Quantification of Phenols in Gas from Rotten Liquid Swine Manure by Computer-controlled Gas Chromatography-Mass Spectrometry

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(Received April 10, 1979)

Analytical studies on phenol, *o*-cresol, *m*-cresol, *p*-cresol, and *p*-ethylphenol from liquid swine manure were performed with selected ion monitoring in computer-controlled gas chromatography-mass spectrometry. Phenol, *p*-cresol, and *p*-ethylphenol in effluent gas from liquid swine manure and in the head-space gas over liquid swine manure were determined.

Some odorous phenols have already been detected in liquid swine manure.[1] Phenols contributed greatly to malodor of liquid swine manure, because there is a relationship between the nature of the putrid odor and the quantity of phenols present.[2] Phenols are present at a relatively high concentration in liquid swine manure. It is very valuable to quantify phenols in gas from rotten liquid manure in order to estimate the role of phenols on the malodor from the piggery. The analytical methods reported for phenols are mainly gas chromatography (GC).[3-5] Selected ion monitoring (SIM) in gas chromatography-mass spectrometry however has the advantage of higher selectivity and sensitivity, when compared to GC. SIM controlled by computer has been shown to have sufficient accuracy and stability for long-time measurement in the quantification of geosmin.[6]

This paper reports an analytical method for phenols by SIM and the results of measurements on phenols in the gas from liquid swine manure.

Experimental

Gas Chromatography. A 3 m×2 mm i.d. glass column packed with KG-02[7] was used. The column temperature was 170 °C, the injection port temperature was 250 °C and the carrier gas was helium at a flow-rate of 30 ml/min (2.4 kg/cm^2).

Computer-controlled Selected Ion Monitoring. A JEOL Model JMS-D 100 mass spectrometer was connected with a JEOL Model JGC-20 K gas chromatograph and a JEOL Model JMA-2000 mass data analysis system. The mass spectrometer was operated with a resolution (10% valley) of *ca.* 1000. The magnetic field was set at *m/e* 93 and the accelerating voltage and electric field were changed at intervals of 0.3 s. Six-time repetitions of a small range sweep (1 mass unit) on each mass number setting (94, 105, 107) were carried out and the latter four values were averaged for the correction of deviations of the magnetic field. The ionizing current was 3×10^{-4} A and the ionizing energy was 75 eV.

Absorption Process and Extraction of Phenols. A fixed volume of gas was passed through a glass filter and then into sodium hydroxide solution (20 ml, 1 M) to trap phenols. After acidification of the solution with concd hydrochloric acid (5 ml), phenols were extracted with dichloromethane (10 ml) twice. The combined solution after drying over anhydrous sodium sulfate was concentrated to a few millilitres using a Kuderna-Danish concentrator under atmospheric pressure. One μg of butyl benzoate was added as an internal standard to 1 ml of the sample solution.

Isolation of Phenols from Rotten Liquid Manure by a Gas-stripping Method. Liquid swine manure (2.5 l) which had been digesting anaerobically or aerobically was transfered to a three-necked flask (3 l) and warmed to 35 °C. Nitrogen or air was passed into the flask at a rate of 220 ml/min for 3 h. The effluent gas was treated with the absorption process described above.

Isolation of Phenols from Head-space Gas over Rotten Liquid Swine Manure in the Pigsty. The head-space gas over the reservoir of liquid manure in a pigsty near Tsukuba New Town, Ibaraki, was passed into sodium hydroxide (20 ml, 1 M) at a rate of 1 l/min for 1 h. Subsequent procedures were the same as described above.

Results and Discussion

It has already been reported that the column packing material, KG-02, used here had excellent ability for the separation of several phenols.[8]

The mass numbers used for ion detection were 94 for phenol and 107 for three cresols and *p*-ethylphenol. As the dynamic range in the mass spectrometer is very narrow and injection of an exact volume with a microsyringe is not sufficiently accurate, quantitative analysis was carried out using an internal standard method. Butyl benzoate was selected as the internal standard, since the retention times of phenols and butyl benzoate in the gas chromatogram were close and a base peak at *m/e* 105 in the mass spectrum of butyl benzoate was close to the mass numbers of the selected ions for phenols.

Extended measurements by SIM with a magnet-type mass spectrometer has been considered to be difficult until a few years ago, because the magnetic field is not so stable at a resolution (10% valley) over 1000. Improvements of instruments have now enabled

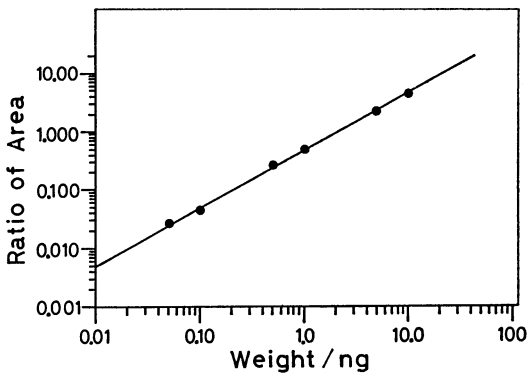

Fig. 1. Calibration curve for the analysis of *p*-cresol by selected ion monitoring.

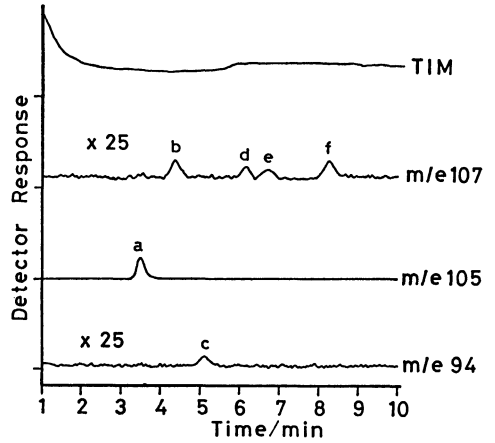

Fig. 2. Typical example of selected ion monitoring in GC/MS.
a: Butyl benzoate (1 μg/ml), b: *o*-cresol (50 ng/ml), c: phenol (50 ng/ml), d: *p*-cresol (50 ng/ml), e: *m*-cresol (50 ng/ml), f: *p*-ethylphenol (50 ng/ml).

TABLE 1. COEFFICIENT OF VARIATION FOR MEASUREMENT OF PHENOLS BY SELECTED ION MONITORING

Concentration	Phenol	Cresol			*p*-Ethylphenol
		o-	*m*-	*p*-	
10 μg/ml	13.5%	8.1%	8.7%	9.2%	7.4%
5 μg/ml	12.9	6.0	10.4	12.5	10.6
1 μg/ml	8.2	2.8	5.4	5.7	3.8
500 ng/ml	8.4	2.8	8.3	17.3	8.9
100 ng/ml	3.1	7.1	12.2	7.5	5.9
50 ng/ml	5.9	1.6	15.7	14.9	7.6

TABLE 2. RECOVERY OF PHENOLS FROM ALKALINE AQUEOUS SOLUTION

Run No.	Recovery/%				
	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol	*p*-Ethylphenol
1	86	89	89	92	95
2	92	93	95	97	99
Average	89	91	92	95	97

extended measurements over 10 h to become possible, since deviations of the magnetic field can now be corrected by computer. This is achieved by generating the electric field and accelerating voltage as a continuously varying triangular wave function which sweeps over a small mass range (1 mass unit). The sweep correction technique is described in the experimental section.

The calibration curve for each phenol was prepared using the ratio of the peak areas of the component and butyl benzoate. An example of the calibration curves is shown in Fig. 1. The detection limit of each compound was 50 ng/ml and an example of SIM is shown in Fig. 2. The precision of measurement was obtained by making measurements on six samples five times respectively. The coefficients of variation are shown in Table 1.

A standard gas containing a fixed amount of phenols

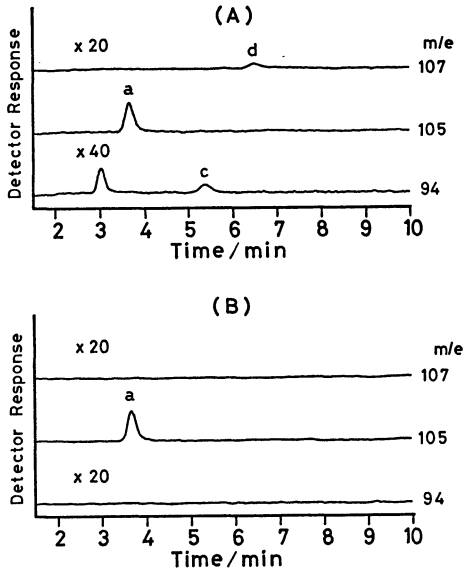

Fig. 3. Selected ion monitoring for phenols in effluent gas from liquid swine manure.
(A): The case of aerobic digestion, (B): background.
a: Butyl benzoate, c: phenol, d: *p*-cresol.

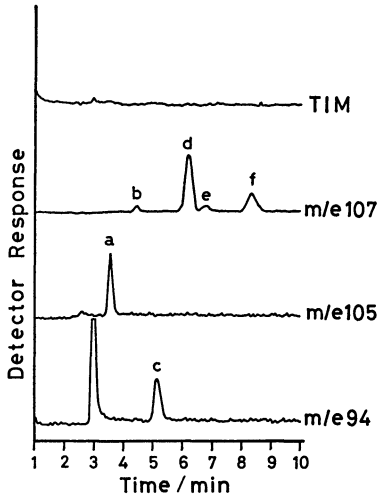

Fig. 4. Selected ion monitoring for phenols in effluent gas from anaerobically digested liquid swine manure.
a: Butyl benzoate, b: *o*-cresol, c: phenol, d: *p*-cresol, e: *m*-cresol, f: *p*-ethylphenol.

cannot be prepared because of the low volatility of phenols and also because of adsorption loss on the container walls. Therefore, a fixed volume of gas containing a suitable amount of phenols was passed consecutively through two bottles containing sodium hydroxide solution (20 ml, 1 M). This extraction procedure was the same as those of the samples and extracted phenols were measured by SIM. Phenols were not detected from the second trap so that subsequent experiments utilized only one bottle containing sodium hydroxide solution (20 ml, 1 M).

Next, to test whether phenols trapped in alkaline aqueous solution are oxidized by aeration, air was passed into 1 M aqueous solution (20 ml) of sodium hydroxide containing phenol (6.2 μg), *o*-cresol (4.2

Table 3. Concentration of phenols in the effluent gas from anaerobically or aerobically digested liquid swine manure by gas-stripping method[a)]

Run No.	Anaerobically			Aerobically	
	Phenol	*p*-Cresol	*p*-Ethyl-phenol	Phenol	*p*-Cresol
1	27.4	163	16.6	ND	3.0
2	33.1	201	20.1	ND	5.1
3	35.8	215	22.1	6.3	13.1
4	39.3	225	24.2	7.1	15.2
5	37.4	191	19.3	ND	3.5
6	42.8	201	19.9	ND	3.5
7	43.0	212	21.9	ND	9.7
8	46.3	219	27.1	ND	5.5
9	47.3	218	28.4	ND	4.4
10	44.1	222	24.0	ND	10.1
11	40.9	226	22.6	ND	3.7
12	41.7	237	24.8	ND	6.4
13	44.1	233	28.4	ND	3.0
14	42.5	232	26.7	ND	3.7
15	42.8	245	25.9	ND	3.5
16	39.8	212	23.0	ND	9.7

a) Unit of concentration is volume ppb (10^{-9}). ND means "not detected."

μg), *m*-cresol (6.9 μg), *p*-cresol (8.3 μg), and *p*-ethylphenol (19.4 μg) under the same conditions as those of measurements. The results are shown in Table 2.

Figures 3 and 4 show the SIM for the phenols isolated from aerobically or anaerobically digested liquid manure by gas stripping. Phenol and *p*-cresol were detected under aerobic digestion, whereas five phenols were sometimes detected from anaerobically digested manure. Phenol, *p*-cresol, and *p*-ethylphenol were always detected at a higher concentration under anaerobic digestion than under aerobic digestion. The results of measurements are shown in Table 3.

Phenols in the head-space gas over the reservoir of liquid manure, in which a small amount of fresh manure was continuously poured, were measured according to this procedure. The results are shown in Table 4. The concentration of phenol was greater than that of *p*-ethylphenol in the head-space gas, compared with the gas-stripping method.

Table 4. Concentration of phenols in head-space gas over the reservoir of liquid swine manure[a)]

Run No.	Phenol	*p*-Cresol	*p*-Ethylphenol
1	13	0.83	0.86
2	11	0.35	0.38
3	9	ND	0.31
4	13	ND	ND

a) Unit of concentration is volume ppb (10^{-9}). ND means "not detected."

Quantification of carboxylic acids by SIM was unsuccessful, because the concentration of carboxylic acids in liquid manure or head-space gas was lower than that of phenols. For the analysis of carboxylic acids it is necessary to use an adsorption method with a precolumn rather than the absorption method with an alkaline aqueous solution.

The authors wish to thank Mr. Minoru Kuriyama, a hog raiser near Tsukuba New Town, Ibaraki Prefecture, for his offer of liquid swine manure and for his permission on the measurements in his pigsty.

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