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Note

Determination of micro amounts of acrolein in air by gas chromatography

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Although acrolein is an important air pollutant, there are few selective and sensitive methods for its analysis in air. Suzuki *et al.*[1] determined acrolein in air, but the analytical results involve the α,β-unsaturated aldehydes. Magin[2] analysed simple aldehydes involving acrolein in cigarette whole smoke, and Saito *et al.*[3] performed similar analysis in auto exhaust by gas chromatography (GC). On the other hand, high-performance liquid chromatographic methods have also been used for measurement of aldehydes in auto exhaust and/or polluted air[4,5]. However, the separation of acrolein and other compounds was not sufficient in these methods. We have described[6] a method of analysis of acrolein in auto exhaust based on bromination followed by GC with electron-capture detection (ECD). It was not possible to analyse acrolein in ambient air because the determination limit was about 5 ppb* with a 40-l sample of air. This paper deals with a sensitive and selective method for GC–ECD determination of micro amounts of acrolein in air as the brominated O-methyloxime derivative.

EXPERIMENTAL

Reagents and materials

Ethanol was of analytical reagent grade from Kanto Chemical (Tokyo, Japan). Methoxylamine hydrochloride (MOA · HCl), supplied by Wako Pure Chemical Industries (Osaka, Japan), was dried under reduced pressure. The other reagents used were of analytical reagent grade. A standard solution of acrolein was prepared by dissolving 100 mg of acrolein in distilled water and diluting to 100 ml. The brominated derivative of acrolein O-methyloxime was supplied by Tokyo Kasei Kogyo (Tokyo, Japan). The Sep-Pak C_{18} (SP) cartridge was from Waters Assoc. (Milford, MA, U.S.A.).

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

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Preparation of standard gas

A 10-μl volume of acrolein solution was vaporized in a 1-l evacuated sampling bottle, and the bottle filled with nitrogen, yielding about 3300 ppm (v/v) of the first standard gas. A known volume of this gas was injected into a 100-l Tedlar bag filled with nitrogen to give the second standard gas. The concentration of the latter was analysed by a fluorimetric method with *m*-aminophenol[1].

Equipment, apparatus and conditions

A Gifu-Aichi Electric GA-2F handy sampler was used for sample collection. The volume of the bubbler used was about 30 ml.

An Hitachi 073 gas chromatograph with a ^{63}Ni electron-capture detector was used. The GC conditions were as follows: 2-m glass column packed with 3% silicone GE XE-60 on Chromosorb W AW DMCS (60–80 mesh); column temperature, 90°C; injection and detector temperatures, 170°C; carrier gas (nitrogen) flow-rate, 40 ml/min.

Collection and general procedure

Sample gases (3–40 l) were collected at a rate of 0.5–1.0 l/min in two bubblers containing 10 ml ethanol. After sampling, the absorption solution was made up to 25 ml with ethanol. Then 4 ml of this solution were diluted with 20 ml distilled water, 1 ml of 2 *M* sodium acetate and 1 ml of MOA · HCl (5 mg/ml) were added. The mixture was allowed to stand for 10 min at room temperature. Then, 1.2 ml of 3 *N* sulphuric acid, 0.3 ml of 0.2 *M* potassium bromate and 3 g of potassium bromide were added and dissolved by stirring. After standing for 15 min at room temperature, the excess of bromine was removed with 0.05 *M* sodium thiosulphate. After reaction, the solution was forced through an SP cartridge. The derivative in the cartridge was eluted with 1.5 ml of diethyl ether. A 4-μl aliquot of the eluate was analysed by GC.

RESULTS AND DISCUSSION

Sample derivatizations

Levine *et al.*[7] reported the GC analysis of aldehydes as their O-methyloxime. However, their method was not able to determine micro amounts of acrolein. So, an improved method involving the formation of a brominated derivative of the O-methyloxime of acrolein was investigated in this work. The use of ECD resulted in a highly sensitive and selective analysis of acrolein. The derivatization conditions were established as described in the Experimental. The efficiency of the whole reaction was about 92% for 1 mg of acrolein dissolved in 4 ml of the absorption solution.

Absorption solution and collection efficiency

Ethanol was used as an absorption solution to collect acrolein in air. Several kinds of ethanol supplied from different companies were investigated for their blank peaks. The reagent supplied by Kanto Chemical (Tokyo, Japan) showed the minimum blank peak. Fig. 1 shows the chromatograms of the blank and standard solutions.

The collection efficiencies for acrolein from the second standard gases at the levels of 4.4, 15.4 and 247 ppb were 81, 85 and 96% respectively, and the relative

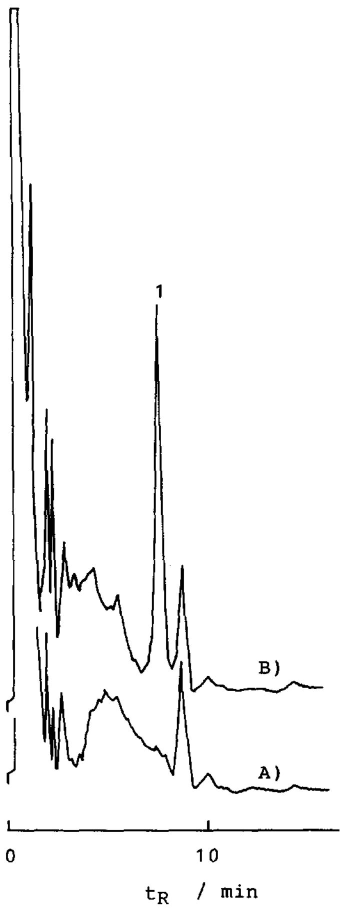


Fig. 1. The chromatograms of the products obtained from a blank (A) and a standard solution (B). Peak 1: acrolein derivative.

standard deviations of five determinations were 10.9, 9.2 and 6.1% respectively at a rate of 1.0 l/min. The collection efficiency was slightly decreased at low concentrations.

Reaction in ethanol–water

In order to prevent the precipitation of sodium sulphate and for adequate dissolution of potassium bromide, the absorption solution (ethanol) was diluted in distilled water, and the derivatization reaction was investigated in ethanol–water. The reaction efficiency for 0.2 μg acrolein in this medium was 98% of that in aqueous solution. This shows that the derivatization reaction proceeds adequately in ethanol–water.

The peak due to the acrolein derivative was sharp and separated from impurities as is seen in Fig. 1.

TABLE I

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF ACROLEIN

Ion	*Amount added (μg)*	*Recovery of acrolein (%)*	
		Proposed method	*Bromination method*[6]
–*	–	100	100
Cl^-	2	98	100
NO_3^-	2	97	103
NO_2^-	2	102	88
SO_3^{2-}	2	99	96

* A 0.2-μg amount of acrolein was added to 4 ml of absorption solution.

Separation of similar compounds and effect of diverse ions

The separation of the acrolein derivative and those of similar compounds with ethylenic bonds, such as methacrolein and crotonaldehyde, was sufficient to analyse acrolein under the GC conditions proposed here.

The interference from co-existing ions was investigated. Chloride, nitrate, nitrite or sulphate ion was dissolved in 4 ml of the absorption solution, and their influence was studied. The results are shown in Table I. None of these ions interfered with the determination of acrolein in this method, though nitrite ion interfered slightly in the previous method[6].

Calibration graph

The calibration graph obtained showed a good linearity over the range 0–0.3 μg of acrolein in 4 ml of absorption solution. The regression equation was: $y = 243x + 1.25$, where x = content (μg) in 4 ml of absorption solution, y = peak height (mm) and the correlation coefficient was 0.991 ($n = 10$).

The determination limit was about 0.001 μg/ml of acrolein in the absorption solution.

Determination of acrolein in polluted air

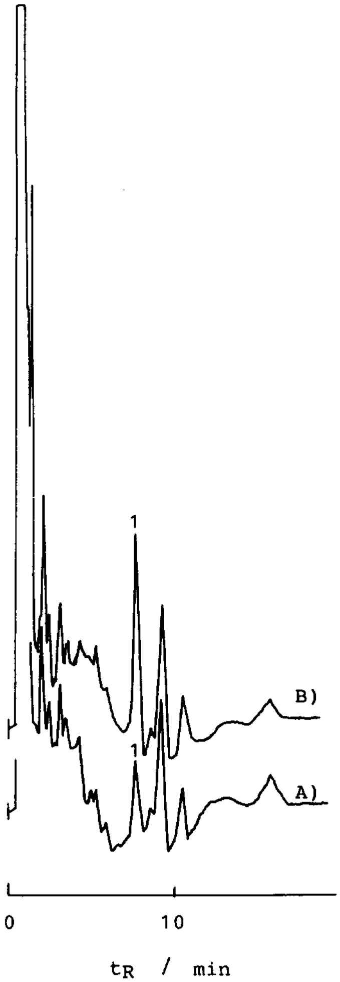
The proposed method was applied to the determination of acrolein in ambient

TABLE II

ANALYSIS OF ACROLEIN IN VARIOUS KINDS OF AIR SAMPLES

Sample	*Acrolein found*	
	*Mean**	*Range*
Urban air A	1.0 ppb	0.9–1.1 ppb
B	1.2 ppb	1.1–1.3 ppb
Air in road tunnel	1.7 ppb	1.4–1.8 ppb
Auto exhaust A	1.7 ppm	1.5–1.9 ppm
B	3.4 ppm	3.3–3.6 ppm

* Mean of three determinations.



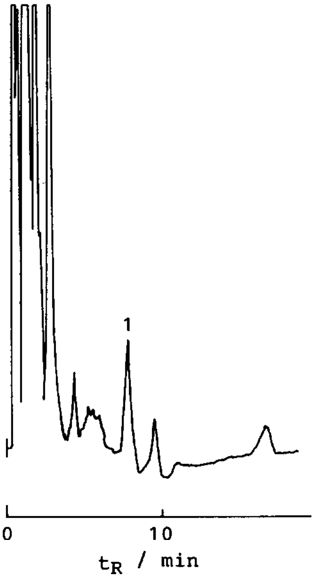


Fig. 2. Typical chromatograms of the air in a road tunnel (A) and of acrolein (0.05 μg) added to an air sample (B). Peak 1: acrolein derivative.

Fig. 3. Typical chromatogram of auto exhaust. Peak 1: acrolein derivative.

air and auto exhaust. The results are shown in Table II. The chromatograms of a sample of air from a road tunnel and of a sample from 4 ml of the absorption solution to which 0.05 μg of standard acrolein had been added are shown in Fig. 2. The peaks of acrolein in the chromatograms were coincident and the analytical results calculated from the calibration graph agreed with that obtained by addition of the standard solution. So, the proposed method is considered to be reliable. Fig. 3 shows a typical chromatogram of auto exhaust.

CONCLUSIONS

A gas chromatographic determination of micro amounts of acrolein in air was investigated. Acrolein collected in ethanol was analysed by GC with ECD as the brominated O-methyloxime derivative. This method is highly sensitive and selective and reproducible for the determination of acrolein in air.

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