Short Communication

# Gas chromatographic determination of trace amounts of aldehydes in automobile exhaust by a cysteamine derivatization methods ☆

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## Abstract

Low-molecular-mass aldehydes present in automobile exhaust from vehicles with three different mileages were collected in a 1000-ml bottle and then determined as thiazolidine derivatives. Aldehydes were derivatized with cysteamine to the corresponding thiazolidines, which were subsequently determined using a gas chromatograph with a nitrogen–phosphorus detector. A car driven 50 000 km emitted high concentrations of formaldehyde (13.6 $\mu$g/l) and acetaldehyde (6.6 $\mu$g/l) and trace amounts of propionaldehyde, isobutyraldehyde, butyraldehyde, pentanal and benzaldehyde. Formaldehyde and acetaldehyde were also found in the exhaust from a car driven 20 000 km at levels of 4.33 and 1.32 $\mu$g/l, respectively. On the other hand, a car driven 5000 km did not emit any aldehydes.

## 1. Introduction

Some low-molecular-mass aldehydes such as formaldehyde and acetaldehyde may cause environmental problems because they are emitted from incinerator and automobile engines in large amounts. They are also known to produce photochemical smogs. It is therefore important to determine levels of these aldehydes emitted from automobile engines. However, it is extremely difficult to measure some of these low-molecular-mass aldehydes because they are highly volatile and reactive. Several methods have been reported [1–3] and the most commonly used methods involve derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH). However, chromatographic analysis of the 2,4-DNPH derivatives is difficult because they produce syn and anti forms, except in the case of formaldehyde. Moreover, this derivatization requires strongly acidic conditions, which may alter the chemicals of interest.

A simple and specific method that involves derivatization of aldehydes with cysteamine (2-aminoethanethiol) to form stable thiazolidines has been reported [4–6]. The resulting thiazolidines were determined by gas chromatography with a fused-silica capillary column and nitrogen-phosphorus detection (NPD). This method was applied successfully to determine various volatile aldehydes simultaneously in the headspace of heated pork fat [7] and cooking oils

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[8]. In this study, trace volatile aldehydes formed in exhaust from cars with gasoline engines were determined using this cysteamine method.

## 2. Experimental

### 2.1. Materials

Cysteamine and N-methylacetamide were purchased from Aldrich (Milwaukee, WI, USA). Analytical-reagent grade dichloromethane, anhydrous sodium sulphate, sodium hydroxide and aldehydes were obtained from Wako (Osaka, Japan). High-purity water was prepared by passing distilled water through an ion-exchange column and then through an activated carbon column. Thiazolidine derivatives from corresponding aldehydes except benzaldehyde were prepared according to the method reported previously [9]. A stock standard solution of cysteamine was prepared by dissolving 0.5 g of cysteamine hydrochloride in 15 ml of high-purity water. The solution was adjusted to pH 8.0 with 0.1 $M$ sodium hydroxide solution and to 20 ml in volume with high-purity water. A GC internal standard solution was prepared by dissolving N-methylacetamide in benzene (13.8 mg/ml).

### 2.2. Synthesis of 2-phenylthiazolidine

Cysteamine hydrochloride (6.8 g) was dissolved in 100 ml of 50% methanol solution and the pH of the solution was adjusted to 7.5 with 1 $M$ sodium hydroxide solution. Benzaldehyde (6.4 g) in 50 ml of methanol was added dropwise

to the cysteamine solution while stirring at room temperature. After the reaction mixture had been stirred for 10 h, 30 ml of aqueous potassium carbonate solution (0.43 g/ml) were added dropwise to the reaction mixture while stirring. The reaction mixture was diluted with 150 ml of water and then extracted five times with 50-ml portions of dichloromethane. After the extract had been dried over anhydrous sodium sulphate, the solution was concentrated under atmospheric pressure by distillation with a fractionation column. The residual colourless crystals obtained were recrystallized from hexane–benzene (2:1). Colourless needles (7.7 g) with m.p. 112–113°C were obtained. NMR and mass spectral data for 2-phenylthiazolidine are given in Table 1.

### 2.3. Sampling of aldehydes from automobile exhausts

Cars run with regular unleaded gasoline were used. The exhaust gas was collected from an engine at idling speed after the car had been driven for ca. 8 km. A 1000-ml glass bottle sealed with a PTFE plug equipped with a PTFE stopcock was used for sample collection. A glass sample bottle, from which air had been evacuated with a vacuum pump prior to sampling, was placed over the exhaust pipe and the stopcock was opened gradually over 10 min. After exhaust gas had been drawn into the sample bottle, the stopcock was closed and the bottle was brought back to the laboratory. Three bottles were filled with exhaust gas from each car every day for 2 days.

Table 1
Spectral data for 2-phenylthiazolidine

| | |
|---|---|
| $^1$H NMR (in C$^2$HCl$_3$) | $\delta$ (ppm): 7.57–7.54 (m, 2H, $o$-H on benzene ring), 7.43–7.32 (m, 3H, $m$- and $p$-H on benzene ring), 5.63 (s, 1H, methyne), 3.74–3.66 (m, 1H, one of methylene H), 3.22–3.12 (m, 3H, other methylene H), 2.04 (s, 1H, H on NH) |
| $^{13}$C NMR (in C$^2$HCl$_3$) | $\delta$ (ppm): 73.37 (position 2), 36.53 (position 4), 52.83 (position 5), 140.07 (position 1 of benzene ring), 128.13 (position 2 of benzene ring), 128.51 (position 3 of benzene ring), 127.22 (position 4 of benzene ring) |
| Mass spectrum | $m/z$ (relative intensity, %): 15(3), 18(15), 27(4), 28(9), 30(100), 36(10), 38(3), 41(2), 42(9), 43(7), 44(44), 45(4), 46(3), 59(3), 60(2), 75(3), 76(3), 77(21), 78(3), 106(5), 109(22), 111(2), 123(4), 135(3) |

## 2.4. Determination of aldehydes in exhaust gas

After sampling, 15 ml of cysteamine solution were injected into the sample bottle through the stopcock with a syringe. The bottle was shaken vigorously for 5 min and then allowed to stand for 1 h at room temperature. The reaction solution was extracted twice with 10-ml portions of dichloromethane using a separating funnel. The extracts were combined and passed through a small amount of sodium sulphate to remove water. The sodium sulphate was washed with 5 ml of dichloromethane. The dichloromethane solutions were combined and then concentrated to 1 ml under atmospheric pressure by distillation with a fractionation column. A 1-$\mu$l volume of N-methylacetamide solution was added to the sample solution as an internal standard prior to GC analysis.

## 2.5. Gas chromatography

A Hewlett-Packard Model 5890A gas chromatograph equipped with a DB-WAX fused-silica capillary column (30 m × 0.25 mm I.D., film thickness 0.25 $\mu$m) and was used with NPD. The oven temperature was held at 40°C for 2 min and then programmed to 200°C at 6°C/min. The GC peak areas were integrated with a System Instruments Model 7000B integrator. The injector temperature was 250°C and the detector temperature was 300°C. The linear velocity of helium carrier gas was 33.7 cm/s at 40°C. The injector splitting ratio was 1:20.

## 2.6. Measurement of NPD relative response factor

The relative response factor ($RRF$) for each thiazolidine derivative was defined by the following equation:

$$RRF = S_a / S_i$$

where $S_a$ is peak area of each thiazolidine derivative per unit mass and $S_i$ is peak area of 2-methylthiazolidine per unit mass. Measurements were performed for four consecutive days and five runs were carried out each day.

## 3. Results and discussion

The $RRF$ values of 2-alkylthiazolidines are given in Table 2. The deviation in the $RRF$

Table 2
Deviations of relative response factors ($RRF$) of 2-alkylthiazolidines

| 2-Alkylthiazolidine | Deviation of $RRF$ within a day | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1st day | | 2nd day | | 3rd day | | 4th day | |
| | $RRF^a$ | R.S.D.$^b$ | $RRF$ | R.S.D. | $RRF$ | R.S.D. | $RRF$ | R.S.D. |
| Unsubstituted | 0.731 | 6.1 | 0.735 | 3.2 | 0.767 | 3.8 | 0.821 | 1.6 |
| Ethylthiazolidine | 0.913 | 0.34 | 0.902 | 1.2 | 0.902 | 0.47 | 0.897 | 0.79 |
| Isopropylthiazolidine | 0.911 | 0.81 | 0.882 | 2.3 | 0.810 | 1.8 | 0.869 | 1.6 |
| Propylthiazolidine | 0.740 | 0.75 | 0.768 | 0.60 | 0.771 | 0.89 | 0.764 | 1.1 |
| Isobutylthiazolidine | 0.710 | 0.72 | 0.694 | 1.3 | 0.694 | 1.3 | 0.686 | 1.4 |
| Butylthiazolidine | 0.690 | 0.79 | 0.679 | 0.85 | 0.682 | 1.2 | 0.678 | 1.1 |
| Pentylthiazolidine | 0.504 | 1.4 | 0.502 | 1.6 | 0.508 | 1.7 | 0.505 | 1.1 |
| Hexylthiazolidine | 0.459 | 1.8 | 0.457 | 2.4 | 0.469 | 2.5 | 0.466 | 1.8 |
| Heptylthiazolidine | 0.370 | 3.5 | 0.376 | 3.4 | 0.385 | 3.3 | 0.385 | 1.5 |
| Octylthiazolidine | 0.275 | 9.0 | 0.284 | 6.0 | 0.294 | 5.0 | 0.299 | 2.3 |
| Phenylthiazolidine | 0.950 | 4.4 | 0.916 | 3.8 | 0.943 | 4.6 | 0.966 | 4.4 |

$^a$ Values are averages of five replicates. Standard compound in $RRF$ calculation is 2-methylthiazolidine.
$^b$ Relative standard deviation (%).

values is small, indicating that the use of a calibration graph for 2-methylthiazoline to determine other thiazolidine derivatives is acceptable.

A model study using standard chemicals showed that 2-alkylthiazolidines were sufficiently extracted with dichloromethane from an aqueous solution at pH 7 and exhaust gas did not change the pH of the sample solutions.

The recovery of formaldehyde using this method was checked by using a gas sample prepared by heating paraformaldehyde, and the average recovery was 89%. The average recoveries of propionaldehyde and butanal were 98% and 95%, respectively, in recovery experiments in which 10 $\mu$g of each aldehyde were added to clean air in a 1-l glass bottle.

Gas chromatograms of standard derivatives and a typical dichloromethane extract from a sample solution are shown in Fig. 1. The calibration graph for 2-methylthiazolidine is shown in Fig. 2.

Table 3 shows the results for the determination of aldehydes in exhaust gas; the values are means for three samples taken each day and corrected for the background. It is obvious that the older car (A) emitted a considerably high concentration of aldehydes, particularly formaldehyde (13.6 $\mu$g/l) and acetaldehyde (6.6 $\mu$g/l). It is noteworthy that there is an interference in the determination of formaldehyde and acetaldehyde due to the background of both aldehydes in the laboratory atmosphere and the reagents used. As the deviation of the background levels is fairly high (12–41%), the accuracy of the determination of both aldehydes becomes lower.

There are several reports on the determination of aldehydes in automobile exhaust [10–15]. Results of aldehyde determinations are summarized in Table 4. The presence of pentanal in automobile exhaust has not been reported prior to this study. Benzaldehyde, which has also been reported in exhaust gas by several researchers [12,13], may be formed from toluene in gasoline by oxidation. The amount of benzaldehyde determined in this study is consistent with those reported previously. The concentration levels of each aldehyde reported in many studies are fairly
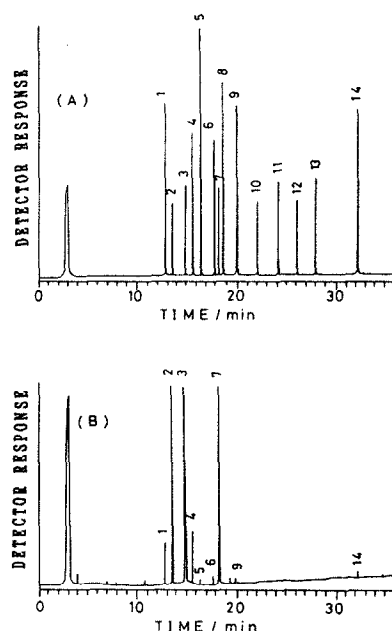


Fig. 1. Gas chromatograms of (A) a dichloromethane solution of thiazolidine standards and (B) a dichloromethane extract of automobile exhaust collected from car A. Peaks: 1 = 2,2-dimethylthiazolidine from acetone; 2 = 2-methylthiazoline from acetaldehyde; 3 = unsubstituted thiazolidine from formaldehyde; 4 = 2-ethylthiazolidine from propionaldehyde; 5 = 2-isopropylthiazolidine from isobutyraldehyde; 6 = 2-propylthiazolidine from butyraldehyde; 7 = N-methylacetamide (internal standard); 8 = 2-isobutylthiazolidine from isovaleraldehyde; 9 = 2-butylthiazolidine from valeraldehyde; 10 = 2-pentylthiazolidine from hexanal; 11 = 2-hexylthiazolidine from heptanal; 12 = 2-heptylthiazolidine from octanal; 13 = 2-octylthiazolidine from nonanal; 14 = 2-phenylthiazolidine from benzaldehyde.

similar and the relative abundances of the aldehydes show the same pattern.

The proposed method for the determination of low-molecular-mass aldehydes in exhaust gas is simple, highly sensitive and specific to aldehydes. Also, a simple quantitation method for various aldehydes was established using a single calibration graph and the relative response factor.

Table 3
Concentrations of formaldehyde (FA), acetaldehyde (AA), propionaldehyde (PA), isobutyraldehyde (IBA), butyraldehyde (BA), pentanal (PA) and benzaldehyde (BzA) found in exhaust gas from different cars

| Model | Piston displacement (cm$^3$) | Year of manufacture | Mileage (km) | Sampled on | Aldehyde concentration ($\mu$g/l) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | FA | AA | PA | IBA | BA | PA | BzA |
| A | 550 | 1986 | 50 000 | 1st day | 13.6 | 6.60 | 3.13 | 0.73 | 0.81 | ND[a] | 0.92 |
| | | | | 2nd day | 10.4 | 6.22 | 2.28 | 0.37 | 0.54 | 0.25 | 0.43 |
| B | 1800 | 1990 | 20 000 | 1st day | 4.33 | 1.32 | 0.17 | ND | ND | ND | ND |
| | | | | 2nd day | 4.25 | ND | ND | ND | ND | ND | ND |
| C | 1500 | 1989 | 5000 | 1st day | ND | ND | ND | ND | ND | ND | ND |
| | | | | 2nd day | ND | ND | ND | ND | ND | ND | ND |

[a] ND = Not detected.

Table 4
Concentration ranges of several aldehydes in car exhausts reported in the literature

| Ref. | Year | Units[a] | Aldehyde concentration range | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C$_1$ | C$_2$ | C$_3$ | i-C$_4$ | C$_4$ | i-C$_5$ | C$_5$ | C$_6$ | Benzaldehyde |
| 12 | 1981 | $\mu$g/l | 5.1–6.1 | 1.8–5.7 | 0.5 | 0.1 | 0.1 | | | | 3.5 |
| 10 | 1982 | ppm | 0.04–2.54 | ND–0.59 | | | ND–0.03 | ND–0.03 | ND–0.02 | ND–0.01 | ND–0.10 |
| 14 | 1982 | ppm | 3.26–3.56 | 0.56–0.76 | 0.03–0.08 | 0.08–0.20 | | | | | 0.05–0.07 |
| 11 | 1983 | ppm | 8.95–96.4 | 0.568–7.29 | ND–0.756 | ND–0.126 | | | | | |
| 15 | 1983 | $\mu$g/l | 17.2 | 4.03 | 0.644 | | 0.588 | | | | 0.886 |
| 13 | 1992 | ppm | 6.7–14.1 | 1.2–6.3 | ND–1.1 | ND–0.8 | | | | | |
| This work | 1992 | $\mu$g/l | ND–13.6 | ND–6.50 | ND–3.13 | ND–0.783 | ND–0.805 | | ND–0.253 | | ND–0.924 |

[a] All ppm values are v/v.
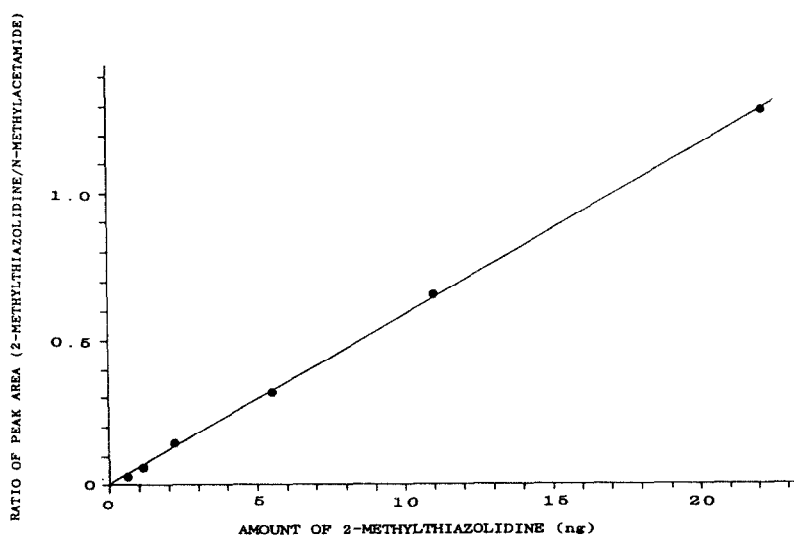
Fig. 2. Calibration graph for 2-methylthiazolidine. A 1-$\mu$l volume of standard solution was injected into the GC instrument. Each standard solution contained N-methylacetamide at 13.8 $\mu$g/ml as an internal standard. All thiazolidines were subsequently quantified using this calibration graph and the relative response factor (*RRF*).

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