Odor and Volatile Compounds in Liquid Swine Manure. I. Carboxylic Acids and Phenols

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Seventeen carboxylic acids and four phenol compounds were isolated from liquid swine manure by steam distillation and identified by gas chromatography-mass spectrometry. The major components are butyric, isovaleric, benzoic, phenylacetic acids, and *p*-cresol. The only carboxylic acid fraction has the same odor as liquid acidic swine manure. The odor of the phenols is rather pleasant and sweetish. The butyric, isovaleric, and phenylacetic acids have a very strong malodor, while the odor of phenylacetic acid is identical with that of liquid acidic swine manure.

The large quantities of manure produced by modern confinement swine buildings evolve a very strong and offensive odor by means of anaerobical microbial decomposition. The odor which is discharged into the atmosphere of the adjacent residential area is nuisance and polluting.

Little is known about the chemical nature of the odor of swine manure. Information on the nature of the odor would, however, be valuable for odor control and deodorization in confinement swine buildings.

The identification of some components in swine manure has been carried out by several research workers. Amines,[1] alcohols,[2] aldehydes,[2] acids,[2] ketones,[3] and other substances[4] which contain hydrogen sulfide, methane, *etc.* have been detected in the atmosphere of confinement swine buildings. However, in those studies only highly volatile components were caught because of the use of the head-space method. There is a possibility, therefore, that swine manure contains some other odorous components, because odor does not always result from major components. Another method is, then, required in order to isolate minor components possessing malodors.[5] Steam distillation is another useful method for isolating odorous compounds.[6,7]

An intolerable odor results from the acidification of swine manure. The acidic volatile compounds reported in poultry liquid manure[8] are acetic, propionic, isobutyric, butyric, isovaleric, and valeric acids, while in swine manure formic, acetic, propionic, and butyric acids have been reported.[2] However, none of these compounds explains the odor of acidic swine manure.

This paper will deal with the separation of odorous components by steam distillation and with the results of the application of gas chromatography-mass spectrometric and organoleptic techniques to the determination of the important compounds responsible for the malodor of liquid swine manure.

Experimental

Gas Chromatography. A Model Shimadzu GC-5A gas chromatograph was equipped with dual-flame ionization detectors, dual-thermoconductivity detectors, a matrix temperature programmer, a dual-pen recorder, and a Takeda Riken -*tr*-2215A degital integrator. The flame detectors were operated using a hydrogen-flow rate of 50 ml/min and an air-flow rate of 0.5 l/min. Thermoconductivity detectors were used for the organoleptic tests.

The gas-chromatographic conditions were as follows on the carboxylic acid fraction: injector and detector temperatures, 250 °C; column temperatures, 50 °C for 3 min, followed by an increase to 180 °C at a rate of 8 °C/min, and then held at 180 °C until the completion of the analysis; carrier-gas (nitrogen) flow rate, 20 ml/min at 6 kg/cm^2.

On the phenol fraction the gas-chromatographic conditions were as follows: injector and detector temperatures, 200 °C; column temperature, 160 °C; carrier-gas (nitrogen) flow rate, 20 ml/min at 6 kg/cm^2.

A 3m×3mm i.d. glass column packed with 2% DEGS+0.5% H_3PO_4 on 60- to 80-mesh, acid-washed, DMCS-treated Chromosorb-W was used for the analysis of the carboxylic acids and phenols.

Mass Spectrometry. A Model JEOL JMS-D 100 mass spectrometer was connected with a JEOL JGC-20K gas chromatograph. The gas-chromatographic conditions were the same as above. The mass-spectrometric conditions were as follows on both carboxylic acid and phenol fractions: ion-source temperature, 140°C; ionizing current, 3×10^{-4} A; ionizing voltage, 75 eV; accelerating voltage, 3 kV; scan speed, 5 sec from *m/e* 0 to 800.

Sampling Procedure and Fractionation. The experiments reported here were performed using accumulating liquid swine manure collected from pits under confinement swine buildings. Liquid manure (36 l) was acidified with concd hydrochloric acid in order to move its pH below 1.0 and was then shaken two times with dichloromethane (4.8 l). The resultive slurry was separated and steam-distilled. The distillate was saturated with sodium chloride and extracted two times with dichloromethane. The extract was evaporated by means of a Kvrderna-Danish concentrator under atmospheric pressure. The concentrated residue was dissolved in ether (50 ml) and fractionated as will be described below.

(a) Phenol Fraction. The ether solution was washed several times with a potassium hydroxide aquous solution. The organic layer was used for the neutral fraction. Sodium hydrogencarbonate was added to the aquous layer until saturation, and then carbon dioxide gas was passed into it. Then, the separate phenol compounds were extracted with ether (50 ml). The extract was washed, dried, and concentrated.

(b) Carboxylic Acid Fraction. After the extraction of the phenol compounds, the aquous layer was acidified with concd hydrochloric acid until it showed a pH below 1.0; then it was extracted with ether (50 ml). After washing and drying, the extract was evaporated to a small volume and then injected into the gas chromatgraph and the gas chromatograph-mass spectrometer without any protection of the carboxyl group.

(c) Neutral Fraction. The organic layer obtained in

Operation *(a)* was washed, dried, and concentrated.

Organoleptic Test for Odor. This test was carried out by means of smelling the odor of compounds progressively eluted from the outlet of the gas chromatograph.

Results and Discussion

The steam distillate has the same odor as acidic swine manure. In this case, steam distillation has been proved to be a useful method of obtaining odorous compounds.

Separation and Identification of Volatile Carboxylic Acids. From several microlitres of the prepared sample solution injected into the gas chromatograph, seventeen peaks were obtained on the DEGS+H_3PO_4 column. Figure 1 shows the gas chromatogram, while the table shows the results of the identification, which was performed by a comparison of the measured mass spectra with the standard mass spectral data and by a comparison of the retention times with those of authentic samples.

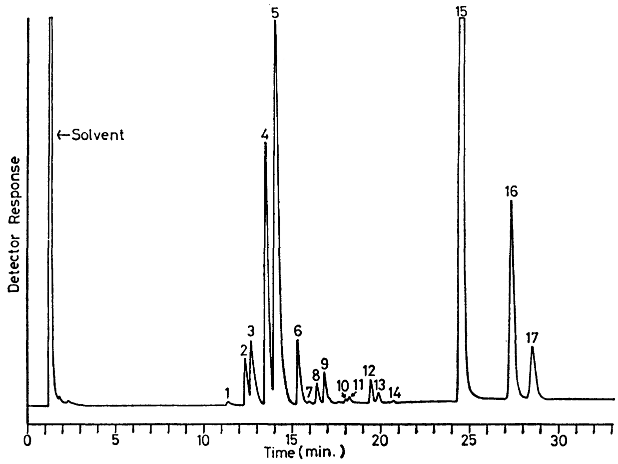

Fig. 1. Gas chromatogram of volatile carboxylic acids in swine manure.

TABLE 1. RESULTS OF IDENTIFICATION OF VOLATILE CARBOXYLIC ACIDS

Peak number	Name of compound	Content ratio (%)
1	Acetic acid	0.2
2	Propionic acid	1.6
3	Isobutyric acid	2.8
4	Butyric acid	10.1
5	Isovaleric acid	20.6
6	Valeric acid	2.2
7	2-Methylbutyric acid	0.1
8	2,2-Dimethylpropionic acid	0.6
9	Hexanoic acid	1.1
10	4-Methylhexanoic acid	0.1
11	Heptanoic acid	0.2
12	Octanoic acid	0.7
13	$C_8H_{16}O_2$	0.4
14	Nonanoic acid	0.1
15	Benzoic acid	45.8
16	Phenylacetic acid	9.9
17	3-Phenylpropionic acid	3.1

The main components are butyric, isovaleric, benzoic, and phenylacetic acids. The compound with the peak number of 13 was not identified, but it was confirmed to have the molecular formula of $C_8H_{16}O_2$, according to its mass spectrum, which is as follows: *m/e* (rel. intensity), 144 (2), 128 (35), 110 (15), 101 (17), 99 (29), 83 (44), 73 (100), 68 (32), 55 (54), 43 (29), 41 (34).

The organoleptic test shows that butyric, isovaleric, and phenylacetic acids have very strong malodors. The odor of phenylacetic acid is the most offensive among them; it is the same as that of acidic swine manure. Although butyric and isovaleric acids are recently considered as malodorous air pollutants, phenylacetic acid must be taken into consideration. Phenylacetic acid plays a very significant role in the malodor of liquid swine manure, although neutral or alkaline swine manure has a different order.

The origin of the carboxylic acids is considered to be proteinaceous material.[2]

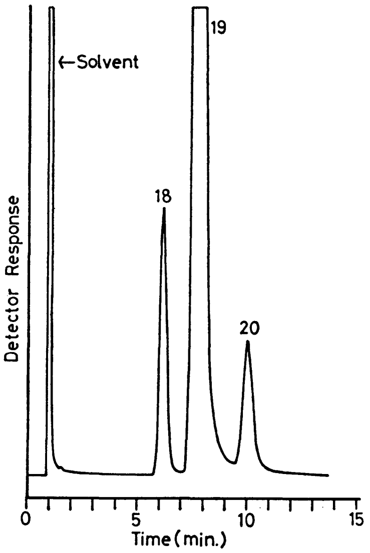

Fig. 2. Gas chromatogram of volatile phenols in phenol fraction of swine manure. (18): Phenol, (19): *m*- and *p*-cresols, (20): *p*-ethylphenol.

Separation and Identification of Volatile Phenols. Three peaks were obtained from the phenol fraction by gas chromatography using a DEGS+H_3PO_4 column. Identification was carried out by gas chromatograph-mass spectrometry. Figure 2 shows the gas chromatogram. It was confirmed by the use of a Golay R column (45 m×0.25 mm i.d.) that *p*-cresol was the major component, *m*-cresol was the minor component, and *o*-cresol was not present. Furthermore, another phenol compound was observed in the neutral fraction. It is 2,6-di-*t*-butyl-*p*-cresol, which is a well-known synthetic antioxidant. 2,6-Di-*t*-butyl-*p*-cresol is absent in the phenol fraction because of an obstruction of the dissociation of the hydroxyl group by the steric hindrance of the two tertiary butyl groups and the hydroxyl group.

Most of the phenols come from the disinfectant used in the confined swine buildings.

Organoleptically, phenols have a rather pleasant and sweetish odor. Although they evidently do not contribute any offensive notes to the odor of swine manure, they most certainly contribute to the total odor.

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