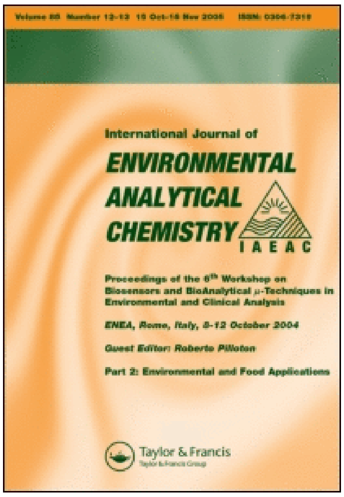

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Habboush, Albertine E. , Farroha, Sabri M. , Naoum, Osama F. and Kassir, Abdul-Ahad F.(1988) 'The Collection and Direct Analysis of Low Molecular Weight Aldehydes from Automobile Exhaust Gases by GLC', International Journal of Environmental Analytical Chemistry, 32: 2, 79 — 85

To link to this Article: DOI: 10.1080/03067318808078418

URL: http://dx.doi.org/10.1080/03067318808078418

Intern. J. Environ. Anal. Chem., Vol. 32, pp. 79–85
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Printed in Great Britain

The Collection and Direct Analysis of Low Molecular Weight Aldehydes from Automobile Exhaust Gases by GLC

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(*Received 9 March 1987; in final form 10 July* 1987)

In this investigation low molecular weight aldehydes from automobile exhaust gases were collected in bisulfite solution and analyzed directly by GLC after liberation of the compounds with sodium carbonate solution.

A special collection device was developed for this purpose. Laboratory studies on the efficiency of collection of propion aldehyde, valeraldehyde and acrolein were made in laboratory setup.

Reproducibility and recovery were excellent. Data on the concentration of these compounds in automobile exhaust gases collected from an Iraqi Reem bus running on diesel fuel are presented.

KEY WORDS: Low molecular weight aldehydes, exhaust gases.

INTRODUCTION

Aldehydes are important constituents of automobile exhaust because several of these compounds are known to be toxic, odorous, and believed to be a cause of eye irritation. Various methods have been

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reported for determining these materials as 2,4-dinitrophenyl hydrazone derivatives. These are paper chromatography,[1] spectroscopy,[2] gravimetry,[3] colorimetry,[4] and gas chromatography.[5,6]

The present investigation concentrated on devising a direct quantitative GLC method for the determination of low molecular weight aldehydes extracted from automobile exhaust condensate without converting them into 2,4-dinitrophenyl hydrazone derivatives, since this conversion is time consuming, involving several separation steps and is not suitable for routine analysis of large numbers of samples.

EXPERIMENTIAL

Apparatus

A Beckman GC-45 gas chromatograph equipped with a flame-ionization detector was used, with a 10 mV recorder. The optimal carrier gas (nitrogen) flow rate of 30 ml/min at NTP was used. The columns were made of stainless-steel tubing (6 ft long and $\frac{1}{4}$ in o.d.) filled with 20% W/W liquid phase on chromosorb W (80–100 mesh). The column temperature was controlled to within ±1%.

Materials

The pure aldehydes used were obtained from Fluke AG. Ltd. no further purification was needed as each of the compounds gave only one peak with a stable base line.

Procedure

Preparation and measurements of synthetic standards A synthetic mixture of known amounts of the expected low boiling carbonyl compounds present in exhaust gases according to preliminary work (*n*-valeraldehyde, acrolein and propionaldehyde) was prepared and added to a three-neck round bottom flask (A) containing 15 ml of 15% sodium bisulfite. A side arm of this flask was immersed into another three-neck bottom flask (B) containing 8 ml of ether which in turn was connected to a condenser and side arm immersed into a two-neck flask (C) containing 8 ml of ether, also equipped with condenser, as shown in Figure 1. The flasks B, and C were immersed

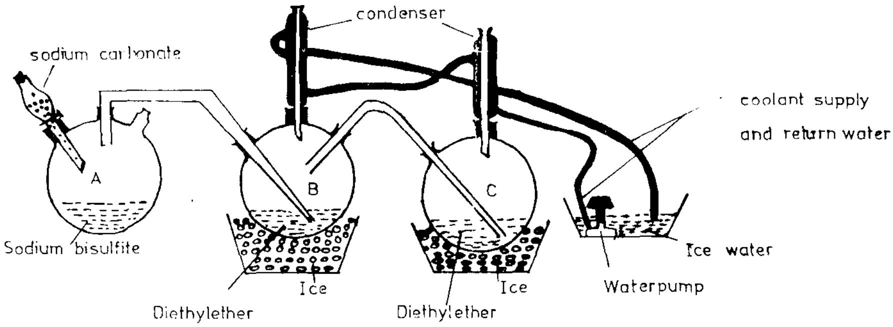


Figure 1 Schematic diagram for the recovery system of carbonyl compounds in free state.

in an ice bath to ensure the complete trapping of the aldehydes liberated by the addition of 15% sodium carbonate in ether to flask (A). The remaining mixture in flask (A) was extracted by another 4 ml of ether. The combined portions recovered were mixed and kept in a refrigerator at 5 °C for GLC analysis.

The optimum experimental conditions for the GLC analysis (Table 1) were selected according to the results of a previous study of aldehydes on a series of polysiloxane and polyester liquid phases.[7]

Table 1 Conditions for chromatography of free aldehydes

Column type	OV-101
Column temperature	120 °C
Detector temperature	170 °C
Carrier gas-flow	30 ml/min
Sample size	1 uL

One uL portions of the recovered standard samples were injected directly into the gas chromatograph using 1 uL Hamilton syringe, and the area under the peaks were calculated from the chromatogram. A calibration curve was established for the individual standard aldehyde and the percentage recoveries are shown in Table 2.

Table 2 Recovery of aldehydes from synthetic standard samples

Compound	*Weight taken (mg)*			*Percentage recovery*			*Mean percentage*
	Exp. 1	*Exp. 2*	*Exp. 3*	*Exp. 1*	*Exp. 2*	*Exp. 3*	
n-valeroaldehyde	1.061	1.017	0.968	94	97	96	96
acrolein	1.269	1.091	0.731	93	95	97	95
propionaldehyde	1.168	1.496	1.197	103	105	105	104

Mean of three runs for each experiment.

Preparation and measurement of automobile exhaust gases samples The sample volumes (2–3 m^3) of raw automobile exhaust gases taken at idle mode were measured by means of a flowmeter. The average exhaust flow through the traps was from 0.011–0.017 m^3/min. The aldehydes were trapped in two 500 ml round bottom flasks connected in series (Figure 2) and each one contained 15 ml of 15% sodium bisulfite. For the recovery of the aldehydes and analysis, the same steps in the preparation and analysis were followed as described for the standards.

A typical chromatogram of the free aldehydes present in exhaust gases condensate is shown in Figure 3 which represent *n*-

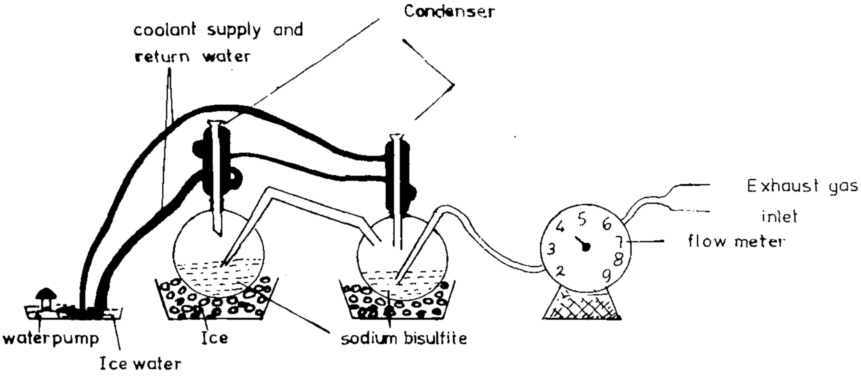


Figure 2 Schematic diagram for the collecting system of the exhaust gases.

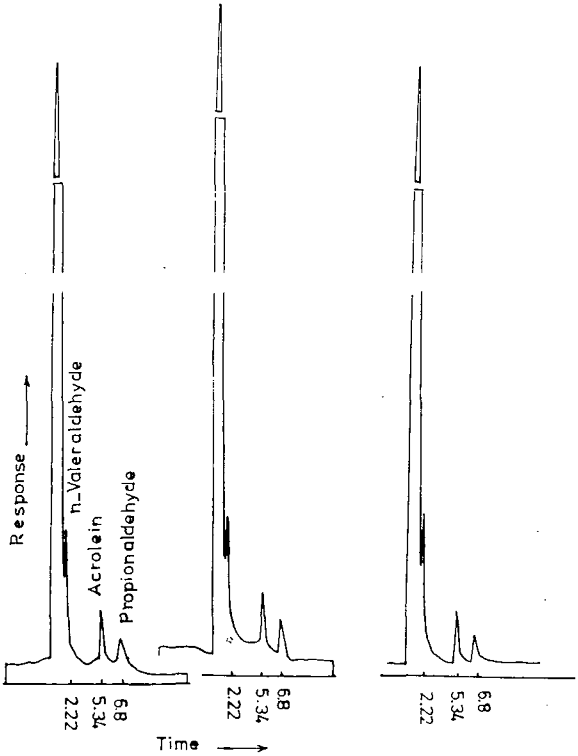


Figure 3 Chromatogram of exhaust gases (from Iraqi Reem bus) on OV-101 at 120 °C. Samples (1, 2, 3.)

valeraldehyde, acrolein and propionaldehyde respectively. The quantities of these three aldehydes were calculated from the appropriate peak areas on the chromatogram. The results obtained are shown in Table 3. These results are in good agreement with the results obtained by the standard addition method, that is by mixing 0.08 uL valeraldehyde, 0.09 uL acrolin and 0.15 uL propionaldehyde with 1 ml of the collected sample of the exhaust gas, then 1 uL of this sample was injected into the gas chromatograph and the quantity of each aldehyde was calculated from the established calibration curves for the individual standard aldehyde.

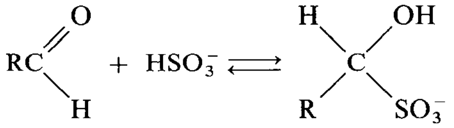
Table 3 Levels of aldehydes in exhaust gases condensate collected from an Iraqi Reem bus operated on idle mode with diesel fuel

Compounds	*Area* (cm^2)	*Weight recovered* (*Yield*)[a]	*Corrected weight recovered* (*Yield*)[a]	*Weight by stand. add.* (*Yield*)[a]
n-valeroaldehyde	4.5	2.2	2.3	2.4
acrolein	2.1	5.3	5.6	5.8
propionaldehyde	1.6	9.5	9.1	8.6

[a] Yield is expressed as mg of aldehyde per liter of fuel burnt.

RESULTS AND DISCUSSION

The optimal conditions for the quantitative collection and analysis of automobile exhaust gases condensates were carefully investigated. These are the composition of the solutions used for trapping of aldehydes and liberation of the trapped aldehydes and the choice of solvent for the absorption of the liberated aldehydes for GLC analysis, in addition to the technique of collecting of samples. It was found that a freshly prepared 15% $NaHSO_3$ in water and 15% $NaHCO_3$ in ether with ether as absorbing solvent gave very good recovery, since aldehydes are firmly bound as bisulfite addition complexes:



and the aldehydes generated quantitatively by sodium bicarbonate.

The standard experiments which were performed gave an average percentage recovery of 96%, 95%, 104% for valeraldehyde, acrolein and propionaldehyde respectively (Table 2). The efficiency of each cooled flask (B and C in Figure 1) for the absorption of the liberated aldehydes were: 88 and 8 for valeraldehyde, 90 and 5 for acrolein and 95 and 9 for propionaldehyde. No detectable amount of aldehyde were found when a third flask was connected.

The average percentage recovery was used for correcting the quantity of each aldehyde recovered from the automobile exhaust gases condensate.

Table 3 shows the mean results of analysis obtained in three samples of exhaust gases condensate collected from an Iraqi Reem bus operated on idle mode with diesel fuel. Three runs were performed for each collected sample. The values were expressed as mg of aldehyde produced by combustion of 1 liter of diesel fuel.

The relative standard deviation did not exceed ±4%.

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