THE USE OF REVERSE PHASE MICROCOLUMNS IN THE SAMPLING OF ALDEHYDES (AS 2,4-DINITROPHENYLHYDRAZONES) EMITTED FROM ALCOHOL-FUELED MOTOR VEHICLES.

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Abstract. A rapid new analytical protocol was developed for the sampling and determination of aldehydes in exhaust gases from ethanol-fueled vehicles. The procedure involves collection of samples with two SEP PAK microcolumns, connected in series, coated with 2,4-dinitrophenylhydrazine , followed by quantification by HPLC.

INTRODUCTION

Recently, the analysis of carbonyl compounds (CC) has received a great deal of attention, especially with regard to the determination of these compounds in both exhaust gases and in the atmosphere because of their recognized importance as precursors in the production of photochemical smog. In countries where ethanol is added to gasoline as an octane booster or, such as is the case in Brazil, where gasohol (gasoline with 22% v/v ethyl alcool) for automobiles is increasingly being substituted with hydrated ethyl alcohol, the problem of photochemical smog is of great recent concern.

A common analytical procedure employed in the speciation and determination of CC involves their reaction with 2,4-dinitrophenylhydrazine(2,4-DNPHi) to form corresponding 2,4-dinitrophenylhydrazones (2,4-DNPHos). The hydrazones thus formed are then separated, before quantification, by HPLC or GC.

The derivatization reaction of CC in microimpingers during the sampling has been widely studied in aqueous media[1-8] . The use of microcolumns or cartridges in the sampling of atmospheric CC has been recently reported[9-11] .

In the present work we report on a new, inexpensive, rapid and accurate procedure for sampling and determination of CC at ppmv levels. The procedure was used in the determination of gaseous formaldehyde and acetaldehyde in exhaust gases from ethanol-fueled vehicles operated on a chassis dynamometer equipped with a constant volume sampler (CVS).

EXPERIMENTAL SECTION

Reagents and Materials

All organic solvents used were chromatography grade (Grupo Química, RJ), further redistilled in the presence of a small amount of 2,4-DNPHi to remove carbonyl compoud impurities. 2,4-DNPHo standards were precipitated using chromatography grade 2,4-DNPHi following a method described elsewere[12] . The hydrazone standards were dissolved in acetonitrile. Reverse phase SEP PAK C18 microcolumns were obtained from Waters Associates.

Microimpingers (25 mL capacity) adapted with coarse porous frits were also used for sampling.

Preparation of the SEP PAK Microcolumns for Sampling.

Prior to use the SEP PAK microcolumns were washed with 2 mL of methanol and 2 mL of acetonitrile. A 3 mL portion of a solution containing 0.2% 2,4-DNPHi and 1% of phosphoric acid in acetonitrile was passed at 5 mL/min through the microcolumn. The end part of the microcolumn was plugged with a piece of filter paper. The microcolumn was then placed inside a vacuum filtration flask and, under reduced pressure provided by an aspirator, dried under a constant stream of nitrogen gas.

Apparatus

A Waters Associates liquid chromatograph equipped with a U6K injector and a model 240 variable wavelength UV/VIS detector set at 365 nm was used. The analytical column used was a Spherical C18 5 um, 15 cm x 3.9 mm i.d. (Waters Associates). The mobile phase was methanol/water (57/43 v/v) at 1.0 mL/min. Detector sensitivity was 0.1 AUFS. In all cases 20 uL aliquots were used for analysis.

A Clayton model ECE-50 chassis dynamometer equipped with an Horiba Instruments model 20 B CVS was used for the simulation of the urban driving conditions as prescribed by the U. S. Environmental Protection Agency urban dynamometer driving schedule for light duty vehicles. The driving schedule consists of a non-repetitive series of idle, acceleration, cruise and deceleration modes of various time sequences and rates. In three separate phases (1st, 2nd and 3rd phases, respectively) it simulates an average trip in an urban area of 12.1 kilometers (7.5 miles). Using the CVS system, a proportional part of the diluted exhaust is collected continuously in Tedlar bags for subsequent analysis.

Two fleet passenger automobiles designed to operate with hydrated ethanol fuel were used . Both had four cylinder engines and four-speed manual transmissions. One was a 1980 GM Opala equipped with a 2.5 L engine with 110 412 Km and the other a 1982 VW Gol equipped with a 1.6 L engine with 43 946 Km. Both vehicles were equipped with catalytic converters.

Sampling and Analytical Procedure

Carbonyl compounds contained in the exhaust gases of the alcohol fueled vehicles were sampled using two SEP PAK microcolumns (coated with 2,4-DNPHi) connected in series or two microimpingers in series, each containing 25 mL of an aqueous solution of 2,4-DNPHi (2N HCl).

Sampling was conducted during 10 minutes at a flow rate of 0.5 mL/min. After sampling the microcolumns were eluted separately with dichloromethane (using a syringe) to a final volume of 10 mL. The aqueous solution from the microimpingers were passed through a SEP PAK microcolumn, without previous treatment, as described elsewere[8] . The retained 2,4-DNPHos were eluted with dichloromethane to a final volume of 10 mL. All sampled gas volumes were corrected for 25 °C and 1 atm.

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RESULTS AND DISCUSSION

In a previous work[8] we have reported on the precision and accuracy of sampling of CC using microimpingers containing an **aqueous** acid solution of 2,4-DNPHi or a binary solvent system containing an aqueous solution of 2,4-DNPHi and toluene, dichloromethane or cyclohexane. We reported that the single aqueous solution of 2,4-DNPHi was efficient in the trapping of gaseous CC emitted from ethanol-fueled vehicles.

The use of microimpingers containing an acid solution of 2,4-DNPHi involves the recovery of 2,4-DNPHos from the aqueous media. This can be done by either liquid-liquid extration[1-7] or by using reverse phase microcolumns[8] .

The use of SEP PAK microcolumns coated with 2,4-DNPHi for trapping gaseous CC, involves only the elution (with an organic solvent) of 2,4-DNPHos formed in the microcolumn, into a calibrated volumetric flask, followed by injection in the HPLC system without further handling.

Comparison of the use of SEP PAK microcolumns (coated with 2,4-DNPHi) with microimpingers (containing an acid solution of 2,4-DNPHi) in the trapping of formaldehyde and acetaldehyde contained in exhaust gases from both ethanol-fueled vehicles (a GM Opala and a VW Gol) operating in all three phases of the urban driving schedule showed that, for formaldehyde, the SEP PAK microcolumns trapping system was more efficient for both automobiles in all three phases (Tables I and II). For acetaldehyde no significant differences were observed.

Each SEP PAK microcolumn retained up to 216 ug of total aldehydes without breakthrough. The used microcolumns can be reused after washing first with methanol and then acetonitrile without loss in trapping efficiency.

TABLE I. Concentrations of formaldehyde and acetaldehyde (ppm v) emitted by an alcohol-fueled VW Gol during the three phases of the urban driving schedule.

Trapping system	FORMALDEHYDE I	FORMALDEHYDE II	FORMALDEHYDE III	ACETALDEHYDE I	ACETALDEHYDE II	ACETALDEHYDE III
MI	0.477	0.502	0.392	13.2	3.79	7.60
MC	1.28	0.703	0.531	10.7	3.51	7.60

MI= microimpinger trapping system.
MC= SEP PAK microcolumn trapping system.
I, II and III represent 1st, 2nd and 3rd phases of the urban driving schedule.

TABLE II. Concentrations of formaldehyde and acetaldehyde (ppm v) emitted by an alcohol-fueled GM Opala during the three phases of the urban driving schedule.

Trapping system	FORMALDEHYDE I	FORMALDEHYDE II	FORMALDEHYDE III	ACETALDEHYDE I	ACETALDEHYDE II	ACETALDEHYDE III
MI	0.966	0.076	0.076	31.6	5.33	10.3
MC	1.37	0.255	0.102	29.5	4.82	10.3

Based on the results presented above, it is possible to conclude that the use of reverse phase SEP PAK C18 microcolumns coated with 2,4-DNPHi can trap gaseous formaldehyde from ethanol-fueled vehicles with greater efficiency than microimpingers containing a single aqueous 2,4-DNPHi solution or a binary system. The efficiency of the SEP PAK C18 microcolumns is about equivalent to that of the microimpingers for the trapping of gaseous acetaldehyde . However, for both gases the SEP PAK C18 microcolumns present the advantage of lower cost and shorter analysis time when compared with the microimpingers. This is of paramount importance in monitoring programs which require routine analysis of hundreds of samples.

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