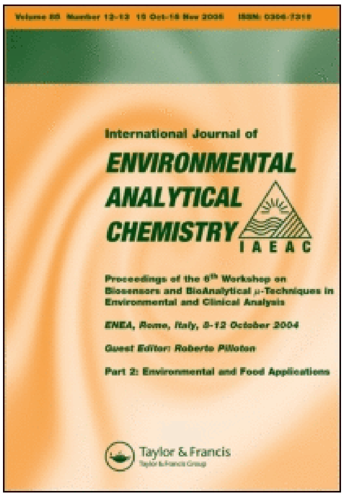

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Determination of Carbonyl Compounds in Exhaust Gases from Alcohol-Fuelled Vehicles Equipped with Three-Way Catalytic Converters†

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A rapid new analytical protocol was developed for the determination of aldehydes and ketones in exhaust gases from alcohol-fuelled motor vehicles equipped with three-way catalytic converters. The procedure involves collection of samples with two microimpingers (connected in series) containing an acid solution of 2,4-dinitrophenylhydrazine (2,4-DNPHi), recovery of the corresponding 2,4-dinitrophenylhydrazones (2,4-DNPHo) by retention on reverse phase microcolumns (Sep-Pak C18) and elution with dichloromethane or methanol. Separation and quantitation of the 2,4-DNPHo were done by reverse phase HPLC using methanol:water (57:43) as the mobile phase at 1.0 mL/min and absorbance detection at 365 nm. The results obtained in the recovery of formaldehyde and acetaldehyde from the exhaust of automobiles submitted to typical urban driving conditions indicate that the new analytical protocol compares favorably in terms of accuracy, precision, cost and speed of analyses when compared with binary solvent collection and liquid–liquid extraction procedures.

KEY WORDS: Acetaldehyde, formaldehyde, Sep-Pak, carbonyl compounds, dinitrophenilhydrazones.

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INTRODUCTION

Recently, the analysis of carbonyl compounds 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 alcohol) 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 carbonyl compounds involves their reaction with an acid solution of 2,4-DNPHi (contained in microimpingers) to form corresponding 2,4-DNPHo.[1–7] The hydrazones thus formed are recovered by liquid/liquid extraction using organic solvents such as dichloromethane:cyclohexane (30:70 v/v),[1] hexane,[2,3] pentane,[4] isoctane,[5] chloroform,[6] and dichloromethane.[7] After extraction, the solvents are evaporated to dryness and the 2,4-DNPHo taken up with a solvent which is compatible with the chromatographic procedure used or analysed directly by HPLC or GC. Besides being time consuming, these liquid/liquid extraction procedures make use of expensive solvents and involve many manipulations which tend to decrease the accuracy and precision of the analysis. In the present work we report a new, inexpensive and rapid procedure which makes use of reverse phase microcolumns in the recovery of 2,4-DNPHo from aqueous media. The procedure was used in the determination of carbonyl compounds emitted by alcohol-fuelled vehicles (equipped with three-way catalytic converters) operated on a chassis dynamometer which simulates typical urban driving conditions.

EXPERIMENTAL SECTION

Reagents and materials

All organic solvents used were chromatography grade (Grupo Quimica, R.J.) and were further redistilled with 2,4-DNPHi. 2,4-DNPHo standards were precipitated using chromatographic grade

2,4-DNPHi following a method described elsewhere.[8] The hydrazone standards were dissolved in dichloromethane or acetonitrile. Reverse phase Sep-Pak C18 microcolumns were obtained from Waters Associates.

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

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 μm, 15 cm × 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 μL aliquots were used in the analysis.

A Clayton model ECE-50 chassis dynamometer equipped with Horiba Instruments model 20 B constant volume sampler (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 it simulates an average trip in an urban area of 12.1 kilometers (7.5 miles). A proportional part of the diluted exhaust is collected continuously in Tedlar bags for subsequent analysis, using the CVS system.

Two fleet passenger automobiles designed to operate with ethanol fuel were tested. 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.

Sampling and analytical procedure

Carbonyl compounds contained in the alcohol fuelled exhaust gases were sampled using two impingers connected in series, each containing 25 mL of an aqueous solution of 2,4-DNPHi (2N HCl), or a binary system containing 10 mL of cyclohexane and 15 mL of an aqueous solution of 2,4-DNPHi (2N HCl). After sampling the phases were separated using the binary system. The organic phase was injected directly in the HPLC system. In both systems, either the whole aqueous phase or an aliquot containing the 2,4-DNPHo was passed through Sep-Pak microcolumns (using a 30 mL glass syringe) at an approximate flow rate of 3 mL/min. The retained 2,4-DNPHo were then eluted with dichloromethane, methanol or acetonitrile to a final volume of 10 mL. Liquid/liquid extractions were made taking 5 mL aliquots of the aqueous solution containing, 2,4-DNPHo and extracting 3 times with 5 mL portions of pentane, which was then evaporated at room temperature using a flow of nitrogen gas. The 2,4-DNPHo were redissolved in dichloromethane before HPLC analysis.

Known concentrations of propanone in nitrogen were generated at the ppm level using a diffusion cell described elsewhere.[9]

RESULTS AND DISCUSSION

Collection efficiencies

In non-isokinetic analytical procedures based on the reaction of a compound of interest and a derivatizing agent the limiting accuracy parameter is obviously the efficiency of the reaction. For derivatization using 2,4-DNpHi it has been established that while the collection of aldehydes at ppm v levels is nearly 100% efficient, that of ketones is significantly smaller (as low as 18% for propanone).[7] At lower levels (ppb v) it has been shown that full recovery of acetaldehyde and benzaldehyde was not obtained but that it could be increased by addition of an organic phase to the aqueous 2,4-DNPHi solution.[1]

Aldehyde emissions from alcohol-fuelled automobiles operated under typical urban driving conditions are at the ppm v level. For this reason we initiated our study evaluating the collection efficiencies of propanone at 34 ppm v using single aqueous or binary (aqueous/organic) solvent systems. Propanone was chosen because of the reported lower recoveries amongst the carbonyl compounds of interest,[7] and ease of generation of known concentrations using a diffusion cell. Binary solvent systems containing an aqueous 2,4-DNPHi solution and toluene, dichloromethane or cyclohexane were evaluated. No significant differences were found among any of these three systems in the recovery of propanone. Use of dichloromethane was discarded because of high solvent losses during collection. Under the chromatographic conditions used, during the elution of a mixture of hydrazones of formaldehyde, acetaldehyde and propanone, a negative toluene solvent peak eluted directly under the acetaldehyde derivative peak, causing severe area subtraction. For these reasons cyclohexane was the organic solvent of choice.

The accuracy of propanone collection, as determined by comparison of the analysed with the calculated values using the diffusion equation,[9] was 98.4%±3.3% and 99.0%±4.0%, respectively for the single aqueous and the aqueous/cyclohexane binary system. Thus, similar or higher collection efficiencies can be expected for both formaldehyde and acetaldehyde.

Comparison of single aqueous versus aqueous/cyclohexane binary solvent system in the collection of formaldehyde and acetaldehyde from an alcohol-fuelled automobile operated under simulated urban driving conditions (Table I) showed that the recoveries using the single aqueous system were, respectively, 27% and 11% higher for formaldehyde and acetaldehyde. For this reason and because it is easier and faster to use a single phase, the single aqueous collection system was used throughout this study.

TABLE I

Comparison of single versus binary solvent in the collection of acetaldehyde and formaldehyde from an alcohol-fuelled automobile.

	Mass of 2,4-DNPHo recovered, μg	
Collection system	Formaldehyde	Acetaldehyde
Single (aqueous)	49.1 (3.5)	462 (8.1)
Binary (aqueous/cyclohexane)	38.7 (12.3)	417 4.3)
Single/binary ratio	1.27	1.11

Numbers in ( ) are the (%) r.s.d.

The 2,4-DNPHo from the aqueous phases were recovered using Sep-Pak microcolumns.

Recovery of 2,4-DNPHo from aqueous media

Comparison of the use of Sep-Pak microcolumns with liquid/liquid extraction in the recovery of 2,4-DNPHo of formaldehyde and

TABLE II

Comparison of liquid/liquid extraction (LL) with pentane versus retention in Sep-Pak (SP) microcolumns in the recovery of 2,4-DNPHo from an aqueous solution.

	μg/mL 2,4-DNPHo found[a]	
Type of recovery	Formaldehyde	Acetaldehyde
LL extraction	26.3 ± 0.45	10.1 ± 0.08
SP retention[b]	26.2 ± 0.42	10.6 ± 0.07
LL/SP ratio	1.00	0.95

[a] Average results of three determinations.
[b] Hydrazones eluted with dichloromethane.

acetaldehyde from aqueous solutions showed no statistically significant differences with respect to precision and accuracy (Table II).

Dichloromethane, methanol and acetonitrile were evaluated as eluents for the 2,4-DNPHo retained in the microcolumns. The average results for four separate aliquots of aqueous solutions containing 2,4-DNPHo of formaldehyde and acetaldehyde showed (Table III) higher precision for dichloromethane (c. 1.5%) followed by methanol (0.2–5.0%) and acetonitrile (1.4–10.0%). For both formaldehyde and acetaldehyde derivatives any of the three solvents provide similar results Table III). Use of acetonitrile for the elution

TABLE III

Comparison of elution solvents in the recovery of 2,4-DNPHo of formaldehyde, acetaldehyde and propanone retained in Sep-Pak microcolumns.

	μg/mL 2,4-DNPHo found[a]		
Sep-Pak eluent	Formaldehyde	Acetaldehyde	Propanone
DCM	25.6 ± 0.39 (1.52)	11.5 ± 0.14 (1.22)	18.1 ± 0.23 (1.27)
MeOH	26.0 ± 1.30 (5.00)	11.3 ± 0.02 (0.18)	19.7 ± 0.24 (1.22)
MeCN	25.8 ± 0.36 (1.40)	11.1 ± 0.21 (1.89)	13.0 ± 1.31 (10.0)

[a] Average results of four determinations.
Numbers in ( ) are the (%) r.s.d.
DCM = dichloromethane MeOH = methanol MeCN = acetonitrile.

of the propanone derivative is both less accurate and significantly less efficient (c. 69%).

Comparison of liquid/liquid extraction versus Sep-Pak microcolumn retention in the recovery of formaldehyde and acetaldehyde (as their 2,4-DNPHo derivatives) emitted from an alcohol-fuelled automobile under the conditions of urban driving showed that the use of microcolumns resulted in consistently more precise results (better than 2.5% r.s.d.) and recoveries between 18% and 21% higher (Table IV).

TABLE IV

Comparison of liquid/liquid extraction versus Sep-Pak retention in the recovery of formaldehyde and acetaldehyde (as 2,4-DNPHo) emitted from an alcohol-fuelled automobile.

Method	μg 2,4-DNPHo found	
	Formaldehyde	Acetaldehyde
LL extraction[a]	48.0 ± 1.70 (3.54)	353 ± 29.7 (8.41)
SP retention[b]	56.4 ± 0.85 (1.51)	428 ± 10.6 (2.48)
SP/LL ratio	1.18	1.21

[a] Using pentane for the extraction and cyclohehane for take up.
[b] Using dichloromethane as eluent.
Numbers in ( ) are the (%) r.s.d.

"Aging" of the microcolumns evaluated by retention and elution of 2,4-DNPHo of formaldehyde, acetaldehyde and propanone four consecutive times showed no decrease in either recovery efficiencies or precision. After passage of 42 mL of an aqueous solution containing, respectively 36 and 29.5 μg/ml of 2,4-DNPHo of formaldehyde and acetaldehyde—which corresponded to 2.78 mg of total hydrazone retained in the microcolumn—no breakthrough was observed.

Composition of aldehydes in the automobiles exhausts

Typical concentrations of formaldehyde and acetaldehyde in the exhaust emissions of both vehicles, operated on the chassis dynamometer under typical urban driving conditions, are shown in

Table V. Typically, formaldehyde and acetaldehyde comprised about 99% of the exhaust's carbonyl compounds. Acetaldehyde made up between 88.3 and 99.3% of the total aldehydes determined.

TABLE V

Concentrations of formaldehyde and acetaldehyde (ppm v) emitted by alcohol-fuelled vehicles in the three phases of the urban driving schedule.[a]

	Vehicle: GOL	
Phase	Formaldehyde	Acetaldehyde
1	0.477 (3.49)	13.2 (96.5)
2	0.502(11.7)	3.79(88.3)
3	0.392 (4.90)	7.60(95.1)
	Vehicle: OPALA	
Phase		
1	0.966(2.97)	31.6(97.0)
2	0.076(1.40)	5.33(98.6)
3	0.076(0.73)	10.3 (99.3)

[a]Each vehicle was equipped with a three-way Pt/Rh (5:1) catalytic converter installed about 15.000 Km prior to this test.

Numbers in ( ) represent percent aldehyde of total in each phase.

CONCLUSIONS

Collection of carbonyl compounds as 2,4-DNPHo derivatives using an aqueous phase solution of 2,4-DNPHi in 2 M HCl, followed by recovery of the hydrazones by retention on reverse phase Sep-Pak microcolumns is both more efficient, faster and cheaper than liquid/liquid extraction procedures. These considerations are of paramount importance in routine monitoring programs which require the analysis of hundreds of samples.

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