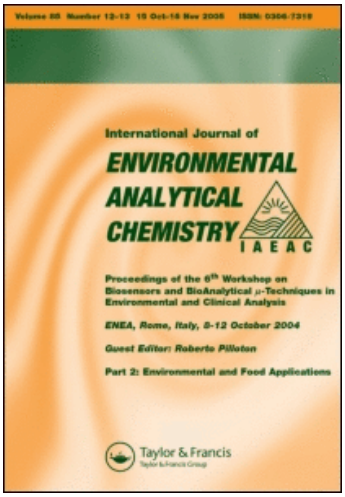

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Determination of Carbonyl Compounds in Automobile Exhausts and Atmospheric Samples†

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Two new methods were developed to determine carbonyl compounds in auto exhaust and atmospheric samples. A gas chromatographic system using a quartz glass capillary column combined with selective and sensitive electron capture detection was used. 2,4-Dinitrophenylhydrazone derivatives of the carbonyl compounds are electron capture sensitive. The aldehydes and ketones were trapped in impinger sampling flasks containing the reagent solution. The excess of reagent was removed before injection onto the glass capillary column. A reversed phase high performance liquid chromatographic system for separation of fluorigenic dansylhydrazones is presented. With this system a complete separation of 17 carbonyl compounds was achieved. The reaction conditions for the dansylhydrazine reagent was studied and compared to the 2,4-dinitrophenylhydrazine reagent.

The gas chromatographic method was also compared to the different liquid chromatographic methods applied on some atmospheric and auto exhaust samples. The methods are selective and sensitive thus a small sample volume of air is sufficient for quantitative determinations.

KEY WORDS: Carbonyl compounds in air, capillary gas chromatography, Electron capture detection, 2,4-dinitrophenylhydrazones, Dansylhydrazones, high performance liquid chromatography, fluorescence labelling.

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INTRODUCTION

Carbonyl compounds are formed by the combustion of organic materials and by photooxidation of hydrocarbons. They are a class of highly reactive compounds present in small amounts in foods, tobacco smoke, car exhaust and atmospheric samples. Some of the carbonyls have attracted special attention since they possess allergenic properties, may cause respiratory problems and are irritant to the eyes. Acrolein is on the EPA Priority Pollulant List. Formaldehyde yields the carcinogenic bis (chloromethyl) ether upon photoreaction with hydrogen chloride in moist air.[1] The growing interest of determining carbonyl compounds in car exhaust is connected with new alternative fuel mixtures containing ethanol and methanol. Fuel saving motors, such as Diesel engines, are believed to produce higher amounts of carbonyl compounds.

The analytical methods commonly used are based on derivatization of the carbonyls to 2,4-dinitrophenyl (DNP) hydrazones and subsequent determination of the derivatives with gas chromatography (GC) or with high performance liquid chromatography (HPLC). A number of gas chromatographic[2–6] and liquid chromatographic [7–10] works have been published.

The aim of this work is to apply highly sensitive chromatographic methods to the determination of small amounts of carbonyl compounds. This can facilitate the sampling and with reduced sample volumes it would be possible to obtain the spreading pattern of the carbonyls in the atmosphere. To date there are few studies on such air samples except for samples from extremely polluted urban areas.[10]

High resolution glass capillary GC combined with electron capture EC detection, GC/GC/EC, has turned out to be very sensitive and selective.[11] The classic DNP-hydrazones are EC sensitive thus making them adequate for GC/GC/EC-studies. Fluorigenic labelling techniques in combination with reversed phase HPLC is another effective analytical tool.[12] Fluorescent dansyl (DNS) hydrazones of aldehydes have been separated on a HPLC system.[13]

EXPERIMENTAL

Reagents and materials

The 2,4-dinitrophenylhydrazin (DNPH) reagent p.a. grade (Merck) as well as the DNP-hydrazone derivatives were recrystallized from carbonyl-free ethanol. The water, ethanol and methanol were purified by refluxing with DNPH reagent and sulphuric acid followed by distillation. n-Hexane HPLC grade (Rathburn Chemicals Walkeburns Peeblesshire G.B.) was

made carbonyl-free according to Hornstein and Crowe[14] with some small modifications. The solvent was purified on a column (2 cm i.d., 9.5 cm length) with Celite 545 mixed with conc. sulphuric acid. At the top was a 1.5 cm layer of water free sodium sulphate. The Celite was first washed with conc. sulphuric acid followed by several washings with distilled water and dried at 110°C. Then 14.5 g Celite was mixed with 16 ml conc. sulphuric acid and hexane was added. The slurry was then transferred to the column. The first fraction of hexane was discarded. The purified hexane was checked on the HPLC system.

The 1-dimethylaminoaphtalene-5-sulfonylhydrazin (dansylhydrazin abbr. DNS-hydrazin) reagent was prepared according to Seiler and Demisch.[15]

The aldehydes C_5-C_9 and benzaldehyde were of purum quality and obtained from Fluka, Germany. The other carbonyl compounds were from Merck. The formaldehyde solution 35% was of analytical grade.

The solvents acetonitrile and dichloromethane were of HPLC quality and obtained from Rathburn Chemicals.

Apparatus

A Carlo Erba Fractovap 4160 with ^{63}Ni electron capture detector and split/splitless injector was used. Different glass capillary columns were prepared and tested. Finally, a 16 m quartz column with SP 2100 stationary phase employed.

A Varian 5000 HPLC system equipped with a Valco injector was used. A variable UV detector (Spectra Physics 770) and a fluorescence detector (Schoeffel FS 970) equipped with a Corning 7-54 primary filter and a 500 nm cut off emission filter were employed. An analytical column 200 × 5 mm i.d. was packed with Nucleosil 50–5 straight phase material (Machery-Nagel, Düren, Germany). The reversed phase column was packed with Nucleosil 5 C_{18}. The recorders were Perkin-Elmer 56 for both the GC and HPLC systems.

Sampling procedure

The sampling device consisted of impinger flasks (one or two in series) so-called Midget Bubbler with porosity A (145–175 μ) and were purchased from ACE Glass Inc. N. J., USA. The air sampling pumps employed were a Sipin personal sampler pump model SP-1 (Sipin Co N.Y., USA) for the range 0.1–0.3 l/min and a MSA portable pump model G (Mine Safety Appliance Co., Pittsburgh, USA) for a flow about 1 l/min. The impinger flasks were filled with reagent solutions and the air samples were pumped through the flasks at different flow rates measured with a flow meter.

DNPH reagent

The reagent solution was prepared by dissolving 2.5 g reagent in one litre of 2M HCl solution. The solution was further purified by extracting three times with carbonyl-free hexane which reduced the background from contaminant hydrazones. The reagent itself is poorly extracted with hexane. Two impinger flasks in series, each containing 20 ml of reagent solution, are used to collect car exhaust and air samples. The pump flow rate was 0.2–1.0 litres per minute. The reagent solutions were combined after the sampling and extracted twice with 20 ml portions of hexane. For HPLC reversed phase mode the hexane solution is evaporated under dried nitrogen and redissolved in methanol.

Removal of the excess of the DNPH reagent

Three different methods were tested to remove the reagent without loss of the hydrazone derivatives. According to Reich *et al.*[16] the excess of reagent was converted with pyruvic acid to its hydrazone, which was then extracted with sodium carbonate solution. Another method tested was oxidation of the reagent with Benedict's reagent.[16] Both methods were unsuccessful since some hydrazone derivatives were lost. However, with the pyruvic acid the unsaturated carbonyl compounds were unaffected and thus might be isolated. The third method employed, described by Schwartz *et al.*,[17] was successful in removing the reagent. A strong cation exchange resin Amberlite AG 50 W-X8 was effective in adsorbing the basic reagent while the weakly acidic hydrazones were passing through the resin. As a column a Pasteur pipet filled with carefully washed ion exchange materials was used. The column was finally washed with hexane prior to use. The DNPH reagent was irreversibly adsorbed on the resin. The hexane solution with the hydrazone derivatives is then ready for GC separation.

DNSH reagent

The reagent solution was prepared by dissolving 10 mg reagent in 20 ml water: methanol: 2%w/v trichloro acetic acid (12:4:4) solution. In this case, one impinger flask is sufficient. As a result of the methanol content, the carbonyl compounds of higher molecular weight are better dissolved in the trapping reagent solution. Ten μl of the sample solution is finally directly injected onto the HPLC reversed phase column.

Gas chromatography procedure

One μl samples were injected with 1:16 split ratio or in splitless mode. After the injection, the column temperature was programmed from 180° to

250° with 2.5°/min, whereafter the column was operated isothermally to the end of the analysis. The injector and detector temperatures where 300°. Hydrogen was employed as a carrier gas with a flow rate of 0.9 ml/min. The make up gas was argon/methane (95:5) with a flow rate of 27 ml/min. As internal standard 2,2′, 4,4′, 5,5′-hexachlorobiphenyl was used. The compound is sensitive to electron capture detection and stable.

Liquid-chromatographic separation

Straight phase separation of the DNP-hydrazones: The mobile phase was a mixture of hexane dichloromethane 15% pumped with a flow rate of 2 ml/min. The wavelength setting was 360 nm. Standard solutions for calibration and evaluation were prepared from recrystallized DNP-hydrazones. Calculation of amounts were made by comparing peak heights. Injected volumes were in the range 10–25 μl.

Reversed phase separation of the DNP-hydrazones: Different mobile phases with either methanol/water or acetonitrile/water were employed. The gradient elution with the acetonitrile water system started with 50% and ended after 10 minutes with 70% acetonitrile. The flow rate of the mobile was 1 ml/min.

Reversed phase separation of fluorigenic DNS-hydrazones: The mobile phase composition was based on water acetonitrile mixtures, run with different gradients. Isocratic separation was perfomed with 50% acetonitrile. The flow rate of the mobile phase was 1 ml/min. Excitation wavelength was 360 nm and the emission was registered above 500 nm. A standard solution was prepared with the underivatized carbonyl compounds in methanol. From this solution derivatization was carried out under the same conditions as the samples. The evaluation was made by comparing peak heights.

RESULTS

The sampling procedure with DNPH-reagent was examined by passing air containing a known amount of propanal through three impinger flasks in series at a flow rate of 1 l/min. The propanal was trapped to 94.5% in the first flask and 5.5% in the second flask; thus two flasks in series are sufficient for sampling.

The extraction efficiency of the DNP-hydrazones with hexane was investigated. Propanal hydrazone at the concentrations of 1.6 μg/ml, 0.28 μg/ml, respectively, (20 ml volume) were three times extracted with 10 ml hexane portions. The yield at the higher concentration was 92.5%, 6.8% and 0%, respectively, and at the lower concentration 85%, 15.9% and 0%, respectively.

Reaction conditions for the DNSH reagent

The reaction time dependence of the DNS-hydrazine reagent is illustrated in Fig. 1. The reaction with a tenfold excess of DNS-hydrazin is completed in five to ten minutes. The excess of reagent should be at least tenfold. The concentration of trichloro acetic acid in the reagent mixture

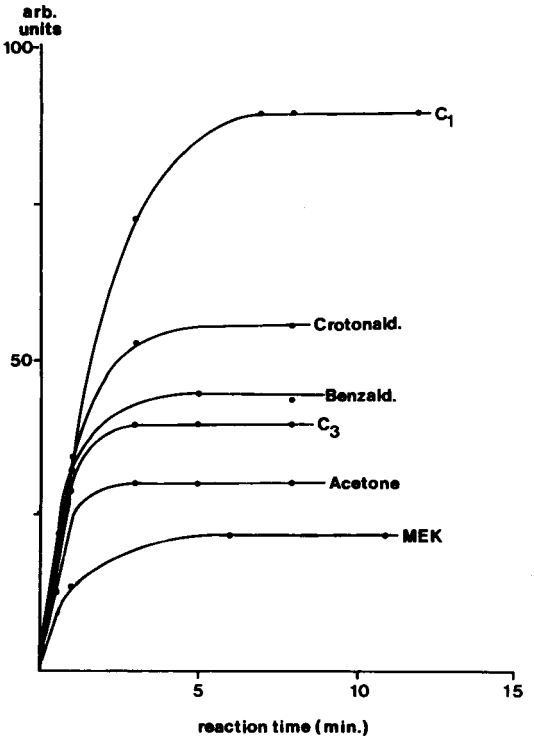

FIGURE 1 Plot of maximum response versus reaction time for different DNS-hydrazones (conc. in the range of 0.1–0.2 nmole). C_1 = formaldehyde, C_3 = propanal, MEK = methyl ethyl ketone.

should be 0.1–0.2%, while higher concentrations affect the subsequent chromatographic separation. The methanol concentration in the water reagent solution was found to be most favourable at about 20%. Methanol was added to dissolve the reagent which is not soluble in water.

The formation of the DNS-hydrazones was affected by heating of the reaction mixture. At 75° the derivatives are gradually decomposed. Already at 50° after a 30 minute period of reaction time, a slight reduction is observed. Room temperature was found to be suitable. The formed DNS-hydrazones were stable for several hours.

Gas chromatography

The separation of 10 carbonyl compounds as DNP-hydrazones is shown in Fig. 2. The peaks have good Gaussian symmetry and the column

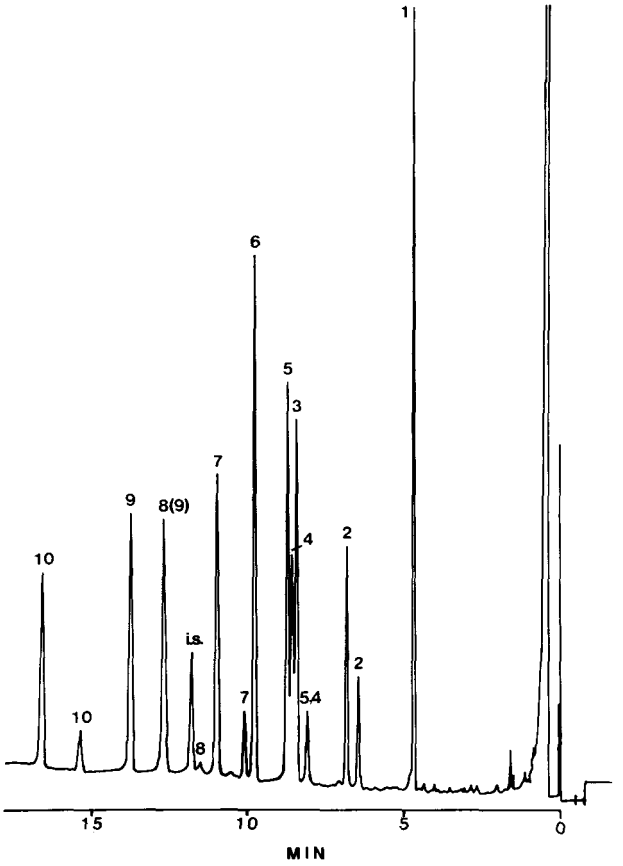

FIGURE 2 Gas chromatogram of a standard solution of 2,4-dinitrophenylhydrazones (6 nmole/ml of each). 1 μl injected.

1 = C_1, 2 = C_2, 3 = Acetone, 4 = Acrolein, 5 = C_3, 6 = iso-C_4, 7 = n − C_4, 8 = Crotonaldehyde, 9 = n − C_5, 10 = n − C_6. Capillary column: 16 m quartz, stat. phase SP 2100. GC condition: carrier gas H_2, flow rate 0.9 ml/min, temp. program. 180° to 250° with 2.5°/min, split ratio 1:16.

separation efficiency is good. Double peaks from unsymmetrically substituted carbonyls appear in the chromatograms for all carbonyl compounds but for formaldehyde and acetone, which yield symmetrical derivatives. The small peak of acrolein is, however, overlapped by the

small peak of propanal, and the small peak of n-pentanal is overlapped by the large crotonaldehyde peak. The ratios of the syn- and anti-isomers are presented in Table I at different concentrations. Propanal, acrolein and crotonaldehyde showed some ratio variations at different concentrations.

TABLE I

Peak ratio of the syn and anti geometrical isomers of the DNP-hydrazones obtained by glass capillary GC separation on 16 m quartz column coated with SP 2100

DNPH derivatives	Concentration interval		
	2–3 μg/ml	0.4–0.7 μg/ml	0.15–0.27 μg/ml
Acetaldehyde	1:0.45	1:0.43	1:0.47
Propanal	1:0.07	1:0.10	1:0.20
Acrolein	1:0.07	1:0.14	1:0.14
iso-Butanal	1:0.06	1:0.07	1:0.06
n-Butanal	1:0.16	1:0.21	1:0.21
Crotonaldehyde	1:0.04	1:0.10	1:0.11
n-Pentanal	1:0.18	1:0.20	1:0.24
n-Hexanal	1:0.20	1:0.17	1:0.20

TABLE II

Gas chromatographic limit of detection calculated as free carbonyls

Carbonyl compound	Detectable amount pg Split ratio 1:16 Signal noise ratio 10:1
Formaldehyde	1
Acetaldehyde	8
Propanal	8
Acrolein	11
Acetone	10
iso-Butanal	7
n-Butanal	9
Crotonaldehyde	12
n-Pentanal	14
n-Hexanal	30

The minimum detectable quantity for different carbonyl compounds, obtained with a split ratio of 1:16, is shown in Table II. Splitless injection technique results in approximately a decade higher sensitivity. A chromat-

TABLE III

Comparison of the GC/GC/EC and the HPLC methods using DNP-hydrazones (calc. as free carbonyls)

Carbonyl compounds	Car exhaust Sample vol. 5 litres mg/m³ HPLC	GC/GC/EC	% rel. stand. dev. n = 4[x)]	Urban air Sample vol. 11 litres µg/m³ HPLC	GC/GC/EC
Formaldehyde	5.1	5.5	3	650	600
Acetaldehyde	1.8	3.5	5	12	15
Acetone	0.5	0.8	2	7	41
Acrolein		0.8	2		trace
Propanal	0.4	0.5	3	9	10
Crotonaldehyde	0.1	0.2	6		
n-Butanal	0.2	0.1	9		
iso-Butanal		0.1	6		

[x)]GC/GC/EC precision

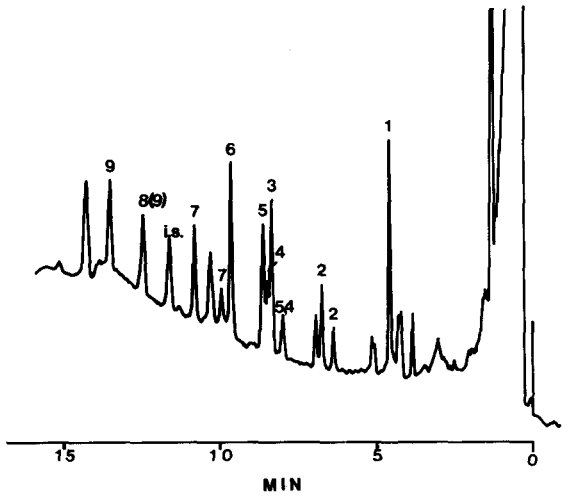

FIGURE 3 Splitless injection of 2 µl of the same solution as in Fig. 2, but diluted 50 times. GC conditions the same as in Fig. 2.

ogram with 0.24 pmoles of each carbonyl splitless injected is shown in Fig. 3. The precision is presented in Table III. Fig. 4 shows a typical separation of the DNP-hydrazones from a 5 litres car exhaust sample. The concentrations are presented in Table III. An 11 litres atmospheric sample

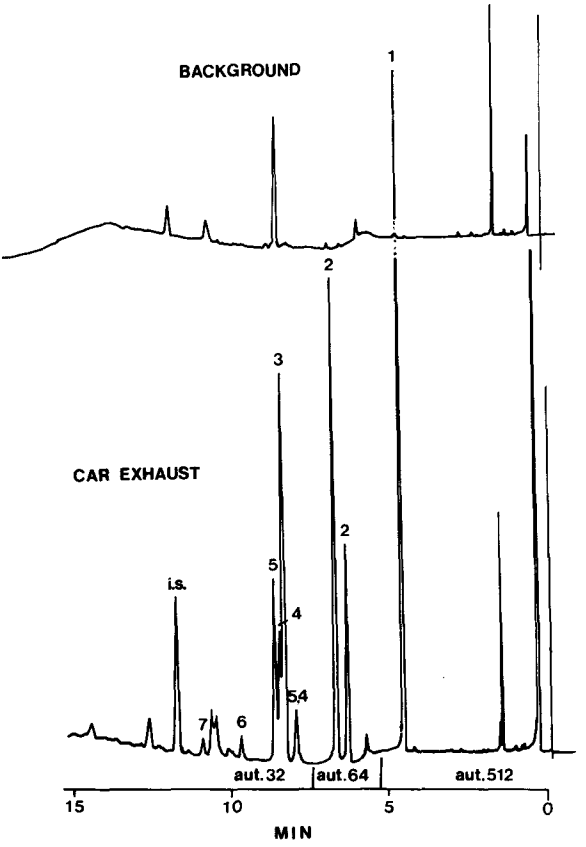

FIGURE 4 Car exhaust sample. Fig. notations and GC conditions the same as in Fig. 2. Background from the reagent solution is inserted.

was analyzed; result of which analysis is shown in Fig. 5. The sample was collected in the center of Göteborg city during daytime. As can be seen in Table III, the formaldehyde predominates.

Liquid chromatography

The separation of the DNP-hydrazones on straight phase column was not complete since acetone and propanal overlapped. In the reversed phase mode acrolein and acetone peaks interferred.

Fig. 6 shows the separation of 17 DNS-hydrazones on a reversed phase column with gradient elution. Isocratic separation of the same sample composition could be achieved in 89 minutes. The k′-values are reported in Table IV.

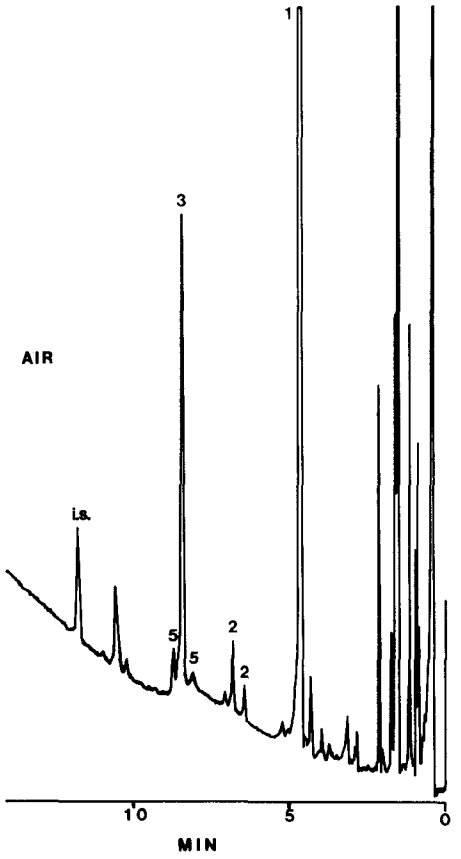

FIGURE 5 Air sample. Fig. notations and GC conditions the same as in Fig. 2.

The minimum detectable quantity for the DNS-hydrazone of formaldehyde $k' = 2.94$ was determined to 10 pg with a signal: noise of 3:1 (calculated as formaldehyde).

In Fig. 7 a chromatogram of carbonyl compounds as DNS-hydrazones from a car exhaust sample is shown. A second impinger flask in series was introduced to study the trapping efficiency in the first flask, which was found to be practically complete. In the same figure the background is also illustrated. The sampling volume was 1 litre, pump flow rate 80 ml/min. A chromatogram of DNS-hydrazones from an air sample of 18 litres is illustrated in Fig. 8 (1:2000 injected). As a comparison, an 11 litres sample of air from a heavy traffic situation is shown with the DNPH reagent and reversed phase separation (Fig. 9). The sample is concentrated

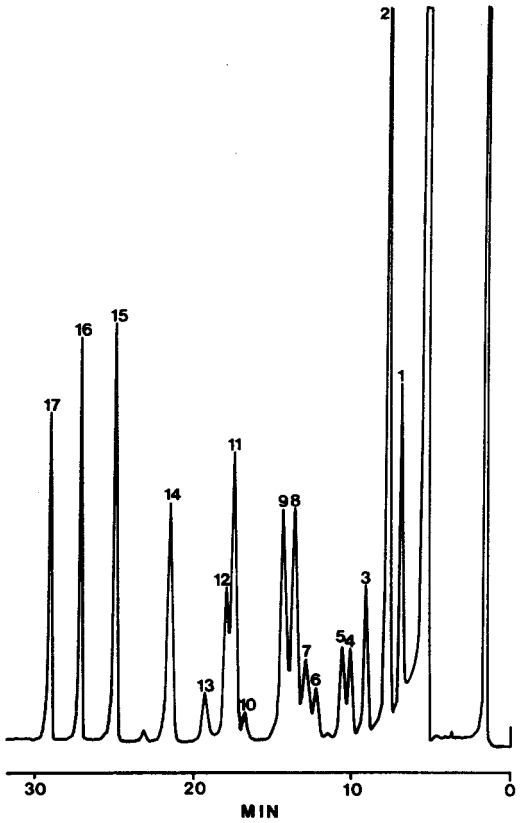

FIGURE 6 Separation of a standard mixture of 17 DNS-hydrazones. Column 200 × 5.0 mm, Nucleosil RP-C_{18} 5 μm. Mobile phase: acetonitrile/H_2O, gradient elution, 50% acetonitrile isocratic in 4 min., then linear gradient to 60% in 14 min. then linear gradient to 80% in 4 min. Flow rate 1 ml/min., 10 μl injected. 1 = C_1, 2 = C_2, 3 = Acetone, 4 = Acrolein, 5 = C_3, 6 = Crotonaldehyde, 7 = Methyl ethyl ketone, 8 = n−C_4, 9 = iso−C_4, 10 = Diethyl ketone, 11 = n−C_5, 12 = Benzaldehyde, 13 = Methyl isobutyl ketone, 14 = n−C_6, 15 = n−C_7, 16 = n−C_8, 17 = n−C_9.

40 times and the background is of importance since contaminants are concentrated simultaneously. The concentrations as free carbonyls are presented in Table III.

An investigation was carried out to study the trapping efficiency and the linear relationship using the DNS-hydrazin reagent. A warmed up car engine was presumed to regenerate constant amounts of carbonyls per time unit. Samples were taken during stable idle running for analysis after 15 min, 30 min etc. The results are shown in Fig. 10. The sampling flow rate was 0.2 l/min.

TABLE IV

k'Values for different DNS-hydrazones. Reversed phase C_{18} column. Mobile Phase: acetonitrile/water 50/50

DNS derivatives	Retention time (min)	k'
Formaldehyde	7.10	2.94
Acetaldehyde	8.00	3.44
Acetone	9.46	4.25
Acrolein	10.48	4.82
Propanal	11.00	5.11
Crotonaldehyde	12.80	6.11
Methyl ethyl ketone	13.60	6.55
n-Butanal	14.40	7.00
i-Butanal	15.38	7.54
Diethyl ketone	18.66	9.37
n-Pentanal	19.80	10.00
Benzaldehyde	20.76	10.53
Methyl isobutyl ketone	23.00	11.78
n-Hexanal	27.90	14.50
n-Heptanal	40.40	21.44
n-Octanal	59.40	32.00
n-Nonanal	89.20	48.55

Comparative studies of the different methods

As a starting point the DNPH reagent was used to perform comparative studies using the same samples. The DNPH reagent is well studied as far as the sampling procedure is concerned. Then the produced DNP-hydrazones from the same samples were run in parallel with the GC and

TABLE V

Comparison of the HPLC/UV method with DNPH-derivatives and the HPLC-fluorescence method with DNS-derivatives. Sample volume 3 1 and the same sampling flow rate 0.2 l/min.

Carbonyl compounds	UV (DNPH) mg/m^3	Fluorescence (DNSH) mg/m^3
Formaldehyde	6.1	5.9
Acetaldehyde	5.7	5.4
Acetone	3.3	1.4
Acrolein	2.4	1.8
Propanal		2.4
Benzaldehyde	3.5	3.5

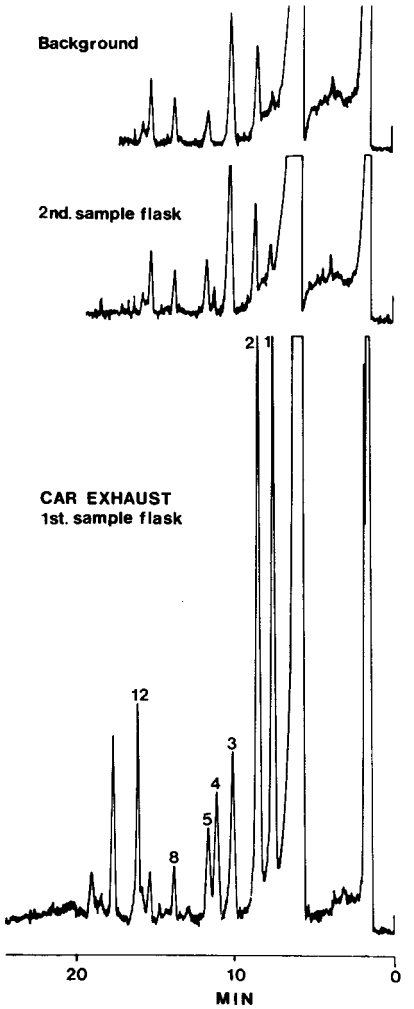

FIGURE 7 HPLC chromatogram of DNS-hydrazones from a car exhaust sample. Sample volume 1 l. Condition as in Fig. 6 except for the gradient elution: acetonitrile/H_2O isocratic 5 min. 50/50, then linear gradient to 80% acetonitrile in 10 min.

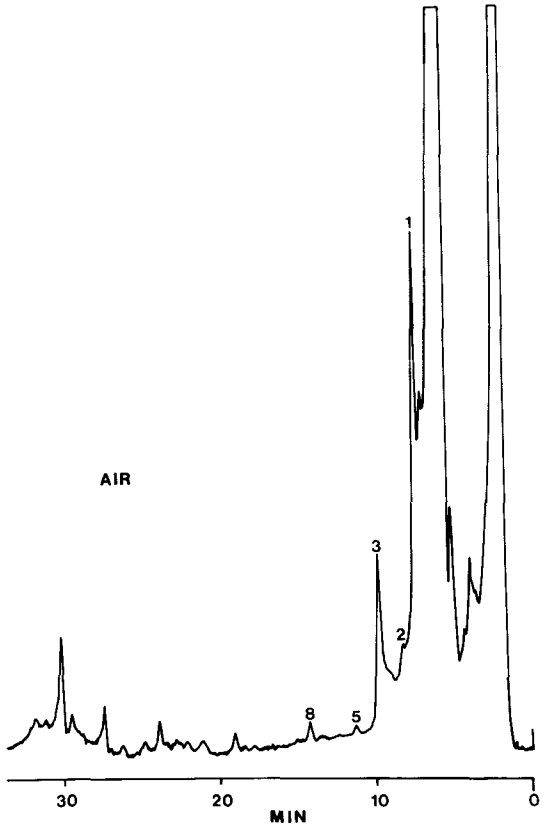

FIGURE 8 HPLC chromatogram of DNS-hydrazones from a sample collected at a low traffic intensity area. Sample volume 18 l. 10 μl untreated sample injected. Conditions as in Fig. 6.

the HPLC systems to compare the instrumental accuracy. The results from the car exhaust and the urban air samples are presented in Table III. There are some discrepancies which cannot be explained from this experiment. For instance, acetone is a serious contaminant in laboratory environment. The high formaldehyde concentrations in the urban air compared to the other carbonyls, show that this compound partly originates from other sources than car exhausts.

The DNPH reagent was compared to the DNSH reagent using the same carbonyl compound producing source. The car was used as in the experiment presented in Fig. 10. The sampling conditions were exactly the same for both the reagents. The results were in good agreement, as can be seen in Table V.

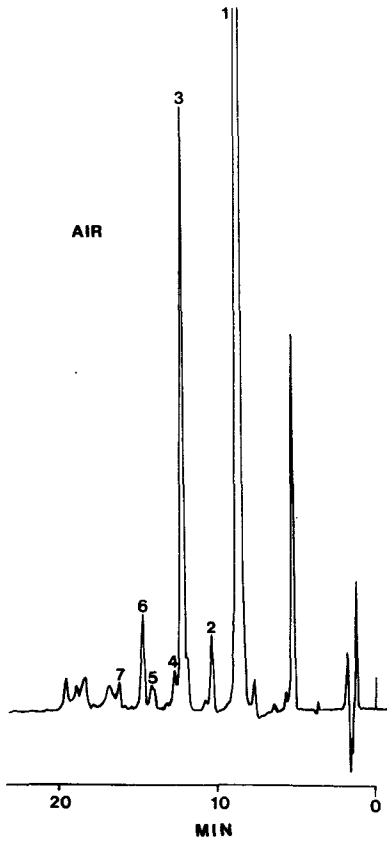

FIGURE 9 HPLC chromatogram of DNP-hydrazones in a sample from urban air with a heavy traffic situation. Column 200 × 5.0 mm Nucleosil RP−C_{18}, 5 μm. Mobile phase: acetonitrile/H_2O linear gradient 50–70% acetonitrile in 10 min. Flow rate 1 ml/min. 10 μl injected.

1 = C_1, 2 = C_2, 3 = Acetone/Acrolein, 4 = C_3, 5 = Crotonaldehyde, 6 = n−C_4/iso−C_4, 7 = Benzaldehyde.

DISCUSSIONS

Sampling procedure

The sampling procedure using impinger flasks and DNPH reagent solution have earlier been studied by Fracchia *et al.*[18] and Kuwata *et al.*[10] The trapping efficiency for 2-pentanone was found to be 71% with two flasks in series and a sampling rate of 1 l/min. At lower pump rate, or 0.85 l/min the recovery was 84%.[18] The pump rate is of importance for quantitative studies and should not exceed 1 l/min. The long chain

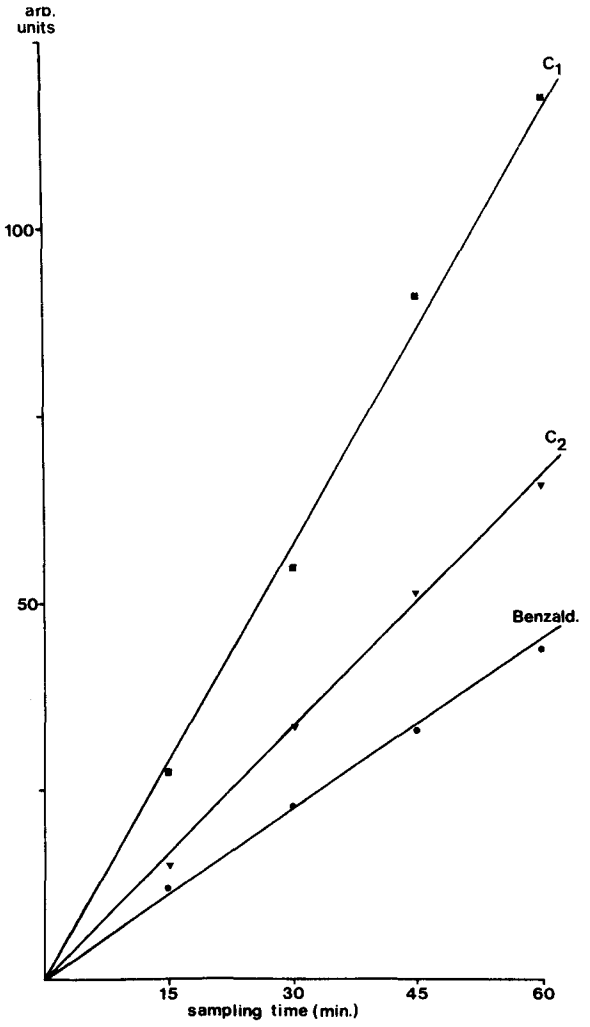

FIGURE 10 Plot of formed quantities of DNS-hydrazones versus sampling time(volume). A stabilized car engine was the carbonyl generator. Sampling volume 31/15 min.

aldehydes or especially the long chain ketones are not quantitatively dissolved and derivatized in one bubble flask because of a stripping effect which carries them over to the next flask. Selim[8] proposed to use a two phase reaction medium using water isooctane which gave better recovery with DNPH reagent. The reaction products, the DNP-hydrazones, were

TABLE VI
The capability of the different methods

Method	Instrumental minimum detection quantity† Free carbonyls	Sample vol. needed litres 100 μg formaldehyde/m³
HPLC/UV, DNPH	100 pg/10 μl	0.4
HPLC/fluorescence, DNSH	10 pg/10 μl	0.1
GC/GC/EC, DNPH	1 pg/μl	0.4
Splitless injection	0.1 pg/μl	0.04

†HPLC signal/noise 3:1
GC signal/noise 10:1

partitioned into the organic phase thus causing a favorable shift in the reaction equilibrium. In our experience the solubility of the carbonyls in the water phase is the important factor when trace amounts are considered. The DNSH reagent dissolved in a water methanol mixture was more efficient to trap carbonyls since they were better dissolved in the trapping solution. Thus in this case one impinger flask was sufficient to trap the carbonyls.

Recovery studies done by injecting known amounts of carbonyls into a purified air stream followed by trapping are difficult to interpret. The long chain carbonyls are easily adsorbed on glass surfaces and lost before they reach the reagent solution. Aldehydes are the most readily auto-oxidizable substances yielding peroxy acids with air. Our experiments with the addition of a known amount of propanal yielded a total recovery which varied between 75–100%. Kuwata *et al.*[10] studied the precision of the sampling and the subsequent analysis by preparing a 50 litres plastic bag containing aldehydes in air as a sample source. Five litre samples were then repeatedly collected and analyzed. The result showed good precision of the method. We used a idle running car engine as a carbonyl generating source for methodological studies. Since a certain amount of carbonyls were generated per time unit the experiment serves as a standard addition technique (Fig. 10). The experiment is more realistic than the injection of a known amount of carbonyls into an air stream.

The GC/GC/EC/ and the HPLC/UV methods are including an extraction step with hexane. The formed DNP-hydrazones were quantitatively extracted with hexane. Hexane was selected since this solvent was easily purified and proper for GC/GC/EC studies. Moreover, hexane is a better extractant for the hydrazones than for the reagent. The derivatives are stable in the hexane solution.

GC-GC-EC studies

The elimination of the excess of the DNPH reagent is a prerequisite for GC/GC/EC studies since the reagent, which is weakly basic and aggressive, rapidly attacks the glass capillary column. The separation of the acidic derivatives is carried out on a quartz column with acidic properties. By eliminating the reagent the separation conditions can be maintained constant. A large amount of the reagent is also badly affecting the EC detector. Benzaldehyde was eluted very late with the GC conditions used and is thus not shown in Figs. 2–5. The selected conditions were optimized to give acceptable resolution with the common aliphatic carbonyls including its syn- and anti-isomers for reproducible quantitative measurements. When packed GC-columns are employed propanal, acrolein and acetone overlap.[3] Another advantage with glass capillary columns is that a higher sensitivity is obtained especially with splitless injection.

Both straight phase and reversed phase HPLC can be used to separate DNP-hydrazones. However, problems due to overlapping peaks occur. Though it is possible to achieve separation of the most common carbonyls, acetone and propanal interfer in straight phase HPLC. In reverse phase mode n-butanal and iso-butanal as well as acrolein and acetone merge. With the latter system the hexane solvent has to be changed to methanol before injection.

HPLC studies

The HPLC separation of the DNS-hydrazones on a reversed phase system yields complete resolution in contrary to the DNP-hydrazones. However, too large an excess of reagent yields a broad peak which interferes with the DNS-formal-dehyde-hydrazone peak as can bee seen in Fig. 8. This problem may be partly overcome by proper selection of reagent concentration in the sampling flask. The reverse phase HPLC separation of the DNS-hydrazone is carried out by direct injection of the sampling solution without an extracting step which is a great advantage. The interferences of trapped substances other than the carbonyls are reduced with fluorescence detection since both excitation and emission wavelengths had to coincide. The DNS-hydrazones could not be isolated for recovery studies, therefore comparative studies with the DNP-hydrazones were needed.

In Table VI the capability of the different methods is compared with respect to instrumental minimum detection quantity and sample volume needed. The values presented in the Table VI are calculated from the used procedures and should not be considered as definite for the different methods. By using various extraction and concentration steps the de-

tection limit may be further enhanced. The hexane extract (40 ml) in the HPLC/UV and GC/GC/EC methods may easily be further concentrated. Furthermore larger injection volumes can be used especially in the HPLC reversed mode. The practical limit of detection is mostly dependent on the achievement of a low background from solvents, reagents etc.

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