CHROM. 12,309

GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC ANALYSIS OF FORMALDEHYDE IN AMBIENT AIR USING A SAMPLING TUBE

YOKO YOKOUCHI, TOSHIHIRO FUJII, YOSHINARI AMBE and KEIICHIRO FUWA

The Division of Chemistry and Physics, National Institute for Environmental Studies, Yatabe, Ibaraki 300-21 (Japan)

(Received July 16th, 1979)

SUMMARY

A gas chromatographic–mass spectrometric technique for the analysis of trace concentrations of formaldehyde in air is described. Molecular Sieve 13X was found to be an excellent adsorbent. The collected samples were thermally desorbed onto the analytical column (Porapak T) for separation, and quantified by mass fragmentography (m/e 29 and 30). Advantages of the technique include ppb sensitivity, selectivity and quantitative recovery. Experimental results are given for air samples in a rural area.

INTRODUCTION

Formaldehyde and other volatile aldehydes are present in car exhaust gas, tobacco smoke[1] and air, and have been reported as important chemical species in photochemical air pollution[2–4]. Formaldehyde is the most abundant of the aldehydes in the atmosphere and its undesirable effects upon the human body have been investigated[5].

A reliable and simple method for gaseous formaldehyde analysis is needed to determine its origin and contribution to photochemical pollution. To date, the available methods for the analysis of formaldehyde in ambient air are colorimetric techniques[6–10] and gas chromatographic (GC) analysis of derivatives (*e.g.*, 2,4-dinitrophenylhydrazone method[11–13]). The former suffer from large interferences due to a number of organic species present in the samples, and the latter methods are tedious requiring chemical reaction, extraction and concentration steps.

It is an interesting approach to apply the GC–mass spectrometry (MS) method in the mass fragmentography (MF)[14] or selective ion monitoring (SIM) mode for the analysis of formaldehyde in air. The inherent advantages of this technique are its sensitivity and selectivity. However, even the sensitivity offered by direct ambient air sampling is insufficient for the analysis of sub-ppb* levels of gaseous formaldehyde. In the method described here, this problem was resolved by preconcentrating the

---

* Throughout this article, the American billion (10^9) is meant.

gaseous formaldehyde on a solid adsorbent prior to GC–MS analysis. Another problem is the separation of formaldehyde from the large quantity of water vapor present in air. To avoid interference from water, it is required that water be excluded from the sampling adsorbent during concentration of formaldehyde, or that elution of water from the GC column occurs much later than formaldehyde.

This paper reports a sensitive GC–MS procedure for the determination of formaldehyde in ambient air. It is based upon MF technique, with an initial trapping of formaldehyde on an adsorption tube filled with Molecular Sieve 13X, and separation from water on a GC column packed with Porapak T.

EXPERIMENTAL

Apparatus

A microprocessor controlled Hewlett-Packard 5992A GC–MS instrument equipped with MF function was used to perform analyses. A schematic diagram of the GC–MS instrument is shown in Fig. 1. The system contains a two-way valve to switch over the carrier gas and a block heater [Shimadzu (Kyoto, Japan) FLS-3 flush sampler] for desorption of the sample from the adsorption tube.
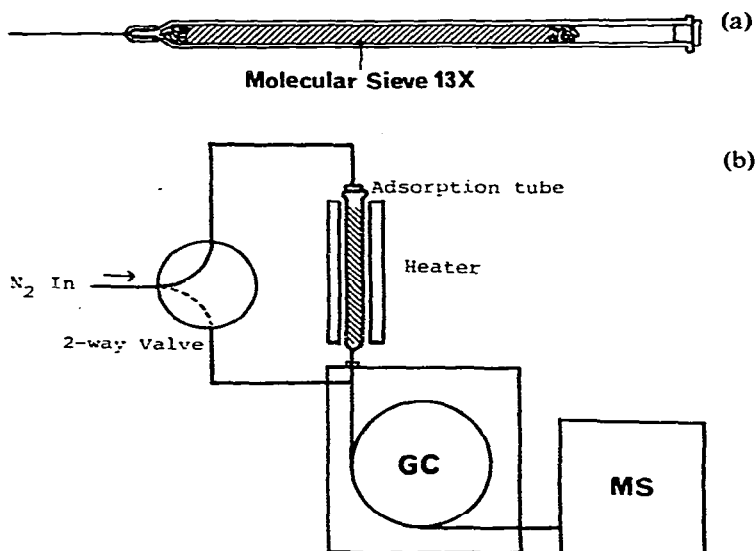

Fig. 1. Experimental GC–MS system (b) and adsorption tube (a).

Adsorption tube

A 1-g amount of Molecular Sieve 13X was packed into a Pyrex tube (15 cm × 4.5 mm I.D.) to form a bed *ca.* 10 cm long, and the tube was secured at both ends with glass wool plugs. A diagram of the adsorption tube is presented in Fig. 1. The tube was connected to the analytical column by inserting the needle end into the GC injection port.

Prior to use, tubes were conditioned by heating at 330° overnight and passing

nitrogen gas at a flow-rate of 30 ml/min. The nitrogen gas had been purified carefully by passing through a Molecular Sieve trap in dry ice–ethanol (−72°) in order to prevent adsorption of trace formaldehyde from the nitrogen gas during the cooling process.

Standards

A stock solution of formaldehyde was prepared by mixing 1.3 ml formalin (about 35%, w/w, HCHO; Wako, Osaka, Japan) and 1 l water. The accurate concentration of formaldehyde in the solution was determined by titration before use. Standards were made up by adding appropriate amounts of this solution to distilled water.

Analytical procedure

One litre of air was drawn through an adsorption tube packed with Molecular Sieve 13X by a portable pump (Charles Austen Pumps). The sampling flow-rate of 100 ml/min was controlled by a needle valve. The sampled tubes were sealed with silicone rubber and GC–MS analysis was performed as soon as possible after sampling.

Chromatographic separations were accomplished on Porapak T (80–100 mesh) packed in a glass column (6 ft. × 2 mm I.D.). Desorption of the sample from the adsorbent was carried out at 240° with the carrier gas of high-purity helium flowing at a rate of 20 ml/min for 2 min. During thermal desorption, the formaldehyde transferred onto the analytical column was temporarily trapped at the top for 2 min at a temperature of 30°, and the carrier flow was then switched to the bypass. The mass fragmentograms of the m/e 29 and 30 ions were obtained by temperature programming at 16°/min to 150°. The concentrations of formaldehyde in the samples were determined from the peak heights of the mass fragmentograms of the m/e 30 ion, using a calibration curve prepared from the standard solutions.

Measurement of breakthrough volume

Breakthrough volumes of adsorption tubes were measured in the following two manners. (1) The elution volumes of the tubes were monitored for formaldehyde with the GC–MS system (Fig. 1) when helium gas was flowing through the tube at room temperature (25°). When formaldehyde vapor was injected (*ca.* 100 μg) onto the top of the tube, the elution volume was taken as the product of flow-rate (20 ml/min) and the elution time from the tube which was obtained by subtracting the retention time of formaldehyde on the GC column from the total elution time. (2) In addition, a tandem tube arrangement was utilized[15] in order to observe the breakthrough volume greater than the 1 l of the former experiment. Formaldehyde vapor (*ca.* 100 μg) was loaded onto the tube containing the adsorbent and the tube was placed in front of an unloaded tube packed with Molecular Sieve 13X. Passing a known volume of air through both tubes at 100 ml/min, the Molecular Sieve 13X tube was analyzed to determine the amount of vapor which has been released from the adsorbents under investigation. In both cases, breakthrough volume was taken as that volume of air which released a detectable vapor (0.2 ng) from the adsorbent tube.

RESULTS AND DISCUSSION

Adsorption tube

The selection of a solid adsorbent for sampling was one of the first steps in the development of a method for formaldehyde in air. Table I lists the results of the breakthrough studies of several adsorbents. Of the adsorbents having a large breakthrough volume of formaldehyde, only the Molecular Sieve 13X was further studied. Carbosieve B and charcoal were found to retain some formaldehyde in spite of overnight conditioning at 320°, so they were not further investigated.

TABLE I

BREAKTHROUGH DATA FOR FORMALDEHYDE EVALUATED ON SEVERAL ADSORBENTS AT ROOM TEMPERATURE (25°)

Adsorbent	Breakthrough volume (l/g)
Porapak N (80–100)	0.6*
Tenax GC (80–100)	0.1*
Chromosorb 105 (80–100)	0.8*
Carbosieve B (60–80)	>5**
Charcoal (30–60)	>3**
Molecular Sieve 13X (60–80)	>3**

* Values at a sampling rate of 20 ml/min.
** Values at a sampling rate of 100 ml/min.

At a flow-rate of 100 ml/min, the passage of 3 l of air on Molecular Sieve 13X did not cause any loss of formaldehyde, which had been injected at the end of the tube as a vapor. However, it was considered that a high humidity or high concentrations of other organic contaminants in the air being sampled, may have an adverse effect on the breakthrough volume of formaldehyde on the Molecular Sieve tube. Gold et al.[16] have reported a 60% reduction of the breakthrough volume of acrolein on Molecular Sieve 13X when the relative humidity was increased from 30 to 100% at a sampling flow-rate of 20 ml/min. A similar effect was also expected for formaldehyde. So, we examined the breakthrough volume of formaldehyde in the presence of 20 μl of water (this corresponds to the amount of water vapor contained in 1 l of air with 100% relative humidity at 25°). A breakthrough volume of more than 2 l was obtained in this case. This suggests that a maximum of 1 l of atmosphere containing formaldehyde may be routinely sampled at a flow-rate of 100 ml/min without breakthrough. These values are considered to incorporate a large safety factor to compensate for the possibility of interferences.

Calibration curve and detection limit

The peak shape of the gas sample adsorbed on the tube and liquid samples were found to be virtually identical. This permitted the use of calibration curves prepared from formaldehyde solution standards. Use of solution standards avoids the difficulty of generating precise formaldehyde gas concentrations at the ppb level. A calibration curve was constructed from the peak heights of the $m/e = 30$ ion mass fragmentograms for the direct injection of 2 μl of each standard solution. The curve

was linear in the range 0–50.0 ng. The detection limit of the method was 0.3 ppb at a signal-to-noise ratio >3.

Recovery

A study of the recovery efficiency was carried out for Molecular Sieve 13X adsorbent. Samples of formaldehyde, 5 μl of solutions of concentrations 0.2 ng/μl and 2 ng/μl in water, were transferred by syringe to prepurged adsorbent tubes, and 1 l of pure nitrogen was passed through the tube at 100 ml/min. Desorption was then performed and the amounts of recovered formaldehyde were determined from the peak heights of the *m/e* 30 ions. The efficiencies were determined by comparison with direct injection of 2 μl of standards of concentrations 0.5 ng/μl and 5 ng/μl, respectively.

Essentially, a quantitative recovery was achieved for both high and low loadings of formaldehyde on molecular sieves. Recoveries for three runs with high loadings of 10 ng HCHO/5 μl aqueous solution and low loadings of 1 ng HCHO/5 μl solution were 101%, with standard deviations of 2% and 14%, respectively. Use of aqueous standards should not detract from the results since it is considered that desorption of formaldehyde from Molecular Sieve 13X, is the critical step in the recovery test for sampling of air at volumes less than the breakthrough volume (1 l). Also, the desorption efficiency is probably not influenced by the initial adsorption of either gaseous or liquid formaldehyde.

Storage of sampled adsorption tube

Storage experiments of formaldehyde on Molecular Sieve 13X were performed by injecting known quantities of solution on the adsorption tube, sealing the tube with silicone rubber, and storing at room temperature (25°). Quantitative recoveries were evaluated after certain storage periods.

The results of experiments to determine the stability of formaldehyde-on-Molecular Sieve samples, demonstrated that formaldehyde was stable on Molecular Sieve 13X for at least 24 h at ambient temperature.
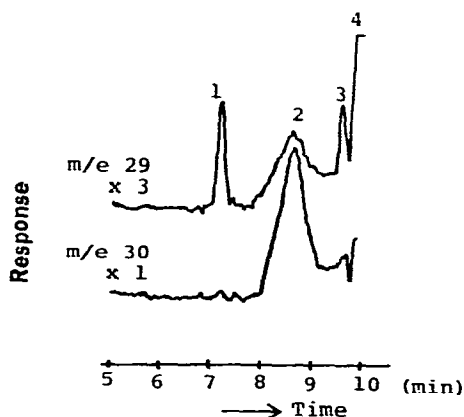

Fig. 2. Mass fragmentograms of air sample collected at Tsukuba, Ibaraki (Japan). Peaks: 1 = propane; 2 = formaldehyde; 3 = *n*-butane; 4 = water peak due to excess source pressure.

Application

    Ambient air samples were collected on Molecular Sieve 13X adsorbents at 2-h intervals, on April 11, 1979 at Tsukuba, Japan. The maximum concentration of formaldehyde, 10.2 ppb, was detected at about noon and the mass fragmentograms of m/e 29 and 30 are shown in Fig. 2. The peaks in the chromatograms are the fragment ions of (1) propane, (2) formaldehyde, and (3) *n*-butane. The detection limit of this method is clearly sufficient to quantify the low ppb levels of ambient formaldehyde gases in rural areas.

REFERENCES

 1 C. T. Mansfield, B. T. Hodge, R. B. Hege, Jr. and W. C. Hamlin, *J. Chromatogr. Sci.*, 15 (1977) 301.
 2 K. L. Demrjian, J. A. Kerr and J. .G Calvert, *Adv. Environ. Sci. Technol.*, 4 (1974) 1.
 3 E. D. Morris and Jr. H. Niki, *J. Phys. Chem.*, 78 (1974) 1337.
 4 P. L. Hanst and B. W. Gay, Jr., *Environ. Sci. Technol.*, 12 (1977) 1105.
 5 M. Omori, Y. Fukui and S. Yamada, *Chemistry*, 32 (1977) 184.
 6 B. W. Baily and J. M. Rankin, *Anal. Chem.*, 43 (1971) 782.
 7 R. G. Dickinson and N. W. Jacobsen, *Chem. Commun.*, (1970) 1719.
 8 E. Sawicki, T. R. Hauser, T. W. Stanley and W. Elbert, *Anal. Chem.*, 33 (1961) 93.
 9 T. R. Hauser and R. L. Cummins, *Anal. Chem.*, 36 (1964) 679.
10 T. Nash, *Nature (London)*, 170 (1952) 976.
11 L. J. Papa and L. P. Turner, *J. Chromatogr. Sci.*, 10 (1972) 744.
12 M. F. Tracchia, F. J. Schuette and P. K. Mueller, *Environ. Sci. Technol.*, 1 (1967) 915.
13 H. Kallio, R. R. Linko and J. Kaitaranta, *J. Chromatogr.*, 65 (1972) 355.
14 C. G. Hammer, B. Holmstedt and R. Ryhage, *Anal. Biochem.*, 25 (1968) 532.
15 E. D. Pellizzari, J. E. Bunch, R. E. Berkley and J. McRae, *Anal. Lett.*, 9 (1976) 45.
16 A. Gold, C. E. Dubé and R. B. Perni, *Anal. Chem.*, 50 (1978) 1839.