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Measurement of Airborne Carbonyls Using an Automated Sampling and Analysis System

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Based upon the well established method of derivitization
with 2,4-dinitrophenylhydrazine, an instrument was developed
for ambient measurement of carbonyls with significantly
improved temporal resolution and detection limits through
automation, direct injection, and continuous use of a single
microsilica DNPH cartridge. Kinetic experiments indicate that
the derivitization reaction on the cartridge is fast enough
for continuous measurements with 50 min air sampling. Reaction
efficiencies measured on the cartridge were 100% for the
carbonyls tested, including formaldehyde, acetaldehyde, propanal,
acetone, and benzaldehyde. Transmission of the carbonyls
through an ozone scrubber (KI) were in the range of 97−101%.
Blank levels and detection limits were lower than those
obtainable with conventional DNPH methods by an order of
magnitude or greater. Mixing ratio detection limits of carbonyls
in ambient air were 38−73 ppt for a 50 min air sample (2.5
L). The instrument made continuous measurements of carbonyls
on a 2 h cycle over a period of 10 days during a field study
in southwestern Ontario. Median mixing ratios were 0.58 ppb
formaldehyde; 0.29 ppb acetaldehyde; 1.14 ppb acetone; and 0.45
ppb glyoxal. Glyoxal shows a significant correlation with
ozone and zero intercept, consistent with a secondary source
and minor direct source to the atmosphere. The method
should easily be extendable to the detection of other low
molecular weight carbonyls that have been previously reported
using the DNPH technique.

Introduction

The atmosphere contains significant burdens of organic
carbonyl compounds that have a variety of primary and
secondary sources including emissions from fuel combustion
(*1*), industrial sources (*2*), biogenic emissions (*3*), and
photochemical hydrocarbon oxidation (*4*). Carbonyl com-
pounds are measured in ambient air (*5*), indoor air (*6*),
scientific mechanism studies (*7−9*), and global monitoring
programs via satellite borne instruments (*10*) to further
understand the role they play in atmospheric chemistry.
Analytical methods for carbonyl compounds include tunable
diode laser spectroscopy (*11*), differential optical absorption
spectroscopy (*12, 13*), Fourier transform infrared spectros-
copy (*14*), the Hantzsch reaction method (*15*), and conven-

tional cartridge methods employing derivitization reagents
such as 2,4-dinitrophenylhydrazine (DNPH) (*7, 12, 16−21*).
More recently, excellent sensitivity and temporal resolution
have been reported for measurement of formaldehyde by
laser induced fluorescence (*22*) and glyoxal by laser induced
phosphorescence (*23*). The spectroscopic methods are
compound specific, nonintrusive, and provide high temporal
resolution measurements. The conventional cartridge method
has lower temporal resolution, but allows simultaneous
measurement of formaldehyde and other carbonyls, the main
reason why it is still used extensively in research applications
(*24*).

In the conventional method, a calibrated volume of air
passes through the cartridge where carbonyls react with
DNPH to form carbonyl−hydrazone derivatives that are
analyzed offline by HPLC. The kinetics of the acid catalyzed
derivitization reaction has been studied in aqueous solution
(*16*), but to date the kinetics of the reaction on silica or C18
silica has not been studied. Quantifying the amount of
carbonyls in the air sample requires either complete trapping
and derivitization, or a reproducible recovery. The collection
efficiency (*25*), measured by using two cartridges in series,
is a common measure of carbonyl recovery that does not
guarantee complete reaction or elimination of interferences,
even if 100% is measured. An example problem in this regard
is the negative ozone interference for formaldehyde collection
on DNPH coated silica cartridges (*26*). Subsequent studies
confirmed that this interference can be eliminated with an
ozone scrubber (*17*). Sirju and Shepson (*17*) first measured
true carbonyl yields on cartridges using a permeation source
to give the overall yield of formaldehyde-hydrazone deriva-
tives collected on coated silica and C18 cartridges. They refer
to carbonyl yield as reaction efficiency, the ratio of moles of
carbonyl−hydrazone recovered to the moles of carbonyl
sampled. The reaction efficiency has been measured for
various carbonyl compounds on C18 cartridges in several
studies (*7, 17, 18*) but there have been few reports on silica
cartridges (*27*).

In this study, we report an instrument developed for
making continuous automated measurements of ambient
carbonyls using a single silica microcartridge, and the reaction
kinetics and reaction efficiencies for various carbonyls
measured with the system. We report transmission efficien-
cies of carbonyls through an ozone scrubber in the system.
The background levels and detection limits are compared to
those obtained using conventional DNPH methods. The
system performance has been demonstrated by ten days of
continuous measurements during a field study in rural
southwestern Ontario.

Experimental Section

Chemicals. The DNPH derivitization solution (0.04M) was
prepared by dissolving 0.2 g of twice recrystallized DNPH
(Sigma-Aldrich, Mississauga, ON) in 25 mL of 90% aceto-
nitrile/10% water with 10 μL of concentrated H_2SO_4.
Carbonyl−hydrazones were synthesized using a previously
published method (*28*). All organic carbonyls were obtained
from Sigma-Aldrich and were typically >99% pure, with the
exception of formaldehyde and glyoxal, which were available
as formalin (37% in water) and glyoxal trimer dihydrate (40%
in water). Standard solutions of the carbonyl−hydrazones
were prepared gravimetrically in calibrated volumetric flasks,
diluted with acetonitrile, and analyzed by HPLC for purity.
Ultrapure air and helium (BOC, Toronto, ON) were used.

Instrumentation. The schematic, Figure 1, illustrates the
instrument developed for the continuous, automated and

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FIGURE 1. Automated Instrument Schematic. Valve positions are those during ambient air sample collection with valve A in air sample position 4, valve B in load position, and valve C in sample position.

unattended sampling and measurement of airborne carbonyls, with a micro-DNPH cartridge being the central component. A series of valves control the following looped cartridge sequence: (i) cleaning with acetonitrile; (ii) loading with DNPH solution; (iii) purging using helium; (iv) air sampling; (v) filling with distilled water; (vi) injection of cartridge contents into the HPLC system. During a blank measurement, the system was carried through the same procedure except air sampling. Three valves and actuators (Valco) and a syringe pump were controlled by four relays from a 24 V power supply. The actuators select the valve position; either load or inject for valves B and C, and sequential advancement from position 1−6 for valve A. The valves (all 1.6 mm tubing) consist of one 6-port multi position valve (A), one high pressure 6-port Cheminert sampling valve with 0.25 mm i.d. flow channels (B), and one 6-port sampling valve (C). The fourth relay controls the syringe pump (Harvard Apparatus, Holliston MA), which delivers water to the cartridge. All solvents in the system are maintained under 420 kPa head pressure of helium, which serves to push solvents through the valve system. The DNPH cartridge (Figure 1) was custom designed, 1.0 mm id. × 30 mm long, 24 µL volume, stainless steel, and packed tightly with 250−350 µm porous silica.

A sampling cycle begins by cleaning the cartridge with acetonitrile (~300 µL) with valve A in position 1, valve B in load position, and valve C in waste position. The cartridge is then loaded with DNPH solution (100 µL) with valve A switched to position 2. The cartridge is adequately purged of liquid by He flow for 12 s with valve A switched to position 3. Air sampling begins with valve A switching to position 4 and valve C to sample position. The sampling pump draws air through the cartridge at a calibrated flow rate (50 mL

min⁻¹) using a Tylan mass flow controller. Ozone in the air sample is removed by a small scrubber consisting of a 0.63 mm i.d. Teflon tube packed with 0.16 g of crystalline KI, with 0.63 mm stainless steel screens with 10 µm openings. Air sampling stops by switching valve C to waste position. The cartridge and loop is filled with a precise volume of distilled water (146 µL) with valve A switched to position 5, via a Gas tight glass syringe in the syringe pump, to avoid air entering the HPLC and to avoid elution of hydrazones to waste. Analysis begins with valve B switched to inject, back flushing the cartridge contents onto the chromatographic system where hydrazones are separated using reversed phase µ-HPLC.

The µ-HPLC system consists of two micropumps, mixer and controller (Micro-Tech Scientific UP200M, Sunnyvale, CA), and a 1.0 × 250 mm LC-18 column (Supelco, Mississauga, ON) with 3 µm packing. The column flow rate was 50 µL/min. The two solvents were A, 100% H₂O; B, 75% ACN, 25% THF. The solvent program was 60% A/40% B from 0 to 40 min, increased linearly to 100% B at 80 min. The flow-cell and total absorbance signal (TAS) detection has been described previously (29, 30). Briefly, light from a deuterium lamp is delivered to, and collected from the custom micro flow-cell (*L* = 12 mm, 30 nL volume) via 400 µm fiber optics with spectral detection using a fiber-optic spectrometer (S2000, Ocean Optics, Dunedin, FL). The spectrometer resolution was 3 nm (10 elements binned) and spectra were collected at a frequency of 1 Hz. The TAS is summed over the region of hydrazone absorption, 292−473 nm. Analytes were identified based on retention time and matching absorbance spectra of peaks to those measured through injection of standard hydrazones. While carbonyl−hydrazone spectra are not highly variable, it is still possible to dif-
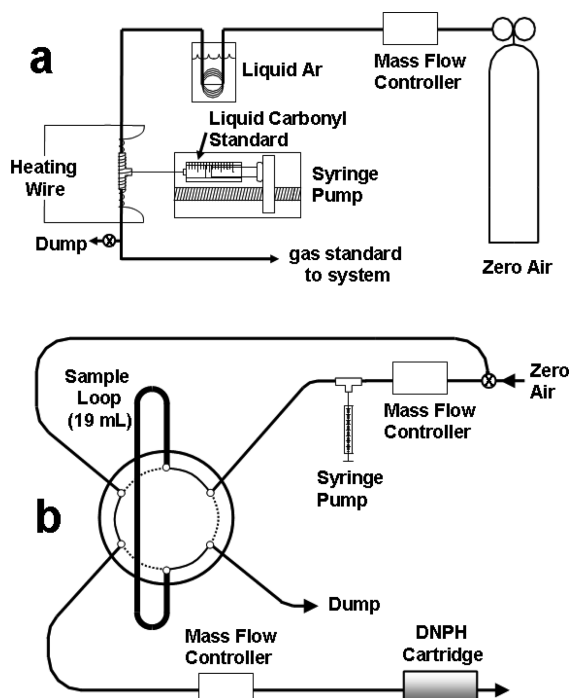
FIGURE 2. Schematics of (a) carbonyl standard gas generation system and (b) injection system for "fast" kinetic experiments of carbonyls on silica cartridge.

ferentiate between aliphatic aldehydes, ketones, aromatic aldehydes, and dicarbonyls (*28*). The spectra of dicarbonyls, such as glyoxal, are very distinctive with peak absorptions at 440 nm, allowing them to be easily differentiated from other carbonyl–hydrazones (*29*). HPLC automation software was written in Visual Basic 4.0.

Standard Gas Generation System. Standard gases of carbonyls in air were generated for gas calibrations, reaction efficiency, and reaction kinetic experiments by evaporating liquid carbonyl standard solutions into flowing air, Figure 2a. The concentration of carbonyls in the air stream are calculated with accuracy knowing the gas flow rate, the liquid flow rate and the concentration of the standard solution. Ultra pure air flowed through a calibrated mass flow controller at 50 mL/min. An in-line liquid argon trap removed trace organic contaminants. A syringe pump was used to inject the diluted standard solution at calibrated flow rates of 0.100 to 1.000 μL/min through a stainless steel tee. The syringe was connected to the tee using a syringe tip with a stainless steel tube silver soldered onto it. The tee piece was gently heated with heating tape to quickly volatilize the liquid entering the air stream. The system was stabilized for 1 h prior to sampling. The air stream was connected to the DNPH cartridge via valve B (Figure 1). For each experiment, the cartridge was loaded with DNPH using the automated system. A thermocouple ensured the temperature of the cartridge remained at room temperature (295 $\pm$ 3 K) throughout reaction efficiency experiments.

Reaction Efficiency Measurements. A standard carbonyl mixture solution composed of ~2% by weight each of formaldehyde, acetaldehyde, propanal, acetone, and benzaldehyde was diluted in 50/50 ACN/H$_2$O. This standard solution was diluted by a factor of 10 000 to yield the solution used in the standard gas generation system. The absolute amount of carbonyl added to the solution is uncertain for compounds which are not pure, i.e., formaldehyde. The standard carbonyl solution was "calibrated" by quantitative conversion of the carbonyls to hydrazones in solution using a small aliquot of the standard solution (5.00 μL) and excess derivitization solution (10 mL). The derivitization reaction

was allowed to proceed overnight, well beyond the 5 min needed for completion typically needed (*16*). This solution, representing a hydrazone equivalent of the diluted carbonyl standard solution, was diluted in steps and injected onto the μ-HPLC system using a calibrated 5.81 μL injection loop. In this way, the response of the analytical system to the same standard liquid carbonyl solution was compared in two ways: (i) gas sampling: volatilization of precise volumes of standard solution followed by gas sampling with the automated system including online DNPH cartridge and (ii) liquid injection: off-line DNPH derivitization of standard solution followed by manual injection of precise volumes onto HPLC system.

Reaction Kinetic Experiments. High concentration standards of carbonyls in air were generated using the setup shown in Figure 2b. A standard carbonyl air sample was generated by injecting liquid carbonyl mixture by syringe pump at a flow rate of 4.0 μL/min into a calibrated air flow of 20.0 L/min. The 19.0 mL sample loop was flushed with the gas sample for a period of time before the loop contents were quickly transferred to the silica cartridge, by switching the valve to inject and purging the loop at 70 mL/min for 2 min. The cartridge was quickly removed from the setup, and placed in the loop of the automated system for analysis of the carbonyl–hydrazones. The reaction time is the time from the start of gas flow through the cartridge to the time when the cartridge is filled with water just before HPLC injection. The experiment was repeated varying the reaction time from 5 to 50 min.

Two liquid carbonyl mixtures were used in the fast kinetic experiments described above. The first contained 5.0 mL each of five carbonyls (formaldehyde, acetaldehyde, propanal, acetone, and benzaldehyde) in a 25 mL flask; 5 mL of this was diluted into 100.0 mL using 50% acetonitrile in water. In the second solution, 5.0 mL of each of four ketones (acetone, 2-butanone, 3-pentanone, and methylvinylketone) were mixed into a 25.0 mL flask; 5.00 mL of this was then diluted as stated above. In each case, the resulting gas phase mixing ratios in the 19 mL loop were ~500 ppb for each compound.

The standard gas calibration system was also used for low concentration kinetic experiments whereby a low concentration standard carbonyl gas mixture (2–4 ppb) was continuously sampled onto the cartridge for 50 min, followed by a variable post sampling reaction time (0–3 h). The post sampling reaction time is the time between the end of gas sampling until analysis on the automated HPLC system. The two kinetic experiments described above were similar in all respects other than the sample concentration and sampling time, which were adjusted to maintain the number of moles of carbonyl equivalent in the two experiments.

Field Measurements. Ambient air samples were collected at Simcoe, Ontario; June 25 to July 20, 2000. The site is in a rural/agricultural environment in southwestern Ontario with few direct sources within a 10 km radius. The site hosts an air monitoring station operated by the Ontario Ministry of the Environment (OME) and experiences some of the highest ozone and particulate matter levels in Canada during regional smog episodes. The automated instrument sampled air directly from the same 10 cm diameter glass manifold as the OME air instrumentation. A 1 m length of 1.6 mm o.d. and 0.76 mm i.d. Teflon line connected valve A to the glass manifold. Air samples were collected at 50 mL min^{-1} for 50 min. The cycle time of the instrument was 2.0 h, limited by the chromatographic separation. The KI in the ozone scrubber was replaced once per week. Approximately 200 samples and 13 blanks were analyzed over the course of the field study. The same cartridge was used continuously for several months without signs of degradation. The silica packing was changed every few months as a matter of preventative maintenance.
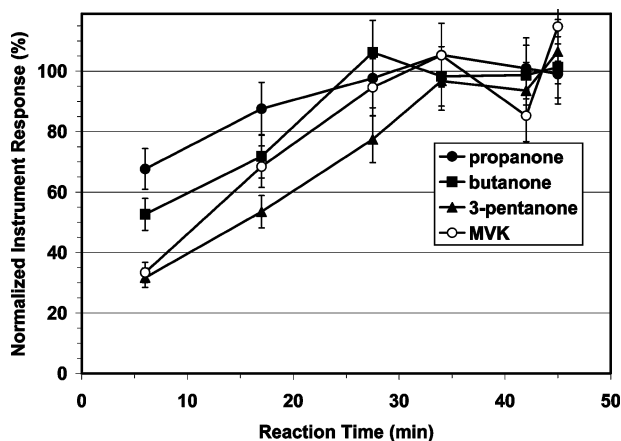
FIGURE 3. Reaction kinetics of ketones on DNPH coated silica cartridge. Reaction time follows the fast injection of a high concentration sample.

Results and Discussion

HPLC System Calibrations. The absorbance detector response was measured by injecting standard solutions of the carbonyl hydrazones in acetonitrile using the manual injector with 5.81 μL loop. Calibrations were linear with statistically insignificant y-axis intercepts except for formaldehyde and acetone that had small but nonzero blank values. The instrument response given by the slope of the calibration line is related to the total integrated molar absorptivity of the hydrazone. The instrument responses for the carbonyl−hydrazones were (AU sec nmole^{-1}): formaldehyde- 9.84; acetaldehyde- 10.7; propanal- 9.89; acetone- 9.87; benzaldehyde- 15.2; glyoxal- 26.5. The responses were checked periodically over a period of two years and were found to be stable within 5%.

The amount of DNPH loaded on the silica cartridge is an important parameter. By dilution and reinjection of a chromatographic eluent fraction containing the DNPH peak, the DNPH loading on the cartridge was determined to be 1.8 $\times$ 10^{-7} moles, with a reproducibility of $\pm$5%. This loading is in excess relative to the expected carbonyl content in an air sample.

Derivitization Kinetics. In contrast to conventional cartridge methods, the rapid repeated use of a single cartridge in the current automated system required us to verify that carbonyls are stoichiometrically converted to hydrazones before injection onto the HPLC. As described in the experimental, kinetic experiments were conducted in two ways to determine the amount of time required for reaction completion. The results of the high concentration standard kinetic experiments are shown in Figure 3 for four ketones. The response for each species is normalized to the response at reaction time >40 min to facilitate comparison. The four aldehydes tested (formaldehyde, acetaldehyde, propanal, benzaldehyde) have been omitted for clarity as the derivitization reactions were complete (>95%) in less than 5 min. The four ketones; acetone, 2-butanone, methylvinylketone, and 3-pentanone have normalized reaction completions of 67, 53, 33, and 30% after 5 min respectively, and 90% normalized reaction completions in 20, 23, 27, and 32 ($\pm$5) min respectively. The observation that ketones react slower than aldehydes on the cartridge, and that the rate of reaction decreases with increasing chain length is in agreement with observations of carbonyl reaction rates with DNPH in solution (16).

The results of varying the post sampling time following a 50 min continuous sampling, were determined by measuring the relative response of formaldehyde, acetaldehyde, propanal, acetone, and benzaldehyde at variable post sampling times from 2 to 180 min. There was no statistical change in the normalized instrument response for any species over these time periods. This suggests that no post reaction time is needed to complete the reaction for these species, under the conditions used for ambient air sampling.

Reaction Efficiency. As mentioned in the Experimental Section, a single standard liquid carbonyl solution was used both for generating a gaseous mixture of carbonyls and a liquid hydrazone equivalent standard solution. The response of the analytical system to a back calculated volume (nL) of the common standard carbonyl solution was compared for the two experiments: (i) evaporation to gas phase and sampling through the silica cartridge with unknown reaction efficiency for 50 min and (ii) manual injection of hydrazone equivalent of standard solution on HPLC. At a constant air flow rate of 50 mL min^{-1}, the gas phase mixing ratios were changed by varying the syringe flow rate from 0.100 to 1.00 μL/min; the syringe containing a 10 000$\times$ diluted sample of the standard carbonyl solution. Final gas phase mixing ratios of the carbonyls were in the range of 0.8−20 ppb (Table 1). For the manual liquid calibrations, the injection volume of the 2000$\times$ diluted sample of the hydrazone equivalent standard carbonyl solution was varied from 0.581−5.81 μL. Calibration curves of HPLC response per volume of standard solution injected (AU sec nL^{-1}) were prepared. All gas and liquid injection calibration curves had statistically insignificant intercepts and were then fit with a linear line, $y = mx$. The gas and liquid calibration statistics and reaction efficiencies are summarized in Table 1. The gas calibrations are linear from the detection limit to the maximum levels tested (10−20 ppb), representing 1−2 orders of magnitude. These concentration levels represent the range over which we expect to apply this system to studies of atmospheric chemistry. Although we have not tested the potential breakthrough at higher concentrations, we anticipate that nonlinearities and/or breakthrough will occur when a significant amount of DNPH has been depleted. With the DNPH loading on the cartridge, and a 50 min sample, 10% depletion of DNPH will occur when the total carbonyl loading in the air exceeds 175 ppbO. Using this system in such polluted environments could be accomplished by shortening the sampling time and/or increasing the size and loading of the cartridge.

The reaction efficiency of the carbonyl on the silica cartridge is given by the ratio of the gas response to the liquid injection response. All five carbonyls tested (Table 1) showed quantitative conversion with reaction efficiencies ranging from 100 to 111%. While formaldehyde and acetaldehyde had reaction efficiencies not different from 100%, the other three had reaction efficiencies just marginally greater than 100% at the 95% confidence level. The result for those three carbonyls likely indicates that there is a small unidentified bias (<10%) in the relative response experiment. The propagated uncertainty of the flow controllers, injection loop volume, calibrated glassware and other factors was estimated to be about 10%. Unfortunately, reaction efficiencies for glyoxal are unavailable due to difficulty in generating a gas standard from the glyoxal trimer dihydrate in water. We expect that reaction efficiencies of glyoxal are close to 100% due to the fast reaction of aldehydes with DNPH and due to recent literature showing recoveries greater than 93% on DNPH coated silica cartridges (31).

To test for potential loss of carbonyls through the ozone scrubber, low concentration (2−4 ppb) carbonyl gas standards were sampled alternately with ($n = 4$) and without ($n = 3$) the KI trap in place using the automated system. The transmission through the trap, calculated as the average response with the trap divided by the average response without the trap, is shown in Table 1 for five carbonyls. The transmissions were all 100% within error, indicating that there are no losses of carbonyls on the KI trap.

	gas calibration[b]			liquid calibration				
compound	slope (AUsec nL^{-1})	n	r^2	slope (AUsec nL^{-1})	n	r^2	reaction efficiency %	O$_3$ trap transmission %
formaldehyde	2.66 ± 0.27	9	0.944	2.65 ± 0.07	7	0.997	100.2 ± 10.5	100.4 ± 9.3
acetaldehyde	3.57 ± 0.19	9	0.984	3.34 ± 0.22	7	0.982	106.9 ± 9.0	96.7 ± 8.6
propanal	2.48 ± 0.17	9	0.985	2.25 ± 0.09	7	0.995	110.2 ± 8.5	100.4 ± 10.5
acetone	3.31 ± 0.17	9	0.978	2.98 ± 0.11	7	0.995	111.1 ± 7.0	100.6 ± 8.1
benzaldehyde	2.83 ± 0.14	9	0.988	2.62 ± 0.13	7	0.991	107.9 ± 7.4	98.0 ± 7.9

[a] Uncertainties expressed at 95% confidence. [b] Ranges of mixing ratios for gas calibrations were formaldehyde (1.1−10.8 ppb), acetaldehyde (2.0−19.8 ppb), propanal (1.5−15.0 ppb), acetone (1.5−15.0 ppb), and benzaldehyde (0.82−8.2 ppb).

TABLE 2. Comparison of Cartridge Blanks, Cartridge Detection Limits and Ambient Detection Limits for Formaldehyde (C1), Acetaldehyde (C2) and Acetone (C3)

		cartridge blanks, nmoles			detection limits, nmoles			detection limit (ppb)[a]		
study	packing	C1	C2	C3	C1	C2	C3	C1	C2	C3
current	silica	0.0014	0.0032	0.0029	0.0073	0.0044	0.0044	0.020	0.012	0.012
ref 17	silica	4.50	1.00	2.25	1.47	0.73	2.94	0.200	0.100	0.400
ref 28	C18[b]	2.83	3.11	2.67	8.00	6.48	4.09	1.089	0.882	0.556
ref 18	silica[c]	1.42			0.96			0.131		
ref 18	C18[d]	2.19			1.26			0.173		
ref 20	silica	1.42	1.01	3.21	0.97	0.68	3.48	0.132	0.092	0.474
ref 20	C18	1.10	0.82	0.97	0.80	0.68	1.55	0.109	0.093	0.211
ref 21	silica	1.47	3.05		1.20	2.45		0.163	0.334	
ref 19	C18	0.30	0.10	0.30						
ref 12	C18	<2						0.333		
ref 33	silica	2.50	1.70	6.00				0.160	0.110	0.169

[a] Based upon 3 h samples, 9 L sample for current, ~180 L sample for other, except ref (33) which is 12 h, 72 L. [b] Average of many lots over several years. [c] Average of four lots. [d] Average of three lots.

Detection Limits. Blank levels and detection limits were assessed in the field over a continuous 10 day period. In total, 13 blanks were taken. For most blank samples, the formaldehyde, acetaldehyde, acetone, and glyoxal-hydrazones were below detection limit. For each chromatogram, the appropriate baseline section of the chromatogram was integrated whether a blank peak was detected or not. Using the detector response, the blank content of the cartridge was calculated along with the standard deviation. The average blank values, Table 2, range from 1 to 3 picomoles for the three prominent carbonyls and detection limits ($3\sigma_{blank}$) range from 4 to 7 picomoles. The average blank is below the detection limit for all three compounds, indicating that the method is not background limited, but is limited by instrumental noise in the detector. The corresponding detection limit in ambient air is dependent on sampling time and total air volume. For a 50 min sample, (50 mL min^{-1}, 2.5 L), the mixing ratio detection limits are 44−73 ppt for the three prominent carbonyls. For glyoxal, the corresponding detection limit was 38 ppt. Estimated detection limits for other carbonyls are in the 30−50 ppt range for a 50 min sample. It is a good approximation that detection limits scale inversely with sampling time. For a 3 h sample, commonly in literature, the corresponding detection limits are 12−20 ppt. For comparison, background levels and 3 h detection limits derived from other studies are summarized in Table 2. The majority of studies utilize commercial cylindrical polymer cartridges of dimensions, 9 mm i.d. × 10 mm, packed with silica or C18-silica, flow rates of 1.0 L min^{-1} and 3 h sampling periods. The range of 3 h detection limits are 100−1100 ppt (Table 2), with median detection limits of 163, 105, and 400 ppt for formaldehyde, acetaldehyde, and acetone, respectively. The 3 h detection limits with the current system are an order of magnitude lower, attributable to two factors. First, the cartridge blank levels are 2−3 orders of magnitude lower than those of conventional cartridges. Lower

blanks lead to smaller blank variance. The lower cartridge blanks might be expected due to the smaller size of the micro cartridge; with smaller mass of silica and smaller DNPH loading. The volume of the micro cartridge is 27 times smaller than the typical cartridge (24 uL vs 640 uL), and the amount of DNPH loaded is 28 times smaller (0.18 μmoles vs 5.0 μmoles). Taking this into account, the blank amount per unit volume or DNPH loading are still 1−2 orders of magnitude lower than those with the conventional cartridges. This reduction in unit blank amount is attributable to several factors including use of a steel cartridge that minimizes cartridge contamination by diffusion; repeated use of a single cartridge with automated and repeated cycling; and protection of stock DNPH and ACN solutions with helium, minimizing growth of background impurities. It is noted that low cartridge background levels were also evident in the study by Zhou (19), which were attributed to a novel extractive cleaning procedure, and loading of cartridges within two hours prior to use.

The second factor leading to low detection limits is the complete injection of the entire cartridge contents. With conventional methods, the cartridge is eluted with 2−5 mL of acetonitrile, followed by manual injection of only 20 μL. If the method is blank limited, complete injection of the sample does not offer any advantage since both the signal and blank signal noise scale with the injection volume. Conversely, if the background noise is instrumental, an advantage is afforded by complete injection since the signal-to-noise ratio increases with aliquot size.

The reproducibility of the instrument was tested by repeatedly sampling a constant 4.0 ppb gas mixture of acetone, generated by diluting a standard lab made mixture of acetone in a high pressure cylinder (200 ppbV) using pure air and two mass flow controllers. The automated instrument sampled the same gas standard continuously for 36 h on the 2 h cycle time. The chromatograms were analyzed for
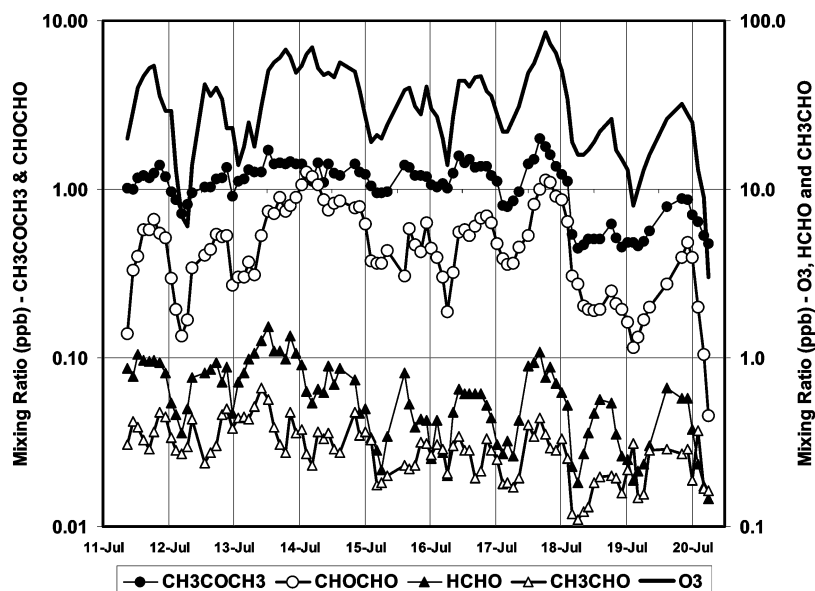
FIGURE 4. Time series of carbonyls and ozone measured with the automated instrument in Simcoe, ON during SONTAS 2000.

TABLE 3. Observations of Carbonyls at Simcoe, ON, July 11–20, 2000. Correlations of Carbonyl Mixing Ratio vs. 50 min Average O_3 Include the Intercept, b; Slope, m; and Correlation Coefficient, r^2

species	mixing ratios (ppb)					correlations with O_3		
	min	10%	median	90%	max	b (ppb)	$\pm m$ (ppb ppb$O_3{}^{-1}$)	r^2
formaldehyde	0.15	0.242	0.575	0.99	1.52	0.25 ± 0.05	$(1.09 \pm 0.18) \times 10^{-2}$	0.40
acetaldehyde	0.11	0.175	0.288	0.45	0.66	0.24 ± 0.02	$(0.18 \pm 0.06) \times 10^{-2}$	0.10
acetone	0.45	0.508	1.14	1.44	1.99	0.55 ± 0.05	$(1.56 \pm 0.13) \times 10^{-2}$	0.62
glyoxal	0.04	0.189	0.445	0.89	1.29	0.01 ± 0.02	$(1.46 \pm 0.07) \times 10^{-2}$	0.84

acetone–hydrazone. The integrated peak areas had a relative standard deviation of 4.3% for 18 samples.

Field Study Data. The retention times of formaldehyde, acetaldehyde, acetone and glyoxal on the HPLC were 28.8, 32.0, 35.2, and 41.1 min, respectively. Glyoxal was found to be ubiquitous throughout the study, its peaks were identified by the UV-spectra of the carbonyl–hydrazone. Example spectra from the field are presented elsewhere (29, 30). The mixing ratios of ozone and four carbonyls are illustrated in Figure 4 for a 10 day continuous period. A statistical summary of the observations is given in Table 3. The range of ambient levels of formaldehyde, acetaldehyde, and acetone are similar to those reported for another rural site in eastern North America (32). A diurnal pattern is apparent with maxima occurring early to late afternoon each day; typical of a secondary source via photochemical hydrocarbon oxidation. Ozone is casually correlated with the carbonyls since the same conditions are necessary for production of O_3; high temperatures, photochemical activity, and precursors. Of interest is the extremely high correlation between glyoxal and ozone, Table 3, much more significant than the other carbonyls. Glyoxal is also the only carbonyl that does not show an intercept. A positive intercept in the correlation can indicate other sources of carbonyls not linked to photochemistry such as direct anthropogenic or biogenic sources, or high background values. It is well-known that glyoxal has significant secondary sources due to OH initiated oxidation of acetylene, benzene, toluene, o,m,p-xylene, and trimethyl benzenes (8, 9), and known sinks including reaction of OH, photolysis, and uptake on particles (34). The observation of high correlation of glyoxal with ozone, and zero intercept, are consistent with the recent view that glyoxal is a good indicator of fast VOC chemistry with significant secondary sources, short lifetime and absence of significant direct

anthropogenic sources (13). The range of ambient glyoxal mixing ratios measured here, 0.04 to 1.26 ppb, are within the range of observations seen in Mexico city; <0.15 ppb (detection limit) to 1.82 ppb (12).

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