PEROXYACETYL NITRATE AND METHANOL DATA FROM

FT-IR SPECTRAL RECORDS DURING THE 1986

CARBONACEOUS SPECIES METHODS COMPARISON STUDY

Final Report

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ABSTRACT

Peroxyacetyl nitrate (PAN) and methanol (CH_3OH) concentrations were derived from the longpath FT-IR spectra which were recorded during the Carbonaceous Species Methods Comparison Study (CSMCS) held on August 12-21, 1986 at Glendora, California. Both the detailed instantaneous and hourly average values of PAN and CH_3OH were determined.

The PAN concentrations during the CSMCS ranged from levels below a detection sensitivity of ~1.5 ppb at night to a maximum of 17 ppb during the peak of a smog episode. These FT-IR PAN data did not agree with measurements by another laboratory using gas chromatography with electron capture detection (EC-GC), with a regression analysis showing essentially zero correlation between the two sets of data and a large positive bias of the EC-GC data with respect to the FT-IR data. During the second half of the field study, in addition to maxima which corresponded to peaks of photochemical activity, smaller PAN maxima of 3-6 ppb were observed between midnight and dawn, with the pattern being coincident with the similar, but more pronounced behavior observed previously for formic acid (HCOOH).

The observed CH_3OH concentrations ranged from occasional levels below detection (<2 ppb) to momentary levels as high as 94 ppb which were attributed to local sources. Measurements in the range 2-10 ppb comprised 75% of the CH_3OH data, with 20% being in the 10-20 ppb range. The small maxima observed in the methanol concentration profile were distinctly non-coincident with the maxima of photochemical pollution. A search was carried out for absorptions due to dimethyl sulfate [$(CH_3O)_2SO_2$], but the results of the FT-IR analysis suggested that this species was not present in the gas phase at levels ≥ 3 ppb during the CSMCS.

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ACKNOWLEDGMENTS

DISCLAIMER

The statements and conclusions in this report are
those of the contractor and not necessarily those
of the California Air Resources Board.   The
mention of commercial products, their source or
their use in connection with material reported
herein is not to be construed as either an actual
or implied endorsement of such products.

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I. INTRODUCTION

Objectives. The main objective of this work was to derive the quantitative data for peroxyacetyl nitrate [PAN; $CH_3C(O)OONO_2$] and methanol (CH_3OH) from the longpath FT-IR spectra which were recorded during the Carbonaceous Species Methods Comparison Study (CSMCS) held in Glendora, California, August 12-21, 1986. As a further objective, the spectral analysis was extended for possible detection of gas-phase dimethyl sulfate [$(CH_3O)_2SO_2$].

Background. Our group at the Statewide Air Pollution Research Center (SAPRC) conducted ambient air measurements by longpath FT-IR spectroscopy during the 1986 Carbonaceous Species Methods Comparison Study with the primary task of providing benchmark data for formaldehyde (HCHO), nitric acid (HNO_3) and ammonia (NH_3) (Atkinson et al., 1987; Winer et al., 1987). Very recently, the same infrared spectral records were analyzed for formic acid (HCOOH) (Tuazon, 1989), resulting in the only set of HCOOH data against which the measurements of a filter collection/wet-chemical method could be compared. In principle, quantitative data for a number of other species are also contained in these spectra, among them PAN, methanol and possibly, dimethyl sulfate.

In previous longpath FT-IR studies, PAN concentrations of 3-37 ppb were measured during smog episodes in the California South Coast Air Basin (Tuazon et al., 1981; Tuazon et al., 1980). PAN was measured during the CSMCS by electron capture gas chromatography (EC-GC) with on-site calibration of the instrument, using a portable PAN generator, the output of which was determined by ion chromatography following alkaline hydrolysis of PAN to acetate (Grosjean et al., 1984). The California Air Resources Board (ARB) expressed the need for an independent set of PAN data to be used in an evaluation of the above EC-GC method. Thus, as the only source of comparison data for the measurements by the above method, the FT-IR spectra from the study period were analyzed for PAN concentrations.

There appears to be no substantive ambient air data that have been published previously for methanol. For example, in the latest update on the national ambient volatile organic compounds data base, published by the U.S. Environmental Protection Agency (Shah and Heyerdahl, 1988), methanol is not in the list of more than 300 chemicals for which data are

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available. It is anticipated that the current high interest in methanol as an alternative fuel (Coordinating Research Council, Inc., 1988) will lead to studies of future environmental impacts, the proper assessment of which should start with a knowledge of current ambient levels of methanol. The present analysis of the longpath FT-IR spectra from the CSMCS provided an opportunity to generate the first detailed set of baseline data for methanol which is applicable to the Los Angeles area.

Dimethyl sulfate is a highly toxic compound and a suspected carcinogen (Hoffmann, 1980). It was reported to be present in both gas phase and particulate samples of the Los Angeles atmosphere, with observed gas-phase concentrations of up to 4 ± 0.6 ppb for a 4-hr sampling period (Eatough et al., 1986). In the procedure indicated below, the search for the strongest infrared absorption band of dimethyl sulfate becomes straightforward following the analysis for methanol.

II. PROCEDURE

As described previously (Atkinson et al., 1987), the FT-IR spectra were recorded during the CSMCS at a pathlength of 1150 m and resolution of 0.13 cm^{-1}, at the rate of four to five spectra per hour, with a Sirius 100 (Mattson Instruments, Inc.) spectrometer interfaced to an open 25-m base-path multiple-reflection optical system.

To facilitate spectral processing, a truncated segment of the spectrum in the 750-1250 cm^{-1} region was generated from the original (256 kilobyte-length) single-beam spectrum. This was converted to an absorbance spectrum, baseline corrected, and then examined for the presence of absorptions by PAN, methanol and dimethyl sulfate after subtraction of interferences from the absorption lines of atmospheric H_2O, NH_3, CO_2 and O_3. Reference spectra for all the above compounds, used in processing the ambient air spectra, were generated in the laboratory at pathlengths of 180-240 m by injection of known amounts of samples into SAPRC's 5800-L evacuable chamber which was equipped with a set of 3.77 m basepath multiple-reflection optics. The reference spectra were recorded with the same FT-IR instrument used in the CSMCS, operated with the same spectral parameters (i.e., resolution, scan velocity, apodization, etc.). Through an interactive subtraction routine the concentrations (absorbances) of PAN and CH_3OH were expressed as fractions of the PAN and CH_3OH concentrations in the reference spectra.

Figure 1 depicts the infrared region where the absorption bands of PAN, methanol and dimethyl sulfate which are most appropriate for measurements are located. The traces are shown for 0.32 ppm of each compound at 180 m path (absorbances equivalent to those for 0.05 ppm at 1150 m).

PAN was determined from its relatively broad band at 1163.5 cm^{-1}, which has an absorptivity (base 10) of 14.5 cm^{-1} atm^{-1} (Niki et al., 1985; see also Stephens, 1964). In order to define the baseline more accurately, the interferences by H_2O absorptions were reduced by subtraction. The analysis of CH_3OH was based on the height of its Q-branch at 1033.3 cm^{-1}, with an absorptivity (peak-to-valley) of 10.2 cm^{-1} atm^{-1} measured in this work. Ozone absorption was an important interference, particularly in the daytime spectra. Minor interferences by NH_3, CO_2 and H_2O were also

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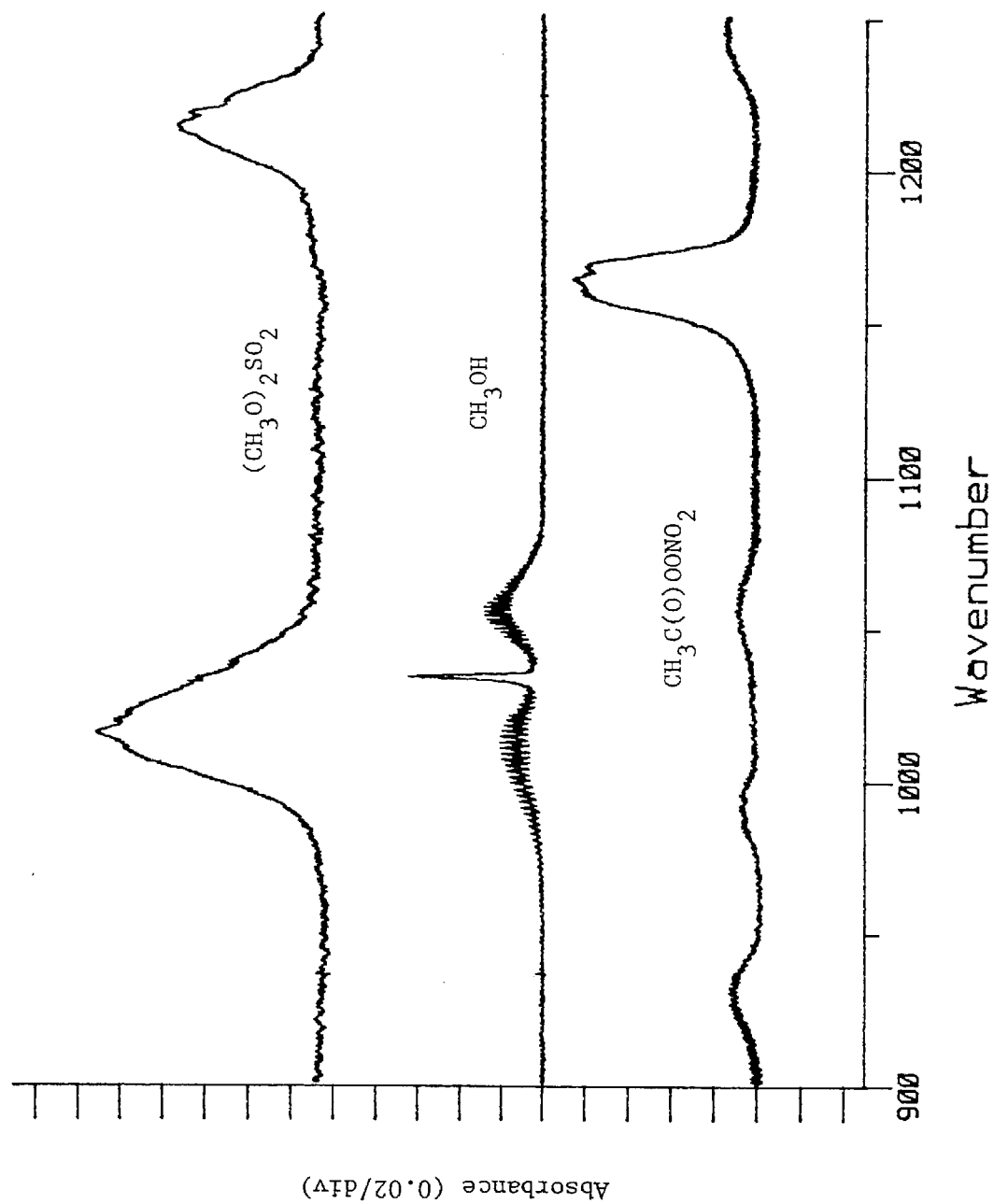
Figure 1. Relative intensities of absorption bands by PAN, methanol and dimethyl sulfate. Concentration = 0.32 ppm for each compound; pathlength = 180 m; resolution = 0.13 cm^{-1}.

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corrected. The interfering absorptions due to the above species were fine structures which were significantly narrower than the 1033.3 cm^{-1} Q-branch of methanol, such that the latter's contour was not adversely affected by all the above subtraction steps. The residual spectra from the CH_3OH analysis were then examined for the presence of the broad band envelope of $(CH_3O)_2SO_2$ centered at ~1015 cm^{-1}, with an absorptivity of 18 cm^{-1} atm^{-1} measured in this work.

PAN samples for reference spectra were prepared and purified according to the method of Stephens et al. (1965). Ozone was generated by flowing O_2 (99.98% min, Liquid Carbonic) through a Welsbach T-408 ozonizer, with the O_2-O_3 mixture being collected in a calibrated 5-L bulb and a 10-cm cell for quantitation by infrared spectroscopy. The sources and purities of the other compounds were as follows: CH_3OH, 99.9%, Aldrich; $(CH_3O)_2SO_2$, 99+%, Aldrich; NH_3, 99.99% min, Matheson; CO_2, 99.8% min, Liquid Carbonic. Partial pressures of these other compounds were measured in calibrated 2-L and 5-L Pyrex bulbs for injection into the 5800-L chamber.

III. RESULTS AND DISCUSSION

The detailed "instantaneous" (5-min measurement time per spectrum) PAN and CH_3OH data for August 12-21, 1986, in Glendora, California, obtained by long pathlength FT-IR spectroscopy are presented in Table 1. As noted previously (Atkinson et al., 1987), gaps in the data, marked by asterisks in Table 1, occurred due to instrument testing on August 12, power interruptions on August 14, and fault in archiving the daytime data to magnetic tapes on August 17.

Peroxyacetyl Nitrate. The instantaneous PAN concentrations during the field study ranged from undetectable levels, generally around midnight, to a maximum of 17 ppb during the smog episode of August 15. (Potentially higher PAN concentrations could have been recorded on August 17, but the data were lost as noted above.) The FT-IR detection sensitivity for PAN was estimated to be 1.5 ppb. The adherence to a consistent procedure during the interactive subtraction of PAN yielded numbers below 1.5 ppb as well, but these lower values are being retained only in Table 1 simply for the purpose of illustrating the trend in concentration. The error e in the concentration c(ppb) is expressed by $e^2 = 2.3 + 0.008c^2$, where the first term is the contribution of random noise in the spectrum and the second term is due to the uncertainty in the absorption coefficient (Tsalkani and Toupance, 1989). Thus, the measurement errors for the range of PAN concentrations observed were within ± 2.5 ppb.

Hourly average concentrations were calculated (by integrated area method) from the instantaneous values and presented in Table 2. Some entries in Table 2 resulted from a mix of values above and below the detection limit, with hourly average values less than 1.5 ppb being retained only to indicate the trend in concentration.

Figure 2 illustrates some of the intensities of the 1164 cm^{-1} band of PAN observed on August 15. The detailed time-concentration profile for PAN by FT-IR during the CSMCS is depicted in Figure 3.

The daytime PAN concentration profile generally tracked that of the previously published CSMCS nitric acid (HNO_3) concentrations (Atkinson et al., 1987), consistent with these species being good indicators of photochemical activity (Tuazon et al., 1981). However, during the second half of the field study, smaller maxima of 3-6 ppb were also observed during

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Table 1. PAN and CH₃OH concentrations (ppb) in Glendora, CA, August 12-21, 1986, by long pathlength FT-IR spectroscopy [Asterisks mark the times where gaps in the data occur. Concentrations below 1.5 ppb for PAN and 2 ppb for CH_3OH are being included only to illustrate the trend in concentrations (see text)]

PDT	PAN	CH_3OH	PDT	PAN	CH_3OH	PDT	PAN	CH_3OH
08/12/86			1816	0.8	1.3	0715	0.4	7.6
			1828	0.6	2.3	0731	0.2	7.1
0758	1.5	9.9	1848	1.2	3.1	0746	0.5	6.6
0811	2.1	10.2	1904	1.7	4.0	0802	0.4	6.9
0825	2.5	9.1	1920	1.1	2.6	0818	0.6	6.8
0837	2.7	9.0	1934	0.5	2.9	0833	1.0	6.4
0851	3.5	9.5	1947	1.5	3.0	0849	1.3	6.8
0905	3.6	8.7	2000	1.0	3.2	0904	1.2	6.9
0917	4.0	8.7	2014	1.2	2.6	0920	1.6	6.6
0930	4.5	9.6	2106	1.0	3.1	0936	2.2	7.1
0944	4.5	8.5	2118	1.0	3.7	0951	3.0	6.5
0957	5.2	10.1	2132	0.8	4.2	1001	3.7	6.6
1010	5.8	7.9	2144	0.8	4.6	1035	4.6	6.8
1024	5.3	8.2	2201	0.9	4.6	1048	5.2	6.7
1037	5.9	6.9	*2215	0.8	5.2	1101	5.6	6.3
1052	5.9	8.5				1114	5.8	6.5
1119	6.6	8.9	08/13/86			1128	5.6	6.2
1136	7.3	7.4				1145	5.7	5.8
1149	6.9	6.2	*0027	0.9	4.8	1158	5.9	5.6
1202	7.2	4.7	0043	0.8	4.9	1211	5.6	5.2
1221	6.0	5.6	0059	0.8	4.8	1229	6.5	5.1
1234	5.3	4.8	0114	0.7	4.6	1248	6.2	4.4
1250	5.3	13.0	0130	0.5	4.7	1309	6.2	4.0
1305	5.4	12.0	0146	0.5	4.7	1331	5.6	5.0
1320	5.9	3.8	0201	0.3	4.6	1344	6.0	4.7
1339	6.3	2.5	0217	0.3	5.0	1357	5.2	4.7
1353	6.6	3.6	0233	0.1	5.1	1410	6.5	3.8
1406	7.9	3.3	0249	0.0	6.8	1423	5.2	3.2
1419	8.4	2.8	0304	0.0	7.0	1440	6.3	2.9
1433	10.8	2.8	0320	0.0	5.3	1453	6.9	3.1
1447	12.6	3.3	0336	0.0	5.4	1506	6.5	3.5
1503	13.1	1.2	0351	0.0	4.4	1522	6.9	3.5
1517	11.3	5.2	0407	0.0	4.4	1535	6.7	3.1
1532	9.3	4.5	0423	0.0	4.0	1548	8.1	4.1
1546	7.8	3.9	0439	0.2	4.1	1601	8.4	3.9
1608	3.6	3.7	0454	0.0	6.6	1614	8.9	3.8
1622	3.5	2.6	0510	0.0	5.5	1630	8.2	3.6
1635	3.3	2.4	0526	0.0	8.1	1643	8.5	3.7
1651	2.3	2.9	0541	0.0	7.7	1655	7.1	4.6
1705	1.2	2.0	0557	0.0	7.2	1706	6.4	4.8
1718	1.0	1.7	0612	0.0	8.9	1718	6.2	5.7
1732	0.9	0.8	0628	0.0	8.0	1734	5.5	4.6
1745	0.5	0.0	0644	0.0	8.4	1747	5.3	4.7
1802	0.6	0.4	0659	0.0	7.6	1800	4.5	5.2

Table 1 (continued) - 2

PDT	PAN	CH$_3$OH	PDT	PAN	CH$_3$OH	PDT	PAN	CH$_3$OH
1813	4.5	4.6	*0914	0.0	7.2	1256	9.4	5.0
1827	4.0	4.3	*2210	2.4	3.1	1309	9.7	4.0
1850	3.0	4.0	2229	2.2	2.9	1325	11.1	4.8
1913	2.7	3.8	2249	2.0	2.2	1341	10.7	3.5
1926	2.8	3.3	2309	1.1	3.1	1353	9.5	4.1
1939	2.9	3.0	2328	1.0	3.1	1410	10.9	4.2
1952	2.4	3.0	2348	0.7	3.3	1425	16.3	3.5
2005	2.1	1.9				1440	15.6	3.3
2018	2.4	2.6	08/15/86			1453	16.5	4.1
2034	2.3	2.2				1505	16.9	4.3
2113	2.5	3.2	0008	0.5	3.3	1518	14.5	4.8
2133	2.1	3.0	0027	0.2	3.6	1530	13.3	6.2
2146	1.5	3.0	0047	0.2	2.9	1542	11.4	6.0
2206	1.3	3.9	0107	0.2	3.4	1604	9.1	5.9
2226	1.4	4.3	0126	0.1	3.9	1616	8.7	6.4
2245	1.2	4.0	0146	0.3	4.2	1629	7.4	4.9
2305	1.3	3.6	0206	0.0	3.4	1641	6.7	3.6
2324	0.9	3.8	0225	0.0	4.0	1653	6.3	2.2
2344	1.0	3.9	0245	0.0	3.5	1707	5.7	3.0
			0305	0.0	5.1	1720	5.3	2.9
08/14/86			0324	0.0	5.0	1732	5.2	2.7
			0344	0.0	4.9	1744	4.9	1.6
0004	0.9	3.6	0404	0.0	5.0	1757	4.5	2.0
0023	0.5	3.9	0424	0.0	4.4	1830	4.4	1.5
0043	0.2	3.2	0443	0.0	4.5	1842	4.4	3.0
0102	0.0	3.9	0503	0.0	5.3	1854	4.1	2.4
0122	0.1	4.7	0523	0.0	5.5	1907	3.8	2.1
0142	0.0	4.2	0543	0.0	4.8	1919	3.6	2.0
0201	0.0	4.9	0602	0.0	4.8	1938	3.3	2.5
0221	0.0	4.1	0622	0.0	5.0	1950	2.8	2.5
0241	0.0	4.0	0641	0.0	5.1	2003	2.5	2.6
0300	0.0	3.5	0701	0.0	4.9	2015	2.1	2.1
0320	0.0	3.3	0721	0.0	5.7	2027	2.0	2.9
0339	0.0	3.2	0741	0.0	4.8	2106	1.0	2.8
0359	0.0	3.4	0800	0.1	5.7	2125	0.8	2.7
0419	0.0	4.0	0820	1.1	5.2	2145	0.8	2.7
0438	0.0	4.3	0840	1.1	28.1	2205	0.5	3.4
0458	0.0	5.4	0859	1.5	5.6	2224	0.5	3.4
0518	0.0	4.4	0919	2.0	5.1	2244	0.5	3.6
0537	0.0	4.7	1016	3.8	5.2	2304	0.5	3.8
0557	0.0	4.8	1029	4.1	35.1	2323	0.4	4.1
0616	0.0	4.8	1043	4.9	6.1	2343	0.5	5.0
0636	0.0	4.4	1100	5.8	4.9			
0656	0.0	5.0	1112	6.2	5.8	08/16/86		
0716	0.0	5.1	1126	6.8	5.2			
0735	0.0	5.2	1138	7.3	5.0	0003	0.4	4.3
			1151	8.2	5.5	0022	0.5	4.4
0755	0.0	5.5	1203	9.6	5.3	0042	0.4	4.8
0815	0.0	5.0	1219	10.5	4.6	0101	0.5	5.0
0834	0.0	6.1	1231	10.2	4.5	0121	0.5	7.0
0854	0.0	6.1	1244	9.5	4.7	0141	0.3	8.7

Table 1 (continued) - 3

PDT	PAN	CH$_3$OH	PDT	PAN	CH$_3$OH	PDT	PAN	CH$_3$OH
0200	0.3	7.7	1558	14.8	4.1	0624	4.7	13.1
0220	0.4	6.1	1610	15.0	3.3	0644	4.7	12.6
0240	0.4	7.1	1623	15.5	2.2	0704	4.5	11.6
0259	0.0	8.5	1635	13.3	2.8	0723	4.7	13.6
0319	0.1	6.3	1647	12.9	3.2	0743	4.7	9.9
0339	0.3	7.8	1659	12.4	2.5	0803	4.9	12.8
0359	0.4	6.1	1711	11.3	3.1	0823	5.4	8.8
0418	0.3	8.9	1724	11.3	4.0	0843	6.1	8.7
0438	0.5	10.2	1736	9.6	3.0	0902	7.0	7.6
0458	0.4	9.0	1748	9.4	3.1	0922	8.4	7.0
0517	0.0	7.5	1800	9.0	2.6	0942	8.8	9.6
0537	0.1	9.5	1812	9.2	2.1	*1002	9.2	32.1
0557	0.4	9.6	1902	5.9	2.6	*2235	1.4	6.8
0616	0.5	9.1	1917	6.0	3.2	2253	1.1	5.7
0636	0.5	7.3	1929	5.9	3.3	2306	1.2	4.2
0656	0.7	9.0	1942	5.0	3.1	2317	1.2	5.3
0715	1.1	9.4	1954	4.7	3.5	2337	1.6	5.8
0735	0.9	6.8	2006	4.5	4.4	2356	1.9	6.0
0755	1.4	7.2	2024	5.1	3.8			
0815	1.3	6.9	2036	4.4	3.9	08/18/86		
0834	1.7	6.8	2049	4.6	4.0			
0854	2.2	6.5	2136	3.6	4.0	0016	2.0	6.1
0914	3.2	5.6	2152	3.8	4.0	0036	1.8	6.9
0933	3.8	5.5	2212	4.1	5.9	0056	1.9	7.4
1015	6.7	5.9	2232	4.0	7.0	0115	2.2	6.9
1028	6.7	8.3	2251	3.3	5.4	0135	2.2	6.5
1048	7.8	6.3	2311	2.6	5.0	0155	2.4	7.8
1100	8.4	6.0	2331	2.5	5.1	0214	2.6	8.6
1118	9.5	6.4	2350	2.1	4.9	0234	2.3	8.9
1131	10.0	5.5				0254	1.8	8.8
1143	10.0	5.2	08/17/86			0313	2.0	9.3
1155	10.3	4.9				0333	1.9	10.5
1207	10.4	4.1	0010	2.2	6.2	0353	1.6	9.9
1219	10.4	4.3	0030	1.6	9.5	0412	1.8	9.8
1231	10.4	4.5	0049	3.8	9.8	0432	1.9	11.7
1243	9.7	3.8	0109	3.4	9.8	0452	1.8	12.7
1255	9.9	3.7	0129	3.5	11.3	0511	1.8	15.0
1308	9.8	2.5	0148	3.5	13.2	0531	1.4	12.9
1320	9.3	3.2	0208	4.5	10.7	0550	1.0	12.4
1332	9.9	2.4	0228	4.4	13.6	0610	1.1	10.7
1344	10.9	6.4	0248	4.4	13.7	0630	0.7	11.3
1356	10.5	3.0	0307	4.9	13.5	0649	0.4	11.7
1409	10.3	2.6	0327	6.1	11.1	0709	0.7	11.9
1421	11.6	3.3	0347	5.9	13.1	0729	0.9	15.4
1433	10.5	3.2	0406	6.4	11.0	0748	0.9	11.2
1445	11.9	2.8	0426	6.3	13.2	0808	0.8	13.5
1457	13.7	2.4	0446	6.3	13.2	0828	1.4	11.4
1509	14.8	3.4	0506	6.0	12.4	0847	1.5	13.1
1522	14.8	2.4	0525	6.0	12.3	0907	1.5	93.7
1534	15.0	3.7	0545	5.3	11.1	0926	1.5	88.5
1546	16.0	3.5	0605	5.3	11.0	0946	1.8	10.1

Table 1 (continued) - 4

PDT	PAN	CH$_3$OH		PDT	PAN	CH$_3$OH		PDT	PAN	CH$_3$OH
1004	1.7	17.0		2124	0.9	4.9		1225	4.7	8.3
1017	1.7	27.3		2206	0.9	21.0		1237	5.0	7.2
1029	2.1	20.5		2226	0.9	26.4		1249	4.2	6.0
1057	3.5	10.5		2246	0.9	20.2		1305	2.5	4.3
1111	4.5	10.3		2305	0.9	10.9		1317	4.6	5.4
1123	5.2	10.2		2325	0.9	12.7		1329	6.7	5.8
1140	5.4	9.4		2345	0.9	12.7		1346	8.6	7.7
1156	4.9	7.6						1355	12.7	8.0
1207	5.5	9.3		08/19/86				1405	11.6	8.9
1220	4.5	7.6						1415	9.1	7.1
1233	3.7	6.9		0004	1.3	11.2		1426	7.4	6.6
1245	2.8	5.5		0024	1.2	9.8		1436	6.0	6.9
1256	4.1	4.9		0044	1.1	15.3		1448	6.1	6.3
1308	3.9	4.3		0103	1.0	12.0		1501	5.2	6.6
1320	3.0	3.0		0123	1.1	11.3		1512	4.6	5.4
1333	2.0	2.5		0143	1.1	12.6		1522	4.3	5.3
1345	2.6	2.0		0202	1.2	13.5		1532	3.3	6.0
1357	2.3	2.1		0222	1.3	13.2		1542	3.0	4.6
1409	1.6	2.0		0242	1.6	12.9		1554	3.0	3.6
1421	2.7	1.9		0301	1.6	11.9		1604	2.1	3.4
1433	3.8	1.1		0321	1.2	11.5		1614	0.9	3.3
1445	3.0	1.1		0341	1.3	12.6		1624	1.1	3.2
1457	3.6	3.1		0400	2.0	13.2		1634	1.0	3.1
1509	5.7	4.5		0420	1.5	12.1		1645	1.0	2.9
1521	7.0	3.1		0439	2.0	11.4		1655	1.0	3.2
1534	8.1	2.4		0459	1.8	13.3		1705	1.0	3.5
1546	9.7	1.6		0519	2.3	13.3		1720	1.0	2.0
1558	7.3	2.2		0538	2.5	12.3		1733	1.5	3.5
1610	7.8	2.0		0558	2.5	15.4		1747	1.3	3.7
1622	6.9	2.1		0618	2.5	14.3		1759	1.4	3.9
1635	4.6	2.4		0637	2.4	15.1		1811	1.1	3.2
1647	3.4	1.9		0657	2.8	16.4		1823	1.1	4.6
1700	3.4	1.9		0717	2.6	14.8		1835	1.1	4.4
1712	2.2	1.6		0737	3.3	17.9		1847	1.3	2.7
1724	2.1	2.2		0757	2.8	70.8		1902	1.0	4.2
1737	1.6	2.1		0816	2.9	16.3		1914	1.0	5.2
1750	1.9	1.0		0836	2.6	11.2		1927	1.0	6.0
1802	1.9	2.4		0855	2.7	11.1		1939	1.0	5.0
1814	1.2	2.0		0915	2.7	9.1		2007	1.0	5.1
1826	1.1	2.0		0935	2.7	10.1		2017	1.0	4.7
1839	1.1	1.6		1006	2.9	10.3		2029	1.0	5.7
1852	1.1	1.9		1018	3.5	8.1		2042	0.9	6.2
1932	1.0	1.1		1030	3.7	8.5		2054	1.1	5.4
1944	0.9	1.1		1043	3.8	9.7		2106	1.0	5.2
1956	1.6	1.4		1057	4.2	9.0		2118	0.8	5.8
2009	1.7	1.1		1109	5.2	10.1		2130	0.8	5.1
2021	1.2	2.7		1121	4.9	8.4		2142	0.8	6.6
2035	1.1	3.1		1133	4.5	8.9		2155	0.8	6.4
2047	1.3	3.7		1148	4.7	7.0		2207	0.9	6.3
2059	0.9	3.7		1200	5.0	7.0		2219	1.1	13.3
2111	0.9	4.6		1213	4.1	7.0		2231	1.1	13.9

Table 1 (continued) - 5

PDT	PAN	CH$_3$OH	PDT	PAN	CH$_3$OH	PDT	PAN	CH$_3$OH
2243	1.1	13.7	1300	9.8	8.6			
2314	1.1	13.8	1311	9.9	7.1	08/21/86		
2334	1.2	13.9	1321	11.1	5.2			
2353	1.5	14.7	1331	10.2	6.2	0006	3.8	11.0
			1341	10.3	6.1	0026	3.9	12.6
08/20/86			1352	10.5	5.6	0046	3.7	14.1
			1402	10.7	5.5	0106	4.0	16.4
0013	1.6	13.9	1414	11.9	6.5	0125	3.8	14.0
0032	1.7	16.6	1424	11.0	6.8	0145	3.8	11.4
0052	1.7	14.3	1434	9.5	6.9	0204	3.7	13.6
0112	3.0	15.5	1444	9.4	5.7	0224	3.8	12.5
0131	2.9	17.2	1454	7.0	5.6	0244	3.5	13.8
0151	2.7	16.1	1507	6.6	6.7	0303	3.8	14.7
0210	3.1	16.9	1517	6.7	7.3	0323	3.5	14.6
0230	3.1	17.5	1530	6.5	7.0	0343	2.6	15.0
0250	3.2	17.8	1540	5.6	5.0	0402	2.8	11.7
0309	3.8	17.0	1550	5.5	5.8	0422	2.6	10.5
0329	3.9	17.6	1600	5.3	4.5	0442	2.7	15.4
0348	3.9	17.6	1610	4.1	3.9	0501	2.7	16.1
0408	3.4	16.7	1621	3.2	3.1	0521	2.6	17.3
0428	3.3	17.2	1631	3.3	2.2	0541	2.6	15.3
0447	3.8	16.3	1643	2.5	2.7	0601	2.7	17.1
0507	4.1	18.1	1656	2.2	2.1	0620	2.5	18.2
0527	3.9	16.4	1706	2.4	3.2	0640	2.5	18.1
0546	3.7	18.0	1716	2.5	3.6	0700	2.5	17.4
0606	3.9	18.1	1727	2.4	3.3	0717	3.1	18.6
0625	3.7	18.0	1737	2.4	3.2	0730	3.4	17.8
0645	3.7	17.6	1747	2.5	3.9			
0705	3.6	18.2	1757	2.8	3.8			
0724	3.4	16.0	1807	3.5	4.8			
0744	3.9	17.8	1817	3.5	2.3			
0803	2.8	15.2	1828	3.4	4.4			
0823	3.3	15.7	1839	3.3	5.2			
0843	3.9	18.3	1849	3.3	5.0			
0902	3.6	18.0	1900	2.9	5.0			
0923	4.3	15.5	1910	3.0	5.2			
0942	4.5	16.2	1920	2.7	5.1			
1001	5.0	15.3	1930	2.8	5.1			
1013	5.1	15.3	1940	3.1	5.6			
1025	5.2	12.8	2023	2.8	4.0			
1038	4.3	9.1	2035	2.5	4.1			
1050	4.7	9.7	2050	2.6	4.2			
1104	4.4	7.7	2110	2.8	7.2			
1117	5.2	8.8	2129	2.9	6.4			
1129	5.7	7.7	2149	3.8	9.4			
1141	6.0	7.5	2209	3.5	8.1			
1153	5.7	9.2	2228	3.1	7.9			
1208	7.5	9.0	2248	2.7	6.8			
1220	9.4	8.4	2307	3.2	9.4			
1232	9.3	9.8	2327	3.0	8.3			
1244	12.6	11.1	2347	3.6	13.5			

Table 2. Hourly average PAN concentrations (ppb) at Glendora, CA, August 12-21, 1986, measured by long pathlength FT-IR spectroscopy[a,b,c]

PDT	Aug 12	Aug 13	Aug 14	Aug 15	Aug 16	Aug 17	Aug 18	Aug 19	Aug 20	Aug 21
0000-0100		0.9	0.4	0.3	0.4	2.5	1.9	1.2	1.7	3.8
0100-0200		0.6	0.0	0.2	0.4	3.5	2.2	1.1	2.8	3.8
0200-0300		0.2	0.0	0.0	0.3	4.4	2.3	1.4	3.1	3.7
0300-0400		0.0	0.0	0.0	0.2	5.7	1.8	1.4	3.8	3.2
0400-0500		0.1	0.0	0.0	0.4	6.3	1.8	1.8	3.6	2.7
0500-0600		0.0	0.0	0.0	0.2	5.7	1.4	2.3	3.9	2.6
0600-0700		0.0	0.0	0.0	0.5	4.8	0.7	2.5	3.7	2.5
0700-0800		0.3	0.0	0.0	1.1	4.7	0.8	2.9	3.5	
0800-0900	2.7	0.9	0.0	1.0	1.7	5.7	1.3	2.7	3.4	
0900-1000	4.3	2.1	ND	2.4	3.9	8.4	1.6	2.7	4.3	
1000-1100	5.7	4.6	ND	4.4	7.0	ND	2.3	3.6	4.8	
1100-1200	6.8	5.7	ND	7.1	9.7	ND	4.9	4.8	5.5	
1200-1300	5.9	6.1	ND	9.9	10.2	ND	4.1	4.4	9.7	
1300-1400	6.1	5.8	ND	10.3	10.1	ND	2.8	6.9	10.4	
1400-1500	10.3	6.1	ND	14.6	11.4	ND	2.9	7.7	9.9	
1500-1600	9.6	7.2	ND	13.2	15.0	ND	7.4	3.8	6.2	
1600-1700	3.2	8.2	ND	7.6	14.0	ND	5.5	1.1	3.2	
1700-1800	0.9	5.7	ND	5.2	10.4	ND	2.1	1.2	2.5	
1800-1900	0.9	3.8	ND	4.4	7.9	ND	1.2	1.2	3.3	
1900-2000	1.2	2.7	ND	3.3	5.5	ND	1.1	1.0	2.9	
2000-2100	1.1	2.3	ND	1.9	4.6	ND	1.3	1.0	2.7	
2100-2200	0.9	2.0	ND	0.8	3.9	ND	0.9	0.8	3.2	
2200-2300	ND	1.3	2.1	0.5	3.8	ND	0.9	1.1	3.1	
2300-2400	ND	1.0	0.9	0.5	2.4	1.5	0.9	1.2	3.3	

[a]Entries <1.5 ppb are included only as indicators of trend in concentration (see text).
[b]Blank means outside the schedule.
[c]ND designates no data due to instrument testing on August 12, power interruptions on August 14, and fault in archiving on August 17.
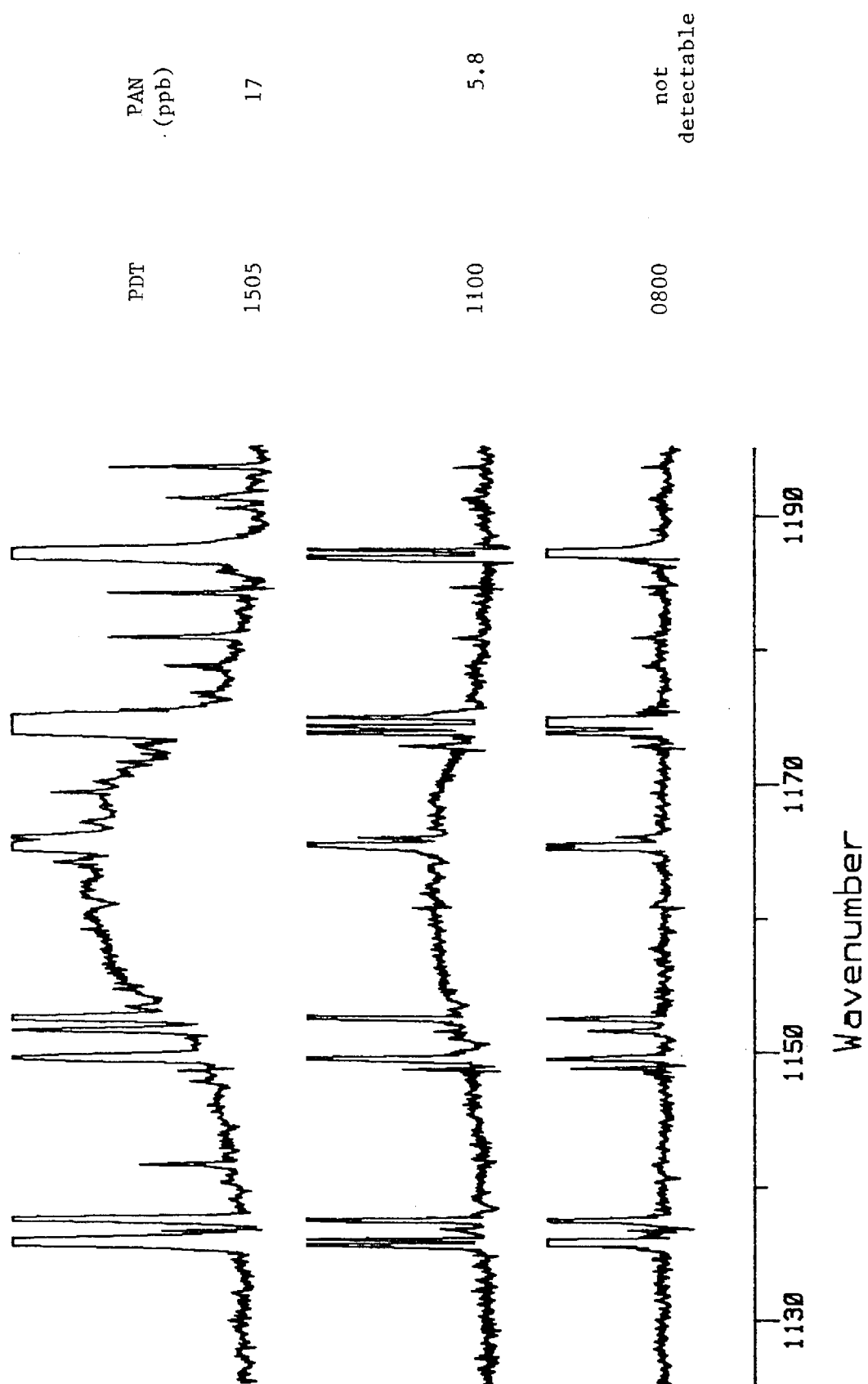
Figure 2. Detection of the 1164 cm^{-1} band envelope of PAN on August 15, 1986, in Glendora, CA.
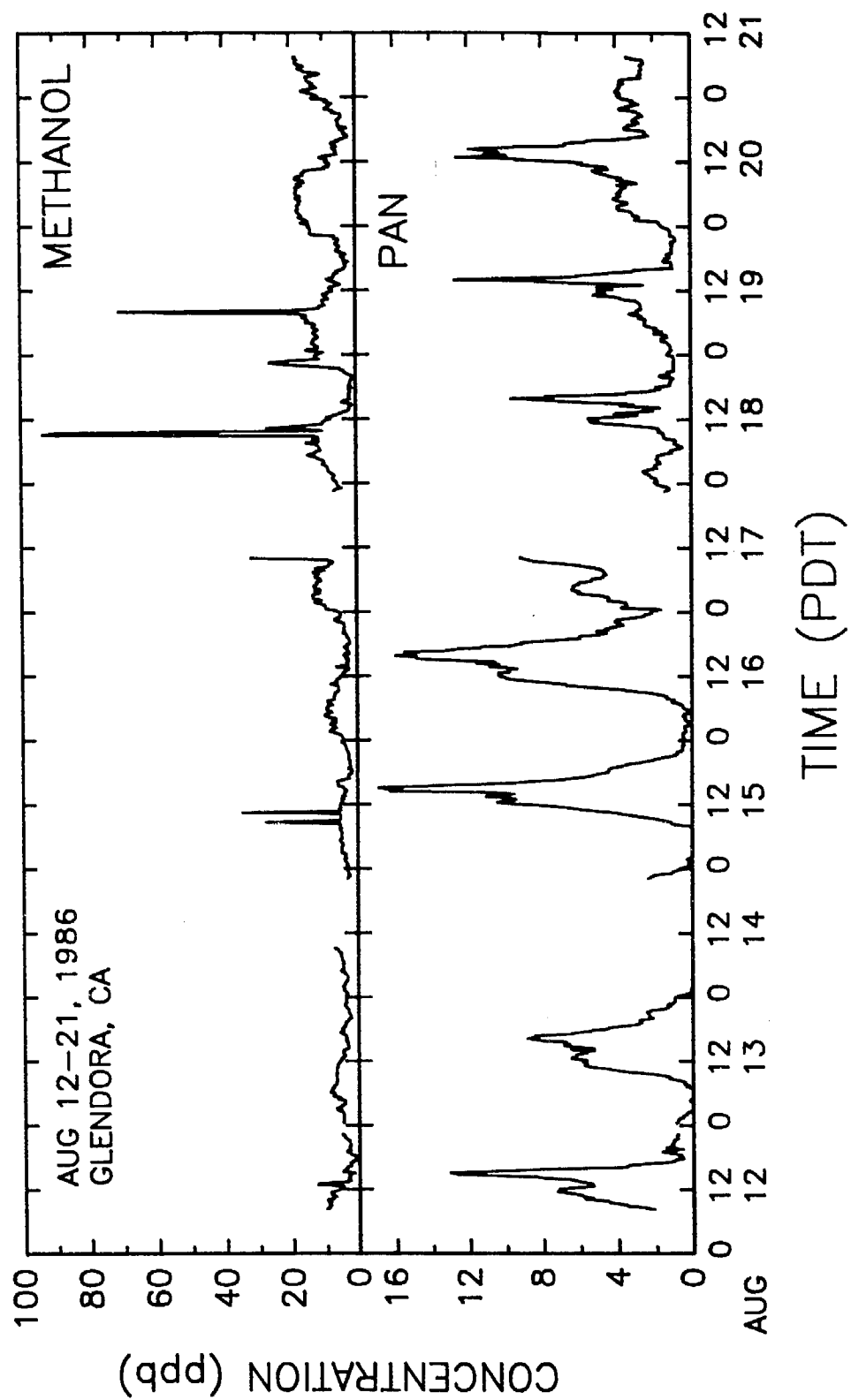
Figure 3. Time–concentration profiles of PAN and CH$_3$OH during the CSMCS.

the hours between midnight and dawn, with the pattern being coincident with that observed for the formic acid (HCOOH) profile which was derived earlier (Tuazon, 1989) from the same CSMCS FT-IR spectral records. An overlay of the time-concentration profiles of PAN and HCOOH is presented in Figure 4. [During the processing of the spectra for this study, most of the August 14 daytime spectral files were rendered unrecoverable from the magnetic tape archive by a power failure, hence the scarcity of PAN (as well as methanol) data relative to HCOOH during this day.] A satisfactory explanation for the occurrence of early morning peaks for both species would perhaps require a study of the more complete CSMCS data (i.e., other chemical species as well as meteorological variables) in the ARB compilation.

The hourly average PAN concentrations by the FT-IR method (Table 2) and those from the EC-GC measurements obtained by DGA, Inc. (Grosjean et al., 1988) are plotted in Figure 5, along with the hourly average O_3 concentrations (from the ARB data compilation) during the CSMCS. The FT-IR PAN profile coincided very strongly with the O_3 profile, even including the early morning maxima noted above, while such correspondence was not consistently observed in the case of the EC-GC PAN data. The regression plot of Figure 6 shows essentially zero correlation between the PAN data by EC-GC (DGA) and the PAN data by FT-IR (UCR), with the former being characterized by a large positive bias with respect to the latter.

Methanol. The instantaneous CH_3OH concentrations are enumerated in Table 1 along with the PAN data. Following a derivation similar to that for PAN, the error e in the methanol concentration c(ppb) is expressed by $e^2 = 4.6 + 0.003c^2$. The instrument's detection sensitivity for CH_3OH was ~2 ppb, but, as in the case of PAN analysis lower readings resulted from following a consistent procedure, and these values are retained in Table 1 to help indicate the trend in concentration. Hourly average CH_3OH values are given in Table 3, with values below ~1.5 ppb not being meaningful and included only for the sake of completeness.

The CH_3OH concentrations ranged from occasional levels below detection (<2 ppb) to momentary "spikes" from local sources of as high as 94 ppb. Measurements in the range 2-10 ppb comprised 75% of the data, with 20% being in the 10-20 ppb range.
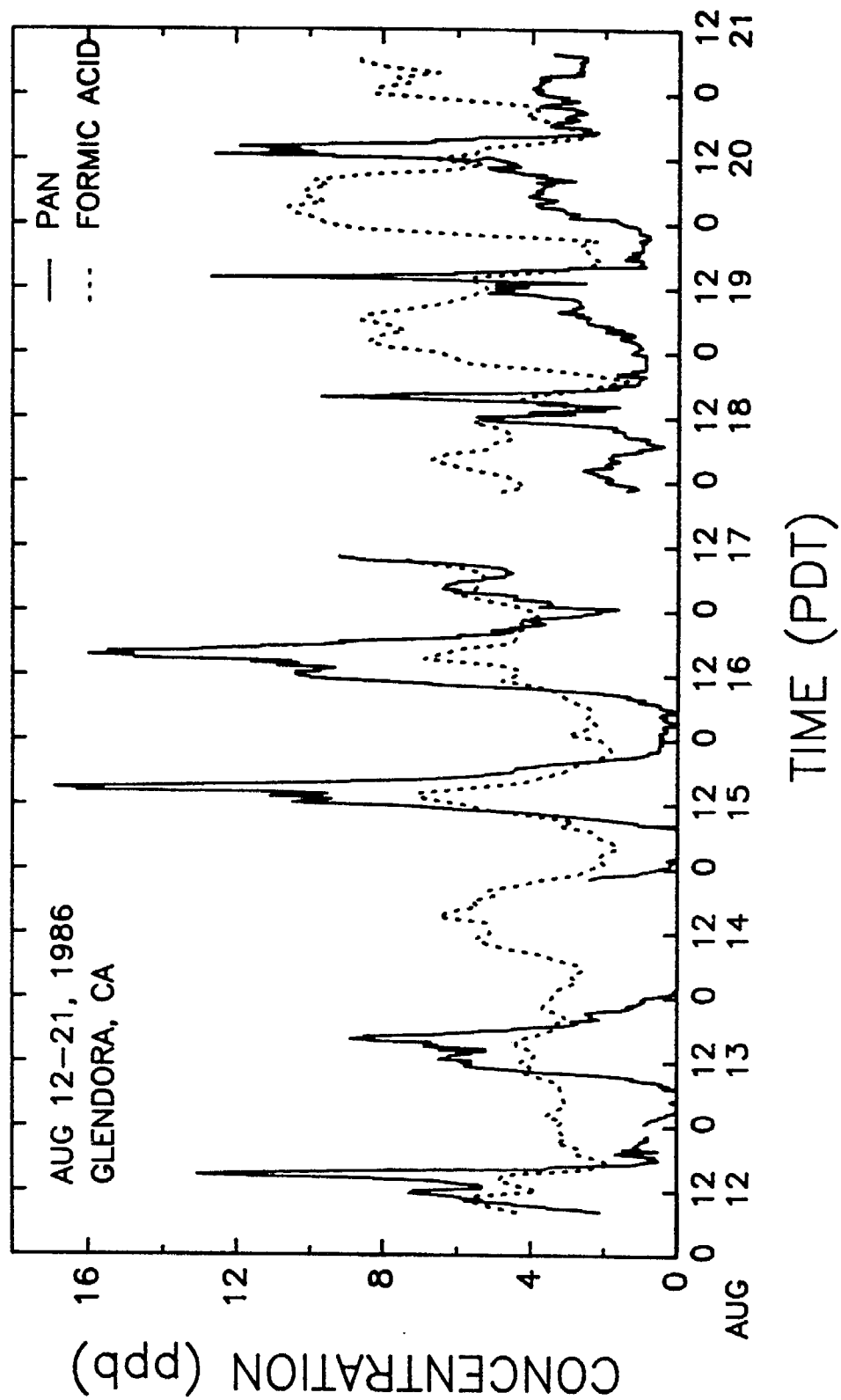
Figure 4. Time-concentration profiles of PAN and HCOOH during the CSMCS.
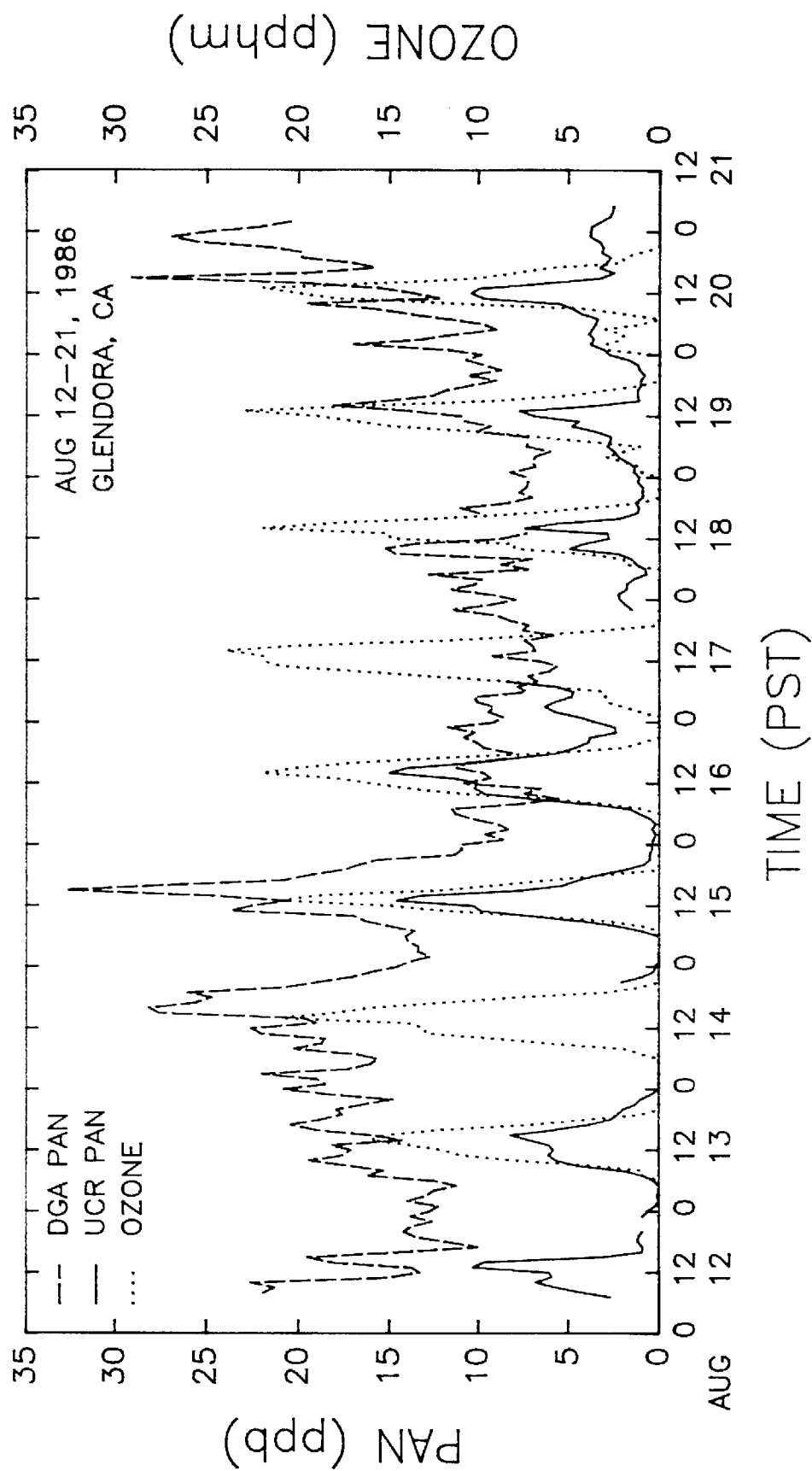
16

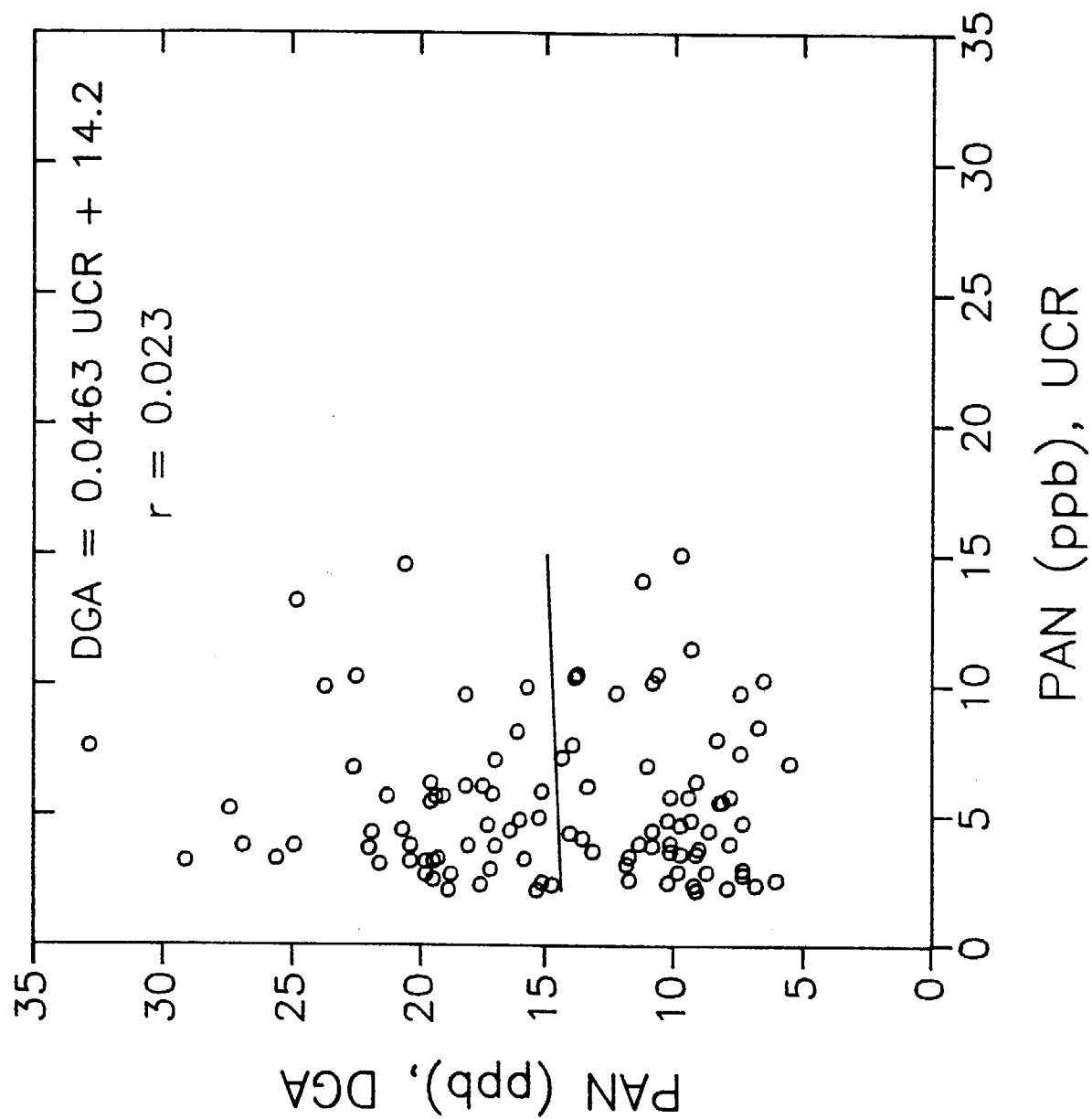Figure 5. Hourly average concentrations of PAN by FT-IR (UCR), PAN by EC-GC (DGA, Inc.), and O₃.

Figure 6. Linear regression plot of PAN by EC-GC (DGA, Inc.) vs. PAN by FT-IR (UCR); only values >2.0 ppb are included.

Table 3. Hourly average CH_3OH concentrations (ppb) at Glendora, CA, August 12-21, 1986, measured by long pathlength FT-IR spectroscopy[a,b,c]

	Aug 12	Aug 13	Aug 14	Aug 15	Aug 16	Aug 17	Aug 18	Aug 19	Aug 20	Aug 21
0000-0100		4.8	3.6	3.3	4.6	8.4	6.7	12.2	15.0	13.0
0100-0200		4.7	4.4	3.8	7.3	11.4	7.0	12.2	16.2	13.7
0200-0300		5.6	4.1	3.8	7.1	12.8	8.7	13.0	17.3	13.4
0300-0400		5.4	3.3	5.0	7.1	12.4	9.8	12.2	17.4	14.4
0400-0500		4.7	4.3	4.7	9.0	12.6	11.4	12.3	16.9	13.1
0500-0600		7.1	4.7	5.1	8.8	11.8	13.3	13.4	17.5	16.4
0600-0700		8.2	4.7	5.0	8.5	12.3	11.3	15.2	17.9	17.8
0700-0800		7.1	5.2	5.3	7.9	11.8	12.9	27.9	17.0	
0800-0900	9.5	6.7	5.7	12.8	6.8	9.5	18.3	19.5	16.7	
0900-1000	9.1	6.8	ND	5.2	5.7	11.4	57.6	9.9	16.2	
1000-1100	8.0	6.7	ND	12.1	6.7	ND	18.4	9.1	11.9	
1100-1200	7.6	6.1	ND	5.3	5.6	ND	9.5	8.4	8.1	
1200-1300	7.4	4.9	ND	4.8	4.1	ND	6.9	6.9	9.6	
1300-1400	5.1	4.6	ND	4.2	3.5	ND	2.9	6.2	6.3	
1400-1500	2.9	3.3	ND	3.8	2.9	ND	1.8	7.0	6.2	
1500-1600	3.9	3.6	ND	5.4	3.3	ND	2.8	5.1	6.2	
1600-1700	2.9	3.9	ND	4.6	2.9	ND	2.1	3.2	2.9	
1700-1800	1.0	5.0	ND	2.4	3.2	ND	1.8	3.2	3.5	
1800-1900	2.2	4.4	ND	2.1	2.3	ND	1.9	3.8	4.4	
1900-2000	3.1	3.3	ND	2.3	3.2	ND	1.3	5.2	5.2	
2000-2100	2.8	2.4	ND	2.7	4.0	ND	2.7	5.4	4.4	
2100-2200	4.0	3.1	ND	2.8	4.1	ND	8.9	5.8	7.5	
2200-2300	ND	3.9	2.8	3.5	6.0	ND	21.6	12.1	7.8	
2300-2400	ND	3.8	3.1	4.4	5.1	5.4	12.2	14.1	10.4	

[a]Entries <1.5 ppb are included only as indicators of trend in concentration (see text).
[b]Blank means outside the schedule.
[c]ND designates no data due to instrument testing on August 12, power interruptions on August 14, and fault in archiving on August 17.

The spectra of Figure 7 illustrate the CH_3OH levels in the morning of August 15. The detailed CH_3OH time-concentration profile is depicted with that of PAN in Figure 1. The methanol concentration profile displayed maxima which were distinctly non-coincident with the peaks of photo-chemical pollution as indicated by the PAN concentration profile.

Dimethyl sulfate. It was necessary to ensure that the broad band of $(CH_3O)_2SO_2$ at 1015 cm^{-1}, if present, was not distorted by any curvature in the absorption spectrum arising from instrumental response. Thus, a reference residual spectrum (after CH_3OH analysis) was chosen for each day, typically one at about midnight, and all residual spectra for that day were ratioed against it. This produced a straight baseline for the ratio plot and would then reflect the difference in the $(CH_3O)_2SO_2$ content, positive or negative, between the reference and the sample spectrum. The reference spectra for all the days were also ratioed against each other. This procedure facilitated a quick way of scanning the spectral records for the presence of $(CH_3O_2)SO_2$. No absorptions at 1015 cm^{-1} were revealed, such that $(CH_3O_2)SO_2$ concentrations ≥ 3 ppb were not detected by longpath FT-IR spectroscopy during the CSMCS. The foregoing comparative method of analysis was based on the assumption that the concentration of dimethyl sulfate was zero at some point during the CSMCS. Clearly, at the low levels near 3 ppb, the more rigorous chemical methods of analysis employed by Eatough et al. (1986) would provide a more positive detection of $(CH_3O)_2SO_2$.

Reaction of Alkenes with O_3 in the Presence of NO_2: A Source of PAN and Methanol? As noted above, the nighttime/early morning PAN peaks coincided with the more pronounced nighttime/early morning HCOOH peaks (see Figure 4). Whereas a significant contribution to the nighttime HCOOH levels can conceivably come from primary emissions, the same conjecture cannot be applied to PAN. The dark reaction of alkenes, such as propene, with O_3 is known to form HCOOH. If the latter reaction is also a significant source of nighttime HCOOH, the coincidence of HCOOH and PAN formation in the dark may suggest that PAN can possibly be generated as well by the reaction of O_3 with alkenes in the presence of NO_2, with the requirement that the alkene contains two terminal carbon atoms. The many pathways by which the energetic intermediate of the ozone-olefin system reacts (see, for example, Finlayson-Pitts and Pitts, 1986) makes PAN formation under these conditions a distinct possibility.
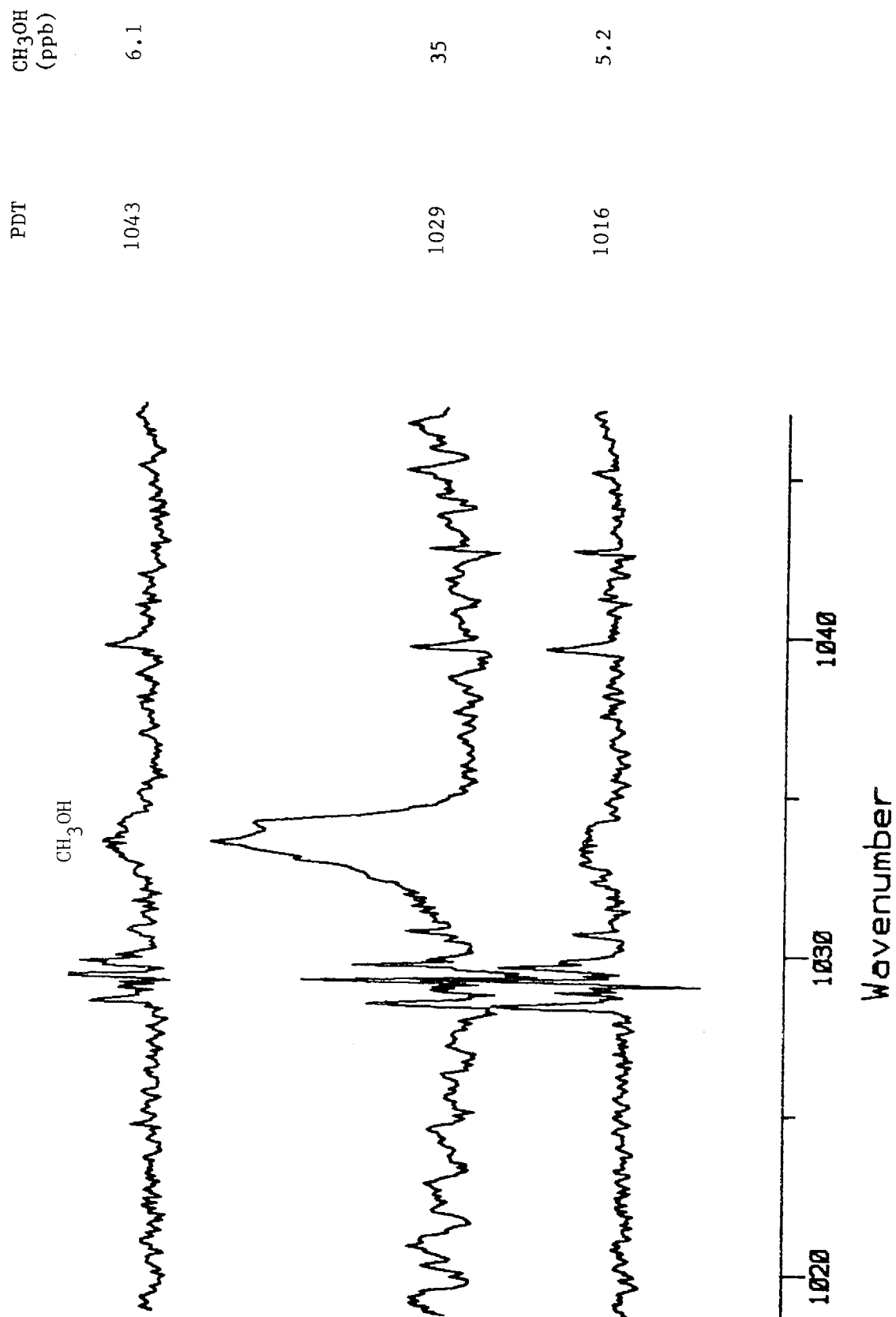
Figure 7. Detection of the 1033 cm^{-1} Q-branch of methanol on August 15, 1986, in Glendora, CA.

To test this hypothesis, an exploratory experiment was conducted in which ~5 ppm O_3 was reacted with a mixture of 20 ppm trans-2-butene and 5 ppm NO_2 in air, at 298 K and 1 atmosphere pressure, in the SAPRC 5800-L evacuable chamber. Reactants and products were monitored by long pathlength FT-IR spectroscopy. The reaction was essentially complete after 1.8 min. The observed concentrations (ppm) of reactants and products are summarized below.

At t = 0:

trans-2-butene	20.0
NO_2	5.1
O_3	~5

At t = 1.8 min:

-Δ (trans-2-butene)	8.6
-Δ(NO_2)	2.5
-Δ(O_3)	~5 (reacted completely)

CH_3CHO	8.1	CH_3OH	0.34
HCHO	1.1	PAN	0.27
CO_2	1.7	HCOOH	0.05
CO	1.3	$ROONO_2$	(formed; conc. unknown)
$CH_2=C=O$	0.35	$HOONO_2$	1.2

Among the products observed were PAN and CH_3OH, in yields which cannot yet be extrapolated to the present ambient data. It is interesting to note that a preliminary calculation (Carter, 1990) indicated that the present photochemical smog model underpredicts the PAN yield from the above chemical system by an order of magnitude. (Although it is also possible to estimate the CH_3OH yield, it was not attempted in this model calculation.)

We are not aware of any previous studies on ozone-olefin reactions which have been carried out specifically in the presence of NO_2. The above chamber experiment shows that these reactions can possibly contribute to the observed nighttime levels of PAN and CH_3OH. It is still not clear, however, whether this is the case for the present data of PAN,

since most of the nighttime peaks occurred after midnight when prevailing low levels of O_3 would not favor the ozone-olefin reactions as sources of PAN.

IV. CONCLUSIONS

PAN concentration data of defined accuracy were derived from the CSMCS FT-IR spectral records. The PAN time-concentration profile was observed to be highly coincident within the O_3 profile. No correlation was observed between the FT-IR PAN data and the EC-GC PAN measurements during the same period by DGA, Inc., with the comparison showing a large positive bias of the EC-GC data with respect to the FT-IR data. The small but definite build-up of PAN, and that of the more pronounced and coincident HCOOH behavior during some of the early morning hours, needs an explanation that will perhaps require a more detailed study of the total CSMCS data. The FT-IR results also highlight the importance of analytical methods with short time-resolution in revealing unique and potentially significant time-concentration behavior of pollutant species.

This study provides the first substantive body of data for ambient methanol concentrations and indicates that 2-10 ppb is the most common range to be expected in the Los Angeles vicinity.

The results of the FT-IR analysis for dimethyl sulfate suggested that this compound probably did not exist in the gas-phase at concentrations ≥ 3 ppb at any time during the CSMCS.

V. REFERENCES

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Peroxyacetyl nitrate (PAN) and methanol (CH_3OH) concentrations were derived from the longpath FT-IR spectra which were recorded during the Carbonaceous Species Methods Comparison Study (CSMCS) held on August 12-21, 1986 at Glendora, California. Both the detailed instantaneous and hourly average values of PAN and CH_3OH were determined. The FT-IR PAN data are compared with measurements by another laboratory using gas chromatography with electron captive detection (EC-GC).

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