

Note

Bromination and gas chromatographic determination of micro amounts of acrolein in rain water

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Acrolein and formaldehyde are irritants of the skin, eyes and nasopharyngeal membranes. Acrolein is formed in the course of the synthesis of resins and other chemicals, during the incomplete burning of organic substances and by the photochemical reaction of hydrocarbons, and is released into the atmosphere and natural waters.

Spectrophotometric determination with 4-hexylresorcinol^{1,2} and a fluorimetric method with *m*-aminophenol³⁻⁶ have been most commonly used for the determination of acrolein. However, gas chromatography (GC) and high-performance liquid chromatography are becoming increasingly applied to this analysis⁷⁻⁹. However, they give poor sensitivity or selectivity. Croll and Simkins¹⁰ and Hashimoto¹¹ developed a method for the determination of acrylamide by bromination and GC. The brominated derivative of acrylamide is stable and easy to measure. Although acrolein is also an ethylenic compound, the brominated product is not fully stable. In this work, we investigated carefully the best conditions for extracting the brominated derivative of acrolein and established a method for the determination of acrolein in rain water based on bromination followed by GC with electron-capture detection. This method is highly sensitive and selective.

EXPERIMENTAL

Reagents

Ethyl acetate and anhydrous sodium sulphate were of analytical-reagent grade for the testing of contamination of pesticide residues (Kanto Chemical). A standard solution of acrolein was prepared by dissolving 100 mg of the purest grade of acrolein available in distilled water and diluting to 1 l. The other reagents used were of analytical-reagent grade.

Apparatus and conditions

A Hitachi 073 gas chromatograph with a ⁶³Ni electron-capture detector was used. The GC conditions were as follows; 2-m glass column packed with 1% PEG-

HT on 60–80 mesh Uniport HP; column temperature, 70°C; injection and detector temperature, 130°C; carrier gas (nitrogen) flow-rate, 30 ml/min.

Procedure

A 25-ml aqueous sample containing 0.2–5.0 μg of acrolein was adjusted to pH 2.0–2.5 with 6 *N* sulphuric acid, then 1 ml of 0.2 *M* potassium bromate solution and 9 g of potassium bromide were added and dissolved with stirring. The mixture was allowed to stand for 20 min in the dark at room temperature. The excess of bromine was reduced with sodium thiosulphate and 4 ml of phosphate buffer (pH 8.0) were added. The brominated derivative was extracted three times with 5 ml of fresh ethyl acetate. The organic solution was dried with anhydrous sodium sulphate and diluted to 20 ml with ethyl acetate. A 5- μl volume of this solution was injected into the gas chromatograph.

RESULTS AND DISCUSSION

Reagent concentration and reaction time

The effect of potassium bromide concentration on the bromination reaction was investigated for a solution containing a known amount of acrolein with the addition of 1 ml of 0.2 *M* potassium bromate, in the pH range 2.0–2.5. The yield of the bromination product was maximal and constant when the amount of potassium bromide was more than 9 g.

Fig. 1 shows the yield of the product as a function of reaction time, keeping the concentration of the reagents added constant. The yield was maximal and constant within 10–30 min after the addition of the reagents, and decreased after 40 min. From this result, it is assumed that the brominated product reacts with water slowly to form hydrogen bromide, and the analysis must be completed within 30 min.

Selection of extraction solvent

Table I shows efficiencies of four solvents for the extraction of the product when a solution containing 2 μg of acrolein in 25 ml of water was sampled. Ethyl acetate is the best solvent. Three successive extractions with 5 ml of fresh ethyl acetate permitted the quantitative extraction of the brominated product from the aqueous medium.

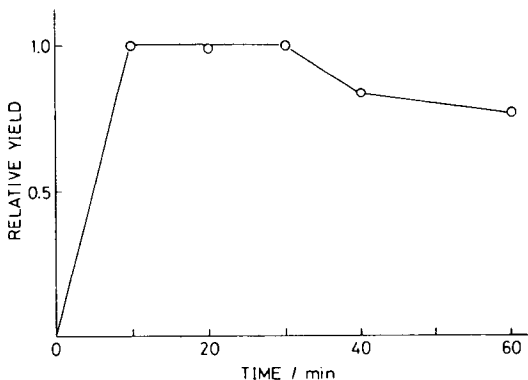


Fig. 1. Effect of reaction time on the relative yield of the bromination reaction.

TABLE I
EFFICIENCIES OF DIFFERENT EXTRACTION SOLVENTS

<i>Solvent</i>	<i>Relative peak height</i>
Ethyl acetate	1.00
Diethyl ether	0.37
<i>n</i> -Hexane	0.05
Benzene	0.47

TABLE II
RELATIVE RETENTION TIME OF DERIVATIVES OF RELATED COMPOUNDS

<i>Parent compound</i>	<i>Relative retention time</i>
Acrolein	1.00
Crotonaldehyde	1.92, 2.64*
Metacrolein	4.08
Acrylic acid	—**

* Double peaks.

** No peaks.

Selection of GC column and separation of related compounds

In order to separate the peak of the product from those of impurities, four columns with different characters were investigated: 20% TCP, 5% Versamide, 1.5% BDS and 1% PEG-HT. It was found that the 1% PEG-HT column was the most efficient for separation of the peaks.

The relative retention times of the derivatives of acrolein and related compounds with ethylenic bonds are given in Table II. The separation of the peaks is adequate for the determination of acrolein.

A calibration graph was constructed by plotting the peak height against the concentration of acrolein, and linearity was observed in the range 4–200 ng/ml of

TABLE III
RECOVERY OF ACROLEIN FROM RAIN WATER

Sample volume: 25 ml.

<i>Rain water sample</i>	<i>pH</i>	<i>Acrolein</i>		<i>Recovery (%)</i>
		<i>Added (μg)</i>	<i>Found (μg)</i>	
A	4.2	—	ND*	—
		0.5	0.44	88
		3.0	2.75	92
B	5.1	—	ND	—
		0.5	0.48	96
		3.0	2.91	97

* ND, Not detected.

TABLE IV

COMPARISON OF RESULTS OF THE DETERMINATION OF ACROLEIN IN RAIN WATER BY DIFFERENT METHODS

Rain water sample	pH	Acrolein ($\mu\text{g/ml}$)*	
		Proposed method	Fluorimetric method
A	5.1	ND**	0.012 ± 0.0004
B	4.1	0.005 ± 0.001	0.080 ± 0.001
C	4.0	0.011 ± 0.001	0.082 ± 0.001
D	4.6	0.008 ± 0.001	0.022 ± 0.0003

* Average \pm standard deviation of four determinations.

** ND, Not detected.

acrolein in aqueous medium. The coefficient of variation from five replicate determinations of $3.0 \mu\text{g}$ of acrolein per 25 ml was 6.5%.

Determination of acrolein in rain water

The method was applied to the determination of acrolein in rain water, and Table III shows the recovery of acrolein on adding known volumes of a standard solution to rain water. The recovery was in the range 88–97%.

Table IV compares the results obtained by this method with those obtained

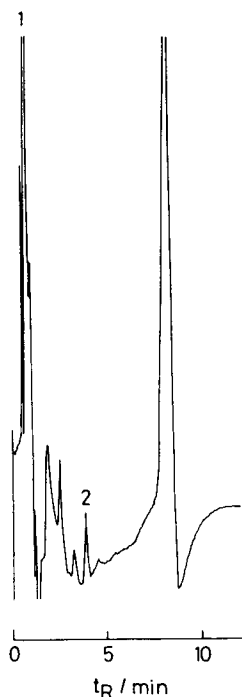


Fig. 2. Typical gas chromatogram of the brominated product of acrolein in rain water. Peaks: 1 = ethyl acetate; 2 = acrolein.

by fluorimetry with *m*-aminophenol, and it can be seen that the former are lower. This result suggests that other related α,β -unsaturated compounds in rain water contribute to the fluorescence intensity, as suggested by Suzuki *et al.*⁵. On the other hand, with the proposed method acrolein can be determined selectively (Fig. 2), but the coefficient of variation of this method is higher than that of the fluorimetric method.

CONCLUSIONS

A method for the determination of acrolein based on the bromination followed by GC with electron-capture detection was developed. This method permits the sensitive and selective determination of 4–200 ng/ml of acrolein in rain water without interference from related compounds. The total time required for the method was about 80 min.

REFERENCES

- 1 I. R. Cohen and A. P. Altshuller, *Anal. Chem.*, 6 (1961) 726.
- 2 *Japanese Industrial Standard*, JIS K 0089, 1983.
- 3 R. A. Alarcon, *Anal. Chem.*, 44 (1968) 1704.
- 4 Y. Suzuki, S. Imai and A. Hamaguchi, *Bunseki Kagaku*, 28 (1979) 445.
- 5 Y. Suzuki, S. Imai and A. Hamaguchi, *J. Jpn. Soc. Air Pollut.*, 12 (1977) 255.
- 6 Y. Suzuki, S. Imai and A. Hamaguchi, *J. Jpn. Soc. Air Pollut.*, 14 (1979) 151.
- 7 T. Saito, T. Takashina, S. Yanagisawa and T. Shirai, *Bunseki Kagaku*, 32 (1983) 33.
- 8 D. F. Magin, *J. Chromatogr.*, 202 (1980) 255.
- 9 S. J. Swarin and F. Kipari, *J. Liq. Chromatogr.*, 6 (1983) 425.
- 10 B. T. Croll and G. M. Simkins, *Analyst (London)*, 97 (1972) 281.
- 11 A. Hashimoto, *Analyst (London)*, 101 (1976) 932.