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**QUALITY ASSURANCE AUDITS FOR THE ARB SPONSORED
CARBONACEOUS SPECIES METHODS COMPARISON STUDY**

AT CITRUS COLLEGE, GLENDORA, CA

August 12-21, 1986

FINAL REPORT

ARB Contract # A5-148-32

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Submitted To:

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E M S I

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C O M B U S T I O N E N G I N E E R I N G

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1.0 INTRODUCTION

EMSI performed the following quality assurance functions for the California ARB sponsored Carbon Species Methods Comparison Study conducted at Citrus College, Glendora, CA between August 12-21, 1986:

- o Preparation of 23 different carbonaceous reference materials for both the study participants and other interested parties for a "round robin" interlaboratory comparison of carbon analysis methods;
- o Audit of sampler flow rates for all study participants including those groups not involved in carbonaceous aerosol measurements;
- o Analysis of the 23 carbonaceous reference materials for organic and elemental carbon; and
- o Analysis of ~ 20% of the samples collected by each of the study participants.

In addition to serving as the QA Contractor for this program, EMSI also operated three PM-10 Hi-vols on loan from ARB-El Monte for the nine study days on a schedule of two samples per day, and analyzed these samples for organic and elemental carbon.

2.0 EXPERIMENTAL METHODOLOGY

This section describes the methodology employed by EMSI to prepare the reference standards, audit sampler flow rates, and analyze samples for organic and elemental carbon.

2.1 CARBONACEOUS REFERENCE STANDARDS

EMSI used the following samples to make up the kits of 23 different carbonaceous reference materials for the interlaboratory round robin analyses:

- o four ambient PM-10 Hi-vol quartz filter samples in triplicate, (Samples 1,10,16; 3,5,14; 6,17,20; 2,4,8) collected by EMSI at Citrus College on August 19 and 20, 1986;
- o three automotive exhaust samples collected on quartz filters by General Motors Research Laboratories from dynamometer tests of a Buick equipped with a catalytic converter burning unleaded fuel (sample #7), a Chevrolet burning leaded fuel (sample #18), and an Oldsmobile diesel (sample #15) (Private communication, Steve Cadle, GMR 6/12/86);
- o two ambient PM-10 Hi-vol quartz filter samples collected by the Oregon Department of Environmental Quality in Medford, OR during the winter of 1986 (samples #13 & 15), to represent carbonaceous aerosol samples dominated by wood smoke emissions (Private communication, Ken McDonald, Oregon DEQ, 5/7/86);
- o one heavily loaded ambient Hi-vol quartz filter sample, heated to 300°C for two hours to remove the organic aerosol fraction, to represent a sample heavily dominated by elemental carbon, i.e., soot (sample #12);
- o one organic aerosol sample (sample #19) collected on a Hi-vol quartz filter generated from the photolysis of trimethylbenzene in an outdoor smog chamber at the California Institute of Technology (Private communication, Jennifer Stern, CIT, 7/29/86);
- o three bulk NBS standards provided by the ARB: NBS 1648 (sample #23), NBS 1649 (sample #21), and NBS 1650 (sample #22); and
- o one blank quartz filter (sample #9).

With the exception of the kit prepared for the Air Industrial Hygiene Laboratory, Berkeley, CA (AIHL), each kit included one 1" diameter aliquot punched from each of the 8" x 10" quartz Hi-vol filters packaged in a labelled petri dish (e.g., sample Y01-14) plus 50 mg of each of the bulk NBS solids in a small vial. The kit prepared for AIHL contained 47mm diameter filter aliquots to accommodate their carbon analyzer.

Each kit of reference material was assigned a letter designation, A-Z, (i.e., one letter per participant). Each sample was assigned a number designation, 1-23, to identify the sample type. In addition, each filter sample was given a two-digit designation which corresponded to the area of each 8" x 10" Hi-vol quartz filters from which each filter aliquot was taken. These reference kits were stored at 5°C or lower, away from solvents, until they were handed directly to each participant in the round robin study or were shipped in an ice chest to interested parties.

All filters used in this project were pre-fired at 600°C for two hours before sampling to reduce the organic carbon background. Hi-vol filter samples were wrapped in clean aluminum foil, placed in Ziplock bags and stored at <5°C prior to preparing the reference kits.

2.2 SAMPLER FLOW RATE AUDITS

On August 11, 1986, EMSI conducted a series of audits of sampler flow rates for approximately 80 samplers for the 22 groups measuring ambient aerosol carbon, H₂O₂, HCHO, C₁-C₁₀ hydrocarbons and other miscellaneous gas phase organic species at the Citrus College site. An additional 10 samplers were audited on August 14, 1986. The audit results are summarized in Table 3-2 of Section 3.

EMSI used three different audit devices for monitoring sampler flow rates, namely:

- (a) a calibrated orifice plate for Hi-vols (20-45 cfm at standard conditions of 25°C and 760 mmHg),

- (b) a calibrated rotameter for moderate flow rates (6-60 lpm at ambient conditions), and
- (c) a series of four calibrated mass flowmeters for low flow rates (0.1-17 lpm at ambient conditions).

Parameters associated with flow measurement traceability include - barometric pressure, temperature, time and volume. Measurements of these parameters are described below.

Barometric Pressure - Measured with a mercurial barometer. The appropriate corrections are made for temperature, latitude and elevation. The accuracy of this barometer is verified by checking the barometer against another mercurial barometer.

Temperature - All temperature measurements are made with thermometers traceable to NBS thermometer #219180.

Time - All stopwatches and electric timers are checked against one another and against station WWV.

Volume - All Hastings Kit volumes are NBS traceable re: Hastings. All Brooks volumes have been checked against NBS approved techniques. All TSP flows are traceable to a primary standard Roots meter.

EMSI flow measurements have repeatedly been demonstrated to agree to within 2% of flows measured by EPA at the EMSL-QAB lab in RTP, NC.

A discussion of the sampler flow rate calibration procedures and the traceability of the audit devices follows.

Audit Orifice for High Volume Samplers

For the Hi-vol audits, EMSI used a General Metal Works, Model GMW 25 orifice kit, Serial #M112. The high volume samplers were audited using those procedures described in "Investigation of Flow Rate Calibration Procedures Associated with the High Volume Method for Determination of Suspended Particulates" (EPA-600/4-78-047). Basically, the procedure

consists of placing an audit high-volume orifice on each sampler inlet with the filter paper in place. The sampler is then turned on and allowed to warm up for about five minutes. At that time the following data are recorded:

1. Orifice pressure drop in inches of water.
2. Ambient temperature and barometric pressure.
3. Indicated station sampler flow as read by the data logger.

The audit flow in SCFM is then calculated using the orifice calibration. This value is compared to the station flow in percent difference. The EPA-recommended range of satisfactory audit results is $\pm 7\%$.

The audit orifice is certified at least every six months in the EMSI Quality Assurance Laboratory using a Dresser Roots Meter, S/N 7659995. This Roots meter is an "authoritative volume" standard which meets all applicable NBS specifications. The orifice calibration used for this audit is presented in Table 2-1 below:

TABLE 2-1. AUDIT ORIFICE CALIBRATION

<u>ORIFICE DESIGNATION</u>	<u>DATE OF CERTIFICATION</u>	<u>CALIBRATION CONSTANTS</u>
B	7/24/86	$Q_{\text{theo}} \text{ (CMM)} = 0.480 \sqrt{P} + 0.015$

The theoretical flow rate Q_{theo} is converted to standard conditions and SCFM using the following equation:

$$Q_{\text{std}} \text{ (SCFM)} = Q_{\text{theo}} \text{ (CMM)} \left[\frac{298}{760} \times \frac{P}{T} \right]^{1/2} \times 35.3$$

where P is ambient barometric pressure in mm Hg, and T is the ambient temperature in °K.

Audit Rotameter

The audit Gilmont rotameter was calibrated on 8/8/86 over the range of 6-60 lpm using the following procedure:

1. Two 0-30 sL/min mass flow controllers were calibrated separately using a 12-liter Brooks volume meter.
2. The two mass flow controllers were then used to calibrate the rotameter.
3. The appropriate temperature and barometric pressure measurements were made in the QA lab during the calibration.
4. During the audits at the field location the temperature and barometric pressure were measured.
5. Ambient audit flow rates (Q_{amb}) were calculated according to the following equations:

$$(a) Q_{std} = 0.771 (\text{Top of Ball}) - 4.21$$

where Q_{std} = standard flow rate in lpm at 25°C and 760 mm Hg

$$(b) Q_{amb} = Q_{std} \left(\frac{760}{298} \right) \left(\frac{T_1}{P_1} \times \frac{T_2}{P_2} \right)^{1/2} = 1.61 \left(\frac{T_2}{P_2} \right)^{1/2} Q_{std}$$

where T_1, P_1 = temperature and barometric pressure in lab during calibration

(i.e. 294.2°K and 741.1mm Hg)

T_2, P_2 = temperature and barometric pressure in field during audit

Audit Mass Flow Meters

Each of the four Tylan mass flow meters used in this audit was calibrated at EMSI against an NBS traceable standard. The 17 L mass flow meter was calibrated 8/7-8/86 using a 4-liter Brooks Volume Meter. The 50 cc, 300 cc, 3000 cc mass flow meters were calibrated 8/8/86 using a Hastings

Bubblemeter Kit. The flows were calibrated in STP conditions (25°C, 760 mm Hg) and were converted to ambient conditions by:

$$\text{ambient flow} = \text{standard flow} \left(\frac{760}{298} \right) \left(\frac{T_2}{P_2} \right)$$

where T_2 was the ambient temperature in °K and P_2 was the ambient barometric pressure in mm Hg.

The calibrations of these mass flow meters were checked after the audit on 8/16/86. Throughout their respective ranges each mass flow meter was found to be accurate to $\pm 1.8\%$ or closer.

2.3 ANALYSIS OF ORGANIC AND ELEMENTAL CARBON

The instrument used was a Dohrmann Model DC-52A carbon analyzer equipped with a Horiba PIR 2000 non-dispersive infrared (NDIR) CO_2 detector. Calibration standards were prepared using potassium acid phthalate (KHP) to form an aqueous 1800 ppm carbon standard stock solution which was diluted with 0.1% phosphoric acid to 400 ppm carbon for the medium range carbon analysis, and diluted to 180 ppm carbon for low range analysis. A separate KHP stock was used to form a 1800 ppm carbon quality control (QC) check solution for high range carbon analysis, 400 ppm carbon medium range QC solution and a 180 ppm carbon low range QC solution. Calibration and QC solutions were introduced into the analyzer using a .50 μl syringe. Carrier gasses were dried upstream of the detector using anhydrous magnesium perchlorate and a Permapure dryer. Calibration was checked using the medium range QC solution after every ten samples.

Filter Sample Preparation - All utensils used in the preparation of quartz filter samples are precleaned and oven dried at 100°C. Gloves are worn during all sample handling processes. A 1/4" punch diameter circle is cut with a paper punch from the original filter sample and placed into a clean prelabeled petri dish with a stainless steel tweezer prior to analysis.

Organic Carbon Determination - A 1/4" diameter punch from the exposed area of a quartz filter is placed into a platinum boat through an inlet port. This port is then sealed and ultra high purity helium carrier gas (10 cc/min) is introduced into the system. The sample boat is advanced to the vaporization zone where samples (and standards) are dried at a temperature of 110°C for two minutes. Next, the sample boat is advanced into a heated furnace zone at a temperature of 600°C for a period of five minutes. Organic compounds on the filter punch are volatilized (but not oxidized) and are transported downstream in the helium carrier gas to a zone packed with manganese dioxide (MnO₂) and heated to 350°C. Here the gaseous hydrocarbon species are converted to CO₂ which is then detected by the NDIR CO₂ detector. At the end of five minutes the sample boat is withdrawn from the furnace to cool down for one minute. When the cycle is completed, the filter punch is taken out of the platinum boat and placed into a pre-labeled petri dish and stored for elemental carbon determination.

Elemental Carbon Determination - The same 1/4" diameter punch analyzed for organic carbon is placed in the platinum sample boat and the inlet port is sealed. The sample boat is advanced into a heated furnace zone at a temperature of 750°C. The carrier gas used in this analysis is helium containing 2% oxygen. This procedure measures graphitic "elemental" carbon, which was left on the filter from the previous organic carbon determination. Total carbon is obtained by adding the organic and elemental carbon values together.

Range and Sensitivity - With a variable injection volume of 5-50 µl for standards, the range of analysis is 0.8-45.0 µg carbon. For filters an area of 0.3137 square centimeters is generally used; however, if the carbon concentration on the filter punch is higher than the highest standard, a smaller portion of the filter is used. The detector responses for the samples are compared to that of a five to six point calibration curve obtained from the standards to determine the carbon content per square centimeter of filter area.

Interferences - There are no known interferences in the NDIR detection of CO₂, except for water, which is removed with a Permapure dryer attached prior to the detection inlet. Carrier gas for the Permapure dryer is 3 cc/min of ultrapure helium. However, atmospheric CO₂ and laboratory solvents can contaminate samples exposed to room air, so it is recommended that samples be kept sealed from the atmosphere prior to analysis.

Bulk Solid Samples - For the bulk solid NBS reference standards, a small aliquot of each material is weighed out into the platinum sample boat. The sample is analyzed for organic carbon in helium and then for elemental carbon by switching the carrier gas to 2% oxygen/98% helium. Results for these standards are reported in percent organic carbon and percent elemental carbon.

3.0 EXPERIMENTAL RESULTS

3.1 AUDIT OF SAMPLER FLOW RATES

The results from audits of sampler flow rates for the 22 groups participating in the carbon study at Citrus College (listed in Table 3-1) are summarized below in Table 3-2.

Flow rates for Hi-vol samplers are given in cfm at standard conditions of 25°C and 760 mm Hg, whereas the flow rates for all other samplers are given in lpm (or cc/min) at ambient conditions.

3.2 ANALYTICAL RESULTS FROM PM-10 HI-VOL OPERATED BY EMSI

During the nine day sampling program it became apparent that one of the three PM-10 Hi-vol samplers on loan from the ARB had a defective flow controller. Thus, EMSI proceeded to analyze only the samples from the two valid samplers. The analytical results from these two samplers are summarized in Table 3-3 in units of $\mu\text{g C/m}^3$.

3.3 EMSI ANALYTICAL RESULTS FOR CARBONACEOUS REFERENCE SAMPLES

The EMSI results for the 20 reference filter samples and the 3 NBS solid standards are summarized in Table 3-4. As part of this task, EMSI also analyzed the same 20 reference filter samples that were recoded (i.e. YA-YT) by ARB's field manager for the Carbon Study, Dr. Susanne Hering. The NBS standards are reported in terms of $\mu\text{g C}$ per μg sample. The lower limit of detection for the EMSI carbon analyzer, based on ten nonconsecutive analyses of the same filter blank, is 0.08 $\mu\text{g C}$. This translates into 0.3 $\mu\text{g/cm}^2$ for the 1/4" diameter filter punches.

3.4 EMSI RESULTS FOR VARIOUS AMBIENT SAMPLES COLLECTED BY OTHER GROUPS

EMSI's analytical results for selected ambient samples (i.e. samples from 8/18-8/19) collected at Citrus College by various participants in the Carbon Study are presented in Table 3-5. Two of the groups collected samples with TSP Hi-vols (AIHL and USEPA); two groups (GMR and EMSI) collected samples with PM-10 Hi-vols. Three groups (OGC, AV, and EMSI) collected ambient samples with samplers having a 2.5 μm diameter cut point, while one group (GGC) operated a sampler with a cut point of 3.5 μm diameter. The University of Minnesota operated a multi-stage micro orifice impactor for which EMSI analyzed samples from the sixth stage corresponding to particles less than $\sim 1 \mu\text{m}$. The results are tabulated in units of $\mu\text{g C/cm}^2$ since the individual sample volumes are not available to EMSI.

3.5 RESULTS OF THE INTERLABORATORY ROUND ROBIN

The analytical results for the interlaboratory round robin comparison of carbonaceous reference materials are summarized for each of 12 participating laboratories in Table 3-6 in units of $\mu\text{g C/cm}^2$. Only Coulometrics and EMSI analyzed the three NBS standards. These results are summarized below:

<u>Sample</u>	<u>EMSI</u>	<u>Coulometrics</u>
NBS 1648	10% OC, 4% EC	7% OC, 7% EC
NBS 1649	14% OC, 4% EC	10% OC, 8% EC
NBS 1650	OC:EC = 4.5:1	60% OC, 18% EC

Note: For sample NBS 1650, EMSI measured the organic carbon to elemental carbon ratio only, rather than the percent composition for the different carbonaceous fractions due to a problem with overloading the NDIR detector for this high carbon content sample.

Table 3-1 LIST OF PARTICIPANTS IN CARBON MEASUREMENT STUDY

<u>Group ID</u>	<u>Participant(s)</u>	<u>Affiliation</u>	<u>Sampled Carbon</u>	<u>Participated In Round Robin</u>
A	Appel	AIHL	x	x
B	Bope	AQMD		
C	Cadle	GMR	x	x
D	Cahill	UC Davis	x	
E	Countess/Howes	EMSI	x	x
F	Fitz/Fung	AV/ERT	x	x
G	Gordon	GGC	x	x
H	Huntzicker/Rau	OGC	x	x
I	Knapp	USEPA	x	x
J	Rasmussen	Biospherics		
K	Pierson	Ford		
L	Holdren	Battelle-Columbus		
M	Grosjean	DGA		
N	Kok	NCAR		
O	Noll	Illinois I.T.		
P	Mackay	Unisearch		
Q	Novakov/Hansen	LBL	x	x
R	Winer	UC Riverside		
S	Ellis	SCE		
T	Kaplan/Sakugawa	UCLA		
U	McMurry	Univ. Minnesota	x	x
V	Shikiya	ARB		
W	Tanner	BNL		
X	Dasgupta	Texas Tech		
Y	Hering/Allen	UCLA		
Z	McTavish	Atmospheric Environment Service (Canada)		

TABLE 3-2. AUDITED FLOW RATES

Group	Sampler	Nominal Flow Rate (lpm)	Audit Flow Rate (alpm)	Flow Rate Difference (%)	Ambient Pressure (mmHg)	Ambient Temperature (°C)	Audit Device ^J
A	AD1	8.0	8.2	+2.5	747.3	34.5	R
	AF2	20.0	21.4	+7.0	"	"	R
	AT3	40 scfm	b	--	--	--	--
	AT4	20.0	21.4	+7.0	747.3	34.5	R
B	BH	40 scfm	41.5 scfm	+3.8	735.7	21.0	0
C	CF1	20.0	19.8	-1.0	747.3	34.5	R
	CF2	7.0	7.1	+1.4	"	"	R
	CP	1.0	0.95	-5.0	"	"	M
	CDC	16.7	16.2	-3.0	"	"	M
	CI	5.0	5.1	+2.0	"	"	M
	CQ	2.0	C	--	--	--	--
	CH	40 scfm	41.7 scfm	+4.2	747.3	34.5	0
	D	DI1	1.1	1.05	-4.5	745.8	31.0
DI2	1.1	1.11	+0.9	"	"	M	
DI3	1.1	1.05	-4.5	"	"	M	
DFM	10.0	10.2	+2.0	"	"	M	
DFO	10.0	9.9	-1.0	"	"	M	
DFD	10.0	9.9	-1.0	"	"	M	
DFC	21.7	20.7	-4.6	"	"	M	
DFS	N/A	--	--	--	--	--	R
E	EF1A	24.3	24.3	0.0	745.8	31.0	R
	EF1B	24.6	24.3	-1.2	"	"	R
	EF2A	24.6	24.3	-1.2	"	"	R
	EF2B	24.3	24.3	0.0	"	"	R
	EF3A	25.8	25.1	-2.7	"	"	R
	EF3B	23.9	23.5	-1.7	"	"	R
	EH1	40 scfm	42 scfm	+5.0	747.3	34.5	0
	EH2	40 scfm	42 scfm	+5.0	"	"	0
	EH3	40 scfm	41.3 scfm	+3.2	"	"	0

TABLE 3-2. (Continued)

Group	Sampler	Nominal Flow Rate (lpm)	Audit Flow Rate (alpm)	Flow Rate Difference (%)	Ambient Pressure (mmHg)	Ambient Temperature (°C)	Audit Device
F	FA/FB	18.6	19.7	+5.9	745.0	26.1	R
	Dilution Air	70.4	69.6	-1.1	"	"	R
	F	1.09	1.12	+2.7	738.0	25.0	M
G	GDIFA1	30.0	29.8	-0.7	747.3	34.5	R
	GDIFA2	30.0	29.1	-3.0	"	"	R
	GDIFA3	30.0	29.8	-0.7	"	"	R
	GDIFA4	30.0	29.8	-0.7	"	"	R
	GDIFA5	30.0	29.1	-3.0	"	"	R
	GHVIR1	34 scfm	32.5 scfm	-4.4	745.0	33.0	O
	GHVCI2	34 scfm	30.3 scfm	-10.9	735.7	21.0	O
H	Dry Gas Meter	30.2	31.2	+3.3	747.3	34.5	R
	"	14.3	15.0	+4.9	"	"	R
I	IHV1	40 scfm	39.0 scfm	-2.5	745.0	33.0	O
	IHV5	40 scfm	41.0 scfm	+2.5	"	"	O
	Dry Gas Meter	17.1	16.2	-5.3	747.3	32.0	R
	"	30.6	29.7	-2.9	"	"	R
J	JC1	--	0.104	--	745.6	34.0	M
	JC2	--	0.108	--	"	"	M
	JC3	--	0.102	--	"	"	M
	JC4	--	0.110	--	"	"	M
	JC5	--	0.053	--	"	"	M
K	BBF	N/A	--	--	--	--	--
L	LK6	--	0.015	--	745.6	34.5	M
	Rotometer #1	--	9.8	--	745.0	29.0	R
M	" #2	--	16.9	--	"	"	R
	" #3	18.3 ^d	19.2	+4.9	"	"	R
	" #4	--	16.1	--	"	"	R
	" Spare	--	15.3	--	"	"	R
N	NPA	1.83	1.76	-3.8	738.0	25.0	M
	NPB	1.81	1.73	-4.4	"	"	M
	NQ	1.19	1.16	-2.5	"	"	M

TABLE 3-2. (Continued)

Group	Sampler	Nominal Flow Rate (lpm)	Audit Flow Rate (alpm)	Flow Rate Difference ^a (%)	Ambient Pressure (mmHg)	Ambient Temperature (°C)	Audit Device ^f
O	ORI	N/A					
P	PC1	11.2 ^e	10.6	-5.4	736.0	21.5	R
	PC2	1.95 ^e	1.78	-8.7	"	"	M
	QCA-1	10.0	10.0 ^f	0.0	747.3	34.5	M
Q	QCA-1	2.8	3.3 ^f	+17.8	745.0	33.0	M
Q	QCA-2	--	Malfunction ^f	--	--	--	--
R	RH5	40 scfm	41.6 scfm	+4.0	745.8	32.0	0
	RH6	"	"	"	"	"	0
	RH8	"	"	"	"	"	0
	RH13	"	"	"	"	"	0
	RH11	"	"	"	"	"	0
	RH14	"	"	"	"	"	0
	RH4	"	"	"	"	"	0
	RH2A	24.7 scfm	21.8 scfm	-11.7	747.3	34.5	0
	RH2B	"	22.7 scfm	-8.1	"	"	0
	RH10A	"	23.3 scfm	-5.7	"	"	0
	RH10B	"	21.5 scfm	-13.0	"	"	0
	Dry Gas Meter	4.5	4.3	-4.4	745.6	33.0	M
	"	12.0	11.0	-8.3	"	"	M
	"	1.79	1.92	+7.3	"	"	M
S	S	N/A					
T	Rotometer #1	2.5	1.8	-25.0	745.8	26.0	M
	"	1.0	0.4	-60.0	"	"	M
	" #2	2.5	1.4	-44.0	"	"	M
U	#1	30.0	33.0	+10.0	747.3	34.5	R
	#2	"	29.8	-0.7	"	"	R
	#3	"	32.3	+7.7	"	"	R
	#4	"	31.4	+4.7	"	"	R
	UFH	N/A	24.6 scfm	--	745.0	29.0	0
UIH	20-25 scfm	8	--	--	--	--	
V	V	N/A					

TABLE 3-2. (Continued)

Group	Sampler	Nominal Flow Rate (lpm)	Audit Flow Rate (alpm)	Flow Rate Difference (%)	Ambient Pressure (mmHg)	Ambient Temperature (°C)	Audit Device ^j
W	WPI	0.50	0.56	+12.0	745.8	26.0	M
	WFS	0.50	0.63	+26.0	"	"	M
	MFC #3	N/A	0.12	--	"	"	M
X	XPI	2.19	2.23	+1.8	738.0	24.0	M
	XQ1	1.12	1.11	-0.9	"	"	M
Y	YFN	4.0	4.0	0.0	745.0	25.0	M
	YI	1.05	1.05	0.0	"	33.0	M
Z	ZF	46.0 ^h	53.0	-15.2	736	21.5	R
	ZCI	7.25 ⁱ	6.14	+15.3	"	"	R

Footnotes:

- a. Percent flow rate difference = (Audit-Nominal) ÷ Nominal x 100%.
- b. Unable to measure flow through 1.5" inlet without restricting flow.
- c. HCHO sampler set up late on 8/15/86 after audits; GMR to calibrate sampler with bubble meter.
- d. According to D. Grosjean, only rotometer #3 used for all samplers after original audit on 8/11/86.
- e. According to G. Mackay, nominal flow rates of 10 lpm and 1.75 lpm are for 0°C and 760 mmHg; therefore corresponding ambient flow rates would be 11.2 lpm and 1.95 lpm, respectively.
- f. Reduced flow through channel #1 since a malfunction was discovered in channel #2.
- g. Sampler located in parking lot behind AIHL trailer. P. McMurry stated that EMSI did not need to calibrate flow rate.
- h. According to D. McTavish, this sampler was 44.3 slpm for 20°C and 760 mmHg, which corresponds to 46.0 alpm.
- i. According to D. McTavish, this sampler was calibrated by G. Mackay with a flow rate of 6.5 slpm at 0°C and 760 mmHg, which corresponds to 7.25 alpm.
- j. Audit devices: O = orifice plate for Hvolts, R = rotometer, M = mass flow meter (0-50 cc, 0-300 cc, 0-3000 cc, 0-17 liter).

Table 3-3 Results for PM-10 HiVol Samplers Operated by EMSI

Sample	Date/Time*	<u>Concentrations (micrograms/cubic meter)</u>		
		<u>Organic Carbon</u>	<u>Elemental Carbon</u>	<u>Total Carbon</u>
26EH	08/12/86 AM	14.3 +/- 0.6	3.0 +/- 0.2	17.3 +/- 0.4
27EH	08/12/86 PM	5.8 +/- 0.2	2.2 +/- 0.1	8.0 +/- 0.4
36EH	08/13/86 AM	13.6 +/- 0.2	4.0 +/- 0.1	17.6 +/- 0.3
37EH	08/13/86 PM	6.3 +/- 0.4	2.5 +/- 0.1	8.8 +/- 0.3
46EH	08/14/86 AM	16.1 +/- 0.7	4.2 +/- 0.5	20.3 +/- 0.7
47EH	08/14/86 PM	5.6 +/- 0.2	1.7 +/- 0.1	7.3 +/- 0.2
56EH	08/15/86 AM	14.9 +/- 0.1	3.2 +/- 0.1	18.1 +/- 0.1
57EH	08/15/86 PM	6.0 +/- 0.2	1.6 +/- 0.1	7.6 +/- 0.2
66EH	08/16/86 AM	13.7 +/- 0.3	2.8 +/- 0.1	16.5 +/- 0.3
67EH	08/16/86 PM	12.3 +/- 0.9	1.5 +/- 0.1	13.8 +/- 0.8
76EH	08/17/86 AM	17.3 +/- 0.3	2.8 +/- 0.1	20.1 +/- 0.3
77EH	08/17/86 PM	8.7 +/- 0.1	1.5 +/- 0.1	10.2 +/- 0.1
86EH	08/18/86 AM	13.6 +/- 0.1	2.7 +/- 0.1	16.3 +/- 0.1
87EH	08/18/86 PM	9.7 +/- 0.4	1.4 +/- 0.1	11.1 +/- 0.4
96EH	08/19/86 AM	12.7 +/- 0.5	2.6 +/- 0.2	15.3 +/- 0.6
97EH	08/19/86 PM	11.2 +/- 0.5	2.1 +/- 0.2	13.3 +/- 0.6
106EH	08/20/86 AM	18.0 +/- 0.8	5.2 +/- 0.3	23.2 +/- 1.0
107EH	08/20/86 PM	13.1 +/- 0.7	3.1 +/- 0.3	16.2 +/- 1.0

*Time: AM = 0800 PDT- 2000 PDT; PM = 2000 PDT-0800 PDT

Table 3-4 EMSI Results for Carbonaceous Reference Samples Analyzed in Duplicate
(micrograms/square centimeter)

Sample Number	Sample	Type Sample	ORIGINAL SET			Sample Number	BLIND SET		
			Organic Carbon	Elemental Carbon	Total Carbon		Organic Carbon	Elemental Carbon	Total Carbon
(I) Filters									
1	01	Ambient: 08/18/86 AM	32.4	6.1	38.5	YT	31.9	6.5	38.4
2	10	" (86 EB)	31.5	6.7	38.2	YK	31.9	6.4	38.3
3	16	"	31.3	7.4	38.7	YE	33.4	8.0	41.5
4	03	Ambient: 08/18/86 PM	19.9	4.4	24.3	YR	19.6	4.8	24.4
5	05	" (87 EB)	19.9	4.3	24.2	YP	19.4	5.2	24.6
6	14	"	19.8	4.0	23.8	YG	18.7	4.3	23.0
7	06	Ambient: 08/19/86 AM	29.2	6.1	35.3	YO	29.8	5.0	34.8
8	17	" (96 EB)	28.8	5.7	34.5	YD	29.4	6.3	35.7
9	20	"	29.8	5.7	35.5	YA	28.9	5.2	34.1
10	02	Ambient: 08/19/86 PM	24.4	5.5	29.9	YS	25.0	5.1	30.1
11	04	" (97 EB)	24.0	5.0	29.0	YQ	23.5	4.9	28.4
12	08	"	24.0	5.6	29.6	YM	22.0	5.8	27.8
13	07	Catalyst: Buick	11.0	23.4	34.4	YN	11.0	25.3	36.3
14	18	Leaded: Chevy	56.1	12.2	68.3	YB	52.0	12.8	64.8
15	11	Diesel: Olds	14.0	84.0	98.0	YJ	14.0	88.3	102.3
16	13	Wood Smoke	89.5	9.2	98.7	YH	85.7	10.2	95.9
17	15	Wood Smoke	366.3	16.7	383.0	YF	363.0	16.9	379.9
18	12	Soot Aerosol	5.4	8.9	14.3	YI	6.3	7.6	13.9
19	19	Organic Aerosol	9.6	0.2	9.8	YC	9.1	0.0	9.1
20	09	Blank	0.0	0.0	0.0	YL	0.2	0.1	0.3
(II) NBS Standards									
21	21	NBS 1649*	0.14	0.04	0.18		-	-	-
22	22	NBS 1650*	-	-	-		-	-	-
23	23	NBS 1648*	0.10	0.04	0.14		-	-	-

Lower limit of detection = 0.08 microgram C = 0.3 microgram C/square centimeter

* Reported as microgram C/microgram sample except for NBS 1650 for which the ratio of organic carbon to elemental carbon is 4.5:1

Table 3-5 EMSI Results for Various Ambient Samples

Carbon Concentration (microgram/square centimeter)				Carbon Concentration (microgram/square centimeter)					
Group	Sample Number	Organic Carbon	Elemental Carbon	Total Carbon	Group	Sample Number	Organic Carbon	Elemental Carbon	Total Carbon
A: AIHL (HiVol)	81AT3P	12.4	2.0	14.4	G: GCC (3.5 um)	82-3GHMCI2	18.8	1.6	20.4
"	82AT3P	14.8	1.7	16.5	"	87GMCI2	17.1	1.9	19.0
"	83AT3P	11.2	1.3	12.5	"	91GHMCI2	11.1	0.9	12.0
"	84AT3P	7.8	0.6	8.4	"	92-3GHMCI2	18.4	1.9	20.3
"	85AT3P	11.1	1.3	12.4	"	97GHMCI2	20.8	2.5	23.3
"	91AT3P	13.1	1.5	14.6	"	Blank	1.4	0.0	1.4
"	92AT3P	14.5	1.2	15.7	H: GCC (2.5 um)	86H	10.9	0.8	11.7
"	93AT3P	7.8	0.5	8.3	"	87H	7.6	0.3	7.9
"	94AT3P	7.8	0.5	8.3	"	96H	10.8	0.4	11.2
"	95AT3P	15.2	2.5	17.7	"	97H	9.2	0.3	9.5
"	Blank	0.4	0.0	0.4	"	Blank	0.0	0.0	0.0
I: USEPA (HiVol)	86IHV5	44.0	6.7	50.7	F: AV (2.5 um)	86FAD-1	14.8	2.1	16.9
"	87IHV5	26.4	2.8	29.2	"	87FAD-1	10.1	1.0	11.1
"	96IHV5	36.8	5.6	42.4	"	96FAD-1	14.1	1.8	15.9
"	97IHV5	32.2	5.4	37.6	"	97FAD-1	12.1	1.6	13.7
"	Blank	0.0	0.0	0.0	"	Blank	0.0	0.0	0.0
C: GFR (RM-10)	86GH	38.0	6.6	44.6	E: EMSI (2.5 um)	86EFIB	31.0	5.7	36.7
"	87GH	15.1	2.0	17.1	"	87EFIB	19.4	3.1	22.5
"	96GH	27.5	5.4	32.9	"	96EFIB	28.5	4.6	33.1
"	97GH	24.1	3.5	27.6	"	97EFIB	23.0	3.9	26.9
"	Blank	0.0	0.0	0.0	"	Blank	0.1	0.0	0.1
E: EMSI (RM-10)	86EH	31.7	6.7	38.4	U: Univ. of MN (microgram for 6th stage)	86UII-6	122.2	44.9	167.1
"	87EH	19.9	4.2	24.1	"	87UII-6	59.2	26.9	86.1
"	96EH	29.3	5.8	35.1	"	96UII-6	104.2	49.9	154.1
"	97EH	24.1	5.4	29.5	"	97UII-6	92.6	20.3	112.9
"	Blank	0.0	0.0	0.0					

Note: Period 1 = 0800-1200; Period 2 = 1200-1600; Period 3 = 1600-2000; Period 4 = 2000-2400; Period 5 = 0000-0800; Period 6 = 0800-2000; Period 7 = 2000-0800.

Table 3-6. INTERLABORATORY ROUND ROBIN RESULTS FOR CARBONACEOUS SPECIES (microgram/square centimeter), BLANK CORRECTED

Sample Type	AIHL	Coulom.	DEQ	EMSI	EPA	ERT	G G C	GMR	LHL	O G C	Sunset	U of M
01,10,16*	29.9	29.2	19.0	31.7	32.4	29.3	28.2	27.5	N/A	25.7	32.4	39.7
"	8.6	7.9	6.7	6.7	4.5	7.6	11.7	10.1	7.6	10.8	6.5	3.1
"	38.5	37.1	25.7	38.4	36.9	36.9	39.9	37.6	N/A	36.5	38.9	42.8
03,05,14*	18.7	13.7	13.3	19.9	19.5	18.9	18.7	17.8	N/A	18.6	19.8	24.5
"	5.9	5.3	2.7	4.2	3.6	4.2	7.4	5.6	5.1	6.5	3.2	2.0
"	24.6	19.0	16.0	24.1	23.1	23.1	26.1	23.4	N/A	25.1	23.0	26.5
06,17,20*	27.0	21.8	17.3	29.3	29.0	26.0	24.7	26.6	N/A	24.8	28.4	28.7
"	7.6	10.5	4.4	5.8	3.1	6.1	10.4	6.7	6.2	8.8	3.8	6.3
"	34.6	31.5	21.7	35.1	32.1	32.1	35.1	33.3	N/A	33.6	32.2	35.0
02,04,08*	21.9	23.9	15.3	24.1	24.6	22.9	22.6	21.3	N/A	18.9	24.1	29.1
"	6.8	6.1	1.4	5.4	2.5	4.2	7.9	5.5	6.0	7.5	4.3	1.8
"	28.7	30.0	16.7	29.5	27.1	27.1	30.5	26.8	N/A	26.4	28.4	30.9
07	22.8	0.6	8.0	11.0	13.9	8.5	8.3	9.6	N/A	5.6	9.7	32.0
"	16.5	25.3	17.0	23.4	17.7	23.1	25.3	36.0	11.3	26.7	20.9	3.7
"	39.3	25.9	25.0	34.4	31.6	31.6	33.6	45.6	N/A	32.3	30.0	35.7
18	62.2	50.7	36.0	56.1	64.0	54.1	46.5	44.8	N/A	45.5	50.1	60.5
"	8.0	21.5	0.0	12.2	2.0	10.4	28.0	19.0	5.8	22.8	13.5	4.7
"	70.2	72.2	36.0	68.3	66.5	64.5	74.5	63.8	N/A	68.3	63.6	65.2
11	N/A	8.2	12.0	14.0	29.7	15.6	15.4	18.8	N/A	37.8	12.6	29.9
"	N/A	97.5	28.0	84.0	71.6	85.7	83.7	84.7	15.5	82.1	88.5	78.7
"	128.0	105.7	40.0	98.0	101.3	101.3	99.1	103.5	N/A	119.9	101.1	108.6
13	83.0	88.0	47.0	89.5	83.8	86.1	92.9	82.4	N/A	71.8	82.7	92.5
"	17.0	8.3	16.0	9.2	6.1	3.8	6.6	22.1	11.2	26.6	8.5	3.4
"	100.0	96.3	63.0	98.7	89.9	89.9	99.5	104.5	N/A	98.4	91.2	95.9
15	N/A	398.0	195.0	366.3	257.6	364.7	392.1	390.5	N/A	299.2	300.5	371.8
"	N/A	9.3	33.0	16.7	108.6	1.5	12.0	79.0	12.0	97.7	11.8	4.9
"	387.0	407.3	228.0	383.0	366.2	366.2	404.1	469.5	N/A	393.9	332.3	376.7
12	7.5	1.6	3.0	5.4	5.0	4.3	4.1	2.5	N/A	2.9	2.9	15.9
"	5.1	11.1	2.0	8.9	8.5	9.2	9.4	8.2	3.2	12.1	10.8	0.5
"	12.6	12.7	5.0	14.3	13.5	13.5	13.5	10.7	N/A	15.0	13.7	16.4
19	10.2	2.2	2.0	9.6	8.2	8.8	7.8	7.8	N/A	6.7	7.9	8.2
"	0.0	0.0	0.0	0.2	1.4	0.8	1.1	1.3	0.0	0.0	0.0	1.6
"	10.2	2.2	2.0	9.8	9.6	9.6	8.9	9.1	N/A	6.7	7.9	9.8

OC = Organic Carbon; EC = Non-Volatile/Elemental Carbon; TC = Total Carbon

* Average of samples submitted in triplicate to all laboratories except Coulometrics and Sunset Labs.

4.0 DISCUSSION AND CONCLUSIONS

4.1 SAMPLER FLOW RATE AUDITS

Audits of the different participants' sampling flow rates (see Table 3-2) for the most part agreed within 7% of the nominal flow rates reported by each participant. The major exceptions include:

- o GGC's (Group G) 3.5 μm cut point Hi-vol sampler GHVCIZ: 10.9% low
- o LBL's (Group Q) black carbon sampler QCA-1: 17.8% high below 3 lpm
- o UC Riverside's (Group R) PM-10 Hi-vol samplers RH2A and RH10B: 11.7% low and 13.0% low, respectively
- o UCLA's (Group T) rotameters: 25-60% low
- o Texas Tech's (Group W) peroxide samplers WPI and WPS: 12% high and 26% high, respectively
- o McTavish's (Group Z) filter pack sampler ZF and TDLAS sampler ZCI: 15.2% low and 15.3% high, respectively.

4.2 PM-10 HI-VOL RESULTS

The precision of the two collocated ARB PM-10 Hi-vol samplers operated by EMSI for the 18 sampling periods was excellent. The standard error for the 18 sets of duplicate measurements was 4.9% for organic carbon and 8.5% for elemental carbon. The average airborne PM-10 carbonaceous concentration, during this nine day period, were 11.8 $\mu\text{g}/\text{m}^3$ organic carbon/ m^3 and 2.7 μg elemental carbon/ m^3 . Daytime concentrations were typically double the night time concentrations for those two species. Organic carbon predominated over elemental carbon by a ratio of approximately 4:1.

4.3 EMSI RESULTS FOR CARBONACEOUS REFERENCE SAMPLES

Overall there was excellent agreement between the duplicate sets of 20 filter samples (#01-#20 versus #YA-#YT) analyzed by EMSI. Differences were within the range of the precision for the ambient PM-10 samples analyzed in triplicate. The standard deviation based on triplicate analyses of the same sample ranged from 0.2 to 0.8 $\mu\text{g}/\text{cm}^2$ for organic carbon and from 0.3 to 0.5 $\mu\text{g}/\text{cm}^2$ for elemental carbon.

4.4 EMSI RESULTS FOR AMBIENT SAMPLES COLLECTED BY OTHER GROUPS

Without having access to the individual participant's data sheets for sampling at Citrus College, it is almost impossible to compare the analytical results given in $\mu\text{g C}/\text{cm}^2$ for the different aerosol samplers. Besides, this is beyond our original scope of work. However, we have attempted to compare these results by normalizing the results to sample volume based on our best estimates of sampling flow rate and sampling duration. These estimates of carbonaceous concentrations in units of $\mu\text{g C}/\text{m}^3$ are summarized in Table 4-1.

Based on this limited amount of data, it appears that most of the particulate elemental carbon is in a size mode below 1 μm (i.e. the cutoff for stage #6 of the UM impactor). Also it appears that the particulate organic carbon is bimodal: $\approx 50\%$ below 1 μm and $\approx 50\%$ between 1.0 μm and 2.5 μm , with just a hint of a supermicron organic mode based on the USEPA TSP Hi-vol results. The elemental carbon values for the AV 2.5 μm cut point sampler look low by comparison with other samplers with similar cut points.

4.5 INTERLABORATORY ROUND ROBIN CARBONACEOUS ANALYSES

Overall, the agreement between laboratories for the total carbon content of the 20 reference filter samples is quite good. For the four ambient PM-10 samples provided to each laboratory in triplicate (as blind samples), the results are internally very consistent with the exception of OGC ($\pm 10\%$), and Coulometrics ($\pm 14\%$), and the Oregon DEQ ($\pm 12\%$). In

addition, the results from the Oregon DEQ are at least 30% lower than the other laboratories for all samples. Other outliers include GM's total carbon values for sample #7 (i.e. catalyst auto) and sample #15 (i.e. woodsmoke), AIHL's total carbon value for sample #11 (i.e. diesel auto exhaust sample), and both OGC's and Coulometric's values for total carbon for sample #19 (i.e. organic aerosol).

Due to the analytical methodology employed by the USEPA, i.e. switching from helium carrier gas to helium/oxygen carrier gas between samples, it appears that the USEPA results overestimate the organic aerosol fraction at the expense of the elemental carbon fraction. It is possible that any residual oxygen in the system from a previous analysis will remove some of the elemental carbon from the fresh sample, thereby overestimating the organic carbon fraction.

GGC's elemental carbon values for the ambient PM-10 samples tend to be higher than the other laboratories by 2-3 $\mu\text{g C}$.

The largest differences in the organic/elemental carbon split occurred for samples 7 (i.e. catalyst auto), 18 (leaded auto), 11 (diesel), 13 and 15 (woodsmoke samples), and 12 (soot sample). The results from the Oregon DEQ, Coulometrics and the University of Minnesota for the organic/elemental carbon split had the largest deviation from that of the other eight laboratories that reported both organic and elemental carbon. If we ignore the results from these three laboratories, the outliers in the organic/elemental carbon split for the different laboratories are:

- o Sample 7: AIHL, OGC, EPA
- o Sample 18: OGC, EPA, GGC
- o Sample 11: OGC, EPA, LBL
- o Samples 12, 13, and 15: No consensus between laboratories.

Table 4-1 ENSI Results for Various Ambient Samples Normalized to Sample Volume

12 Hour Sampling Period	Analyte	Group/Sampler							U of M* <1.0 um	
		AHHL HiVol	USEPA HiVol	ENSI HiVol	SMR RM-10	GCC 3.5 um	ENSI 2.5 um	OGC 2.5 um		AV 2.5 um
86.0	OC	37.2	44.0	31.7	38.0	-	30.9	10.9	14.8	122.2
86.0	EC	5.0	6.7	6.7	6.6	-	5.7	0.8	2.1	44.9
86.0	TC	42.2	50.7	38.4	44.6	-	36.6	11.7	16.9	167.1
87.0	OC	18.1	26.4	19.9	15.1	15.7	19.3	7.6	10.1	59.2
87.0	EC	1.9	2.8	4.2	2.0	1.9	3.4	0.3	1.0	26.9
87.0	TC	20.0	29.2	24.1	17.1	17.6	22.4	7.9	11.1	86.1
96.0	OC	34.2	36.8	29.3	27.5	26.7	28.4	10.8	14.1	104.2
96.0	EC	3.2	5.6	5.8	5.4	2.8	4.6	0.4	1.8	49.9
96.0	TC	37.4	42.4	35.1	32.9	29.5	33.0	11.2	15.9	154.1
97.0	OC	22.2	32.2	24.1	24.1	19.4	22.9	9.2	12.1	92.6
97.0	EC	3.0	5.4	5.4	3.5	2.5	3.9	0.3	1.6	20.3
97.0	TC	25.2	37.6	29.5	27.6	21.9	26.8	9.5	13.7	112.9

(I) Net Concentrations (microgram C/square centimeter)

(II) Sample Volumes (cubic meter) and Filter Area (square centimeter)

ALL	Flow Rate	40 scfm	41 scfm	42 scfm	41.7 scfm	32.5 scfm	24.3 lpm	8.3 lpm	19.7 lpm	30 lpm
ALL	Volume	821	841	862	856	667	17.5	6.0	14.2	21.6
ALL	Area	406	406	406	406	406	6.6	7.4	14.0	N/A

Table 4-1 EMSI Results for Various Ambient Samples Normalized to Sample Volume - continued

12 Hour Sampling Period	Analyte	Group/Sampler										U of M* <1.0 um
		AIHL HVol	USEPA HVol	EMSI HVol	SMR PM-10	GCC 3.5 um	EMSI 2.5 um	OCC 2.5 um	AV 2.5 um			
(III) Net Concentrations (microgram C/cubic meter)												
86	OC	18.4	21.2	14.9	18.0	-	11.7	13.4	14.6	5.7		
86	EC	2.5	3.2	3.2	3.1	-	2.1	1.0	2.1	2.1		
86	TC	20.9	24.4	18.1	21.1	-	13.8	14.4	16.7	7.8		
87	OC	9.0	12.7	9.4	7.2	9.6	7.3	9.4	10.0	2.7		
87	EC	0.9	1.4	2.0	0.9	1.2	1.2	0.4	1.0	1.2		
87	TC	9.9	14.1	11.4	8.1	10.8	8.5	9.8	11.0	3.9		
96	OC	16.9	17.8	13.8	13.0	16.2	10.7	13.3	13.9	4.8		
96	EC	1.6	2.7	2.7	2.6	1.7	1.7	0.5	1.8	2.3		
96	TC	18.5	20.5	16.5	15.6	17.9	12.4	13.8	15.7	7.1		
97	OC	11.0	15.5	11.4	11.4	11.8	8.6	11.3	11.9	4.3		
97	EC	1.5	2.6	2.5	1.7	1.5	1.5	0.4	1.6	0.9		
97	TC	12.5	18.1	13.9	13.1	13.3	10.1	11.7	13.5	5.2		
Average	OC	13.8	16.8	12.4	12.4	~12.5 †	9.6	11.8	12.6	4.4		
	EC	1.6	2.5	2.6	2.1	~1.5 †	1.6	0.6	1.6	1.6		
Periods	TC	15.4	19.3	15.0	14.5	~14.0 †	11.2	12.4	14.2	6.0		

* Results have not been corrected for a blank since there was no blank for this sampler; all analyses performed on samples collected on 6th stage of impactor; net concentrations given in micrograms C per stage.

† Not a complete data set.