

**LIBRARY - AIR RESOURCES BOARD**

**DERIVATION OF FORMIC ACID DATA FROM FT-IR SPECTRA RECORDED  
DURING THE 1986 CARBONACEOUS SPECIES METHODS COMPARISON STUDY**

Final Report

California Air Resources Board

Contract No. A733-167

(through the University of California, Irvine)

Ernesto C. Tuazon  
Principal Investigator

February 1989

Statewide Air Pollution Research Center  
University of California  
Riverside, CA 92521

TD  
890  
T839  
1989

## ABSTRACT

Formic acid (HCOOH) concentrations were derived from long-path FT-IR spectra which were recorded during the Carbonaceous Species Methods Comparison Study held in Glendora, CA, August 12-21, 1986. Both the detailed instantaneous and the hourly average HCOOH values are presented here. HCOOH concentrations during the study were in the range 1-11 parts per billion (ppb). The detection sensitivity was 1 ppb and the measurement errors were within  $\pm 1.5$  ppb. During the first 5-6 days of the study, the HCOOH concentration profiles were generally coincident with photochemical activity. During the remaining days, HCOOH levels were found to be highest in the very early morning hours, presumably as a result of build-up from as yet undetermined primary sources.

## ACKNOWLEDGMENTS

The author acknowledges helpful consultations with Dr. Michael Kleinman, CCM Community and Environmental Medicine, UC Irvine, and with Drs. Eric Fujita and Douglas Lawson, Research Division, California Air Resources Board.

I wish to thank Drs. Roger Atkinson and Arthur M. Winer for spontaneous discussions and their continued interest in spectroscopic studies. Thanks are due to Ms. Minn P. Poe and Mr. Brett McMillan for carrying out the final tabulation and plotting of data, and Ms. Diane L. Skaggs for presiding over fiscal matters.

This report is being submitted in fulfillment of Contract No. A733-167 by the Statewide Air Pollution Research Center, UC Riverside, under the sponsorship of the California Air Resources Board through UC Irvine.

## 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.

TABLE OF CONTENTS

	<u>Page</u>
Abstract.....	ii
Acknowledgement.....	iii
Disclaimer.....	iv
List of Figures/List of Tables.....	vi
I. INTRODUCTION.....	1
II. PROCEDURE.....	1
III. RESULTS AND DISCUSSION.....	3
IV. CONCLUSIONS.....	11
V. REFERENCES.....	12

LIST OF FIGURES

	<u>Page</u>
Figure 1. Reference spectrum of HCOOH monomer; equivalent to 14.9 ppb at 1150 m (296 K, 740 torr).....	2
Figure 2. Intensities of the HCOOH 1105-cm <sup>-1</sup> peak during the evening of August 19 and early morning of August 20, 1986 at Glendora, CA.....	9
Figure 3. Time-concentration profile of HCOOH measured by long pathlength FT-IR spectroscopy on August 12-21, 1986 at Glendora, CA.....	10

LIST OF TABLES

	<u>Page</u>
Table 1. HCOOH Concentrations (ppb) in Glendora, CA, August 12-21, 1986 by Long Pathlength FT-IR Spectroscopy.....	4
Table 2. Hourly Average HCOOH Concentrations (ppb) at Glendora, CA, August 12-21, 1988 Measured by Long Pathlength FT-IR Spectroscopy.....	8

## I. INTRODUCTION

During the California Air Resources Board (ARB) funded Carbonaceous Species Methods Comparison Study (CSMCS) in August 1986 at Glendora, CA, our research group employed long-path Fourier transform infrared (FT-IR) spectroscopy to measure formaldehyde (HCHO) as well as nitric acid (HNO<sub>3</sub>) and ammonia (NH<sub>3</sub>). The data for the above species have already been reported earlier (Atkinson et al. 1987, Winer et al. 1987) and satisfied the stated task for the FT-IR technique. We recognized, however, that the infrared spectral records contained potential quantitative information for other gaseous species.

The ARB recently expressed a need for an independent set of data for formic acid (HCOOH) during the CSMCS that can be compared with the results of wet chemical techniques. In response to this need, we derived the HCOOH data from the FT-IR spectra recorded during that period and present the detailed results in this report.

## II. PROCEDURE

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

To facilitate spectral processing, a truncated segment of the spectrum in the 850-1250 cm<sup>-1</sup> 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 HCOOH absorption peak at 1105.0 cm<sup>-1</sup>. An interference on this signal by a very weak H<sub>2</sub>O peak was corrected by subtracting the H<sub>2</sub>O contribution based on adjoining, nonsaturated H<sub>2</sub>O bands. Finally, an interactive subtraction routine was employed which expressed the HCOOH sample absorbance as a fraction of a known HCOOH reference absorbance.

Figure 1 shows a reference spectrum of gaseous HCOOH at a concentration equivalent to 14.9 parts per billion (ppb) at 1150 m. The calibration for the present analysis was carried out at part-per-million

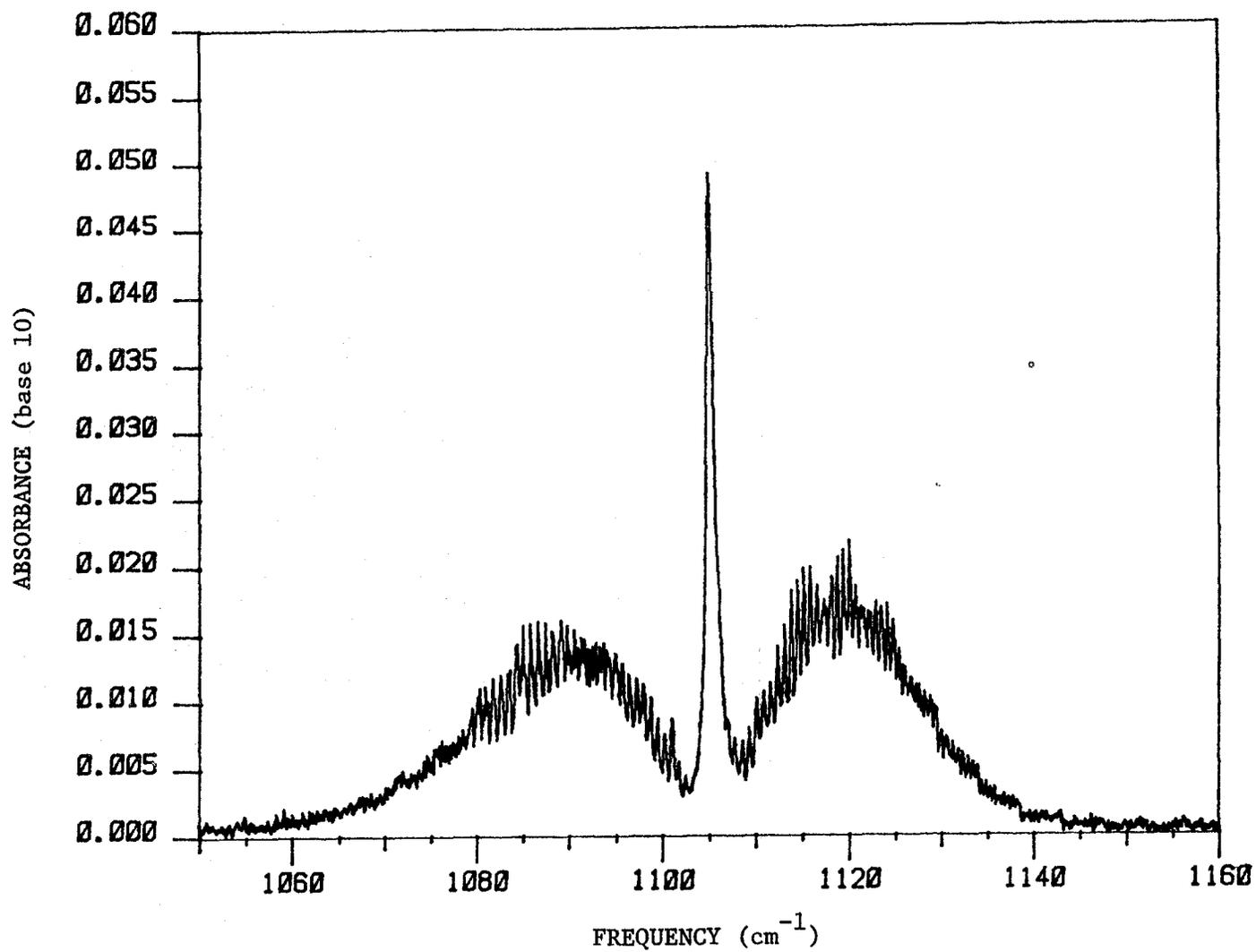


Figure 1. Reference spectrum of HCOOH monomer; equivalent to 14.9 ppb at 1150 m (296 K, 740 torr).

(ppm) concentrations employing our 5870-liter evacuable chamber equipped with long path optics. HCOOH vapor (derived from reagent-grade 80% HCOOH-20% H<sub>2</sub>O sample dried over CuSO<sub>4</sub>) was condensed into a vial using a vacuum line and then weighed prior to injection in the chamber for a reliable measure of the concentration of gas-phase HCOOH monomer.

At the resolution and pathlength employed during the 1986 Glendora study, the analysis of the spectra indicated a detection sensitivity of ~1 ppb. An error limit of ±1.5 ppb was estimated for the current HCOOH measurements.

### III. RESULTS AND DISCUSSION

The detailed "instantaneous" HCOOH data (each data point corresponds to a measurement time of five minutes) for August 12-21, 1986 in Glendora, California obtained by long pathlength FT-IR spectroscopy are presented in Table 1. Except for periods of power disruption on August 14 and the loss of most of the daytime data on August 17 due to a fault in archiving the data onto magnetic tapes, the FT-IR system provided continuous coverage of the HCOOH concentration since HCOOH was above the detection limit of ~1 ppb throughout the entire study period.

To facilitate the comparison of these FT-IR measurements with those by methods involving time-integrated sampling, hourly average concentrations were calculated from the instantaneous values, and these are presented in Table 2.

The instantaneous HCOOH concentrations during the field study were in the range 1-11 ppb. Figure 2 illustrates some of the intensities of the HCOOH Q-branch at 1105 cm<sup>-1</sup> observed on the evening of August 19 and early morning hours of August 20, the latter period being characterized by the highest instantaneous as well as the highest hourly average HCOOH levels throughout the study.

The concentration vs. time plot of Figure 3 shows that the daily HCOOH maxima occurred during about noon to mid-afternoon hours for the days August 12-16 (and possibly including August 17). The HCOOH concentration profiles for these days are roughly coincident with the levels of photochemical activity, as indicated by the O<sub>3</sub> readings and our own HNO<sub>3</sub> concentration-time data (Atkinson et al. 1987). [This was also the

Table 1. HCOOH 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 (see text). Digits beyond two significant figures are retained only for the sake of format and to reduce round-off errors in ensuing calculations.]

PDT	HCOOH	PDT	HCOOH	PDT	HCOOH	PDT	HCOOH
<u>8/12/86</u>		1816	2.1	0715	2.9	1813	3.6
		1828	2.2	0731	3.3	1827	3.4
0758	4.0	1848	2.4	0746	3.4	1850	3.1
0811	4.3	1904	2.7	0802	3.5	1913	3.8
0825	4.1	1920	2.6	0818	3.3	1926	3.2
0837	4.5	1934	2.8	0833	3.0	1939	3.3
0851	4.5	1947	3.2	0849	3.2	1952	3.3
0905	5.2	2000	2.7	0904	3.5	2005	3.1
0917	4.8	2014	2.8	0920	3.7	2018	3.3
0930	5.1	2106	2.6	0936	3.6	2034	2.9
0944	5.0	2118	3.3	0951	3.8	2113	2.8
0957	5.3	2132	3.9	1007	3.7	2133	3.2
1010	5.4	2144	3.5	1035	4.2	2146	3.6
1024	5.3	2201	3.3	1048	4.7	2206	3.6
1037	5.2	*2215	2.9	1101	4.4	2226	3.7
1052	6.7			1114	3.7	2245	3.8
1119	6.1	<u>8/13/86</u>		1128	4.0	2305	3.6
1136	5.4			1145	3.7	2324	3.6
1149	4.6	*0027	3.5	1158	4.3	2344	3.5
1202	4.1	0043	3.2	1211	4.4		
1221	4.0	0059	3.1	1229	4.9	<u>8/14/86</u>	
1234	3.7	0114	2.9	1248	3.9	0004	3.6
1250	3.3	0130	3.2	1309	2.8	0023	3.6
1305	4.9	0146	3.2	1331	4.6	0043	3.3
1320	4.1	0201	3.3	1344	4.1	0102	3.1
1339	4.7	0217	3.6	1357	4.3	0122	3.5
1353	3.9	0233	3.7	1410	4.0	0142	3.4
1406	4.5	0249	3.7	1423	3.4	0201	3.3
1419	5.2	0304	3.4	1440	4.1	0221	3.4
1433	4.7	0320	3.4	1453	4.2	0241	3.0
1447	4.8	0336	3.1	1506	4.1	0300	2.6
1503	5.8	0351	3.5	1522	4.3	0320	2.9
1517	4.9	0407	3.3	1535	4.5	0339	2.6
1532	4.7	0423	3.0	1548	4.6	0359	2.8
1546	4.2	0439	3.0	1601	4.5	0419	3.1
1608	2.9	0454	2.7	1614	4.8	0438	2.6
1622	3.0	0510	2.9	1630	3.8	0458	3.2
1635	2.3	0526	3.4	1643	3.9	0518	2.5
1651	2.1	0541	3.2	1655	5.0	0537	2.8
1705	1.8	0557	3.1	1706	4.1	0557	2.3
1718	1.8	0612	3.5	1718	3.5	0616	2.5
1732	1.7	0628	2.9	1734	4.0	0636	2.6
1745	1.7	0644	3.1	1747	3.8	0656	3.0
1802	1.9	0659	3.1	1800	3.6		

(continued)

Table 1 (continued) - 2

PDT	HCOOH	PDT	HCOOH	PDT	HCOOH	PDT	HCOOH
0716	2.9	2328	2.6	1341	6.7	0220	2.7
0735	3.6	2348	2.4	1353	6.8	0240	2.1
0755	3.4			1410	6.6	0259	2.4
0815	3.8	<u>8/15/86</u>		1425	7.6	0319	2.3
0834	3.5			1440	7.5	0339	2.1
0854	4.0	0008	2.5	1453	6.9	0359	2.1
*0914	4.4	0027	2.4	1505	6.1	0418	2.3
*1033	5.3	0047	2.5	1518	5.5	0438	2.8
*1059	5.4	0107	2.1	1530	5.9	0458	2.6
*1153	5.6	0126	2.0	1542	5.5	0517	1.6
1208	5.0	0146	2.0	1604	4.7	0537	2.6
1221	4.9	0206	1.9	1616	4.6	0557	2.6
1240	5.1	0225	2.4	1629	3.7	0616	2.6
1253	5.3	0245	2.3	1641	4.1	0636	2.0
1309	5.4	0305	2.3	1653	4.0	0656	2.4
*1322	5.1	0324	2.1	1707	4.4	0715	3.0
*1520	5.3	0344	1.9	1720	4.3	0735	2.7
1531	7.3	0404	1.6	1732	3.5	0755	3.0
1543	7.9	0424	1.9	1744	3.3	0815	3.1
1555	6.8	0443	1.2	1757	3.0	0834	3.1
1606	6.9	0503	1.5	1830	3.4	0854	3.1
1620	6.3	0523	1.6	1842	2.6	0914	3.2
1632	6.0	0543	2.2	1854	3.3	0933	3.3
1643	6.0	0602	2.0	1907	2.7	1015	3.7
1655	5.9	0622	2.3	1919	2.8	1028	4.0
1711	4.5	0641	2.2	1938	3.3	1048	3.9
1723	4.8	0701	2.0	1950	2.5	1100	4.9
1735	6.2	0721	2.4	2003	2.7	1118	5.3
1746	5.4	0741	2.3	2015	2.4	1131	4.8
1801	6.3	0800	2.3	2027	2.5	1143	4.8
1818	5.2	0820	3.0	2106	2.2	1155	4.2
1830	5.8	0840	3.9	2125	2.1	1207	4.8
1842	5.4	0859	3.3	2145	1.9	1219	4.5
1853	5.8	0919	2.5	2205	1.8	1231	4.3
1925	4.9	1016	3.4	2224	1.6	1243	4.0
1938	4.7	1029	4.3	2244	1.9	1255	4.3
1951	5.0	1043	4.4	2304	2.0	1308	3.8
2004	5.0	1100	5.0	2323	2.0	1320	4.4
2017	5.6	1112	4.8	2345	1.8	1332	4.0
2030	5.2	1126	5.4			1344	4.8
2044	5.3	1138	5.6	<u>8/16/86</u>		1356	4.4
2057	4.9	1151	5.7			1409	3.9
2110	4.8	1203	5.6	0003	1.9	1421	4.6
2123	4.1	1219	5.8	0022	2.3	1433	5.4
2136	4.2	1231	6.0	0042	2.0	1445	5.5
2210	3.8	1244	5.9	0101	1.9	1457	5.8
2229	3.6	1256	6.0	0121	3.3	1509	6.5
2249	3.7	1309	5.9	0141	3.3	1522	7.5
2309	3.2	1325	8.3	0200	3.2	1534	6.6

(continued)

Table 1 (continued) - 3

PDT	HCOOH	PDT	HCOOH	PDT	HCOOH	PDT	HCOOH
1546	7.0	0525	5.4	0828	4.5	1956	1.8
1558	7.0	0545	5.5	0847	4.4	2009	1.7
1610	6.4	0605	5.4	0907	4.3	2021	2.3
1623	6.3	0624	5.0	0927	5.2	2035	2.9
1635	6.3	0644	5.6	0946	4.3	2047	2.3
1647	6.1	0704	5.3	1004	4.5	2059	3.1
1659	7.0	0723	5.1	1017	4.3	2111	3.0
1711	6.0	0743	5.2	1029	5.1	2124	3.2
1724	6.0	0803	6.1	1057	5.5	2206	5.7
1736	5.5	0823	5.8	1111	5.6	2226	5.2
1748	5.5	0843	5.7	1123	6.1	2246	6.2
1800	4.9	0902	6.5	1140	5.5	2305	5.9
1812	4.8	0922	6.9	1156	5.2	2325	6.2
1902	4.0	0942	7.8	1207	5.8	2345	6.0
1917	4.5	*1002	7.7	1220	4.9		
1929	4.6	*2235	5.1	1233	4.5	<u>8/19/86</u>	
1942	4.1	2253	3.9	1245	4.1		
1954	4.6	2306	3.9	1256	4.7	0004	6.2
2006	4.3	2317	4.1	1308	3.8	0024	6.2
2024	4.3	2337	4.2	1320	3.0	0044	6.9
2036	4.8	2356	4.5	1333	2.8	0103	6.8
2049	4.2			1345	2.7	0123	8.1
2144	3.9	<u>8/18/86</u>		1357	3.0	0143	8.1
2152	4.4			1409	2.5	0202	9.0
2212	4.5	0016	4.3	1421	2.2	0222	8.2
2232	4.7	0036	4.4	1433	2.5	0242	8.2
2251	4.0	0056	4.5	1445	3.0	0301	8.8
2311	4.1	0115	4.4	1457	3.5	0321	8.1
2331	3.8	0135	4.8	1509	4.3	0341	7.7
2350	3.4	0155	4.9	1521	4.1	0400	7.9
		0214	5.3	1534	4.7	0420	7.7
<u>8/17/86</u>		0234	5.6	1546	4.8	0439	6.8
		0254	5.8	1558	4.4	0459	7.6
0010	3.7	0313	5.9	1610	4.1	0519	7.7
0030	3.6	0333	6.6	1622	4.6	0538	7.9
0049	4.8	0353	6.0	1635	3.6	0558	7.9
0109	4.3	0412	6.2	1647	4.0	0618	8.4
0129	4.5	0432	7.0	1700	3.1	0637	8.9
0148	4.7	0452	6.9	1712	3.2	0657	8.7
0208	5.1	0511	6.9	1724	2.7	0717	8.2
0228	5.3	0531	6.5	1737	2.6	0737	8.9
0248	5.3	0550	5.5	1750	2.4	0757	8.0
0307	6.2	0610	5.0	1802	2.9	0816	7.1
0327	6.4	0630	5.0	1814	2.3	0836	7.4
0347	5.4	0649	5.4	1826	1.9	0855	7.3
0406	5.8	0709	5.4	1839	1.8	0915	6.3
0426	5.4	0729	5.2	1852	1.5	0935	6.4
0446	5.5	0748	4.9	1932	1.3	1006	6.1
0506	5.3	0808	4.6	1944	1.4	1018	5.9

(continued)

Table 1 (continued) - 4

PDT	HCOOH	PDT	HCOOH	PDT	HCOOH	PDT	HCOOH
1030	5.7	2029	2.9	1013	7.3	1920	4.0
1043	5.9	2042	2.7	1025	6.1	1930	3.5
1059	6.0	2054	2.5	1038	5.3	1940	3.5
1109	5.8	2106	2.0	1050	5.5	2023	4.1
1121	5.7	2118	2.2	1104	5.2	2035	4.8
1133	4.8	2130	2.2	1217	5.4	2050	4.0
1148	5.6	2142	2.2	1129	6.2	2110	3.8
1200	5.4	2155	2.1	1141	5.8	2129	3.6
1213	5.4	2207	2.8	1153	6.1	2149	4.1
1215	5.5	2219	6.1	1208	5.7	2209	3.9
1237	5.3	2231	6.5	1220	6.9	2228	3.9
1249	5.1	2243	6.9	1232	6.8	2248	4.5
1305	3.4	2314	8.4	1244	7.5	2307	4.9
1317	4.6	2334	8.3	1300	6.5	2327	5.0
1329	5.6	2353	9.8	1311	5.8	2347	8.0
1346	6.1			1321	5.5		
1355	8.2	<u>8/20/86</u>		1331	5.3	<u>8/21/86</u>	
1405	7.3			1341	5.1		
1415	6.6	0013	10.1	1352	5.1	0006	7.8
1426	5.4	0032	9.5	1402	5.1	0026	7.9
1436	5.0	0052	9.1	1414	5.4	0046	8.6
1448	5.2	0112	9.4	1424	6.4	0106	9.6
1501	3.8	0131	10.3	1434	6.0	0125	8.3
1512	4.5	0151	9.8	1444	5.3	0145	7.3
1522	4.3	0210	10.2	1454	4.4	0204	7.7
1532	4.1	0230	10.7	1507	4.0	0224	6.6
1542	3.4	0250	10.8	1517	3.8	0244	7.6
1554	2.8	0309	10.8	1530	3.3	0303	7.8
1604	3.3	0329	10.8	1540	3.7	0323	8.0
1614	2.5	0348	10.3	1550	4.3	0343	7.4
1624	2.3	0408	9.8	1600	4.1	0402	6.4
1634	2.6	0428	9.6	1610	3.3	0422	5.4
1645	2.5	0447	9.1	1621	2.7	0442	7.3
1655	2.0	0507	10.3	1631	2.9	0501	7.6
1705	1.6	0527	10.1	1643	2.0	0521	7.9
1720	1.9	0546	10.0	1656	1.8	0541	8.0
1733	2.3	0606	10.0	1706	1.9	0601	8.2
1747	2.2	0625	10.6	1716	1.3	0600	8.8
1759	2.7	0645	10.1	1727	2.3	0640	8.6
1811	2.0	0705	10.0	1737	2.4	0700	8.5
1823	2.3	0724	9.2	1747	2.6	0717	8.5
1835	2.6	0744	9.7	1757	2.5	0730	8.8
1847	2.4	0803	9.1	1807	2.8		
1902	2.4	0823	9.6	1817	3.6		
1914	2.3	0843	10.7	1828	3.5		
1927	2.4	0902	9.8	1839	3.6		
1939	2.6	0923	8.8	1849	3.2		
2007	2.9	0942	7.8	1900	3.0		
2017	2.5	1001	7.3	1910	3.3		

(continued)

Table 2. Hourly Average HCOOH Concentrations (ppb) at Glendora, CA August 12-21, 1986, Measured by Long Pathlength FT-IR Spectroscopy<sup>a,b,c</sup>

PDT	Aug 12	Aug 13	Aug 14	Aug 15	Aug 16	Aug 17	Aug 18	Aug 19	Aug 20	Aug 21
0000-0100		3.3	3.4	2.4	2.1	4.0	4.4	6.5	9.6	8.2
0100-0200		3.1	3.4	2.0	3.0	4.5	4.7	7.9	9.8	8.2
0200-0300		3.6	3.1	2.2	2.5	5.3	5.5	8.4	10.5	7.3
0300-0400		3.3	2.7	2.0	2.2	6.0	6.2	8.1	10.6	7.6
0400-0500		3.0	2.9	1.6	2.5	5.5	6.7	7.4	9.6	6.5
0500-0600		3.1	2.6	1.8	2.3	5.4	6.3	7.8	10.1	7.9
0600-0700		3.1	2.6	2.2	2.4	5.3	5.2	8.6	10.2	8.6
0700-0800		3.2	3.3	2.3	2.8	5.3	5.1	8.4	9.5	
0800-0900	4.4	3.2	3.7	3.2	3.1	5.9	4.5	7.3	9.9	
0900-1000	5.1	3.7	x	2.8	3.3	7.2	4.6	6.4	8.5	
1000-1100	5.6	4.2	x	4.1	3.9	x	4.9	5.9	6.1	
1100-1200	5.5	4.0	x	5.3	4.8	x	5.6	5.5	5.3	
1200-1300	3.8	4.3	5.1	5.9	4.4	x	4.8	5.2	6.7	
1300-1400	4.4	3.9	x	6.9	4.3	x	3.1	5.5	5.5	
1400-1500	4.9	3.9	x	7.1	5.0	x	2.7	5.7	5.4	
1500-1600	4.7	4.4	x	5.6	6.9	x	4.4	3.8	3.8	
1600-1700	2.6	4.4	6.2	4.2	6.4	x	4.0	2.5	2.7	
1700-1800	1.8	3.8	5.4	3.7	5.8	x	2.8	2.1	2.1	
1800-1900	2.2	3.4	5.6	3.1	4.5	x	2.0	2.4	3.3	
1900-2000	2.8	3.4	5.0	2.9	4.4	x	1.4	2.5	3.6	
2000-2100	2.7	3.0	5.2	2.4	4.4	x	2.4	2.7	4.2	
2100-2200	3.3	3.2	4.3	2.0	4.1	x	3.8	2.2	3.8	
2200-2300	x	3.7	3.7	1.8	4.4	x	5.7	5.9	4.2	
2300-2400	x	3.6	2.7	1.9	3.8	4.2	6.1	8.7	6.1	

<sup>a</sup>Blank means outside the schedule.

<sup>b</sup>x designates no data due to instrument testing on August 12, power interruptions on August 14 and a fault in archiving on August 17.

<sup>c</sup>Estimates of missing hourly averages for August 12 and 14 may be made from the detailed concentration data of Table 1.

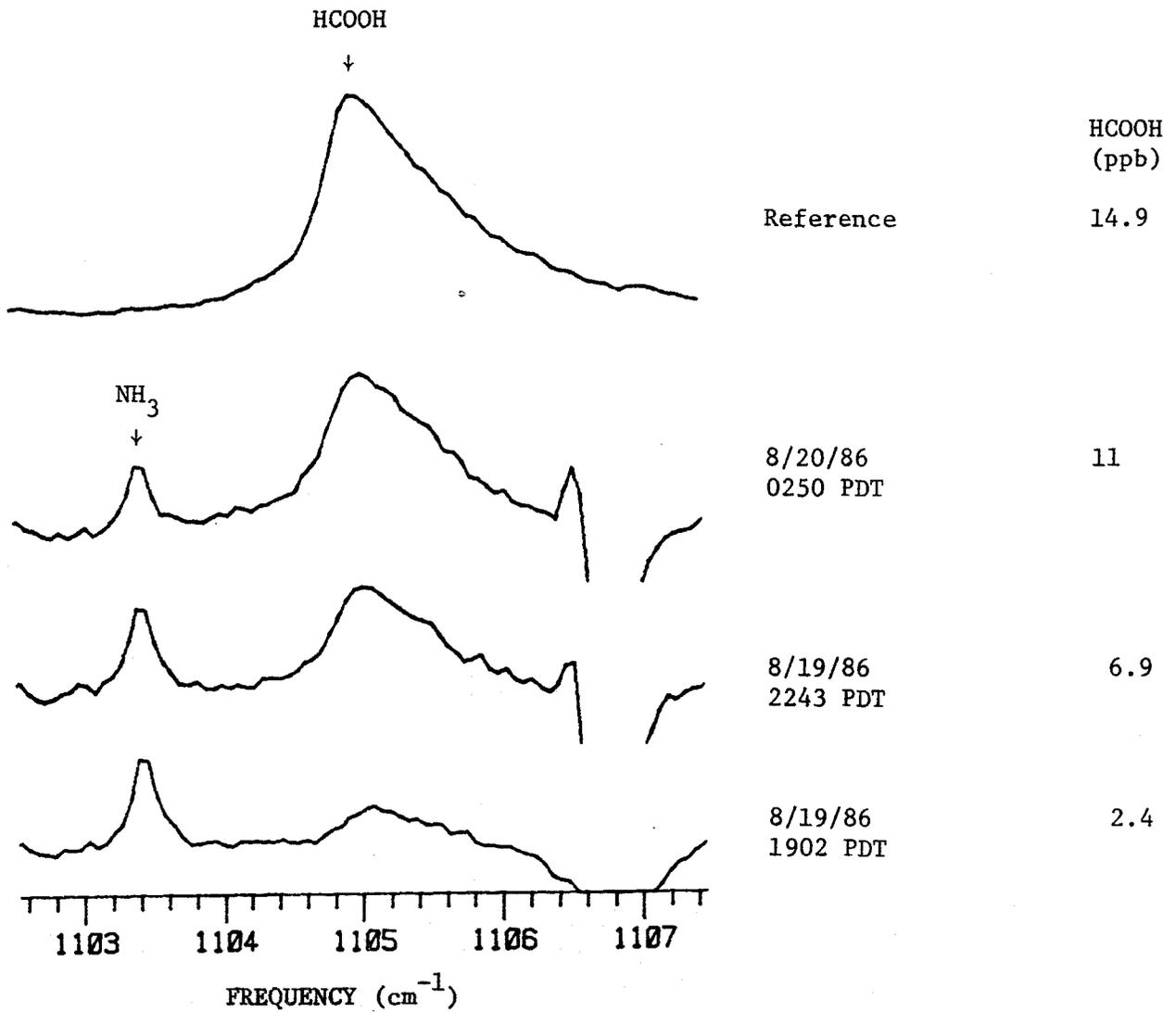


Figure 2. Intensities of the HCOOH 1105-cm<sup>-1</sup> peak during the evening of August 19 and early morning of August 20, 1986 at Glendora, CA. (The discontinuities in the spectra correspond to inexact cancellation of a saturated H<sub>2</sub>O absorption band.)

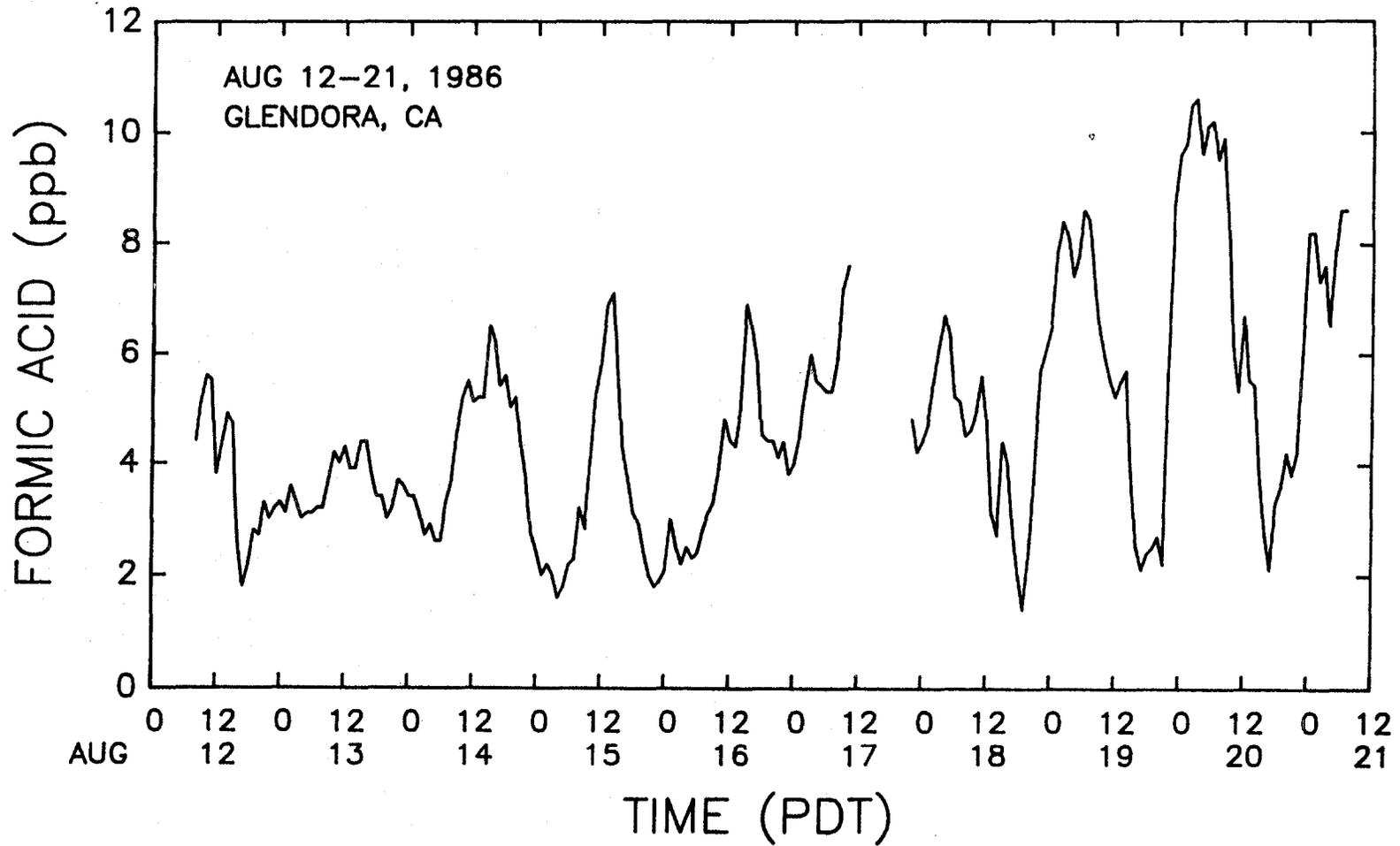


Figure 3. Time-concentration profile of HCOOH measured by long pathlength FT-IR spectroscopy on August 12-21, 1986 at Glendora, CA.

pattern of HCOOH behavior that we observed in 1978 in Claremont, CA during the only other extended (38 hours) spectroscopic measurement of HCOOH (Tuazon et al. 1981), when we reported a maximum HCOOH concentration of 19 ppb, corresponding to an O<sub>3</sub> high of 454 ppb.]

The HCOOH profiles (Figure 3) for the remaining days, August 18-21, are distinctly different from those of the prior days, since they are characterized by a build-up of HCOOH in the late evening hours which led to relatively broad maxima during the early morning hours. Carry-over concentrations seem to contribute significantly to the daytime levels, even though weaker peaks appeared around the noon hours, presumably due to photochemical activity.

There are reactions that could conceivably generate HCOOH at night, such as the reaction of olefins with ozone. However, it is highly doubtful that this reaction could produce a significant fraction of the nighttime HCOOH levels observed during August 18-21. The elevated nighttime concentrations may possibly be traced to primary emissions, and supporting evidence may come from the body of data being compiled by the ARB from the 1986 Glendora study.

#### IV. CONCLUSIONS

The HCOOH data reported here, which covered the period August 12-21, 1986 in Glendora, CA represent the most comprehensive spectroscopic measurement of this species in ambient air to date. The yield of data from the FT-IR measurements is high and the accuracy of the data is defined such that a meaningful comparison can be made with the results of the other HCOOH methods. The short time resolution of the FT-IR spectroscopic technique distinguished between two HCOOH time-concentration profiles, one being essentially coincident with daytime photochemical activity, and the other being dominated by HCOOH build-up from late evening to the morning hours. Extended interpretation of these HCOOH data will be sought through discussion with the ARB staff who can make available pertinent CSMCS data on both directly emitted and photochemically generated species, and the findings will be reported in a peer-reviewed journal article.

## V. REFERENCES

- Atkinson, R., A. M. Winer, J. Arey, H. W. Biermann, T. Dinoff, W. P. Harger, P. A. McElroy, E. C. Tuazon and B. Zielinska, "Intercomparison of Methods for the Measurement of Carbonaceous Aerosol Species," Final Report, California Air Resources Board Contract No. A5-150-32, November 1987.
- Tuazon, E. C., A. M. Winer and J. N. Pitts, Jr., Trace Pollutant Concentrations in a Multiday Smog Episode in the California South Coast Air Basin by Long Path Length Fourier Transform Infrared Spectroscopy, Environ. Sci. Technol., 15, 1232-1237 (1981).
- Winer, A. M., R. Atkinson, J. Arey, H. W. Biermann, W. P. Harger, E. C. Tuazon and B. Zielinska, "The Role of Nitrogenous Pollutants in the Formation of Atmospheric Mutagens and Acid Deposition," Final Report, California Air Resources Board Contract No. A4-081-32, March 1987.

<b>REPORT DOCUMENTATION PAGE</b>		1. REPORT NO. ARB/R-89/388	2.	3. Recipient's Accession No. PB89187165
4. Title and Subtitle Derivation of Formic Acid Data from FTIR Spectra Recorded During the 1986 Carbonaceous Species Method Comparison Study			5. Report Date February 1989	6.
7. Author(s) Ernesto C. Tuazon			8. Performing Organization Rept. No.	
9. Performing Organization Name and Address Statewide Air Pollution Research Center University of California Riverside, CA 92521			10. Project/Task/Work Unit No.	11. Contract(C) or Grant(G) No. (C) A733-167 (G)
12. Sponsoring Organization Name and Address AIR RESOURCES BOARD RESEARCH DIVISION P. O. BOX 2815 SACRAMENTO, CA 95812			13. Type of Report & Period Covered Final Report	
14.				
15. Supplementary Notes				
16. Abstract (Limit: 200 words) Formic acid (HCOOH) concentrations were derived from long-path FT-IR spectra which were recorded during the Carbonaceous Species Methods Comparison Study held in Glendora, CA, August 12-21, 1986. Both the detailed instantaneous and the hourly average HCOOH values are presented here. HCOOH concentrations during the study were in the range 1-11 parts per billion (ppb). The detection sensitivity was 1 ppb and the measurement errors were within $\pm 1.5$ ppb. During the first 5-6 days of the study, the HCOOH concentration profiles were generally coincident with photochemical activity. During the remaining days, HCOOH levels were found to be highest in the very early morning hours, presumably as a result of build-up from as yet undetermined primary sources.				
17. Document Analysis a. Descriptors Formic Acid Organic Acid Air Pollution  b. Identifiers/Open-Ended Terms  c. COSATI Field/Group				
18. Availability Statement Release Unlimited. Available from National Technical Information Service, 5285 Port Royal Road Springfield, VA 22161			19. Security Class (This Report)	21. No. of Pages
			20. Security Class (This Page)	22. Price \$13.95