An aircraft measurement technique for formaldehyde and soluble carbonyl compounds

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Abstract. An aircraft technique was developed for measuring ambient concentrations of formaldehyde and a number of soluble carbonyl compounds, including glycolaldehyde, glyoxal, methylglyoxal, glyoxylic acid, and pyruvic acid. Sampling was achieved by liquid scrubbing using a glass coil scrubber in conjunction with an autosampler which collected 5-min integrated liquid samples in septum-sealed vials. Analysis was performed on the ground after flight using high-performance liquid chromatography following derivatization of the carbonyl analytes with 2,4-dinitrophenylhydrazine; the limit of detection was 0.01 to 0.02 parts per billion by volume (ppbv) in the gas phase. Although lacking a real-time capability, this technique offers the advantage of simultaneously measuring six carbonyl compounds, savings in space and power on the aircraft, and a dependable ground-based analysis. This technique was deployed on the Canadian National Research Council DHC-6 Twin Otter during the 1993 summer intensive of the North Atlantic Regional Experiment. The data obtained on August 28, 1993, during a pollutant transport episode are presented as an example of the performance and capability of this technique.

Introduction

Atmospheric carbonyl compounds are produced as reaction intermediates from oxidation of hydrocarbons (HC) and play an important role in photochemical reactions because of their properties as free radical sources and sinks [Carlier et al., 1986; Finlayson-Pitts and Pitts, 1986]. Consequently, information on atmospheric distribution of this class of compounds affords mechanistic insights into photooxidation of HC as well as constraints for numerical simulations of photooxidant formation. To acquire this information, we developed and tested an aircraft measurement technique for formaldehyde (FA) and a number of soluble carbonyl compounds, including glycolaldehyde (GA), glyoxal (GL), methylglyoxal (MG), pyruvic acid (PD), and glyoxylic acid (GD). Since FA, a reaction product of a multitude of HC precursors, represents the most abundant aldehyde and contributes pivotally to radical budgets, its concentration is critical to a reliable understanding of photooxidant formation [e.g., Cantrell et al., 1992; Kleinman et al., 1994]. On the other hand, because of the more distinctive precursor-product relationships characterizing the multi-oxygenated carbonyl compounds [Atkinson, 1994], their distributions are potentially useful for discerning HC sources [e.g., Lee et al., 1995] in terms of, for example, man-made versus natural origins.

Previously, a real-time aircraft method has been developed for FA, which is based on a wet chemical technique using the Hantzsch reaction in conjunction with a coil scrubber sampler [Kelly, 1990; Luke et al., 1992]. In contrast, the present technique collects batch samples using the same coil technique and analyzes them after flight using high-performance liquid chromatography (HPLC). Although lacking an on-line capability, this technique has the advantage of simultaneously measuring the multi-oxygenated carbonyl compounds mentioned above in addition to FA. Because of the fact that only the sampler was outfitted on the aircraft, the size and power requirement was fairly modest, making this technique feasible for most aircraft. We tested this technique on the Canadian National Research Council Twin Otter during a joint field program involving Atmospheric Environmental Service (AES) of Ontario, Canada, Institute of Aerospace Research (IAR) of Ottawa, Canada, and Brookhaven National Laboratory (BNL) as part of the 1993 summer North Atlantic Regional Experiment (NARE) in southern Nova Scotia, Canada. In this paper we give a description of the design and operation of this aircraft technique. We also present the data obtained on August 28, 1993, when a distinctive pollutant layer was encountered to demonstrate the feasibility of this method.

Experiment

The aircraft carbonyl method reported in this work is based on a ground measurement technique recently developed [Lee...
and Zhou, 1993], whereby soluble carbonyl compounds are scrubbed into an aqueous solution, derivatized with 2,4-dinitrophenylhydrazine (DNPH), and detected by high-performance liquid chromatography (HPLC) using a UV-visible detector. To adapt this technique to an aircraft platform, we divided the system into two separate modules: a sampling device on the aircraft and an analysis system on the ground.

**Sampling system.** A schematic of the sampling device is given in Figure 1. Ram air flows into the unpressurized cabinet through a piece of 0.95-cm OD Teflon tubing sample manifold, which was housed in a 2.54-cm OD forward-facing aluminum air intake tube located at ~10 cm above the fuselage and lengthwise about 3/5 of the way back from the nose of the aircraft. The liquid scrubber system consisted of a 28-turn Pyrex coil (tubing ID -0.2 cm, coil helix diameter ~2 cm) equipped with an inlet tee for the sample gas and the scrubbing solution to enter and mix [Lee and Zhou, 1993]. The sample gas inlet, which connected the coil scrubber to the ram air Teflon tubing manifold, was comprised of a piece of 2.5-cm-long x 0.125-cm OD Teflon tubing. At cruising speed, the ram airflow was in excess of 100 L min⁻¹ (~60% isokinetic). The excess ram airflow in the sample manifold tubing was vented into the cabin through a rotameter, which permitted easy confirmation of the flow conditions during the flight. The DNPH scrubbing solution (see below) was stored in a Teflon bottle (~500 mL) and pumped into the coil by a peristaltic pump (Rainin, model Rabbit-Plus) through a piece of 0.08-cm OD Teflon tubing at a nominal rate of 0.25 mL min⁻¹. This Teflon bottle was vented to the ambient air through a DNPH-coated C18 sep-pak cartridge to prevent carbonyl compounds present in the cabin air from entering the container. The sample air was pulled through the coil by a diaphragm pump (GAST, model 1531-U107-288) at a preset flow rate of 4.0 standard liters per minute (slpm) controlled by a mass flow controller (Tylan, model FC280, 0-5 slpm). The return liquid from the coil after separation from the sample air was collected in a 2.5-cm-long x 0.125-cm OD Teflon tubing manifold. The DNPH-coated cartridge was replaced at ~2 min before takeoff. The DNPH solution was used up to 48 hours, or in some cases up to 72 hours.

The DNPH solution freshly prepared from a 25 mL acetone solution and 0.05% (v/v) DNPH solution with 900 mL H₂O, yielding [DNPH] = 0.1 mM and pH = 2.5 ± 0.1. The DNPH-Coated cartridge was replaced at ~2 min before takeoff. The DNPH solution was used up to 48 hours, or in some cases up to 72 hours.

**Sampling procedure.** The sampling system was made ready ~30 min before door-close by (1) filling the Teflon bottle with the DNPH scrubbing solution freshly prepared from a concentrated stock (see below), (2) placing 60 clean sealed vials in the autosampler tray, enough for two flight missions (~5 hours), and (3) connecting and priming the liquid plumbing system. The empty vials had been previously weighed using an electronic balance (Ohaus, model TS400D). Approximately 10 min before taking off, the power to the system was turned on and sampling began. However, during this period, while the plane was still on the runway, high-purity N₂ was used to backflush the inlet line at ~5 L min⁻¹ to prevent sample manifold contamination by engine exhaust. Upon airborne the N₂ flow was turned off and the ambient air sampled.

During flight the liquid plumbing system and the autosampler were checked periodically for proper operation. The timing of vial position was automatically registered on the data system and was also manually recorded at least 3 times each flight to ensure correct time sequencing of the vials. Upon landing, the system was turned off and the N₂ flow was turned on to backflush the intake manifold.

**Analysis.** After the final flight of the day the sample vials and the Teflon bottle containing the remaining DNPH solution were taken to an instrumented trailer located at a ground-sampling site (Chebogue Point, ~10 km from the airport) for analysis. Blanks and standards were prepared using this very DNPH scrubbing solution and liquid standards freshly diluted from 10-mM carbonyl standards. The filled vials were weighed to determine the volume of the liquid collected, which in turn gives the liquid flow rate during sampling.

The HPLC analysis was performed using a binary gradient elution (H₂O-CH₃OH) on a Hitachi pump (model L-6200A) equipped with a C18 reverse phase column (cartridge type, Waters RCM 8x10, 4-μm Bondapak) and a 1.0-mL sample loop, in conjunction with a programmable UV-visible detector (Spectra-Physics, model UV2000) which switched from 370 nm to 400 nm after the pyruvic acid peak. Two different elution programs were used: a shorter one (10 min) for FA and OD only, which was used initially. A longer one (20 min) was used later in the study to also elute GA, PD, GL, and MG. Automation of the chromatographic analysis was achieved by using an automatic sample injector (Gilson, model 231XL, programmed to fill the sample loop with 500-μL sample) controlled by software (Rainin, model MacIntegrator) running on a Macintosh computer, which also performed data acquisition and storage. The analysis typically began at ~4 hours after the samples were brought back from the airport and all the samples were analyzed within 12 to 20 hours of collection. The derivatization of the carbonyl compounds in that time frame was complete and the resulting hydrazone derivatives were stable [Lee and Zhou, 1993].

**Scrubbing solution.** The working scrubbing solution was prepared daily by diluting 4.0 mL concentrated DNPH stock solution with 900 mL H₂O₂, yielding [DNPH] = 0.1 mM and pH = 2.5 ± 0.1. The concentrated DNPH stock solution was prepared by dissolving 1.0 g of recrystallized DNPH into 94 mL CH₃CN (HPLC grade, Baker) and 6.0 mL concentrated H₂SO₄.
The purification procedure applied to DNPH has been detailed elsewhere [Keiber and Mopper, 1990]. The water used in the field was ASTM type I water (ion-exchanged, organics-removed filtered water) either brought to the field or prepared in situ.

Collection efficiency. Previously, the collection efficiency (CE) of the 28-turn glass coil for FA, GA, GD, PD, GL, and MG had been determined at ~1 atm pressure [Lee and Zhou, 1993; Zhou et al., 1995]. Except for FA, all the carbonyl compounds exhibited a CE of 100% within experimental uncertainty, consistent with the high Henry’s law solubility of these compounds. Since this efficiency may vary depending on ambient pressure and volume flow rate of the sample air, CE for FA and GL were determined under the aircraft sampling conditions using a walk-in altitude chamber. This chamber which measures 2 m in diameter and 4 m in length can be evacuated to a pressure corresponding to an altitude of 6 km. The CE of GL is to be representative of all the soluble carbonyl measured in this work because of their similarly large Henry’s law solubilities [Betterton and Hoffmann, 1988].

The CE was determined in two different fashions, the first by connecting two 28-turn coils in series and measuring the amount of material collected by each coil when sampling a gas containing a constant concentration of the carbonyl [Lee and Zhou, 1993]. Each coil was plumbed to its own independent scrubbing solution flow and automatic samplers (ISCO, model ISIS and Gilson fraction collector, model 203). This approach affords the convenience of not requiring a precise knowledge of the concentration of the test gas so long as it remains constant. The second method used only one coil and the efficiency was determined by ratioing the amount of the carbonyl collected to the total amount of the carbonyl passing through the coil. This approach, which requires a standard of known concentration, was necessary for conditions when the flow of the standard gas through two coils in series became too restrictive due to the reduced pumping capacity at "higher altitude." The gas standards were prepared by bubbling 1 L min\(^{-1}\) N\(_2\) through an aqueous carbonyl solution (typically 1 mM) maintained at 0°C using an ice-water bath. A diluent N\(_2\) gas was then mixed into the carbonyl carrier gas to yield the desired final concentration. The CE was determined as a function of pressure (0.5 to 1.0 atm), sample gas flow rate (0.8 to 4.0 slpm), and concentration of the gaseous carbonyl standards (0.5 to 5 ppbv).

Results

Collection efficiency. The CE of the 28-turn coil determined for GL was 100 ± 7% under the conditions studied, namely, gas flow rate of 1.0 to 4.0 slpm and concentrations varying between 1 to 5 ppbv. This value was taken as the CE for other soluble carbonyl compounds, i.e., GA, GD, PD, and MG. The CE for FA was 42 ± 3%, over the altitude range upward of 5200 m (Figure 2), independent of the gas phase FA concentration between 0.5 and 5 ppbv. The constancy of the CE for FA was fortuitous as it happened that the pumping capacity diminished with increasing altitude, resulting in a decreased mass airflow through the coil. The amount of FA collected showed a corresponding decrease with altitude (Figure 2) in such a way that the calculated CE remained unchanged over the altitude range. It should be pointed out that the CE of this present system can only be empirically determined, which reflects the operation conditions, including the gas and liquid flow rates in addition to the ambient pressure. Consequently, the CE calibration was performed using an identical plumbing system (in terms of, e.g., the mass flow controller and the sample air pump) to that used on the aircraft to ensure the applicability of the calibration results.

Aircraft operation. The operation of the sampling device was found to be smooth. For the majority of the flights the variability of the liquid flow was <6%; the uncertainty of the individual sample volume collected was ±3%. On the other hand, because of the restriction associated with the gas plumbing system, the air sampling pump was only able to pull a flow at the preset nominal value of 4.0 slpm up to an altitude of 1000 m. Above which the flow rate decreased with increasing altitude, the lowest being ~2 slpm at 5000 m (Figure 2). The delay time was determined to be 150 ± 8 s and the collection time of each vial was 304 ± 1 s.

HPLC analysis. A typical chromatogram of the HPLC analysis of the samples is displayed in Figure 3 along with a blank. The separation is adequate for reliable peak area integration. The only exception is PD which was not baseline separated from FA. The uncertainty associated with PD is therefore somewhat greater than with the rest of the carbonyl compounds (see below). The aqueous concentrations of the carbonyl compounds were determined from the calibration curves established for each carbonyl using the blanks and
standards prepared with the same DNPH scrubbing solution used for sampling. The limit of detection in the liquid phase was estimated to be ~5 nM for all the carbonyl compounds. A peak which appeared immediately before FA and correlated strongly with GD was nearly always seen but has not been positively identified. This peak was also observed in our ground measurement at the Chebogue Point [Zhou and Lee, 1994].

Atmospheric mixing ratios. The gas phase concentrations of the carbonyl compounds were determined from the aqueous concentrations of the liquid sample (±8%), the total volume of air scrubbed (±3%), the liquid volume collected (±3%), and the collection efficiency of the system (±7%), the uncertainties in the parentheses being one-σ values. The limit of detection under typical conditions employed was 0.01 to 0.02 ppbv, depending on the sample airflow rate; since the air flow decreased with altitude, so does the limit of detection of this technique. Taking into account the uncertainties of the individual parameters given above, we estimated the measurement uncertainties to be ±15% ± 0.01 ppbv. It may be noted that FA, GA, and GD were always detected, but PD, GL, and MG were sometimes below their detection limits.

Example of data collected. We present in this section the measurement results obtained from flight 29, August 28, 1993, when a distinctive pollutant transport event was observed [Kleinman et al., this issue; Daum et al., this issue]. There were elevated levels of pollutants in a rather narrowly confined altitude range that provided a unique opportunity for examining the instrument performance. We plotted in Figure 4 the time series of the concentration of FA along with altitude for flight 29: a strong anticorrelation is observed between these two quantities showing a minimum FA concentration of 0.70 ppbv at 3000 m and a maximum of 5.4 ppbv at ~350 m. The concentration of FA was changing very little between 4.8 and 5.4 ppbv during horizontal traverses at ~350-m height in the pollution layer.

To investigate the relationship of FA to other photochemistry-related measurements, we plot in Figure 5 the concentrations of FA together with that of O₃ and the accumulation mode particles (ACP) [Kleinman et al., this issue]. Since the latter quantities...
Figure 6. Time series of the concentrations of five carbonyl compounds measured on flight 29, August 28, 1993.

Table 1. Correlation Coefficients (r) Among Concentrations of Carbonyl Compounds, O₃, and Accumulation Mode Particles (ACP) Measured on Flight 29, August 28, 1993

<table>
<thead>
<tr>
<th></th>
<th>GD</th>
<th>GA</th>
<th>FA</th>
<th>PD</th>
<th>GL</th>
<th>MG</th>
<th>ACP</th>
</tr>
</thead>
<tbody>
<tr>
<td>GD</td>
<td>0.49</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>GA</td>
<td>0.57</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>FA</td>
<td>0.31</td>
<td>0.93</td>
<td>0.95</td>
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<tr>
<td>PD</td>
<td>0.59</td>
<td>0.91</td>
<td>0.95</td>
<td>0.92</td>
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<tr>
<td>GL</td>
<td>0.49</td>
<td>0.97</td>
<td>0.96</td>
<td>0.95</td>
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<tr>
<td>MG</td>
<td>0.58</td>
<td>0.88</td>
<td>0.86</td>
<td>0.89</td>
<td>0.86</td>
<td>0.87</td>
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<tr>
<td>ACP</td>
<td>0.12</td>
<td>0.42</td>
<td>0.31</td>
<td>0.36</td>
<td>0.40</td>
<td>0.42</td>
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</tbody>
</table>

GD, glyoxylic acid; GA, glycoaldehyde; FA, formaldehyde; PD, pyruvic acid; GL, glyoxal; MG, methylglyoxal.

are known to be associated with photochemical reactions [e.g., Finlayson-Pitts and Pitts, 1986], we would take a positive correlation of FA with these parameters as a qualitative indication of consistency of the data. FA indeed showed a vertical distribution paralleling that of ACP for the entire altitude range and the correlation between those two species is highly significant (Table 1). The correlation of FA with O₃ is considerably weaker, arising from the fact that elevated levels of O₃ were also observed in clean air at high altitude. However, the pollution layer at the low altitude is well defined by all three species.

The corresponding time series of the concentrations of GA, GD, PD, GL, and MG are given in Figure 6. The highest concentration observed in this group was exhibited by GA in the pollution layer, reaching 1.3 ppbv, and the lowest was by MG at 3000 m, at its detection limit of ~0.01 ppbv. PD, GL, and MG exhibited maximum concentrations of, in descending order, 0.25, 0.14, and 0.23 ppbv, respectively. The concentration patterns as a function of time are in close correspondence to that of FA (Figure 3), with the exception of GD. The much weaker correlation of GD with other carbonyl compounds (Table 1) suggests that this compound is not strongly influenced by photochemistry and may have a source separate from that for the rest of the carbonyls. This behavior has also been observed on the ground at the Chebogue Point measurement site [Zhou and Lee, 1994]. A detailed analysis of the carbonyl data collected during this NARE intensive in terms of chemistry and transport will be reported in a subsequent publication.

Method evaluation. The method developed here has performed without major technical difficulties. No apparent interference was observed as far as chromatographic analysis was concerned. The batchwise nature of this technique provided only limited time resolution, in this case 5 min. However, this disadvantage is compensated for by the fact that a multitude of carbonyl compounds can be simultaneously determined. The nature of chromatographic separation in principle helps to improve specificity. Although the possibility of coelution cannot be completely ruled out in dealing with atmospheric samples, the DNPH derivatization serves as an additional discrimination step against such an occurrence. Finally, since the analysis was carried out on the ground, potential altitude effects on real-time detection systems in terms of sensitivity and baseline stability are obviated. The simplicity of the system results in significant savings of space and power consumption on the aircraft, as well as the manpower required for the operation, which all contribute to the cost effectiveness of this technique.

Further improvements are being contemplated. As an example: since the concentration of FA was always significantly greater than its limit of detection, the amount of liquid sample needed for the HPLC analysis can be reduced by a factor of 2 to 3, thereby increasing the sampling frequency.

Conclusions

An aircraft technique was developed for simultaneous measurement of formaldehyde, glycolaldehyde, glyoxylic acid, pyruvic acid, glyoxal, and methylglyoxal. A glass coil scrubbing technique was used for collecting discrete 5-min integrated samples, which were analyzed after flight using HPLC following derivatization with DNPH. The limit of detection is approximately 0.01 to 0.02 ppbv. The data obtained from flight 29, August 28, 1993, during which a pollution layer was encountered showed that the concentration levels of the carbonyl compounds corresponded well to other photochemical indicators characteristic of polluted air masses. While detecting substantial concentrations for all the carbonyl compounds in this pollutant layer, we found that these species were present at much lower levels at higher altitudes. This altitude dependence is consistent with prior experience with the distributions of reactive trace species.

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