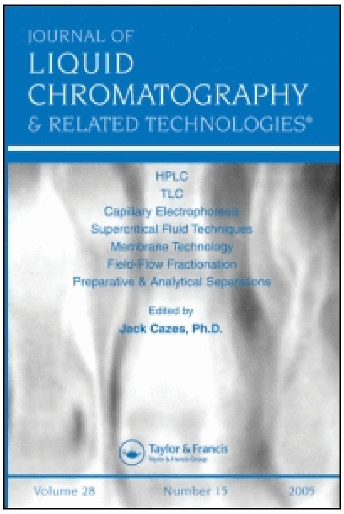

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Aliphatic Aldehydes C_1—C_4 in Waste Gas by HPLC

J. Lehotay[a]; F. Halmo[a]
[a] Department of Analytical Chemistry, Slovak Technical University, Bratislava, Slovakia

To cite this Article Lehotay, J. and Halmo, F.(1994) 'Determination of Aliphatic Aldehydes C_1—C_4 in Waste Gas by HPLC', Journal of Liquid Chromatography & Related Technologies, 17: 4, 847 — 854
To link to this Article: DOI: 10.1080/10826079408013372
URL: http://dx.doi.org/10.1080/10826079408013372

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(4), 847-854 (1994)

DETERMINATION OF ALIPHATIC ALDEHYDES C_1 - C_4 IN WASTE GAS BY HPLC

J. LEHOTAY AND F. HALMO
Department of Analytical Chemistry
Slovak Technical University
Radlinskeho 9
812 37 Bratislava, Slovakia

ABSTRACT

A simple and rapid method for the determination of aliphatic aldehydes (C_1 - C_4) in waste gas was developed. Sample collection and derivatization are performed directly in a sorption tube containing Chromosorb P impregnated with 2,4 - dinitrophenylhydrazine and catalyst. This methods allows direct injection of a methanol extract of a sorption tube into a chromatographic column. Detection limit of aldehydes is below 1 mg/m^3 for a 10 l sample. The technique was used to measure aldehyde emissions from wood fired furnace.

INTRODUCTION

Aldehydes represent a class of chemical compounds of partially oxidized organic substances which react more or less rapidly to form further products. they are produced by many industrial processes and combustion sources. Aldehydes are known contributors to photochemical smog and irritants of the skin, eyes and nasophatyngeal membranes (1,2). Formaldehyde has been identified as a suspected carcinogen, and for this reason the maximum tolerable limit in air must be low (1.2 mg/ m^3) (3).

Concern about environmental pollution and occupational hazards due to the presence of aldehydes in air has led to the development of analytical method for the determination at trace level. The best known method for the determination of aldehydes at trace levels by HPLC is the derivatization which uses 2,4-dinitrophenylhydrazine (DNPH) as reactant (4). Numerous studies have been published which use DNPH as the derivatizing reagent for the collection of carbonyl compounds in impingers and cartridges with subsequent analysis by HPLC (5-7). The anthrone reagent has been utilized as a selective reagent for derivatizing the unsaturated aldehydes to produce fluorometric derivatives (8). Several other techniques have been reported for the derivatization of aldehydes (9-11).

The aim of this paper is to describe a method for the determination of aliphatic aldehydes (C_1 - C_4) by HPLC in which the sample collection and the derivatization reaction are performed directly in a tube containing a sorbent which is impregnated with DNPH reagent. This technique was used to measure aldehyde emissions from wood fired furnace.

EXPERIMENTAL

In sampling the highest efficiency of aldehydes trapping from the waste gas using a sorption equipment is required.The sampling system consists of the sampling probe from stainless steel (inside diameter 10 mm). The suction tube is heated to such a degree that the temperature of the aspirated gas stream corresponds to that in the waste gas channel.The waste gas passed trough 2 sorption tubes ordered one after other in order that the determination of aldehyde sampling could be tested. The flowmeter was used for the measurement of the waste gas volume. For the measurement of the temperature of the gas in front of the sorption tube a thermocouple was used. An oil diffusion pump was used as a suction aggregate. The emission gas passed trough the sorption system at the rate about 200 ml/min. After 10 minutes the pump is shut off and sample volume as well as temperature and barometric pressure at the sampling site is recorded. The sorption system consists of sorption tubes which are filled with Chromosorb P impregnated with DNPH (50 g Chromosorb P, 50 ml 0.5% DNPH in acetonitrile and 0.3 ml conc. phosphoric acid).

The contents of the sorption tubes were extracted with 3 x 1 ml of methanol. Both sorption tubes of a sample are to be measured separately. If the amount of aldehydes in second sorption tube exceed 10% of the amount found in the first tube then the sample volume of the waste gas must be lower.

The HPLC equipment consisted of a Waters 510 HPLC pump, a sample valve VALCO (10 µl loop), a Waters 484 variable wavelength detector. 2,4-dinitrophenylhydrazones of aldehydes were separated on a 100 x 3 mm I.D./ Tessek SGX C18 column, 5 µm with isocratic elution at 0.5 ml/min. The eluent was methanol - water (7 : 3, v/v). The temperature of column was 25°C. The injected volume was 10 µl and spectrophotometric detection took place at 355 nm.

The standard 2,4-dinitrophenylhydrazones were synthesized by the reaction of carbonyl compounds with DNPH in the presence of hydrochloric acid that promotes the protonation of the carbonyl group. The reaction products were purified by recrystallization from methanol. Standard solutions were prepared by dissolving weighed amounts of the pure hydrazones in methanol

All chemicals must be of analytical grade, distilled water is used for the solutions. Water deionized with synthetic resins may contain formaldehyde.

RESULTS AND DISCUSSION

The chromatographic system was designed for a complete separation of all 2,4-dinitrophenylhydrazones of aldehydes expected as products of the wood fired furnace. Care must be taken to optimize HPLC conditions for sensitivity and selectivity of the separation process. Some absorption maxima of 2,4-dinitrophenylhydrazones can be seen in Fig.1, from which the maxima at 215 and 355 nm are most advantageously. Many organic substances absorb at 215 nm and an interference can be occurred. For this reason the detection will be more selective at 355 nm and possibility of the interference with other compounds is considerably lower. The qualitative evaluation was carried out on the basis of a comparison of the elution time of the standard and the sample. In our experimental conditions, retention times were reproducible within 4.5%.

Prior to measurements the blank value of the sorption tubes employed must be determined. For this purpose the sorption tubes are submitted to the complete analytical

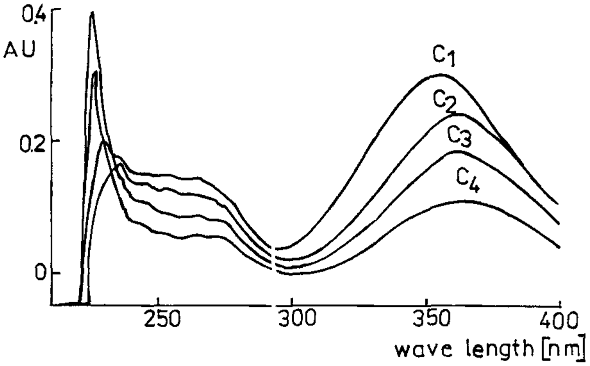

FIGURE 1
Absorption spectra of 2,4-dinitrophenylhydrazones of aldehydes C_1 - C_4.

procedure. The average blank value is to be considered in the calculation of the results.

The calibration mixtures are analyzed by using at least three hydrazone/solvent dilution ratios for each aldehyde. Calibration curves relating the concentration of hydrazone to the ratio of the peak area of the compound to that of the internal standard are constructed by regression analysis. These calibrations cover the range of hydrazone concentrations in samples listed in Table 1. Fig.2 illustrates the separation of hydrazones of C_1 - C_4 aldehydes in

TABLE 1

Determination of aldehydes in the samples

sample	sampling volume [l]	concentrations of aldehydes [mg/m^3]		relative standard deviation (3 measurements)
1	8.0	C_1	1.18	0.06
		C_2	1.30	0.06
		C_3	--	
		C_4	--	
2	6.0	C_1	1.57	0.07
		C_2	0.62	0.08
		C_3	--	
		C_4	--	
3	8.5	C_1	0.71	0.07
		C_2	--	
		C_3	--	
		C_4	--	
4	8.6	C_1	0.83	0.07
		C_2	--	
		C_3	--	
		C_4	--	

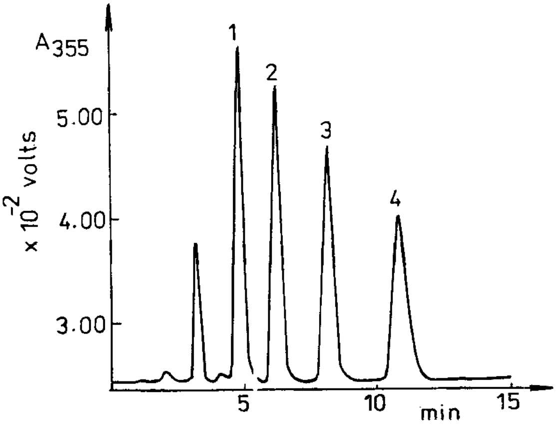

FIGURE 2

Chromatogram of 2,4-dinitrophenylhydrazones of aldehydes separated on a Tessek SGX C18 column: methanol-water (7:3) at 0.5 ml/min.

Formaldehyde (peak 1), acetaldehyde (2), propanal (3) butanal (4), (1 ppm).

less than 15 min. The chromatogram of the sample 1 is shown in Fig.3.

The results of the determination of aldehydes in the samples are given in Tab.1. The concentration of C_3 and C_4 aldehydes was below the limit of the determination. Simultaneously with the extract of the first sorption tube the extract of the second tube was analyzed. It was found that the amount of hydrazones was below the limit of the determination. It can be seen (Tab.1) that the values of the standard deviation depend on the content of aldehydes in the samples. The optimum concentration interval is in the range 0.1 - 100 μg in 1 ml of methanol. The relative standard deviation can be decreased by sampling a greater gas volume but on the other hand the possibility of an interference can increase.

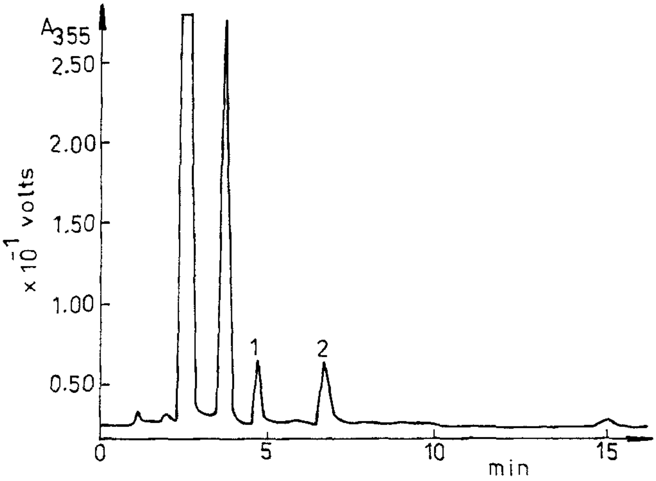

FIGURE 3
Chromatogram of the sample 1.
Formaldehyde (peak 1), acetaldehyde (2).

The limit of the determination depends on the aspirated waste gas volume. The concentration of aldehydes in the waste gas volume of 1.0 mg/m^3 (sampling volume 10 l) can be determined that is in agreement to the requirements given in literature (3). The absolute limit of the determination - the amount, that can be determined in the injected solution (10 µl) is 1 ng. At this injected amount the height of the peak of hydrazones was five time higher than the noise of the base line.

REFERENCES

1. Bailey R.A., Clark H.M., Ferris J.P., Krause S.,Strong R.L., Chemistry of the Environment., Academic Press, New York 1978

2. Sitting M., Pollution Detection and Monitoring Handbook, Noyes Data Corp., Park Ridge, NJ, 1974
3. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 7. International Agency for Research on Cancer. Lyon 1987 p.211.
4. Selim s., J. Chromatogr. 136, 271 (1977).
5. Smith D.F., Kleindienst T.E., Hudgens E.L., J. Chromatogr. 483, 431 (1989).
6. Lipari F., Swarin S.J., J. Chromatogr. 247, 297 (1982).
7. Fung K., Grosjean D., Anal. Chem. 53, 168 (1981).
8. Miller B.E., Danielson N.I., Anal. Chem. 60, 622 (1988).
9. Chao W.F., Kai M., Schida J., Ohkura J., Hara S., Yamaguchi M., Anal. Chim. Acta 215, 259 (1988).
10. Stahovec W.L., Mopper K.J., J. Chromatogr. 298, 399 (1984)
11. Du Val D.L., Rogers M., Fritz J.S., Anal. Chem. 57, 1583 (1985)

Received: June 24, 1993
Accepted: August 2, 1993