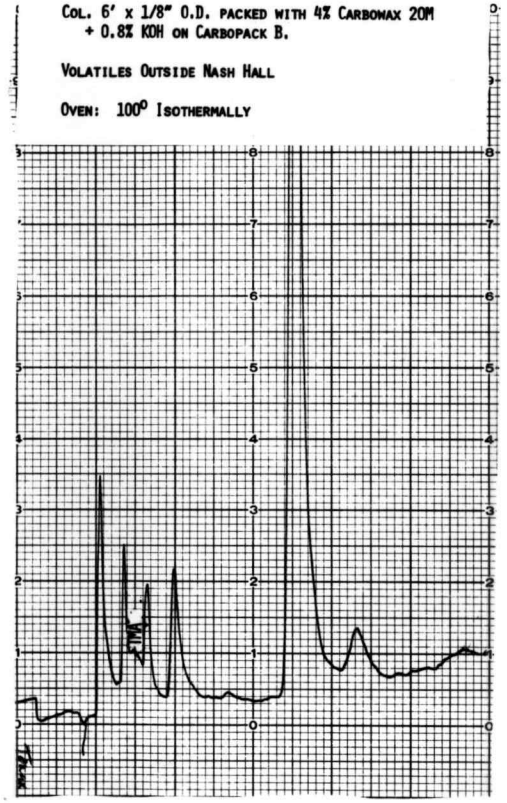


Figure 9. FID chromatogram of volatile compounds from OSU campus run on Carbopack B column.

trimethyl amine was the only compound positively identified and was most prominent in the Swine Center. Isopropyl amine was tentatively identified in both places. Dimethyl was tentatively identified from the Swine Center and ethyl amine from the campus sample.

Usually blank control trap runs to check for column or trap bleed were negative (Figure 10).

By using a gas chromatograph equipped with an integrator, a quantitative check could be made on various compounds. One microliter of standard solution was injected into the gas chromatograph giving concentration readings in millivolts. By using the formula:

$$1\ \mu l \text{ of known} = 3500 \times 10^3 \text{ mvolts (standard value)}$$

$$X\ \mu l \text{ of unknown} = \text{integrator presentation in mvolts}$$

$$X\ (3500 \times 10^3) = (1\ \mu l)\ (\text{integrator presentation of unknown})$$

The amount of unknown is determined in microliters. This amount was converted to micrograms. Approximately 720 l of air passed through each Tenax trap and 500 l through each Porapak Q trap in 24 hours and the fraction of unknown volatiles is given in µg/l (Table 4). Two traps were set up in a series to see if any acids were being missed. The chromatogram from the second trap was either negative or too small to measure for the acids. It was,however, found that not all of the aromatic hydrocarbons were retained on one trap alone.

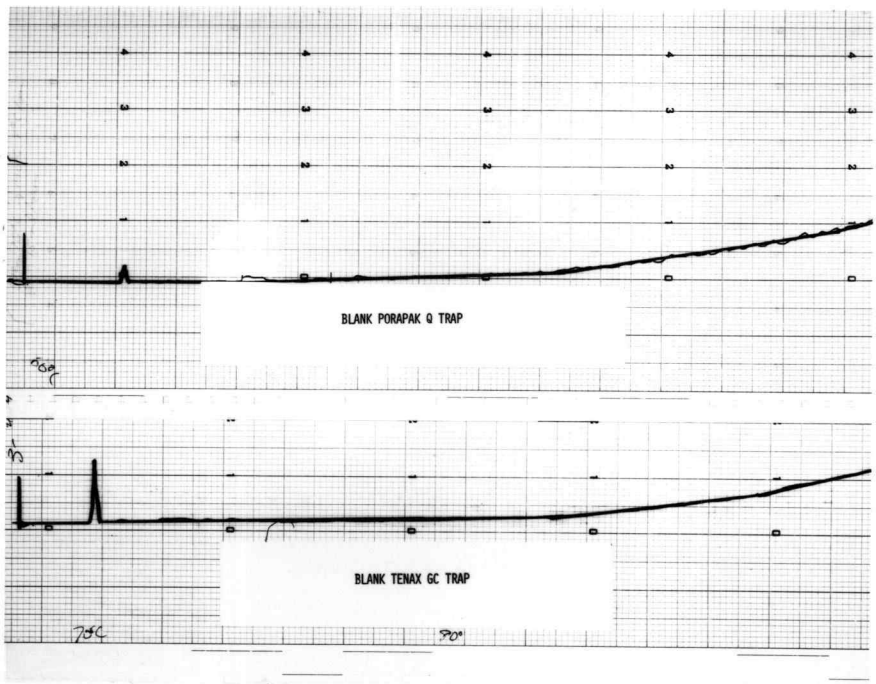


Figure 10. FID chromatogram of blank Porapak Q and Tenax G-C traps. Run under same conditions as full traps.

Table 4. Concentration of volatiles in 500 L of Swine Center air passed through Porapak Q traps in 24 hours.

COMPOUND	DATE	RECORDER PRESENTATION IN MILLIVOLTS	μG x 10^{-4}	μG/L x 10^{-7}
Acetic	5/ 3/74	1140	3.42	6.84
"	5/10/74	1333	4.0	8.0
"	5/17/74	3996	12.0	24.0
"	5/24/74	3990	12.0	24.0
Propionic	5/ 3/74	910	2.6	5.2
"	5/10/74	500	1.43	2.86
"	5/17/74	8738	25.0	50.0
"	5/24/74	8610	23.0	46.0
Butyric	5/ 3/74	1065	2.92	5.84
"	5/10/74	800	2.2	4.4
"	5/17/74	286	0.79	1.58
"	5/24/74	5660	17.3	34.6
Valeric	5/ 3/74	2663	7.17	14.34
"	5/10/74	3863	10.4	20.8
"	5/17/74	485	1.32	2.64
"	5/24/74	1700	4.6	9.2
Phenol	5/ 3/74	2942	9.0	18.0
"	5/10/74	5667	17.4	34.8
"	5/17/74	1910	5.46	10.93
"	5/24/74	5660	17.3	34.6
Cresol	5/ 3/74	3580	10.6	21.2
"	5/10/74	8863	26.0	52.0
"	5/17/74	7878	23.4	46.8
"	5/24/74	8610	23.0	46.0
DMDS	5/17/74	5040	15.2	30.4
"	5/24/74	2663	7.17	14.34
Xylene	5/17/74	6995	17.6	35.2
"	5/24/74	8738	25.0	50.0

The values determined for acids by this method were well below threshold limit values defined as follows: the airborne concentrations under which it is believed that nearly all workers may be repeatedly exposed without adverse effect (16).

Many of the compounds identified (Tables 1 and 2) could come from degradation pathways of carbohydrate metabolism

(Figure 11). A variety of fatty acids of varying chain length could come from lipid decomposition as well as carbohydrate. Proteins are hydrolyzed into amino acids by extracellular enzymes before they can be used as nitrogen sources. The ability to attack amino acids is much more widespread among bacteria than the ability to attack proteins. Bacteria attack amino acids in two main ways: decarboxylation or deamination. Decarboxylation results in the amino acids corresponding amines plus carbon dioxide while deamination gives ammonia and acids. The alkyl benzene and phenolic compounds could come from the aromatic amino acids. Aerobic oxidation of aromatic compounds can also proceed by the β-ketoadipate pathway to yield acetyl-CoA plus succinate which can then go through the TCA cycle. Acids, alcohols and aldehydes could come from the various aliphatic amino acids. The dimethyl disulfide compound would come about from the oxidation of methyl mercaptan, a breakdown product of methionine, cystine, or cysteine (Figure 12). The amines could come about from bacterial transamination or decarboxylation of amino acids (Figure 13). TMA is produced in fish by the reduction of trimethylamine oxide by certain Pseudomonas species (15).

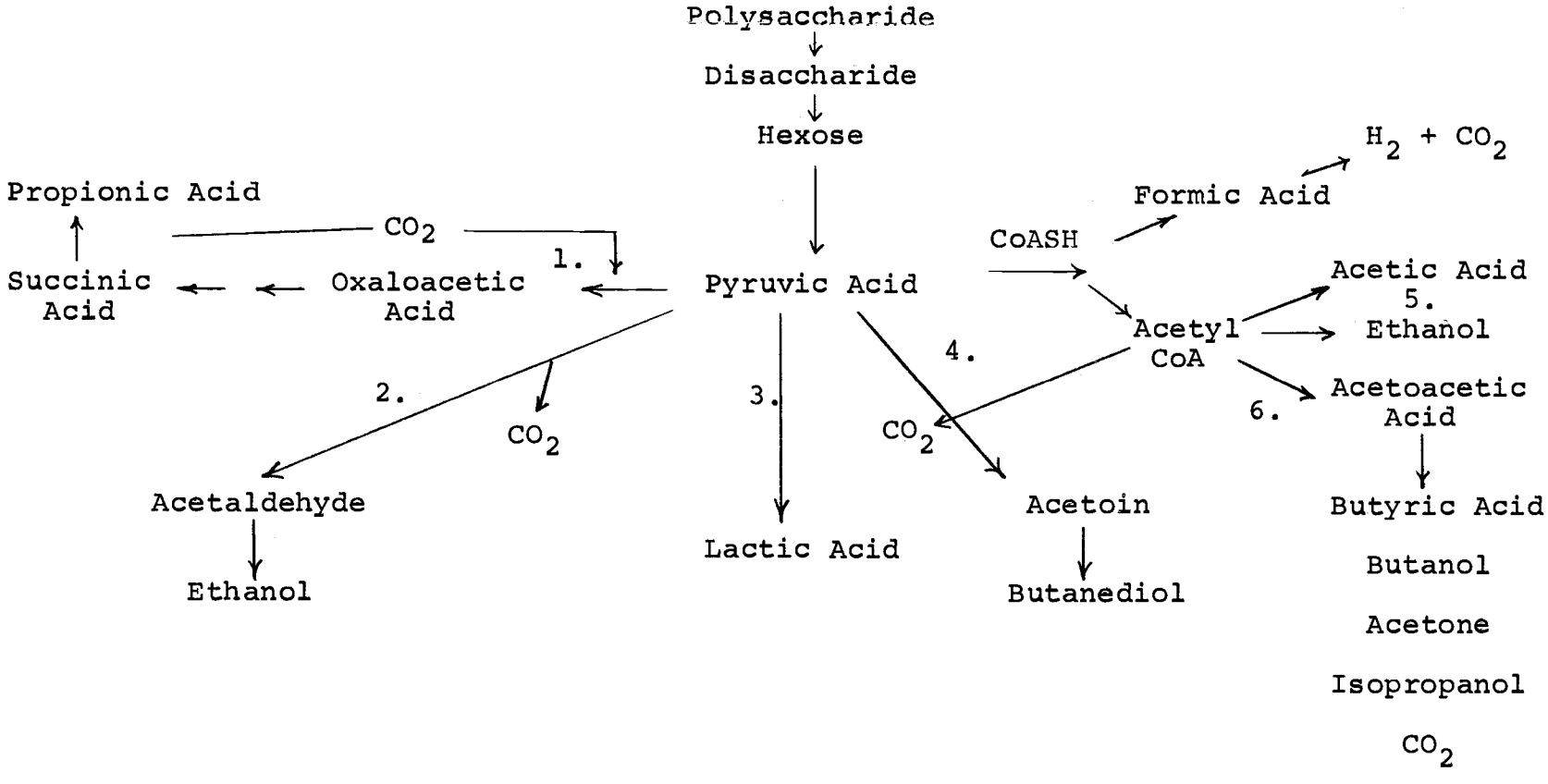
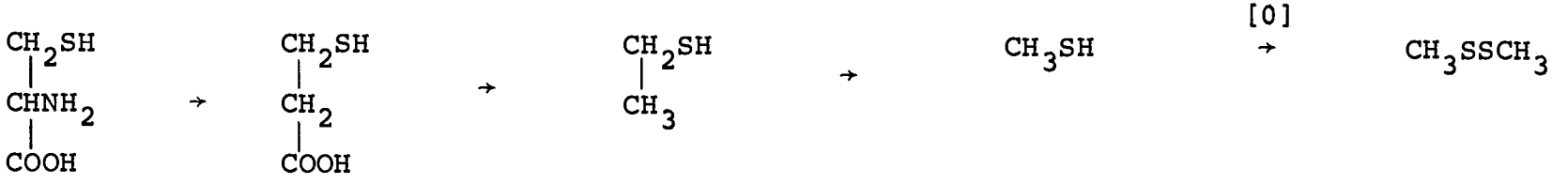


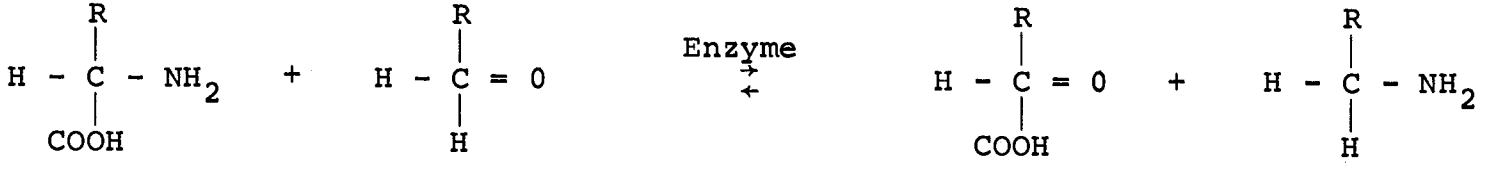
Figure 11. Pathways of carbohydrate decomposition. (1) Propionic (propionic acid bacteria); (2) Alcoholic (yeasts and bacteria); (3) Lactic (Streptococcus and Lactobacillus); (4) Butanediol (Enterobacter); (5) Mixed acid (Enterobacteriaceae) (6) Butyric (Clostridia) (3).



Cysteine — Thiopropionic Acid — Ethyl Mercaptan — Methyl Mercaptan — Dimethyl Disulfide

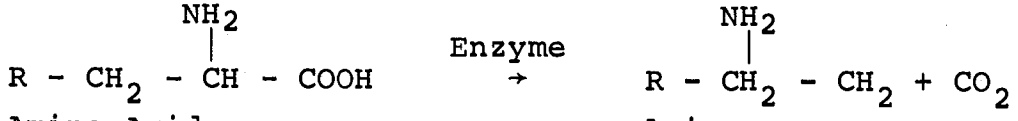
Figure 12. The degradation of cysteine to methyl mercaptan and oxidation to dimethyl disulfide (9).

(a)



Amino Acid — Ketone — α-Keto-Acid — Amine

(b)



Amino Acid — Amine

Figure 13. (a) Bacterial transamination.
(b) Decarboxylatic of amino acids.

SUMMARY

The main difference between the air of the Swine Center and OSU campus was the dimethyl disulfide, the mixed acids and the trimethyl amine. All would result in a marked odor in any area. The DMDS and TMA have a putrid smell and the acids are pungent. The major organic constituents collected at both locations are alkylated aromatic hydrocarbons. Most hydrocarbons have a relatively high odor threshold and do not leave odors characteristic of swine rearing facilities. Exceptions are the napthalene compounds which have a moth-ball odor and the cresols which have a preservative smell.

Many of the compounds identified are well known flavor constituents in food such as diacetyl, butyric acid, and p-cresol which occur in dairy products and hexanal which is a common constituent in vegetables and their fats (6).

Both organic absorbants used, Porapak Q and Tenax, selectively retain those compounds having at least two carbon atoms, and are useful as adsorbants for volatile organic compounds. Most one carbon compounds probably are not retained or may be lost during the water purge. Miller et al., however, did identify methyl mercaptan, a one carbon compound, produced from fish muscle by a bacteria using a Propak Q trap following a water purge of one hour at 55°C (15). Another method may be required in order to efficiently trap one carbon compounds.

The Porapak and Tenax adsorbants differed in their gas flow resistance and temperature limits for desorption. Using the same pressure, gas flowed through Tenax faster than Porapak Q. The only difference this made was in calculating volatile concentrations. Porapak Q had a temperature limit of 200°C and may prevent desorption of higher molecular weight-volatile organics whereas Tenax GC can sustain relatively higher temperature (375°C).

The large number and complexity of compounds of potential importance in odorous air accounts for the difficulty encountered in odor analysis. It also helps explain the variability in the detected odors commonly found in wastes. The objection to manure odors arises from the particular concentration and combination of volatiles present. The compounds found in the Swine Center were each individually below danger threshold for man, however, this does not mean that they are not an odor nuisance. Air in other confinements in which wastes are handled differently may have different odorous constituents.

Further work is planned to refine the monitoring method, and to identify additional compounds responsible for odors. The testing method now in use could be developed to identify routinely, the odorous compounds found. It is possible that one or more of these odorous compounds may prove to be indicators of the level of livestock odor pollution. The main objective of this research was to find

possible ways for the identification, determining of concentrations, and methods of influencing the odor of manure in order to make it less offensive to man physically or esthetically. The identification and concentration monitoring of the odorous compounds from livestock wastes should help establish better methods by which odor can be reduced or altered.

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