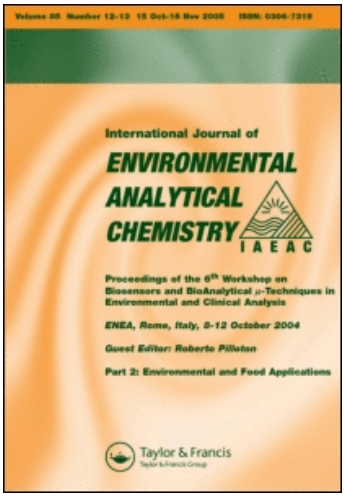

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Cecily M. Druzik[a]; Daniel Grosjean[b]; Antoinette Van Neste[b]; Sucha S. Parmar[b]
[a] The Getty Conservation Institute, Marina del Rey, CA, USA [b] DGA, Inc., Ventura, CA, USA

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SAMPLING OF ATMOSPHERIC CARBONYLS WITH SMALL DNPH-COATED C18 CARTRIDGES AND LIQUID CHROMATOGRAPHY ANALYSIS WITH DIODE ARRAY DETECTION

CECILY M. DRUZIK

The Getty Conservation Institute, 4503 Glencoe Avenue, Marina del Rey, CA 90292, USA

DANIEL GROSJEAN,* ANTOINETTE VAN NESTE and SUCHA S. PARMAR

DGA, Inc., 4526 Telephone Road, Suite 205, Ventura, CA 93003, USA

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Carbonyls in air are sampled using small DNPH-coated C18 cartridges and analyzed by liquid chromatography with diode array detection. Carbonyl structure confirmation is obtained by comparing diode array spectral scans of samples to the uv-visible spectra (190–600 nm) of some 20 carbonyl hydrazones recorded in the $CH_3CN—H_2O$ eluent used for LC analysis. Analytical detection limits are 0.09–3.4 nanograms carbonyl and correspond to 0.14–1.24 ppb in 60 L air samples. Accuracy was ±5% as measured for independently prepared hydrazone standards. The precision was 1–5% for multiple injections of hydrazone standards and 2–10% for replicate analysis of indoor and outdoor air samples. Excellent agreement was obtained in an interlaboratory comparison that included hydrazone standards as well as indoor air samples.

Cartridge collection efficiency has been tested over a range of conditions (sampling flow rate, volume of air sampled, presence of co-pollutants including photochemical oxidants) and is >0.95 for monofunctional carbonyls, unsaturated carbonyls, and alpha dicarbonyls. Carbonyl recovery by cartridge elution is >0.99 for all carbonyls tested. Examples of applications are given in the fields of atmospheric chemistry, indoor air pollution in museums, and outdoor air quality.

INTRODUCTION

The determination of trace amounts of carbonyl compounds is of critical importance in a number of industrial, biomedical and environmental applications. In the field of air quality alone, carbonyls are actively investigated as pollutants emitted by indoor and outdoor sources and as products of hydrocarbon reactions in photochemical smog.[1]

While conventional colorimetric methods are still in use, liquid chromatography analysis of carbonyls as their 2,4-dinitrophenylhydrazones, DNPH-LC, has gained acceptance in recent years.[2–4] Thus, this method is now recommended by the Intersociety Committee and by the US Environmental Protection Agency for the determination of formaldehyde and other carbonyls in air.[5,6]

*To whom correspondence should be addressed.

Early field applications of the method involved sampling with impingers containing acidic solutions of DNPH in appropriate solvents.[7,8] Since impingers are not practical, for example, in large field studies or for sampling at remote locations, subsequent studies have focused on sampling with DNPH coated on solid sorbents.[9-12] In particular, Kuwata *et al.*[12] have proposed the use of small C18 cartridges coated with DNPH to collect airborne carbonyls in urban and industrial atmospheres.

In this article, we present new results concerning both sampling and analytical aspects of the DNPH-LC method. With respect to sampling, we present collection efficiency data for DNPH-coated C18 cartridges as well as validation results obtained under laboratory and field conditions. With respect to analysis, we have for the past three years employed a diode array detector, and have recorded uv-visible spectra of carbonyl 2,4-dinitrophenylhydrazones under conditions identical to those used for LC analysis. Thus, the combination of hydrazone retention time and uv-visible spectrum allows for positive identification of a large number of carbonyls, including dicarbonyls and keto acids, in complex mixtures. Examples of applications are given in the fields of atmospheric chemistry, air pollution and indoor air quality with focus on airborne carbonyls in museums.

METHODS OF PROCEDURE

Synthesis of Hydrazones

All chemicals were obtained commercially in the highest purity available. The reagent 2,4-dinitrophenylhydrazine (DNPH) was recrystallized twice from hot HPLC-grade ethanol. The corresponding carbonyl 2,4-dinitrophenyl hydrazones were synthesized by mixing ethanol solutions of the carbonyl and of acidic DNPH.[13] They were slowly recrystallized from hot ethanol (most carbonyls), ethyl acetate (glyoxylic acid, hydroxyacetone), or 20:1 by volume tetrahydrofuran-chloroform (glyoxal and methylglyoxal), and stored in the dark at refrigerator temperature. Purity checks were carried out by LC analysis of dilute solutions of DNPH and of hydrazones in HPLC-grade acetonitrile. Confirmation of hydrazone structure was obtained by chemical ionization mass spectrometry.[14]

Liquid Chromatography Analysis

Low uv-cutoff HPLC grade acetonitrile and HPLC-grade water (Burdick and Jackson) were filtered through a 0.5 μm pore size polytetrafluoroethylene filter and a 0.45 μm mixed cellulose ester filter, respectively. The eluent was 55:45 by volume acetonitrile-water and was continuously degassed by helium sparge.

The LC system included a Waters 510 pump, a 20 μL Rheodyne loop injector, a Waters Resolve C18 Guard-Pak guard column, a 2 μm stainless steel precolumn filter, a Waters Resolve C18 spherical 5 μm stainless steel column, 3.9 $\times$ 150 mm, kept at 30 °C in a column heater, and a Hewlett–Packard 1040 uv-visible diode

array detector controlled by an HP85 computer. The eluent flow rate was 1.0 mL/min.

Preparation and Use of DNPH-Coated Cartridges

Small polyethylene cartridges (volume 0.5 mL) containing 0.4 gram of neutral, hydrophobic C18 sorbent packed by radial compression (Sep-Pak, Waters) were used in this work. Each cartridge is first cleaned and wetted by slowly pushing 2 mL of HPLC-grade water followed by 2 mL of HPLC-grade acetonitrile, and is then loaded with 2 mL of a solution containing 0.14 g DNPH and 1 mL conc. H_3PO_4 in 100 mL CH_3CN. A batch of 25–50 cartridges is then allowed to dry overnight in a vacuum dessicator. Passive contamination during the drying step is minimized by placing in the dessicator filter paper impregnated with acidic DNPH. The paper acts as a passive collector for airborne carbonyl impurities.[15]

Once dry, each cartridge is sealed with Teflon tape, wrapped in aluminum foil, placed in a glass vial with Teflon-lined screw cap, and stored refrigerated in the dark. Several cartridges from each batch are analyzed for background carbonyl content.

Air samples are collected by removing the Teflon tape, connecting the downstream end of the cartridge to a calibrated flowmeter and a small air sampling pump (e.g. Barnant Air Cadet, or battery-activated "personal" sampling pump, e.g. SKC or Gillian) and activating the pump manually or with a timer.

For indoor sampling, especially in museums where noise is a prime consideration, we have found it advantageous to modify and use quiet, compact aquarium pumps (e.g. Hagen Optima, rating 30 decibels). Pump, timer, flowmeter, cartridge and tubing connections are housed in a compact tool box-size sampling unit for convenient transport and operation in the field. Typical sampling flow rates are in the range 0.25–2.0 L min^{-1}. After sampling, each cartridge is resealed with Teflon tape, wrapped in aluminum foil, returned to its glass vial, and stored refrigerated in the dark.

Cartridge Analysis

Each cartridge is eluted slowly with 2 mL of HPLC-grade acetonitrile, and 100 μL aliquots of the eluate are injected into the sampling loop with a syringe equipped with an in-line 0.2 μm pore size Teflon or nylon filter. As the peaks elute, 190–600 nm uv-visible spectra of each hydrazone are recorded using the diode array detector. Carbonyl identification involves matching the hydrazone spectrum in the sample to that of a reference "library" that we have constructed by diode array scanning of authentic samples synthesized as described above and injected as dilute acetonitrile solutions on the LC, under conditions identical to those used for sample analysis. Carbonyl quantitation involves external standards, i.e. acetonitrile solutions of precisely weighed amounts of the hydrazones of interest. The corresponding response factors (at 360 nm or any other selected wavelength, see

Results and Discussion) are calculated from absorbance vs. concentration plots. Several hydrazones have limited solubility in acetonitrile, e.g. about 85 and 40 μg/mL for the di-hydrazones of glyoxal and methylglyoxal, respectively. Thus, care should be exercised, in preparing hydrazone calibration solutions, to stay below eluent solubility limits. Examples of calibration curves are given in Figure 1.

RESULTS AND DISCUSSION

UV-Visible Spectra of Carbonyl Hydrazones

Spectra of carbonyl hydrazones in 55:45 CH_3CN—H_2O obtained with the diode array detector have been recorded for some 20 carbonyls. Examples are given in Figure 2. Individual spectra for all compounds studied are compiled in a technical report[16] available from the authors. Absorption maxima are summarized in Table 1 along with the corresponding retention times. The relation between carbonyl structure and hydrazone absorption characteristics is apparent from Table 1. Hydrazones of monofunctional aliphatic carbonyls have, like DNPH, adsorption maxima near 360 nm: aliphatic substituents have only a minor effect on the hydrazone chromophore. The introduction of an aromatic substituent shifts the maximum absorption from 360 to about 385 nm, e.g. see benzaldehyde in Figure 2. More substantial chromophore modification results in larger bathochromic shifts, e.g. from 360 to 410–430 nm for the hydrazones of dicarbonyls, e.g. see methylglyoxal in Figure 2.

An advantageous feature of the diode array detection method is the simultaneous recording of chromatograms at several wavelengths (up to 8 with our instrument). By selecting appropriate "diagnostic" wavelengths, e.g. 360, 390 and 415 nm, and by examination of absorbance ratios at any combination of two wavelengths, e.g. 430/360 nm, it is possible to selectively scan complex carbonyl mixture for their aliphatic, aromatic and dicarbonyl components, see example in Figure 3. Detection limits are also optimized by carrying out calibrations at or near the wavelength of maximum absorption. This is particularly useful for hydrazones with lower molar absorptivities such as those of dicarbonyls.

Hydrazone Retention Times and Divide Array Scans: Diagnostic Value

Hydrazone retention times are plotted in Figure 4 according to carbonyl functional group and to number of carbon atoms. Hydrazone retention times, like absorption characteristics, are closely related to carbonyl structure. Thus, structural assignments can be made with great confidence by matching uv-visible spectra *and* retention times of unknown carbonyls in the sample to those of the reference "library" we compiled in the course of this work. As the information is generated on-line during LC analysis of the samples, diode array scans offer a rapid and cost-effective alternative to off-line methods such as IR or mass spectrometry. Isomers and/or structural homologues, which often have identical

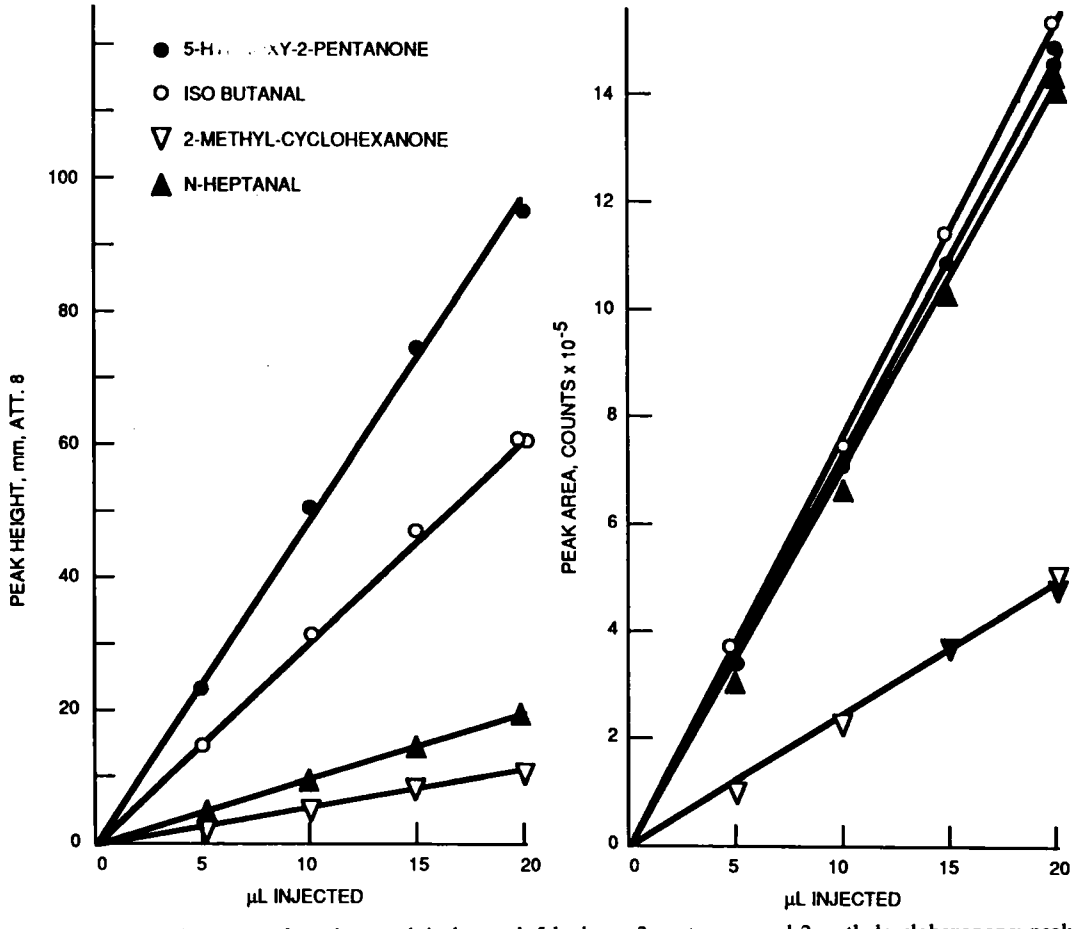

Figure 1 Calibration curves for *n*-heptanal, isobutanal, 5-hydroxy-2-pentanone and 2-methylcyclohexanone: peak height (left) and peak area (right) vs. amount of carbonyl hydrazone injected.

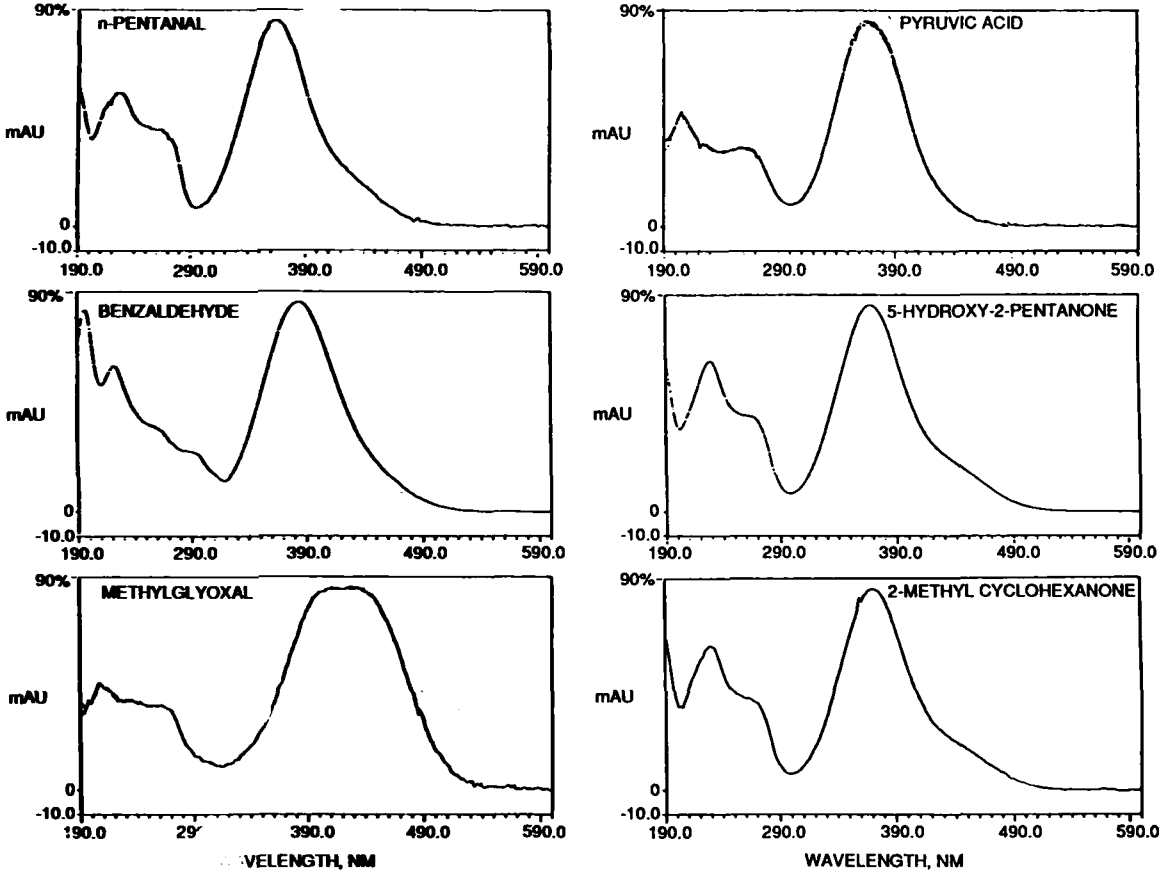

Figure 2 UV-visible spectra (190–600 nm) of selected carbonyl 2,4-dinitrophenylhydrazones recorded with diode array detector. Solvent: 55:45 $CH_3CH—H_2O$.

Table 1 Maximum absorption wavelengths and retention times of carbonyl 2,4-dinitrophenyl hydrazones in 55:45 CH3CN—H20

Carbonyl	*Hydrazone λ max, nm*	*Hydrazone retention time, relative to that of formaldehyde*	
		Method A[a]	*Method B*[b]
DNPH reagent	357	0.63	0.6
5-Hydroxy-2-pentanone	369	0.89	0.9
Formaldehyde	353	(1.00)	(1.00)
Acetaldehyde	363	1.30	1.3
Acrolein	373	1.69	1.7
Acetone	367	1.74	1.8
Propanal	365	1.91	2.0
Glyoxylic acid	355	—	2.2
Crotonaldehyde	—	—	2.4
Methylvinylketone	—	—	2.6
Methacrolein	—	—	2.7
Methyl ethyl ketone	367	2.67	2.8
n-Butanal	363	2.71	2.9
Isobutanal	363	2.75	3.0
Pyruvic acid	369	3.50[c]	3.2
Benzaldehyde	385	3.28	3.5
Glyoxal	437	3.80	3.9
3-Pentene-2-one	—	—	3.9
n-Pentanal	363	4.05	4.3
Methylglyoxal	427	6.00	5.9
n-Hexanal	363	5.99	6.5
2-Methylcyclohexanone	371	6.51	66
n-Heptanal	359	9.41	9.3
Biacetyl	412	11.26	12.5

[a]Method A: conditions given in experimental section, $T = 30\,^{\circ}C$, retention time of formaldehyde hydrazone = 3.47 min.

[b]Method B: 55:45 CH3CN—H_2O eluent, solvents filtered on 0.2 μm Teflon filters, no helium sparging, SSI Model 300 pump, 20 μL Valco injection loop, Whatman Partisphere C18 guard cartridge, Whatman Partisphere 5 μm C18 column, 110 × 4.7 mm, $T = 19$–$22\,^{\circ}C$, Perkin Elmer LC 75 uv-visible detector, absorbance setting 0.01 aufs, Hitachi D-2000 integrator, eluent flow rate 1 mL/min, retention of formaldehyde hydrazone = 3.36 min.

[c]On Radial Pak C18 cartridge with radial compression module, $T = 30\,^{\circ}C$, retention time of formaldehyde hydrazone = 3.73 min.

mass or IR spectra, are less likely to have identical retention times *and* uv-visible spectra. Only small amounts of sample (micrograms) are needed, and the risk of contamination in subsequent sample handling is eliminated. Thus, the diagnostic value of our method compares favorably to that of conventional off-line methods for carbonyl identification in complex mixtures.

Detection Limits

Detection limits for air samples are limited either by the analytical detection limit or by the background carbonyl hydrazone content of the cartridges. We have found the latter to be the determining factor for formaldehyde, acetaldehyde and

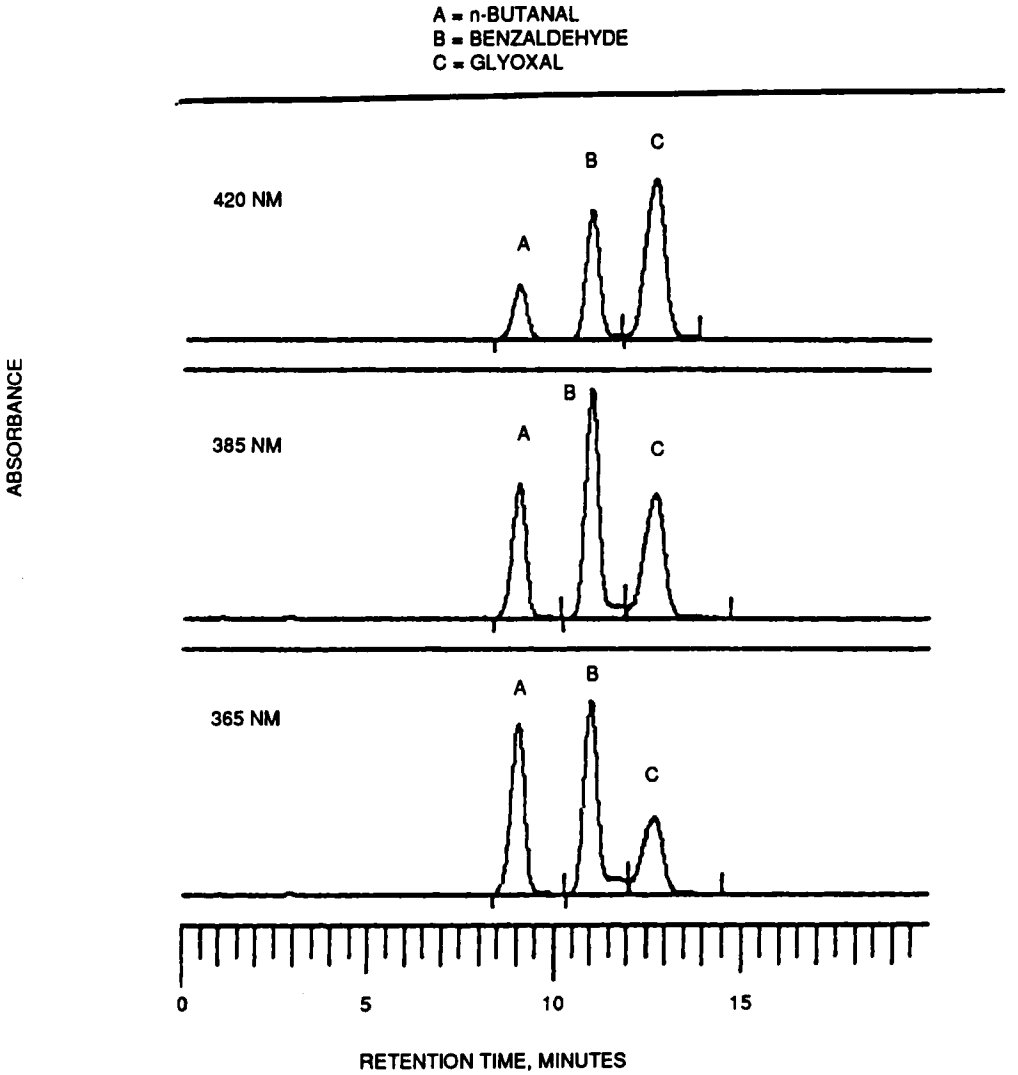

Figure 3 Multiwavelength chromatogram of mixture of *n*-pentanal, benzaldehyde, and glyoxal hydrazones.

acetone, see Table 2. Analytical detection limits are in the range 0.09 to 3.4 nanograms. Ambient air detection limits (in a 60 L sample) range from 0.14 to 1.24 ppb.

Analytical Performance

A measure of accuracy and precision is given by comparing several standard

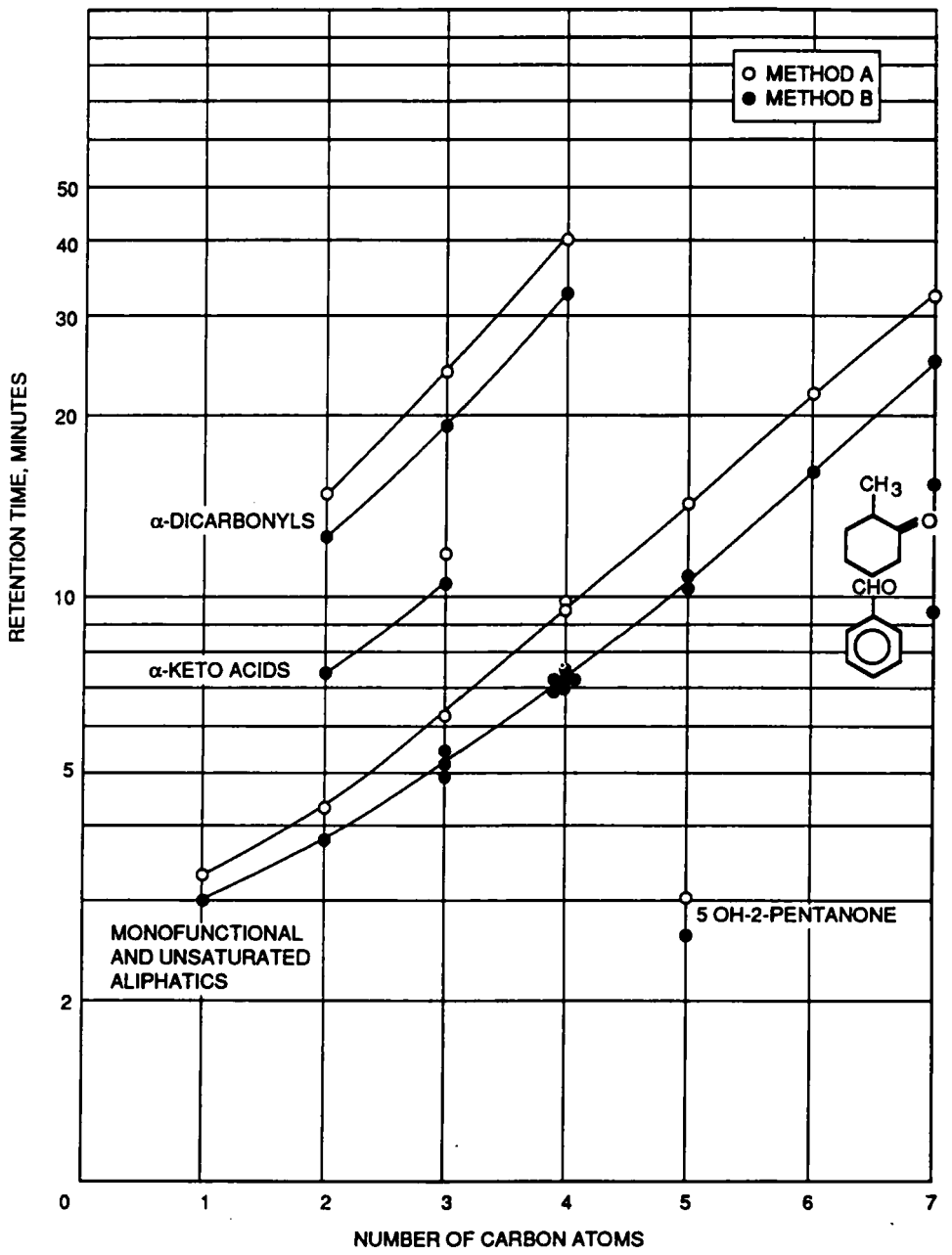

Figure 4 Retention times of 2,4-dinitrophenylhydrazones vs. carbonyl carbon number for aliphatic monofunctional carbonyls, dicarbonyls and ketoacids. Open symbols: method A, conditions given in Experimental Section. Solid symbols: methods B, see Table 1.

Table 2 Analytical detection limits, cartridge background carbonyl content, and lowest quantifiable limit for 60 L air samples

	Analytical detection limit[a]	*Equivalent per cartridge*[b]	*Measured cartridge background*[c]	*LQ L ppb*[d]
Formaldehyde	0.09	9	56[e]	0.76
Acetaldehyde	0.12	12	60[e]	0.55
Acetone	0.21	21	70[e]	0.49
n-Butanal	0.6	60	n.d.[f]	0.34
Pyruvic acid	1.15	115	n.d.	0.53
Benzaldehyde	0.75	75	n.d.	0.29
Propanal	0.20	20	n.d.	0.14
2-Butanone	0.30	30	n.d.	0.17
n-Pentanal	0.65	65	n.d.	0.31
n-Hexanal	0.5	50	n.d.	0.20
5-Hydroxy-2-pentanone	0.60	60	n.d.	0.24
2-Methylpropanal	0.95	95	n.d.	0.54
2-Methyl cyclohexanone	3.4	340	n.d.	1.24
n-Heptanal	2.9	290	n.d.	1.04
Acrolein	0.65	65	n.d.	0.47

[a]At 360 nm, 20 μL injected, S/N = 3, units nanograms carbonyl.

[b]2 mL elution, same units as ref. (a).

[c]15 cartridges from 6 different batches, prepared over a nine-month period, RSD $\leq$ 15%, same units as ref. (a).

[d]LQL = lowest quantifiable limit in a 60 L air sample.

[e]LQL is limited by cartridge background.

[f]n.d. = none detected, LQL is calculated from analytical detection limit.

solutions independently prepared by dissolving recrystallized, dried solid hydrazones in acetonitrile. Results in Table 3 indicate agreement within typically $\pm 5\%$, where the scatter among independently prepared standards reflects mostly gravimetric and volumetric errors. RSDs are 1–5% for multiple injections of standard solutions, and 2–10% for replicate analyses of indoor, outdoor and laboratory-generated (smog chamber) air samples.

The long-term performance of the system is monitored by periodical re-analysis of standard solutions (as a rule we employ at least two independently prepared standard solutions along with each batch of samples). The results in Table 3 indicate good system stability over a nine-month period during which (a) more than 500 carbonyl samples have been analyzed and (b) the LC instrument had been used alternatively for carbonyl analysis and for other applications using different columns and eluents.[17,18]

Another measure of analytical performance involves interlaboratory comparison of calibration mixtures and of field samples analyzed according to a "blind" protocol. Figure 5 summarizes the results of a study involving the analysis, using two different sets of LC equipment, of 8 hydrazone standards and 14 indoor air samples collected at ten Southern California museums. The data shown in Figure 5 show good agreement and can be described by the following unweighed least squares regression parameters (slope $\pm 1\sigma$, intercept $\pm 1\sigma$, correlation coefficient):

formaldehyde, 8 standards: $1.08 \pm 0.10 \quad -0.26 \pm 0.37 \quad 0.974$

Table 3 Analysis of independently prepared hydrazone standards

Standard used[b]	*Peak Height, mm, for 1 μg/mL carbonyl*[a]:								
	Formaldehyde				*Acetaldehyde*				
	5A	*C1C2*	*Others*	*RSD, %*	*5A*	*5B*	*C1C2*	*Others*	*RSD, %*
Date:									
6/88	18.9(2)	21.0(2)	—	5.3	12.7(2)	—	13.9(2)	—	4.5
7/88	19.4(7)	22.0(4)	—	6.3	12.7(6)		13.9(3)	—	5.2
8/88	21.2(3)	23.7(2)	—	5.6	15.2(3)	13.8	15.8(2)	—	2.4
9/88	21.0(2)	23.6(2)	—	5.8	14.4(2)	14.7(2)	15.6(2)	—	4.0
10/88	21.4(8)	21.1(4)	—	0.7	14.8(8)	14.7(3)	15.0(2)	—	1.3
12/88	21.8(7)	25.3(9)	—	7.4	15.6(5)	—	16.6(8)	—	3.1
1/89	20.8(8)	—	B19.1(18)	8.0	14.4(9)	—		B13.6(18)	3.5
			C18.3(6)					C14.5(6)	
		—	U21.6(3)					U14.3(3)	
2/89	17.8(2)	—	D17.5(6)	0.8	12.1(2)			D12.9(6)	4.0

[a]Method B (see Table 1), number of replicates in parentheses.

[b]concentrations, μg/mL formaldehyde and acetaldehyde, respectively: 5A: 5.0, 5.31; 5B: 0, 5.31; C1C2: 2.86, 3.93; U: same as C1C2 but stored refrigerated for 7 months; B: 2.86, 4.71; C: 3.46, 2.51; and D: 3.16, 3.61.

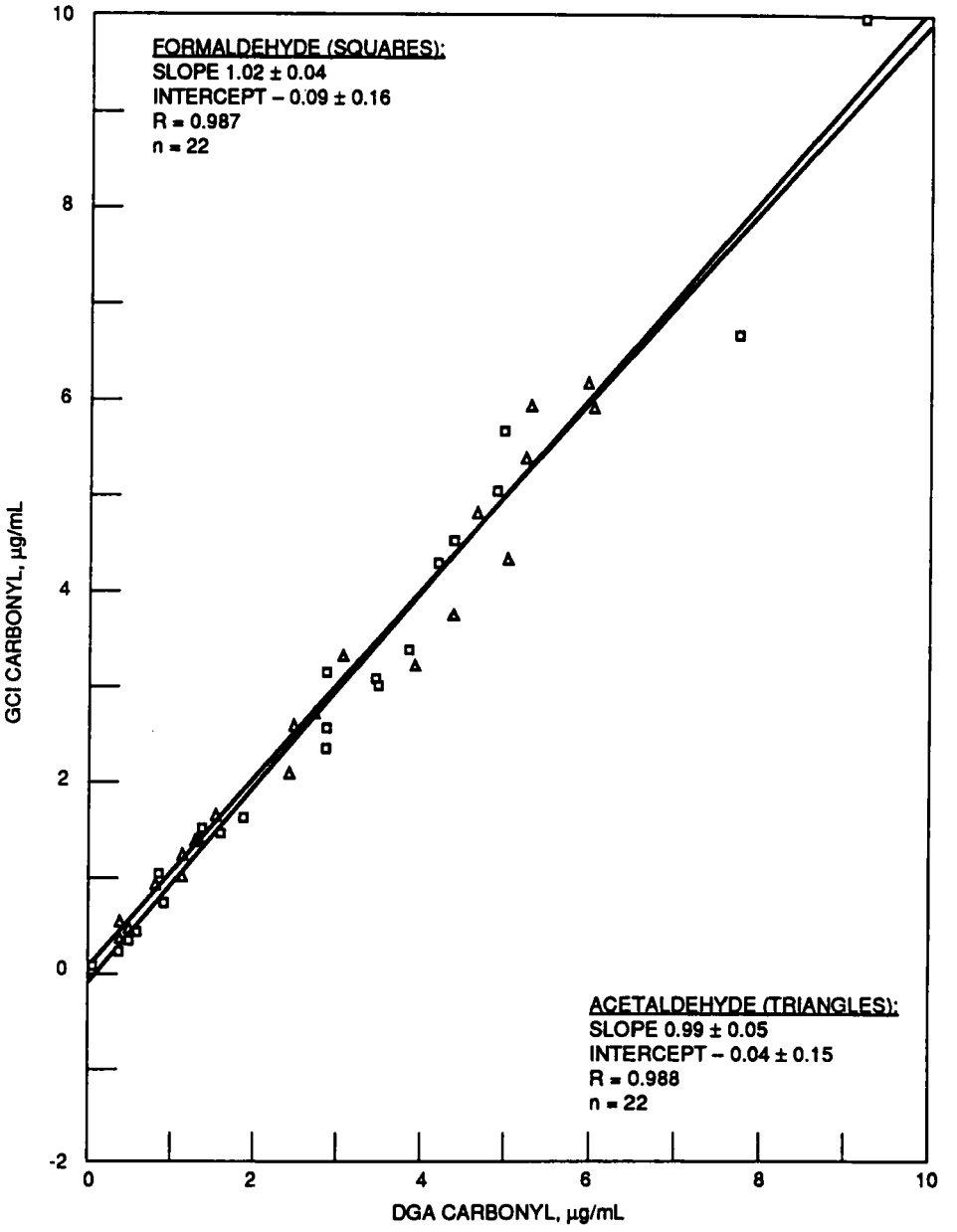

Figure 5 Interlaboratory comparison of hydrazone standards.

14 samples:	1.0 ±0.04	−0.08 ±0.16	0.990
combined ($n=22$)	1.02 ±0.04	−0.09 ±0.16	0.987
acetaldehyde, 8 standards:	1.03 ±0.09	−0.10 ±0.42	0.976
14 samples:	0.947 ±0.034	0.11 ±0.09	0.992
combined ($n=22$)	0.990 ±0.05	0.04 ±0.15	0.988

Cartridge Collection Efficiency

Satisfactory collection of airborne carbonyls requires that the amount of DNPH loaded on the cartridge be in excess of that of the carbonyls to be collected. This condition is indeed satisfied: using calibration mixtures of DNPH reagent in acetonitrile, we have measured the DNPH load to be 0.95–1.0 mg per cartridge, consistent from batch to batch. This compares well to the nominal value of 0.7 mg per cartridge estimated from data in the experimental section. For comparison, a typical 100 L sample of air containing 20 ppb each of formaldehyde and acetone will yield a much smaller amount of carbonyls, 7.2 micrograms per cartridge.

Collection efficiencies, determined experimentally with two cartridges in series, are summarized in Table 4. Quantitative collection on the first (upstream) cartridge was observed in all cases for the six carbonyls tested. As indoor and outdoor air unavoidably contains pollutants other than carbonyls (e.g. NO, NO_2, SO_2, ozone, peroxyacetyl nitrate, hydrocarbons, chlorinated compounds, etc.) our tests were carried out under a range of actual (e.g. ambient air) and simulated air quality conditions (e.g. purified air, or heavily polluted air prepared in 4 m^3 Teflon smog chambers). The data in Table 4 reveal no effect of co-pollutants on carbonyl collection efficiency.

Elution Recovery

Table 5 summarizes the results obtained for two consecutive elutions of cartridges used for the collection of indoor, outdoor and laboratory (smog chamber) air samples, and indicates quantitative recovery for all carbonyl hydrazones studied to date.

Examples of Application

Table 6 presents indoor air concentrations in museums, where formaldehyde is of concern for its adverse effects on collections including corrosion of metals and damage to ethnographic objects. Also included in Table 6 are selected data for carbonyls in urban and non-urban air. For example, we have recorded high levels of acetaldehyde in Brazil as a result of the use of ethanol as a vehicle fuel.[19] Figure 6 shows data for a smog chamber experiment involving sunlight irradiation of ppb levels of a common hydrocarbon air pollutant, toluene, with oxides of

Table 4 Cartridge collection efficiency studies

Matrix air	*Number of samples*	*Volume sampled, L*	*Sampling flow rate, L/min*	*Collection efficiency*[f]			
				Formaldehyde	*Acetaldehyde*	*Acetone*	*Other carbonyls*
Acetaldehyde in pure air[a]	2	6	0.10	—	1.00	—	—
	2	6	0.21	—	1.00	—	—
Indoor air, office bldg.	2	120	2.0	0.96	0.96	>0.90	—
Smog mixture A[b]	2	6	1.3	0.96	1.00	0.97	methylglyoxal 1.00
Smog mixture B[c]	3	18	1.2	0.95	0.97	0.92	methacrolein 1.00, methylglyoxal 1.00
Smog mixture C[d]	2	5	0.6	1.00	1.00	1.00	methylglyoxal 1.00, glyoxal 1.00
Indoor air, museums[e]	26	360	2.0	0.962 ± 0.066	0.969 ± 0.052	—	—

[a]Acetaldehyde permeation tube.

[b]Sunlight irradiated mixture of ppb levels of 2-methyl-2-butene and NO in purified air. Also contained ozone, NO2, peroxyacetylnitrate, and other photochemical air pollutants.

[c]Same as ref. (b) with 100 ppb methacrolein added

[d]Ozone and 2-methyl-2-butene in pure air in the dark.

[e]Range of concentrations: formaldehyde 1–27 ppb, acetaldehyde 0–19 ppb.

[f]2 cartridges in series, CE = upstream/(upstream + downstream).

Table 5 Elution recovery

Matrix air	*Carbonyl content, μg/cartridge*	*Elution recovery*[a,b]		
		Formaldehyde	*Acetaldehyde*	*Other carbonyls*[c]
Acetaldehyde in pure air	0.5–139	—	>0.996(6)	—
Indoor air, office bldg.	0.2–30	0.994(6)	0.996(6)	acetone>0.999(6)
Indoor air, museums		1.00(8)	1.00(2)	—
Outdoor air, Los Angeles area, CA	0.5–60	>0.999(5)	>0.998(5)	acetone>0.998(5) 2-butanone>0.995(5) benzaldehyde>0.985(5) C4 aliphatics>0.992(5) C5 aliphatics>0.988(5)
Outdoor air, Sao Paulo, Brazil	5–120	>1.00(3)	1.00(3)	acetone 1.00(3) propanal 1.0(3) acrolein 1.00(3) benzaldehyde 0.996(3)

[a]2 consecutive elutions with 2 mL CH_3CN. Recovery = first elution/(first elution + second elution); number of experiments in parentheses.

[b]Cartridges properly eluted and cleaned can be re-used many times for sampling.

[c]C4 aliphatics = *n*-butanal, isobutanal, unsaturated isomers; C5 aliphatics = pentanal isomers, 2- and 3-pentanone, and unsaturated isomers.

Table 6 Carbonyls concentrations in indoor (museums) and outdoor air

Location	*Date*	*Formaldehyde, ppb*	*Acetaldehyde, ppb*
Indoor samples (museums)[a]:			
Museum A	2/18/87	2.0	3.6
Museum B	7/29/88	4.7	10
		20	31
Museum C[b]	8/12/88	3.5	4.2
	8/15/88	1.9	4.5
Museum D	8/30/88	17	13
Museum E	9/16/88	20	24
Museum F	10/4/88	55	23
	10/4/88	40	35
	10/5/88	90	14
University campus library	9/15/88	10	13
Outdoor samples:			
Urban:			
Six sites in Los Angeles, CA area[c]	12/11/88	3.0–12.3	3.3–9.9
	12/17/88	2.4–7.9	1.7–5.4
	12/23/88	4.1–9.2	4.0–8.4
	12/29/88	2.1–16.5	2.3–5.0
Brazil[d]			
Sao Paulo, downtown	10/23/86	4.4	19.2
Sao Paulo, University campus	6/29/88	10.7	13.5
Rio de Janeiro, residential area	9/22/87	0.7	4.1
Rio de Janeiro, tunnel	1/8/87	60	231
Salvador, residental area	9/22/88	7.8	15
Non-urban[e]			
Santa Cruz Island, CA	6/88	0.95(3)	0.65(3)
San Nicholas Island, CA	7/87	0.60(2)	0.35(2)
South Pacific (Tahiti and Moorea, French Polynesia)	7/87	0.12 ± 0.04(6)	<0.04(6)

[a]All located in the Los Angeles area except Museum A located in eastern U.S.
[b]Measurements taken in empty building shortly before first opening to the public.
[c]Range of individual values, 24-hour samples.
[d]See ref. 19.
[e]Mean value, number of samples in parentheses.

nitrogen in air. The reaction products formaldehyde, benzaldehyde, glyoxal and methylglyoxal were readily identified from comparison of the sample diode array spectra to those of reference hydrazone standards.

Conclusions

The DNPH cartridge-diode array LC method described here has already found applications in a number of studies including museum air quality, outdoor air pollution, and atmospheric chemistry research. Once carbonyl hydrazone spectra have been recorded, full diode array scans are no longer needed in most applications, and carbonyl samples can be simply analyzed at 2–3 "diagnostic" wavelengths. Thus, the spectral data presented herein can also be used to identify

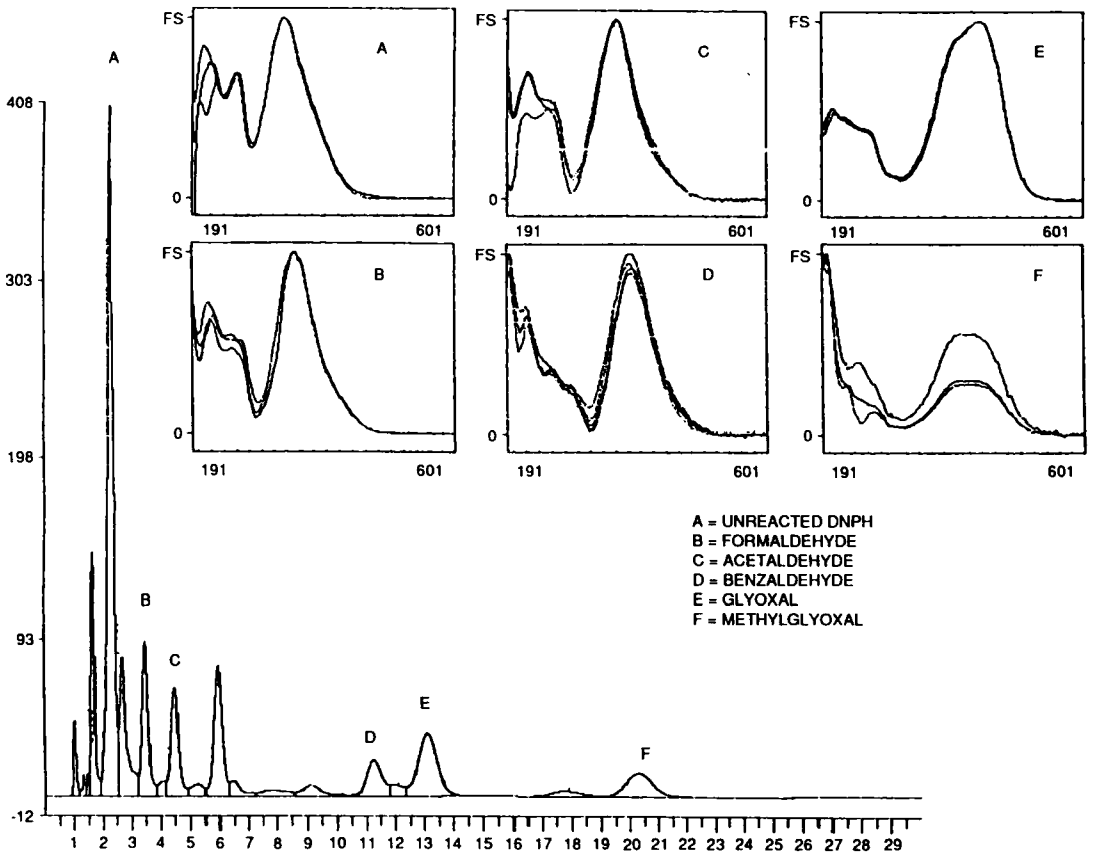

Figure 6 Diode array chromatogram and scans of a sample of atmospheric oxidation products of toluene.

carbonyls in complex mixtures using standard, inexpensive LC hardware. While the focus of our study is on the determination of trace levels of carbonyls in air, the method may be suitable for other environmental applications.

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