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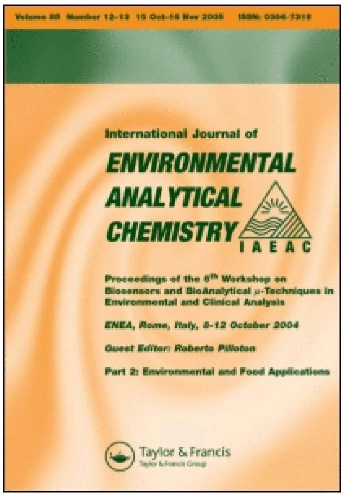

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PERFORMANCE OF DNPH-COATED C_{18} CARTRIDGES FOR SAMPLING C_1-C_9 CARBONYLS IN AIR

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The sampling performance of C_{18} cartridges coated with DNPH has been studied for twenty four C_1-C_9 carbonyls in experiments involving sampling of parts per billion levels of carbonyls in urban air, indoor air and laboratory experiments. The cartridge background carbonyl content in thirty six batches of cartridges averaged 85, 137 and 155 nanogram/cartridge for formaldehyde, acetaldehyde and acetone, respectively, and was below analytical detection for all other carbonyls. Carbonyl-DNPH derivative recovery from the cartridge was complete in the first elution with 2 mL acetonitrile, and this for twenty four carbonyls at concentrations of 0.02–73 μg carbonyl/cartridge. Studies carried out using two cartridges in series showed no breakthrough, for the sixteen carbonyls tested, at concentrations of 0.10–49 μg carbonyl/cartridge and volumes of air sampled = 6–370 L. Average relative standard deviations (RSD) for replicate analyses were 0.20–13.2% for twenty one carbonyls. Average RSD for co-located samples were 0.9–16.2% for eighteen carbonyls. Comparison of RSD for replicates and RSD for co-located samples for thirteen carbonyls indicated that the overall method precision was limited by sampling precision rather than by analytical precision.

KEY WORDS: Aldehydes, ketones, dinitrophenylhydrazine, urban air, indoor air

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INTRODUCTION

Formaldehyde and other carbonyls in air are often measured as their 2,4-dinitrophenylhydrazine (DNPH) derivatives by liquid chromatography with ultraviolet detection[1-20]. An important component of this method is the sampling step. A number of sampling devices have been employed in the past, e.g. impingers containing DNPH in various solvents[3,4] and tubes packed with glass beads coated with DNPH[8]. Work in recent years has focused on the use of small sampling cartridges packed with solid sorbents coated with DNPH[9-15]. Of the several sorbents available, one, the C_{18} (octadecyl) liquid chromatography column packing material, has been employed by a number of investigators[9,11-15]. Thus, cartridges packed with C_{18} and coated with DNPH, first used by Kuwata *et al.*[9] for sampling carbonyls in air, continue to be widely employed for the collection of carbonyls in vehicle exhaust, outdoor air, indoor air and laboratory studies of carbonyls as reaction products of the atmospheric oxidation of hydrocarbons[16-20]

The performance and limitations of the DNPH-coated C_{18} cartridge have been discussed in several studies[9,11,14]. However, these studies were generally limited to a few carbonyls such as formaldehyde and to a few examples given to illustrate method performance. To our knowledge, no comprehensive study of the DNPH-coated C_{18}

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cartridge has been carried out. The objective of this article is to present, for up to twenty four carbonyls, data for cartridge background carbonyl content, cartridge breakthrough, elution recovery, analytical precision and overall (sampling + analytical) method precision.

The twenty four carbonyls studied are important as contaminants in outdoor and indoor air and as major products of the photochemical oxidation of hydrocarbons in the atmosphere. The information may be of value not only to researchers in the field but also to the numerous laboratories, in the U.S. and elsewhere, that have begun routine measurements of carbonyls in air as part of recently implemented air pollution monitoring programs. Some of these programs call for the collection and analysis, every year, of thousands of samples on cartridges packed with C_{18} or other sorbents and coated with DNPH[21,22]

EXPERIMENTAL METHODS

Coating of C_{18} cartridges with DNPH

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All solvents were HPLC-grade (Baker, Burdick and Jackson). Acetonitrile was tested for carbonyl impurities by addition of acidic DNPH followed by liquid chromatography analysis. The C_{18} cartridges employed were Sep-Pak, short body "Classic" (Waters Chromatography Division, Millipore Corp.), particle size 55–105 μm, carbon loading 12%, 360 mg sorbent per cartridge, surface pH = 7. Batches of C_{18} cartridges were washed with 4–5 mL acetonitrile using a glass syringe fitted with a Teflon plunger. The acetonitrile flow rate through the cartridge was 8–10 mL/min. Following this step, 2 mL of a freshly prepared DNPH solution (0.143 g DNPH, recrystallized twice from hot ethanol, in 99 mL acetonitrile + 1 mL conc. H_3PO_4) were loaded on the cartridge at a flow rate of 4 mL/min. Batches of DNPH-coated cartridges were placed in a desiccator on sheets of aluminum foil washed with acetonitrile. The desiccator was kept under vacuum for 48 h. Contamination was minimized by placing several DNPH-coated glass fiber filters or paper filters (47 mm diameter) in the desiccator along with the cartridges and by inserting a DNPH-coated filter or cartridge between the desiccator and the vacuum pump. These filters act as passive samplers for possible carbonyl contaminants. After drying, each cartridge was sealed with Teflon tape, wrapped in aluminum foil washed with acetonitrile, and placed in a clean glass vial which was then sealed with a Teflon-lined cap. Batches of vials containing cartridges coated with DNPH were stored in sealed plastic bags that contained several DNPH-coated filters (again acting as passive samplers for carbonyl impurities). Cartridges prepared in this manner were stored in the dark at 2–4 °C

Cartridge elution

Following sampling, the contents of the DNPH-coated C_{18} cartridges were eluted with 2 mL of acetonitrile at a flow rate of 2 mL/min. The eluate was collected in a 4 mL amber glass vial sealed with a Teflon-lined screw cap and was stored at 2–4 °C in the dark prior to analysis. The sample volume was measured by weighing the eluate and dividing the value obtained by the density of CH_3CN (0.785 g/mL at 20°C). For the C_{18} Sep-Pak "Classic" cartridge, we have measured sample volumes of 1.71 ± 0.06 mL (n = 13, relative standard deviation = 3.4%) for first elutions and 2.05 + 0.07 mL (n = 3, RSD

= 3.4%) for second elutions. Thus, the cartridge "hold-up" volume is 0.29 ± 0.06 mL for the first elution.

Liquid chromatography analysis

The carbonyls employed as starting materials were from commercial sources (Aldrich, Sigma, Fluka, PolyScience, highest purity available). DNPH (Aldrich) was recrystallized twice from hot ethanol, rinsed 2–3 times with ethanol, dried under slight vacuum for 1 min and subsequently for 1–2 hours in a dessicator, and analyzed by LC for possible carbonyl impurities[23]. The carbonyl 2,4-dinitrophenylhydrazones were synthesized as described previously[23].

Acetonitrile solutions of carbonyl-DNPH standards and of air samples were analyzed by liquid chromatography (LC) with uv detection as described previously[23]. The eluent was 55:45 or 53:47 by volume acetonitrile-water, the eluent flow rate was 1.4 mL/min. and the detection wavelength was 360 nm. Two C_{18} analytical columns have been employed: a Whatman Partisphere column (5 µm, 110 × 4.7 mm) with a Whatman Partisphere C_{18} guard cartridge at an eluent flow rate of 1.0 mL/min and an Axxiom ODS column (5 µm, 150 × 4.7 mm, Cole Scientific Inc.) with a C_{18} guard cartridge (Brownlee Applied Biosystems).

Calibration standards were prepared by weighing the solid hydrazones and dissolving them in acetonitrile. Calibration curves were constructed by plotting, at a detection wavelength of 360 nm, absorbance (peak height) vs. concentration for five concentrations of the carbonyl-DNPH standard. Least squares linear regression of the data yielded slopes, i.e. response factors, that were used to calculate the concentrations of carbonyls in the cartridge samples[23].

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Types of samples studied

The performance of the DNPH-coated C_{18} cartridge was evaluated in a number of studies involving the collection of ppb levels of carbonyls in outdoor air, indoor air and laboratory experiments. Outdoor air samples were collected at twelve locations in urban southern California (one sample was collected in a highway tunnel) and at four locations in the urban Atlanta, GA, area. Sampling flow rates were 0.3–0.8 L/min and sampling durations ranged from 2 to 24 h. The volumes of air sampled were 100–460 L. Indoor air samples were collected in an office building in Ventura, CA. The sampling flow rates were 0.3–0.4 L/min, the sampling durations were 4, 24 and 48 h and the volumes of air sampled were 100, 550 and 1,100 L. Laboratory samples were collected for 10, 30 or 60 min at flow rates of 0.5–0.8 L/min. The volumes of air sampled were 6–9 L (10 min samples) and 18–132 L (30 min. and 60 min. samples).

The laboratory samples were collected in four types of smog chamber experiments: (a) sunlight irradiations of mixtures of a reactive organic compound with nitric oxide in purified air; (b) reaction, in the dark, of a reactive organic compound with ozone in purified air; (c) thermal decomposition of peroxyacyl nitrates, $RC(O)OONO_2$, in the presence of excess nitric oxide in purified air, and (d) calibration experiments involving ppb levels of carbonyls, singly or as mixtures, in purified air[24–32]. Reactive organic compounds studied included alkenes, isoprene, terpenes, unsaturated alcohols and unsaturated carbonyls at initial concentrations of 0.1–1.0 ppm. The major carbonyl products of these reactive organics, e.g. methacrolein from isoprene[24] and nopinone from β-pinene[26,27], were also used as starting materials in several experiments. Co-pollutants present in the matrix air included the reactive organic compound studied, oxides of nitrogen (NO and NO_2), ozone, cyclohexane (added to scavenge OH in the ozone-organic compound experiments), several carbonyls formed as reaction products and one or more of the peroxyacyl nitrates present either as reaction products in the organic-NO-sunlight experiments[24–26,29] or as starting materials in the thermal decomposition studies[30–32].

Co-located samples

Co-located samples were collected in ambient air (relative humidity = 40–90%) and in smog chamber experiments (relative humidity = 55 ± 10%). In ambient air, co-located samples were collected using the two lines of dual sampling units, with the cartridge inlets being typically within 0.3 m of each other. In smog chamber experiments, co-located samples were collected in two ways, either as described above for ambient air samples with two short sections of Teflon tubing connecting the cartridge inlets to the sampling ports of the chamber or by sampling from a small glass manifold that was connected to the chamber by a short Teflon line. Sampling durations were identical for co-located samples; sampling flow rates were on occasions slightly different due to differences in pressure drop from one cartridge to the next.

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RESULTS AND DISCUSSION

Cartridge carbonyl background

DNPH-coated C_{18} cartridges contained detectable amounts of three carbonyls: formaldehyde, acetaldehyde and acetone. For all other carbonyls, the cartridge carbonyl content was below the analytical detection limit, which decreases with increasing carbonyl molecular weight since our calibrations are based on peak heights, i.e., the corresponding response factors decrease with increasing retention times[23]. Analytical detection limits for all carbonyls studied here have been given elsewhere[23]. They decrease, for example, from 7–14 nanograms per cartridge for the low molecular weight carbonyls formaldehyde, acetaldehyde, acetone and acrolein to 106 nanograms per cartridge for higher molecular weight carbonyls such as n-hexanal. The corresponding limits of detection for a sampling volume of 100 L range from 0.06 ppb for acrolein to 0.26 ppb for n-hexanal.

For formaldehyde, acetaldehyde and acetone, the limit of detection in air was limited by the cartridge background content, which varies from one batch of cartridges to the next. For thirty six batches of DNPH-coated C_{18} cartridges prepared over a five year period (June 1989–October 1994), the cartridge background contents were 9–423 ng for formaldehyde (consistent with 35–132 ng/cartridge reported in earlier work, see ref. 14), 12–450 ng for acetaldehyde and 84–805 ng for acetone. High values for formaldehyde probably reflect contamination during cartridge coating and handling. High values for acetone, and on occasions for acetaldehyde, often reflect the presence of these carbonyls as impurities in the acetonitrile solvent; the amount of acetone varies from one batch of acetonitrile to the next.

For the thirty six batches analyzed, average cartridge carbonyl contents were 85 ± 80,137 ± 95 and 155 ± 79 ng/cartridge (± one standard deviation) for formaldehyde, acetaldehyde and acetone, respectively. These averages correspond to limits of detection of 0.70, 0.78 and 0.65 ppb for formaldehyde, acetaldehyde and acetone, respectively, in 100 L of air. Lower cartridge background contents, and therefore lower detection limits, can be achieved using more elaborate acetonitrile clean-up procedures, for example CCl_4 extraction[12]. Acceptable detection limits depend on study objectives; those given above as examples are suitable for smog chamber, indoor air and polluted outdoor air (e.g. urban) studies. Our carbonyl background levels for DNPH-coated C_{18} cartridges compare favorably to those of < 150 ng/cartridge for formaldehyde and < 500 ng/cartridge for acetone in commercially available DNPH-coated silica gel cartridges[33].

Carbonyl-DNPH elution recovery

Recovery of carbonyl-DNPH derivatives was investigated by carrying out two consecutive elutions of cartridge samples with 2 mL acetonitrile. The cartridge loading (in fact a lower limit since unidentified carbonyls were not included) ranged from 2–8 µg carbonyl/cartridge for ambient air samples to 50–80 µg carbonyl/cartridge for smog chamber samples. For all carbonyls studied and for all but a few samples, no detectable amounts of carbonyl DNPH could be found in the second acetonitrile elution samples, thus indicating complete carbonyl-DNPH recovery in the first elution.

Data for individual samples are not listed and are summarized in Table 1 for the

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Table 1 Elution recovery of DNPH derivatives of C_1-C_9 carbonyls from DNPH-coated C_{18} cartridges.

Carbonyl	*Range of carbonyl content in first elution, µg carbonyl/cartridge*[a]	*Number of measurements*
Formaldehyde	0.04–42.5	35
3-Hydroxy-2-butanone	1.6 and 3.6	2
Acetaldehyde	0.10–39.3	35
Acetone	0.20–51.8	28
Arolein	0.06–1.2	5
Propanal	0.15–10.0	12
n-Butanal	0.08–32.6	13
2-Butanone	0.14–7.7	5
Methacrolein	0.08–52.3	7
Crotonaldehyde	0.11–0.32	4
Methyl vinyl ketone	18.1–30.1	3
n-Pentanal	0.02–3.4	7
3-Methyl-2-butanone	46.0–73.5	3
Cyclohexanone	0.10–39.2	15
Pyruvic acid	9.0 and 10.8	2
Benzaldehyde	0.27–7.0	3
Glyoxal	0.03–9.8	14
n-Hexanal	0.04–31.5	7
Methylglyoxal	0.05–16.5	7
n-Heptanal	0.42–39.3	4
n-Octanal	0.57	1
Nopinone[b]	3.8 and 32.4	2
4 Acetyl-1-methylcyclohexene	0.4 and 1.9	2
n-Nonanal	5.93	1

[a] the second elution yielded no detectable amount of carbonyl (most samples) or, in a few instances, measurable amounts that were less than 1.0% of the amount recovered in the first elution.

[b] 6,6-dimethyl bicyclo [3.1.1] heptan-2-one.

DNPH derivatives of twenty four C_1-C_9 carbonyls including aliphatic aldehydes (saturated and unsaturated), aliphatic ketones (saturated, cyclic and unsaturated), dicarbonyls, aromatics, hydroxycarbonyls and ketoacids. Also listed in Table 1 for each carbonyl is the range of concentrations measured in the first elution samples. Using the analytical detection limit (or the cartridge background content) as an upper limit for the actual carbonyl-DNPH concentration in the second elution samples, lower estimates of first elution recoveries can be made for all carbonyls listed in Table 1. These lower limits are, for example, > 99% for formaldehyde-DNPH, > 99% for acetaldehyde-DNPH, > 99% for acetone-DNPH, 92.0% for crotonaldehyde-DNPH (limited by the low range of concentrations studied) and 90.4% for n-nonanal-DNPH (limited by the low analytical detection limit). These results are consistent with those of previous studies involving formaldehyde and acetaldehyde in outdoor air samples[20].

Cartridge breakthrough studies

The possibility of breakthrough was investigated by collecting outdoor air, indoor air and smog chamber samples using two DNPH-coated C_{18} cartridges in series. Sampling flow rates were 0.2–0.8 L/min, sampling durations were 0.5–24 h and the volumes of air sampled were 6–370 L. Individual results are not listed and are summarized in Table 2 which includes, for the sixteen carbonyls tested, the range of concentrations tested and the number of experiments. With a few exceptions (reflecting acetone contamination and/or leak in the sampling line that connects the upstream and downstream cartridges), downstream cartridges contained no detectable amounts of carbonyls. Therefore, no breakthrough from the upstream cartridge was observed for any of the sixteen carbonyls studied.

The results summarized in Table 2 are consistent with the simple hypothesis that carbonyl-DNPH derivatives are retained on the cartridge as long as enough DNPH

Table 2 Summary of results for cartridge breakthrough studies.

Carbonyl	*Concentration measured on upstream cartridge, μg carbonyl/cartridge*[a]	*Number of experiments with two cartridges in series*
Formaldehyde	0.13–6.8	22
Acetaldehyde	0.14–38.8	22
Acetone	0.16–49.2	16
Propanal	0.10–2.1	14
n-Butanal	0.14–17.0	14
2-Butanone	0.30	4
Crotonaldehyde	0.11	4
n-Pentanal	0.10–16.3	11
Glyoxal	0.12–1.2	8
Cyclohexanone	0.16–12.4	21
n-Hexanal	0.21–20.1	8
3-Methyl-2-butanone	33.0–35.0	2
Methylglyoxal	0.42	4
n-Heptanal	0.42–15.6	6
n-Octanal	0.57	1
n-Nonanal	5.9	1

[a] absence of breakthrough was verified by measuring the carbonyl-DNPH content of the downstream cartridge.

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reagent is available. The DNPH loading of the C_{18} cartridges prepared in our laboratory is ca. one milligram per cartridge. This amount is sufficient to collect ca. 150 µg formaldehyde using any combination of sampling flow rate and sampling duration. Since the ambient air and smog chamber samples tested contained 2–8 and 50–80 µg carbonyl/cartridge, respectively, a large amount of unreacted DNPH was still available after sample collection and no breakthrough was observed. Breakthrough can occur once the DNPH reagent is depleted, e.g. when sampling larger volumes of air. For example, We have observed breakthrough for formaldehyde (30 ppb) and acetaldehyde (8 ppb) when sampling 1.7 m^3 of indoor air (sampling duration = 72 h): for these samples, liquid chromatography measurements of the amount of DNPH before and after sampling 92% of the DNPH initially present had been consumed.

Replicate analyses

A measure of analytical precision is given by results for replicate analyses. These results are summarized in Table 3 for twenty one carbonyls. Listed in Table 3 are the range of concentrations studied, the range of RSDs for all replicate analyses and the average RSD for each carbonyl. The results in Table 3 are for cartridge samples collected in ambient air and in smog chamber experiments: they do not include data for reference standards and for calibration mixtures, for which the RSD for replicate analyses is typically 1 percent or less[14,19,20]. Examples of individual results are shown in Figure 1 for formaldehyde, acetaldehyde, cyclohexanone and glyoxal.

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Table 3 Summary of results for replicate analyses.

Carbonyl	*Carbonyl concentration ppb*	*Relative standard deviation, percent*		*Number of measurements*
		Range	*Average*	
Formaldehyde	1.5–266	0–8.5	3.0	36
Acetaldehyde	0.6–528	0–25.0	3.6	35
Propanal	0.4–156	0–22.5	4.2	18
n-Butanal	0.3–435	0–13.9	3.9	18
n-Pentanal	0.18–407	0–3.8	1.3	12
n-Hexanal	0.07–400	0–10.8	2.8	12
n-Heptanal	0.76–202	0–6.5	3.8	3
Acetone	0.2–433	0–25.0	3.7	23
2-Butanone	0.34–101	0–1.0	0.20	5
Methyl vinyl ketone	136	2.9	2.9	1
3-Methyl-2-butanone	179–583	2.4–4.5	3.5	4
Cyclohexanone	0.22–384	0–9.8	3.1	23
Nopinone	14, 120	14.3, 5.8	10.0	2
4 Acetyl-1-methylcyclohexene	2.0, 10.6	15.0, 11.3	13.2	2
Methacrolein	365	4.7	4.7	1
Crotonaldehyde	0.20–0.82	6.1–15.0	9.5	3
Glyoxal	0.49–189	0–14.8	4.0	20
Methylglyoxal	1.1–295	0–9.0	2.8	8
3-Hydroxy-2-butanone	42, 130	0, 3.8	1.9	2
Benzaldehyde	0.17–6.2	0–16.1	7.1	4
m-Tolualdehyde	0.22, 0.26	0, 26.9	13.5	2

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1(a)

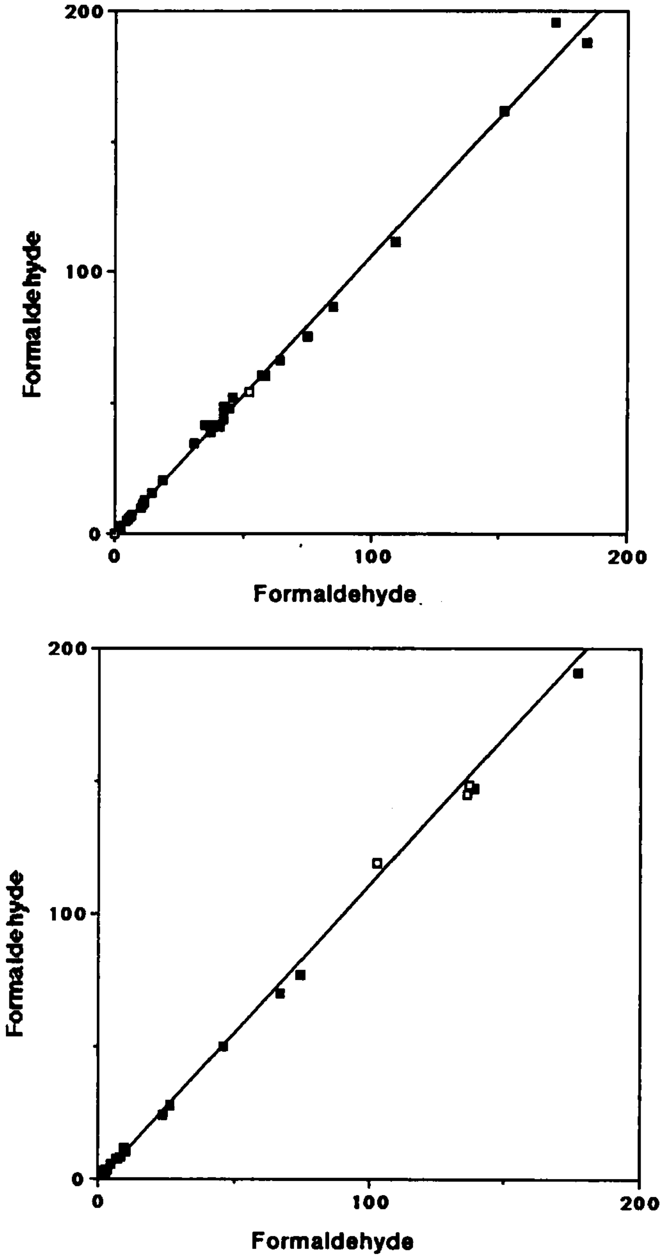

Figure 1 Scatter plots of results for replicate analyses (top) and for co-located samples (bottom) collected on DNPH-coated C_{18} cartridges. Results are shown for formaldehyde (1a), acetaldehyde (1b), cyclohexanone (1c) and glyoxal (1d). Several carbonyl concentrations (in ppb) are shown as one-fifth of actual value for clarity (open symbols). For replicates, linear least squares regression slopes (± one std deviation) were 1.050 ± 0.010 for formaldehyde (R = 0.999, n = 36), 1.013 ± 0.005 for acetaldehyde (R = 1.0, n = 35), 1.014 ± 0.006 for cyclohexanone (R = 1.0, n = 23) and 1.112 ± 0.044 for glyoxal (R = 0.989, n = 20). For co-located samples, linear regression slopes were 1.093 ± 0.009 for formaldehyde (R = 0.999, n = 26), 1.119 ± 0.015 for acetaldehyde (R = 0.998, n = 24), 1.054 ± 0.010 for cyclohexanone (R = 0.999, n = 28) and 1.133 ± 0.010 for glyoxal R = 0.999, n = 23).

1(b)

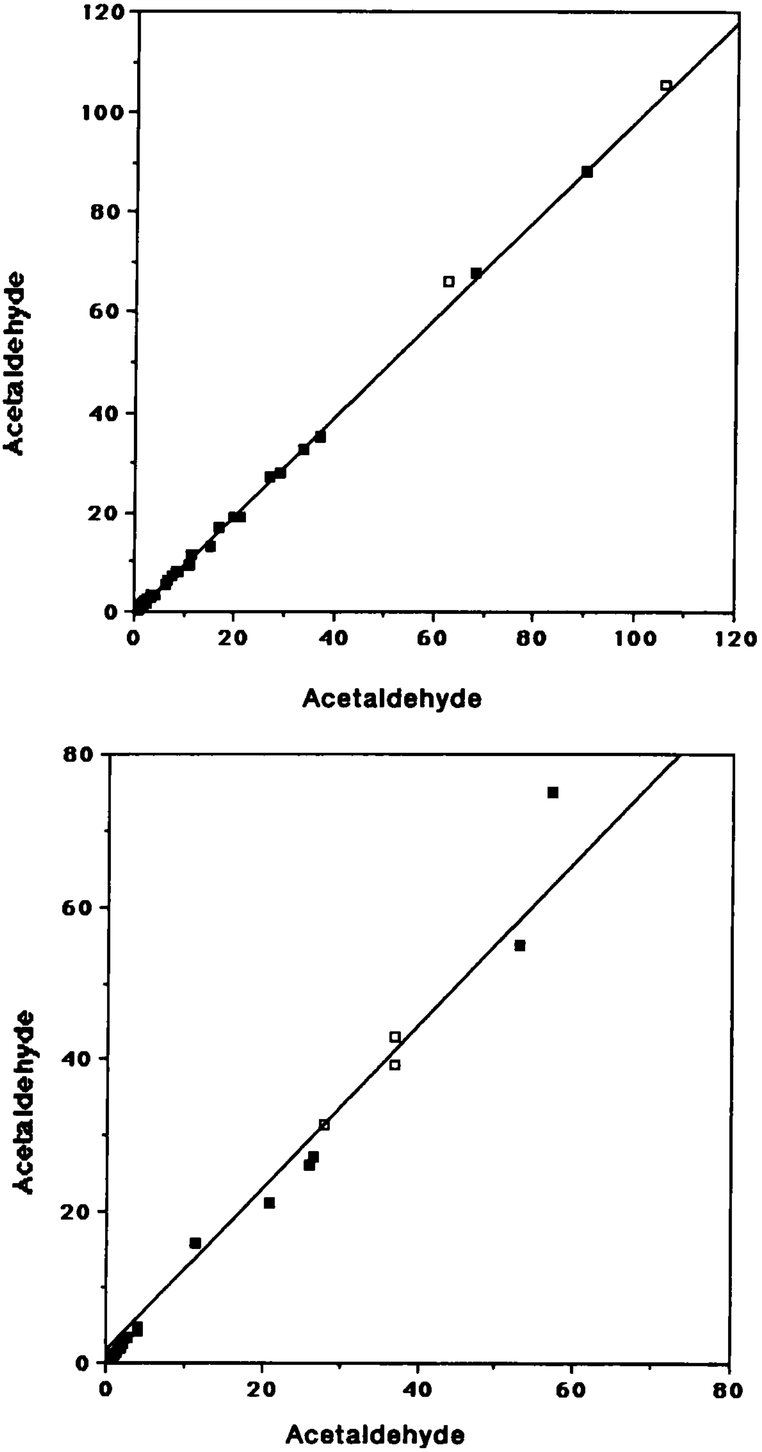

Figure 1 *Continued.*

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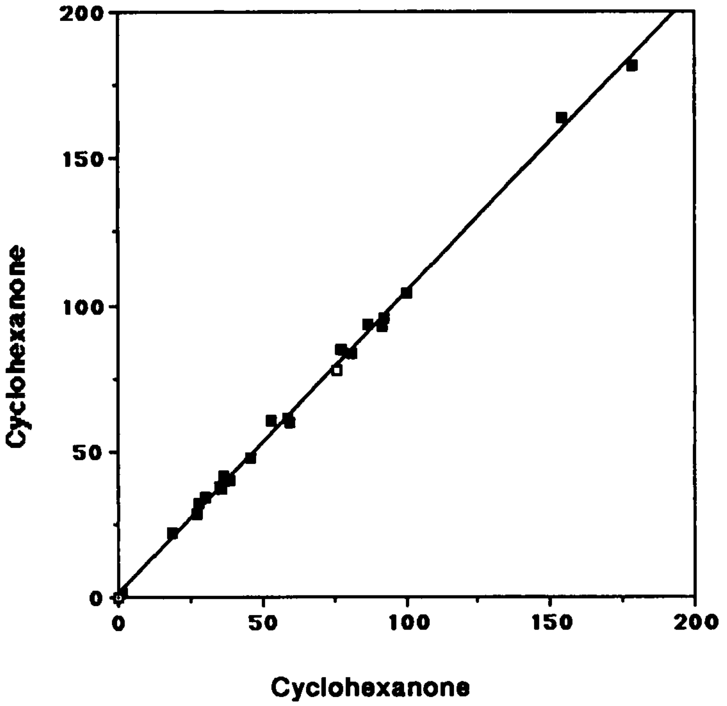
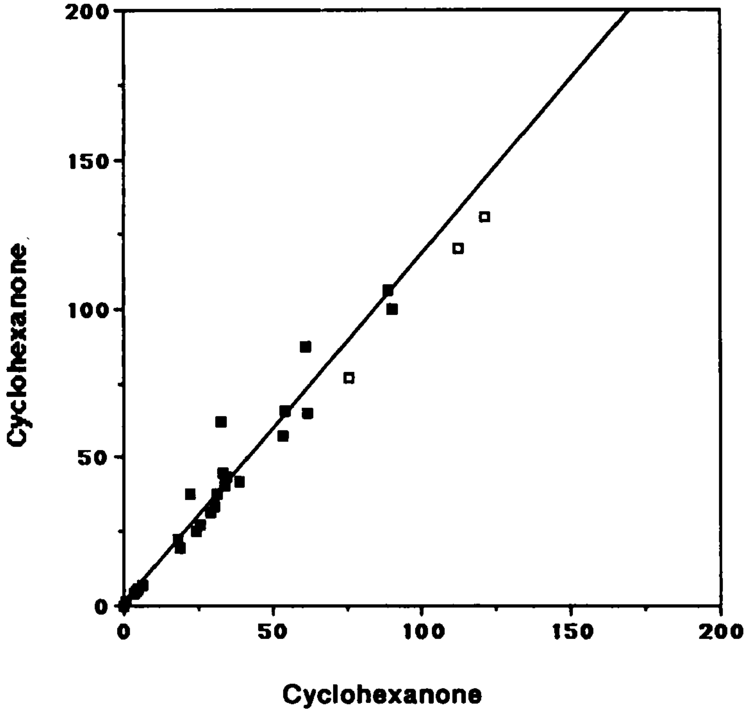
1(c)





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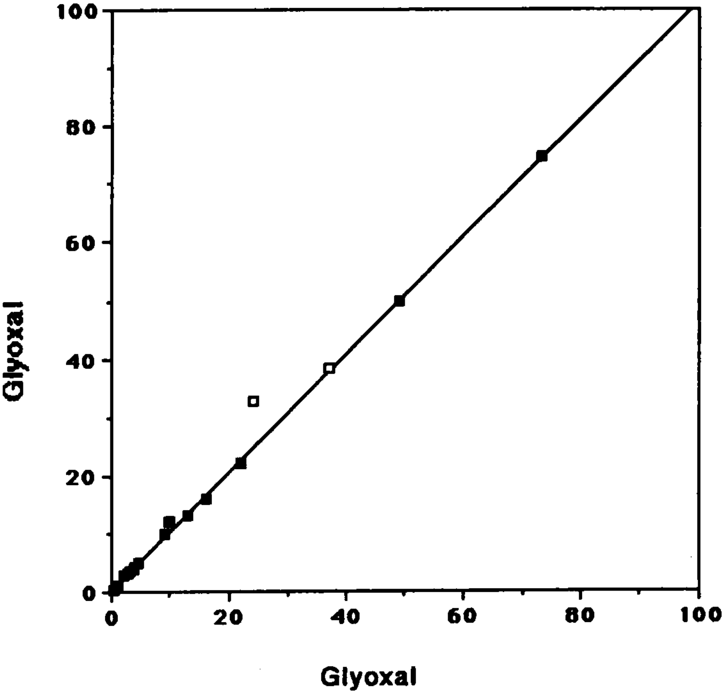
1(d)



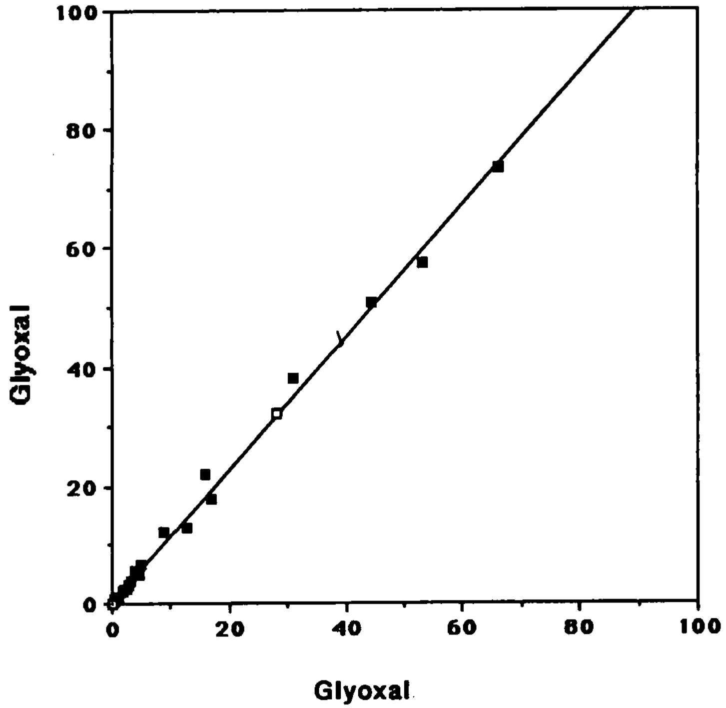


Figure 1 *Continued.*

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Average RSDs of 0.2–4.7% were obtained for sixteen carbonyls including formaldehyde (3.0%) and acetaldehyde (3.6%). Higher RSDs averaging 7.1–13.2% were obtained for the five carbonyls benzaldehyde, m-tolualdehyde, crotonaldehyde, nopinone and 4-acetyl-1-methylcyclohexene. These five carbonyls were tested in only a few samples and at low concentrations that were near the limit of detection. Results for formaldehyde and acetaldehyde are consistent with those obtained in previous work[14,20]. The RSD for replicate analyses was not a strong function of carbonyl concentration, even though several high RSDs were recorded, as would be expected, when the carbonyl concentration was close to the limit of detection. This is illustrated in Figure 2 in which RSDs for formaldehyde, acetaldehyde, cyclohexanone and glyoxal are plotted as a function of the carbonyl concentration.

Co-located cartridges

A measure of overall precision (sampling + analytical) is given by results for co-located cartridges. Individual results are not listed and are summarized in Table 4 for eighteen carbonyls. The results are listed in Table 4 according to range of carbonyl concentrations, range of RSDs, average RSD and number of co-located samples for each carbonyl. Examples of results for individual sets of co-located samples are shown in Figure 1 for formaldehyde, acetaldehyde, cyclohexanone and glyoxal. Average RSDs were 1–16% for the eighteen carbonyls studied including formaldehyde (average RSD = 5.8 ± 4.8%, n = 25), acetaldehyde (6.5 ± 4.9%, n = 24) and acetone (11.4 ± 8.2%, n = 12). As is shown in Figure 2 for formaldehyde, acetaldehyde, cyclohexanone and

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Table 4 Summary of results for co-located samples

Carbonyl	*Carbonyl concentration ppb*	*Relative standard deviation, percent*		*Number of measurements*
		Range	*Average*	
Formaldehyde	1.3–714	0–18.2	5.8	25
Acetaldehyde	0.6–1,123	0–16.8	6.5	24
Propanal	1.5–64.7	0–29.7	8.7	24
n-Butanal	0.58–577	0–17.4	6.1	25
iso-Butanal	37.0	5.9	5.9	1
n-Pentanal	0.33–324	0.6–24.2	7.4	18
n-Hexanal	0.29–461	0–28.4	8.0	13
n-Heptanal	0.60–224	1.0–20.0	9.9	7
n-Octanal	5.7	10.6	10.6	1
n-Nonanal	79.2	0.9	0.9	1
Acetone	0.1–869	0–29.3	11.4	12
3-Methyl-2-butanone	12,584	0, 2.6	1.3	2
Cyclohexanone	0.20–630	0.9–40.0	10.4	29
Acrolein	275	14.5	14.5	1
Glyoxal	0.30–150	0.8–23.3	9.8	24
Methylglyoxal	0.78–54	0–12.8	5.8	5
Pyruvic acid	8.7–9.3	13.4–18.3	16.2	3[a]
Benzaldehyde	6.2–6.8	2.9–6.4	4.1	3[a]

[a] one set of three co-located cartridges.

2(a)

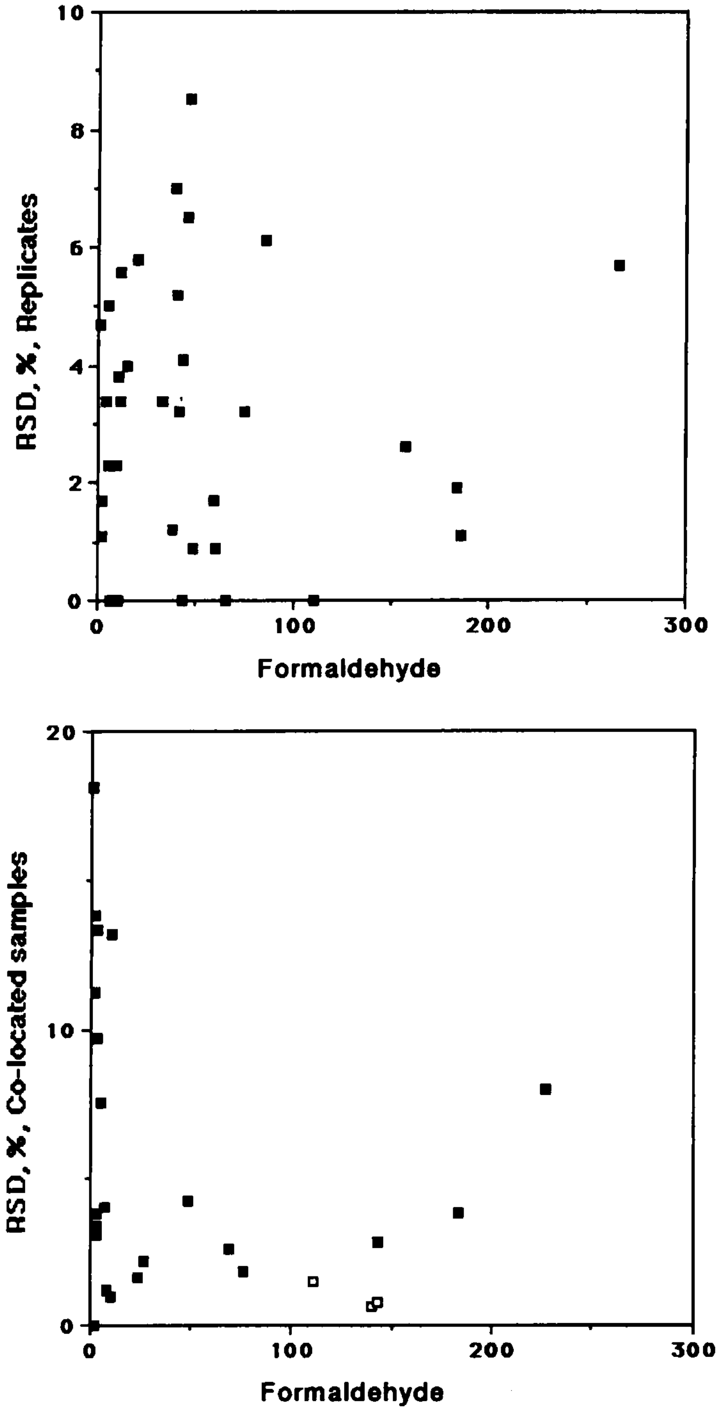

Figure 2 Relative standard deviations (RSD, percent) for replicate analyses (top) and for co-located samples (bottom) vs carbonyl concentration (in ppb) for formaldehyde (2a), acetaldehyde (2b), cyclohexanone (2c) and glyoxal (2d). Several carbonyl concentrations shown as one-fifth of actual value for clarity (open symbols).

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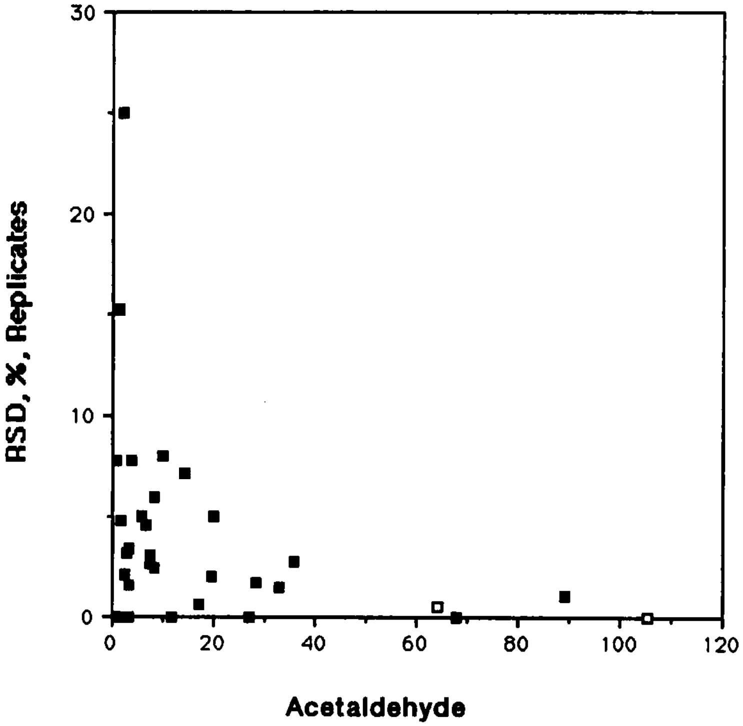
2(b)



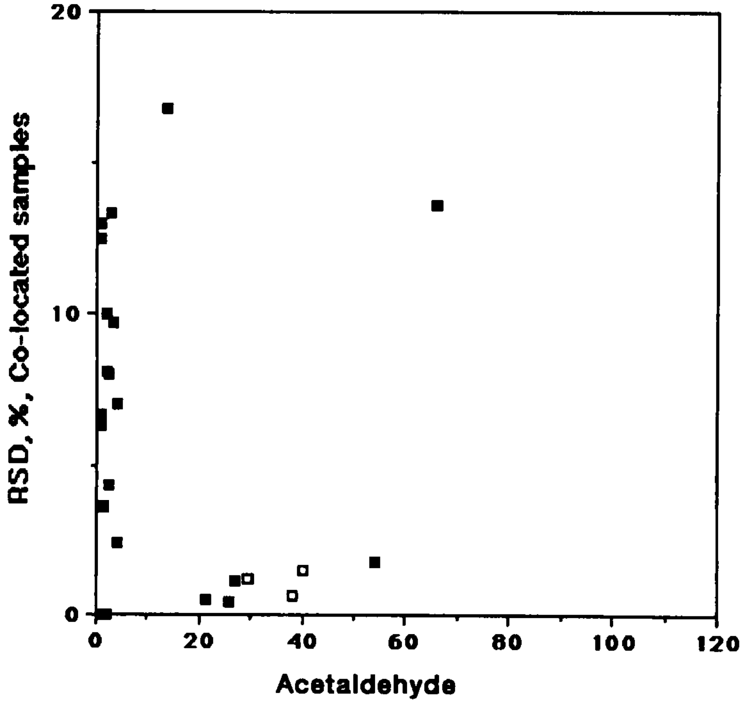


Figure 2 *Continued.*

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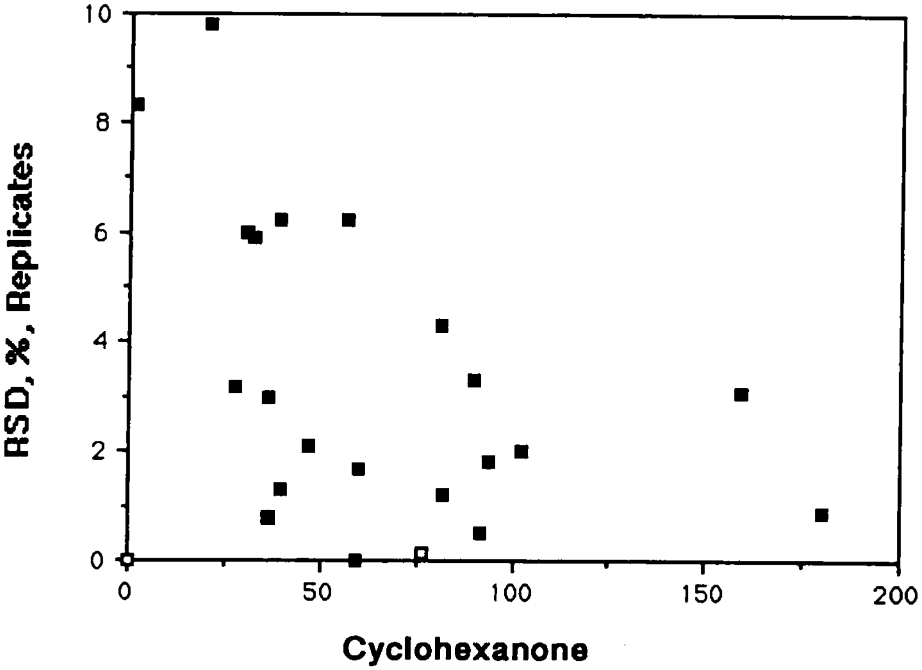
2(c)



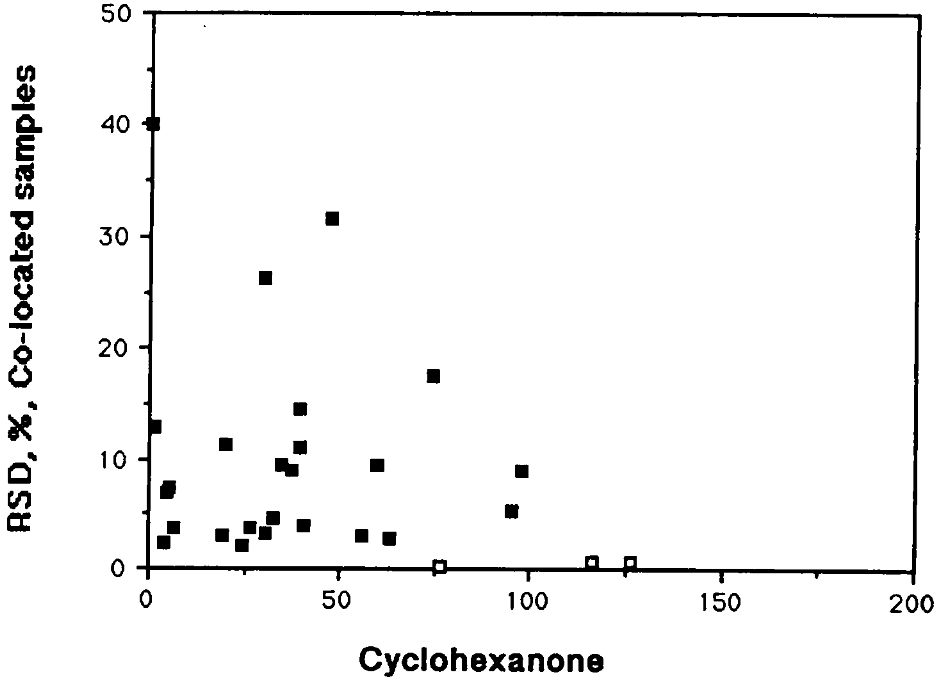


Figure 2 *Continued.*

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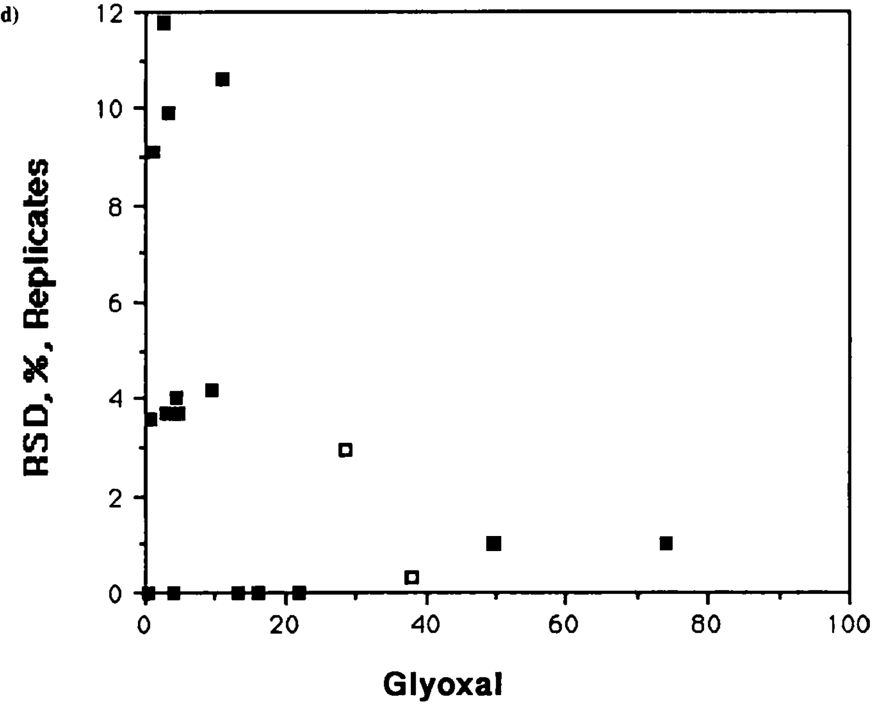
2(d)



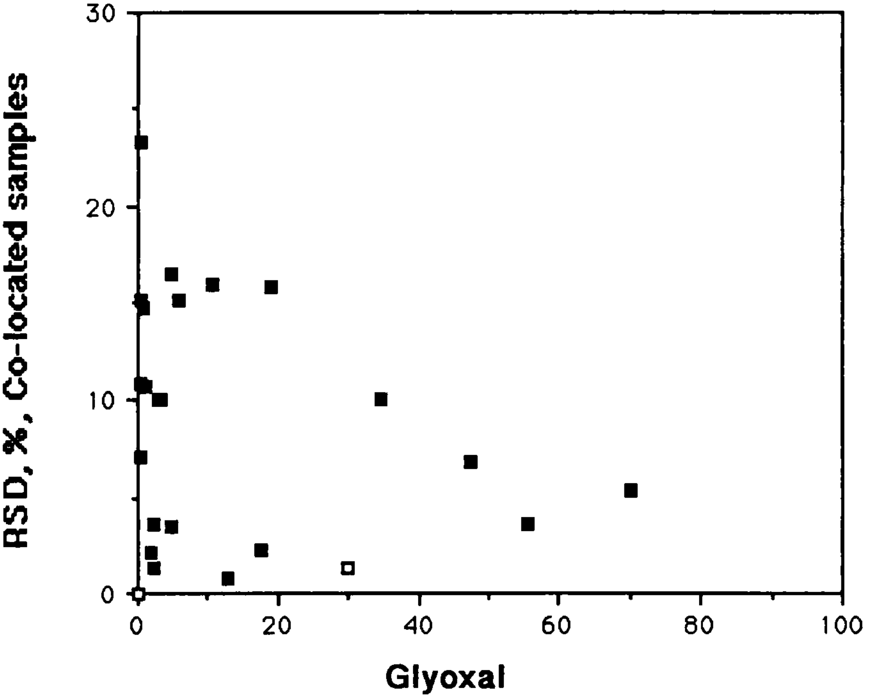


Figure 2 *Continued.*

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glyoxal, RSDs for co-located samples showed no strong dependance on carbonyl concentration, although several high RSDs were, not unexpectedly, recorded at low carbonyl concentrations that were near the limit of detection.

The relative contribution of the analytical and sampling steps to the overall method percision can be assessed by comparing the RSDs for replicate analyses (Table 3) to the RSDs for co-located samples (Table 4). This comparison can be made for thirteen carbonyls and indicates that RSDs for co-located samples are generally higher than those for replicate analyses. The ratios of the average RSD for co-located samples to the average RSD for replicates were 1.9 for formaldehyde, 1.8 for acetaldehyde, 2.1 for propanal, 1.6 for butanal, 5.7 for pentanal, 2.9 for hexanal, 2.6 for heptanal, 3.1 for acetone, 0.4 for 3-methyl-2-butanone, 3.3 for cyclohexanone, 2.4 for glyoxal, 2.1 for methylglyoxal and 0.6 for benzaldehyde. These ratios indicate, for eleven of the thirteen carbonyls studied, a large contribution of the sampling uncertainty to the overall method precision. While average RSDs of 1–16% for co-located samples are in our opinion acceptable, the results in Table 3 and Table 4 indicate a need to improve the sampling precision in future work.

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