

CHROM. 6447

Note

Gas-liquid chromatography-mass spectrometry of organomercury compounds

Recently there has been increased interest in the use of gas-liquid chromatography (GLC) for the detection and analysis of organomercury compounds in environmental samples¹⁻¹⁰. This technique is most widely employed for the determination of methylmercury content of fish⁹. In a detailed study of the gas chromatography (GC) of alkylmercury compounds, NISHI AND HORIMOTO¹⁵ suggested that the compounds decompose on the column. JENSEN¹⁰ reported several potential sources of error in the chromatographic analysis of environmental samples for methylmercury which were possibly due to decomposition of the samples. Prompted by these findings we report our studies of the GLC behavior of organomercury compounds. Analyses were carried out by the use of combined GLC-MS.

*Experimental**

Chemicals. Dimethylmercury and methylmercuric salts were obtained commercially. The phenylmercury compounds were obtained from Dr. A. W. GARRISON of this laboratory. All compounds were used as received. Reference mass spectra obtained for each compound by direct probe or gas inlet techniques indicated no decomposition or impurities.

Apparatus. For reference the compounds were chromatographed on a Tracor MT-220 chromatograph equipped with flame ionization (FID) and ⁶³Ni electron capture (EC) detectors. GLC-MS analyses were performed with a Varian Aerograph Model 1532-B gas-liquid chromatograph and a Finnigan 1015SL quadrupole mass spectrometer having a gas jet separator and a Systems Industries 150 digital computer.

Column conditions. Analyses of the methylmercury compounds were performed on a 6 ft. × $\frac{1}{8}$ in. glass column containing Chromosorb W coated with 5% diethylene-glycol succinate (DEGS) (inlet temperature, 175°; column temperature, 160°). A 6 ft. × $\frac{1}{8}$ in. glass column containing 3% OV-1 on Chromosorb W (inlet temperature, 200°; column temperature, 150°) was used for the phenylmercury compounds. To determine optimum column conditions, benzene solutions of methylmercuric chloride, bromide, and iodide containing 10⁻⁵ g of each had been injected on the DEGS column prior to combined GLC-MS analysis of the methylmercury compounds.

Results

Retention times for methylmercury and phenylmercury compounds are summarized in Tables I and II. The data in Table I confirm the previously reported ob-

* Mention of commercial products does not necessarily constitute endorsement by the Environmental Protection Agency.

TABLE I

GLC^{a,b,c} OF DIMETHYLMERCURY AND METHYLMERCURIC SALTS

Compound	Retention time (min)	
	FID ^b	EC ^c
CH ₃ HgCH ₃ (DMM)	0.6	d
CH ₃ HgI (MMI)	3.7	5.8
CH ₃ HgOH (MMH)	4.7	6.0
CH ₃ HgBr (MMBr)	5.4	6.0
CH ₃ HgOAc (MMA)	4.9 and 5.6	6.0
CH ₃ HgCl (MMC1)	6.0	6.0

^a FID detector employing on-column injection. Column 6 ft. × 1/4 in. glass with 5% DEGS on Chromosorb W (80-100 mesh) at 160°. Nitrogen carrier gas, 60 ml/min. Inlet temperature, 175°. Flame ionization detector temperature, 175°.

^b 1- μ l injections of 0.01 M compound in benzene or hexane.

^c 1- μ l injections of 10⁻⁴ M compound in benzene or hexane.

^d No peak was detected.

servation of NISHI AND HORIMOTO¹⁵ that at low concentrations methylmercury salts of all types give peaks having the same retention time.

The GLC-MS data for dimethylmercury (DMM) and diphenylmercury (DPM) on OV-1 show no peaks that indicate decomposition. The chromatograms have sharp single peaks, the mass spectra of which are identical to those obtained by direct probe for DPM and from the literature for DMM¹⁷⁻²⁰.

However, the phenylmercuric salts were all found to undergo decomposition during chromatography. The GLC-MS data for phenylmercuric acetate (PMA) are shown in Fig. 1. Peak 1 (Fig. 1A) is phenylmercuric chloride (PMCl) ($m/e = 316$) as shown by its mass spectrum (Fig. 1B). Similarly, peak 2 was identified as DPM ($m/e = 356$) by its mass spectrum, shown in Fig. 1C. No peak ($m/e = 338$) corresponding to the molecular ion of PMA appears in either spectrum.

GLC-MS analysis of PMCl, phenylmercuric hydroxide (PMH) and phenylmercuric borate (PMB) resulted in peaks for both PMCl and DPM. As might be expected, PMB and PMH did not elute and no molecular ion peak was found.

TABLE II

GLC^{a,b,c} OF DIPHENYLMERCURY AND PHENYLMERCURIC SALTS

Compound	Retention time (min)
C ₆ H ₅ HgOAc (PMA)	3.3 and 14.5
C ₆ H ₅ HgCl (PMCl)	3.7 and 14.5
C ₆ H ₅ HgBO ₃ (PMB)	3.7 and 14.5
C ₆ H ₅ HgC ₆ H ₅ (DPM)	14.5
C ₆ H ₅ HgOH (PMH)	d

^a FID detector employing on-column injection. Column 6 ft. × 1/4 in. glass with 3% OV-1 on Chromosorb W (100-120 mesh) at 150°. Nitrogen carrier gas, 55 ml/min. Inlet temperature, 200°. Flame ionization detector temperature, 200°.

^b 1- μ l injections of 0.01 M compound in benzene or hexane.

^c Tracor MT-220.

^d No peak was detected.

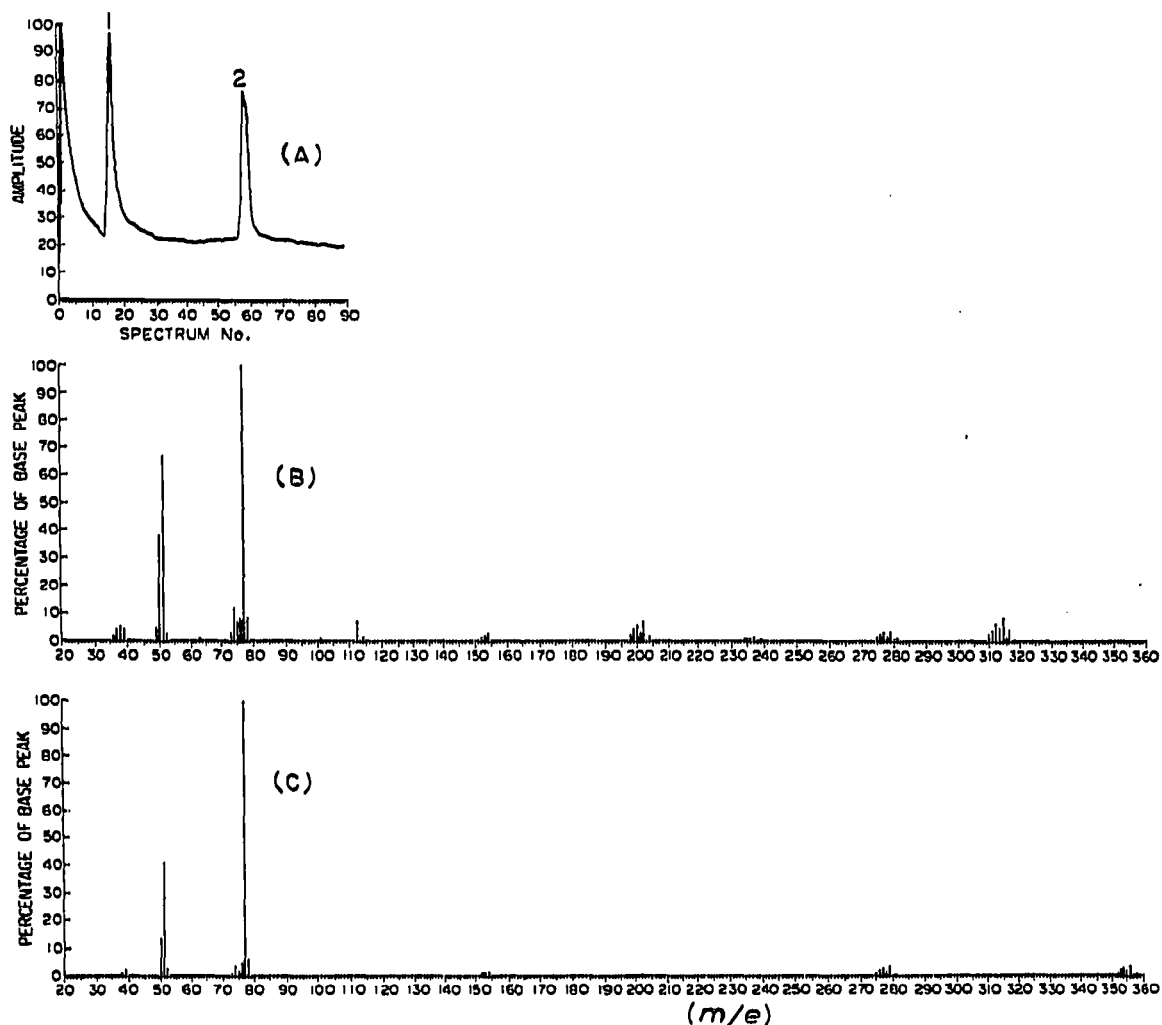


Fig. 1. Phenylmercuric acetate. (A) Chromatogram; (B) mass spectrum No. 16 of peak 1; (C) mass spectrum No. 59 of peak 2.

Methylmercury salts also decomposed during GLC, although methylmercuric chloride (MMCl), methylmercuric bromide (MMBr), and methylmercuric acetate (MMA) each gave only a single chromatographic peak.

Mass spectra of the peak from MMCl show the presence of: methylmercuric iodide (MMI) ($m/e = 344$, 20%); MMBr ($m/e = 298$, 17%); and MMCl ($m/e = 254$, 37%).

Mass spectra of the chromatographic peak from MMA revealed no molecular ion for MMA. However, the following components were detected: MMI ($m/e = 344$, 17%); MMBr ($m/e = 298$, 10%); and MMCl ($m/e = 254$, 46%).

Fig. 2 presents the GLC-MS data obtained for MMI. Mass spectrum 52 (Fig. 2B) of the first chromatographic peak shows the presence of the listed ions (column 1)

below. A second spectrum (54, not shown) of the same peak indicates the same ions, but with changed relative intensities (column 3).

Ion	Spectrum 52	Spectrum 54
MMI	($m/e = 344$, 100%)	43%
CH_3I	($m/e = 142$, 12%)	82%
I	($m/e = 127$, 7%)	100%

The change in intensity may be due to decomposition or change in pressure in the ion source.

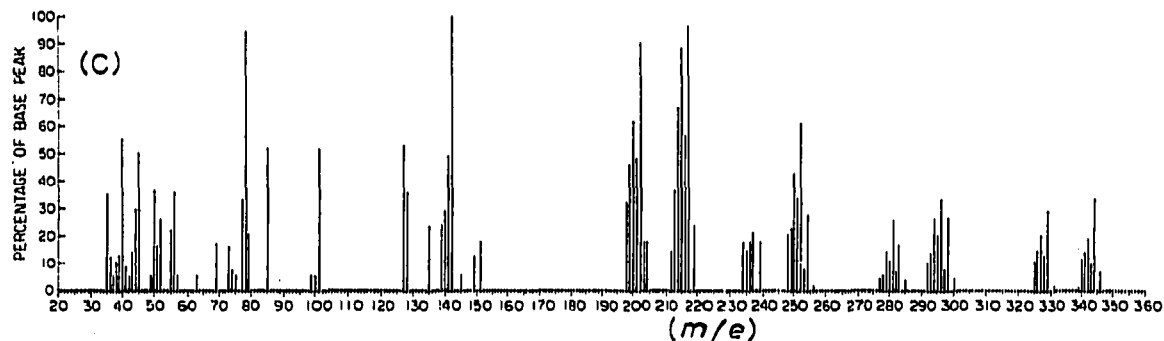
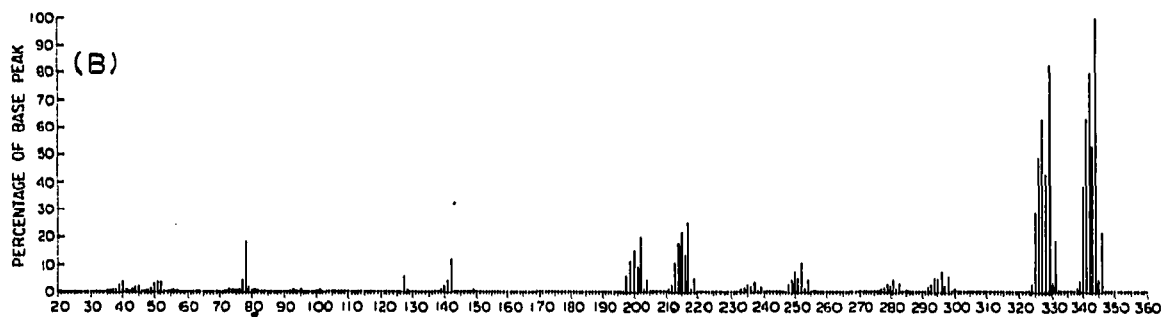
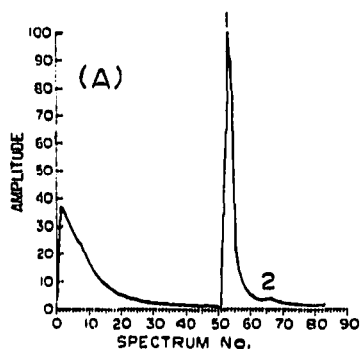


Fig. 2. Methylmercuric iodide. (A) Chromatogram; (B) mass spectrum No. 52 of peak 1; (C) mass spectrum No. 66 of peak 2.

Peak 2 of the MMI chromatogram (Fig. 2A), shown in mass spectrum 66 (Fig. 2C), contains: MMI ($m/e = 344$, 32%); MMBr ($m/e = 298$, 26%); and MMCl ($m/e = 254$, 25%).

Under the GLC-MS conditions specified, no chromatographic peak was observed for methylmercuric hydroxide (MMH). However, under other chromatographic conditions, a peak was observed with the same retention time as MMCl.

Discussion

The results described support the suggestion of NISHI AND HORIMOTO¹⁶ that ionic methylmercury compounds undergo decomposition during GLC. The decomposing proportion appears to increase as the sample size decreases. With larger samples (10^{-5} g), the methylmercury salts (CH_3HgX ; X = Cl, Br, I) elute with characteristic retention times (Table I). When sample sizes are smaller (10^{-8} g) single elution peaks having the same retention time are obtained regardless of X. The more ionic methylmercury compounds (MMH and MMA) are not eluted even at higher concentrations although decomposition products do emerge.

The phenylmercury salts, even at large sample sizes, decompose to give DPM as the major product (Table II). The relatively non-ionic organomercurials DMM and DPM are eluted with no indication of decomposition.

The pathways for the decomposition probably involve free radical or symmetrization reactions in which the Hg-X bond is cleaved^{21,22}. The product ratios are not reproducible and depend on the impurities in the injection port or on the column.

Reliable analyses for methylmercury salts may be achieved using GC but only if specially treated columns are employed to make the decomposition reactions reproducible. WESTÖÖ²⁻⁴, NISHI *et al.*⁸, and UTHE⁷ have shown that valid data can be obtained by treating the column with halide salts. The results of this study emphasize the need for this column treatment. As phenylmercury salts decompose extensively, GLC is not a good method for their analysis.

The authors wish to thank Dr. R. C. DRESSMAN, Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, for communication of his results on the GLC of organomercurials.

U.S. Environmental Protection Agency,
National Environmental Research Center, Corvallis,
Southeast Environmental Research Laboratory,
College Station Road,
Athens, Ga. 30601 (U.S.A.)

G. L. BAUGHMAN
M. H. CARTER
N. L. WOLF*
R. G. ZEPP

- 1 L. FISHER, *Chromatogr. Rev.*, 13 (1970) 82.
- 2 G. WESTÖÖ, *Acta Chem. Scand.*, 20 (1966) 2131.
- 3 G. WESTÖÖ, *Acta Chem. Scand.*, 21 (1967) 1790.
- 4 G. WESTÖÖ, *Acta Chem. Scand.*, 22 (1968) 2277.
- 5 L. R. KAMPS AND B. McMAHON, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 590.
- 6 J. F. UTHE, J. SOLOMON AND B. GRIFF, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 583.
- 7 J. F. UTHE, *Int. Symp. on Identification and Measurement of Environmental Pollutants*, National Research Council of Canada, Ottawa, Canada, 1971, p. 207.

* To whom inquiries should be addressed.

- 8 S. NISHI, Y. HORIMOTO AND R. KOBAYASHI, *Int. Symp. on Identification and Measurement of Environmental Pollutants*, National Research Council of Canada, Ottawa, Canada, 1971, p. 202.
- 9 L. FRIBERG *et al.*, *Nord. Hyg. Tidskr.*, 52, Suppl. 4 (1971) 37.
- 10 S. NISHI AND Y. HORIMOTO, *Bunseki Kagaku (Jap. Anal.)*, 17 (1968) 1247.
- 11 S. NISHI, Y. HORIMOTO AND Y. UMEZAWA, *Bunseki Kagaku (Jap. Anal.)*, 19 (1970) 1646.
- 12 S. NISHI AND Y. HORIMOTO, *Bunseki Kagaku (Jap. Anal.)*, 20 (1971) 16.
- 13 S. YAMAGUCHI AND H. MATSUMOTO, *Kurume Med. J.*, 16 (1969) 22.
- 14 K. SUMINO, *Kobe J. Med. Sci.*, 14 (1968) 115.
- 15 S. NISHI AND Y. HORIMOTO, *Bunseki Kagaku (Jap. Anal.)*, 17 (1968) 75.
- 16 S. JENSEN, *Nord. Hyg. Tidskr.*, 50 (1969) 85.
- 17 D. B. CHAMBERS, F. GLOCKLING AND J. R. C. LIGHT, *Quart. Rev., Chem. Soc.*, 22 (1968) 317.
- 18 W. F. BRYANT AND T. H. KINSTLE, *J. Organometal. Chem.*, 24 (1970) 573.
- 19 R. SPIELMANN AND C. DELAUNOIS, *Bull. Soc. Chim. Belges*, 79 (1970) 189.
- 20 O. HUTZINGER, W. D. JAMIESON AND S. SAFE, *Int. J. Environ. Anal. Chem.*, 1 (1971) 85.
- 21 K. C. BASS, *Organometal. Chem. Rev.*, 1 (1966) 391.
- 22 F. R. JENSEN AND B. RICKBORN, *Electrophilic Substitution of Organomercurials*, McGraw Hill, New York, 1968.

Received September 20th, 1972