Comparison of Exhaust Emission Measurements by the Federal Register Procedures and by a Beckman 6800 Gas Chromatograph

by

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ABSTRACT

This report compares measurements of exhaust emission components made using a Beckman Gas Chromatograph Model 6800 and the Standard Federal Register instrumentation. The Beckman Gas Chromatograph Model 6800 as modified for this comparison is a single instrument capable of measuring total hydrocarbons, methane, CO and CO_2.

In this comparison test, bag samples of CVS collected exhaust from 1975 prototype vehicles were analyzed by both the Federal Register instrumentation and the Beckman Gas Chromatograph. Very good correlation between the two instruments was observed for the total hydrocarbon measurements. The CO measurements showed some variations between instruments, particularly in the high concentration region. The CO_2 measurements showed apparent random fluxuations larger than either the total hydrocarbon or the CO random fluxuations.

It is believed much of the observed measurement variations were a result of less frequent use and less rigorous calibration of the Beckman instrument. If the Beckman instrument was maintained in the manner of the Federal Register certification instrumentation, comparable accuracy and repeatability could probably be achieved. There are no EPA data, however, to experimentally verify this at present.

INTRODUCTION

In 1972 the ECTD Methane Exclusion Study was started to determine the percentage of methane in 1975 prototype automobile exhaust emissions. For this study total hydrocarbons, methane, CO, and CO_2 were measured from bag samples of CVS diluted exhaust using a Beckman model 6800 gas chromatograph. The same bag samples were also analyzed by the Standard Federal Register procedures for total hydrocarbon, CO, CO_2, and NO_x. It is the intent of this report to review this data with the purpose of comparing the two instrument systems.

DATA

From November 1972 to March 1973 a series of thirty three, LA-4 cycles, three bag tests were run; however, one test was voided. The bag samples from the remaining 32 tests were analyzed on the Federal Register instrument train #16 and on the Beckman Gas Chromatograph* instrument train #42. This yielded 96 measurement pairs for each HC, CO, and CO_2. In some instances an apparent error or instrument malfunction had occurred. This was usually characterized by a near zero reading for one of the emissions on one of the instrument trains. It was arbitrarily decided to delete any data where the two values for any one emission component differed by more than a factor of two. This resulted in a deletion of 13 data points and a remaining data field of 83 points for each HC, CO and CO_2.

In order to better visualize the data a scatter plot of each measured component was printed. These plots appear in Appendix I and II. It should be noted the program prints an astrix each time one or more of the data points fall in the computer assigned bins; therefore any astrix may represent more than one data point. From these scatter plots several points on the CO and CO_2 plots were observed to deviate from the obvious grouping of the remaining points. It was decided to delete 7 more data points and then calculate statistics on both the 83 point data field and on the reduced 76 point data field. The reduced data should give better estimation of the experimental parameters since the calculations would not be affected by a few points greatly deviating from the majority; however the statistic tests of the parameters calculated from the 76 point data field would be overally optimistic since all "bad" data had

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*Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

been removed. The data and all calculations pertaining to the 83 point data field are given in Appendix I, while the reduced data and those corresponding calculations based on the 76 point data field are given in Appendix II.

ANALYSIS

The data sets were analyzed using the Multiple Regressions with Case Combinations program from the Health Sciences Computing Facility of UCLA. This program calculates a correlation matrix, a least squares best fit straight line, and associated test statistics.

A table of the correlation coefficients comparing the two different instrument measurements of the same parameter is given below:

	83 Point Data Field	76 Point Data Field
HC	.9975	.9981
CO	.9909	.9973
CO_2	.9650	.9848

As anticipated there is a very good correlation between the two instrument systems. The best correlations occur for total hydrocarbon, and the worst for CO_2. The complete correlation coefficient matrix for the 83 point data field is given in Appendix I. The corresponding correlation coefficient matrix for the 76 point data field is presented in Appendix II.

The method of least squares was used to calculate a regression line of the form:

$$X_{FR} = B_1 X_{gas} + B_o$$

Where:

X_{FR} = Represents the emission component measured by the standard Federal Register analysis.

X_{gas} = Represents the same emission component measured by the Beckman Gas Chromatograph.

B_1 = The slope of the regression line.

B_o = The ordinate intercept.

The following values for slope and intercept were obtained.

	83 Point Data Field		76 Point Data Field	
	Slope	Intercept	Slope	Intercept
HC	.99969	-0.7838	.99737	-0.91211
CO	.91417	8.6167	.90284	5.89731
CO_2	.94201	0.1733	.94191	0.15835

The intercepts are easier to visualize when expressed as a percentage of the maximum ordinant value:

	83 point data field intercept as a percentage of max ordinate value.	76 point data field intercept as a percentage of max ordinate value.
HC	-0.46 %	-0.54 %
CO	1.0 %	0.71 %
CO_2	6.2 %	5.7 %

Since the data represents measurements of the same parameters by different instrument systems, the theoretically expected curve would have intercept of zero and slope of one. It is desirable to test if the calculated experiment values are significantly different from these theoretical values. The hypothesis intercept = 0 and slope = 1 may be tested using the student "t" statistic.[1] A table of the calculated t values and a summary of the above tests for the 83 point data field and the 76 point data field are given in Appendices I and II respectively.

It can be stated with 95% confidence that all experimental intercepts are non-zero and that the CO and CO_2 slopes differ from one. It should be noted from the calculated t values that greater confidence in these predictions can be made with the reduced data field.

DISCUSSIONS

The agreement between the two instruments is best for the total hydrocarbon measurements. This is to be expected since both systems use a similar FID approach to measure total hydrocarbons. The intercept of the HC_{FR} vs. HC_{gas} fitted curve is only 0.5% of the total HC range. This seems within normal experimental accu-

racy, however since the two measurements of total hydrocarbons agree very well, this intercept is statistically significant. The slight non-zero intercept probably represents a zero point mis-calibration of one or both instruments.

The line fitted to the CO data had a slope approximately 9% lower than expected. There are several possible contributing factors. First, the calibration concentration used for the gas chromatograph was only 8% of full instrument scale, since the readable accuracy of the pen is about ± 0.2% of full scale, a calibration error of ± 2.5% is very easy. This may be a contributing factor, but should not be responsible for the observed 9%. A more probable explanation is apparent from the scatter plots where a non-linearity of the data can be noted. Specifically the Beckman gas chromatograph gave higher readings than the standard Federal Register instruments and this effect was more pronounced in the high concentration range. The least squares fitted straight line is quite sensitive to extreme points hence the few non-linear appearing points in the high concentration region would cause the fitted line to have a reduced slope and a positive intercept.

Several observations are consistent with the non-linear data hypothesis. First the percentage difference between the means of the measurements from the two instruments is only 3.7% vs. the 9.0% variation in the slope. Second the intercept of the CO fitted line is about 1% of the maximum value. Also the calibration concentration is only about 1/4 of the maximum measured concentration hence non-linear deviations in the high concentration regions are very plausible.

As evident from the scatter plots, the CO_2 data showed the greatest random variation between instruments. Consequently the correlation coefficients were lower for CO_2 than either HC or CO. These variations may represent instrument fluxuations or drift. The CO_2 reading of a Beckman gas chromatograph monitoring a calibration gas was observed to drift downward about 4% in one hour. At the time this was attributed in insufficient instrument warm-up time which might be a problem of the test data.

The fitted straight line had a 6% lower slope than expected, and the intercept was high, approximately 6% of the maximum measured concentration. The means of the two measurements showed the same discrepancies, the mean of gas chromatograph data was 6% higher than the mean of the Federal Register instrument data. This is significant and the 6% error is consistent, however it is difficult to draw any conclusion about the source of this error because of the scatter of the data points. It would be very difficult to get an accurate instrument calibration if drift or non-reproducability is a problem.

CONCLUSIONS

The total hydrocarbon measurement agreed very well and no improvements appear easily available.

The CO measurement problem occurs in the high concentration region. More data points in the region would be necessary to ascertain if the apparent non-linearity is a systematic effect. Additional gas chromatograph calibration points in the high concentration range would be most useful, however the present calibration point near the data mean should not be eliminated. It was noted the maximum concentration measured by the gas chromatograph was about 40% of the instrument recorder scale. If no higher concentrations are routinely encountered, changing the recorder scale could improve accuracy.

Removing the random fluxuations would be a major improvement in the CO_2 data. The Federal Register procedure uses NDIR to measure CO and CO_2, while the Beckman gas chromatograph uses a methanator and FID to measure both CO and CO_2. It would therefore seem possible for the CO_2 data to have as low random fluxuations as the CO data. If this were the case, better calibration could result.

SUMMARY

The Beckman Gas Chromatograph Model 6800 when modified as supplied to the MVEL is capable of measuring total hydrocarbons, methane, CO, and CO_2. The Beckman 6800 is designed as an ambient air quality instrument, hence no sensitivity problems were expected or observed. Also no problems of exceeding the operating range were encountered.

When comparing bag sample measurements made on the Federal Register instruments and on a Beckman model 6800 gas chromatograph significant differences were found for CO and CO_2. It is felt these variations represent fluxuation of insufficient calibration of one of the instruments, probably the gas chromatograph. Investigation of more thorough calibration and adjustment of the gas chromatograph is recommended if better agreement is desired.

REFERENCE

[1]Ostle, B Statistics in Research, The Iowa State University Press Ames, Iowa 1963.

APPENDIX I

(83 Point Data Field)

Table 1

(83 Data Points)

	Federal Registral Instrumentation			Beckman Gas Chromatograph		
No.	HC PPM	CO PPM	CO_2 %	HC PPM	CO PPM	CO_2 %
1	97.01	556.98	1.71	101.23	637.50	1.62
2	4.45	12.33	1.13	3.81	10.00	1.08
3	10.31	62.21	1.48	11.62	60.00	1.39
4	43.55	168.09	1.65	42.46	182.50	1.56
5	10.20	61.43	1.41	11.80	72.50	1.35
6	117.65	436.39	1.70	117.14	497.84	1.64
7	12.17	40.18	1.18	14.16	42.50	1.11
8	54.26	94.76	1.41	58.89	100.00	1.33
9	53.95	246.25	1.65	54.52	227.50	1.61
10	3.84	1.64	1.13	3.89	2.72	1.08
11	8.04	80.41	1.46	9.04	77.50	1.37
12	96.50	445.14	1.71	93.65	495.00	1.61
13	4.25	11.81	1.14	4.55	7.50	1.08
14	8.64	55.52	1.45	9.72	57.50	1.39
15	76.85	566.08	1.63	81.48	530.00	1.70
16	14.81	47.58	1.27	16.14	52.50	1.18
17	92.04	94.05	1.43	96.40	100.00	1.34
18	169.25	831.40	1.60	172.07	908.48	1.61
19	2.93	30.58	0.97	2.07	17.50	1.09
20	10.07	79.69	1.46	19.90	90.00	1.39
21	117.11	404.14	1.55	119.58	450.31	1.51
22	3.38	0.33	1.14	3.55	2.50	1.10
23	6.25	56.24	1.45	7.04	55.00	1.33
24	93.01	578.48	1.83	96.22	657.50	1.75
25	16.64	93.15	1.30	18.52	100.00	1.28
26	44.14	134.37	1.55	44.90	140.00	1.45
27	64.11	235.62	1.63	65.26	265.00	1.56
28	2.92	3.60	1.04	3.29	2.50	0.83
29	7.55	51.50	1.46	8.77	55.00	1.44
30	113.71	666.32	1.63	110.87	737.50	1.57
31	3.98	13.02	1.11	2.37	12.50	1.08
32	9.39	57.07	1.35	10.29	60.00	1.16
33	15.79	312.06	2.76	17.52	375.00	2.80
34	33.25	215.11	2.29	35.29	215.00	2.25
35	56.86	612.06	1.51	58.01	690.00	1.43
36	50.68	284.83	1.99	48.82	320.61	2.00
37	1.11	1.77	1.19	0.86	0.93	1.14
38	10.55	63.55	1.62	10.88	56.88	1.36
39	32.45	479.69	2.66	37.05	478.02	2.67
40	5.13	22.33	1.40	5.32	17.77	1.37
41	19.74	43.52	1.59	22.15	45.38	1.93
42	19.27	295.26	2.10	21.49	307.50	2.24
43	5.62	3.31	1.76	6.93	2.50	1.88
44	60.34	548.77	1.85	63.66	616.47	1.58
45	13.17	81.33	1.49	12.49	68.09	1.21
46	21.28	340.48	2.16	22.15	335.00	2.12
47	2.63	10.71	0.94	2.67	7.50	0.88
48	5.80	4.17	1.75	4.51	5.00	1.28
49	110.62	315.02	2.14	102.99	262.91	1.96
50	3.25	9.17	1.50	4.12	5.00	1.38
51	11.90	51.90	2.03	14.58	47.50	1.87
52	67.51	195.17	2.27	72.57	180.00	2.16
53	2.65	2.92	1.53	3.69	2.50	1.39
54	21.30	57.01	1.58	26.65	47.50	1.85
55	55.67	222.70	1.71	58.94	247.50	1.57
56	14.41	48.24	1.43	15.76	45.55	1.15
57	36.04	282.67	2.24	38.32	317.50	2.64
58	5.57	3.85	1.59	5.91	2.50	1.36
59	43.36	40.82	2.04	43.20	35.00	1.67
60	58.51	253.01	1.64	55.96	312.50	1.53
61	54.65	210.11	1.41	56.53	200.00	1.24
62	30.53	500.63	2.36	30.51	493.89	2.20
63	9.45	126.43	1.40	6.28	153.58	1.56
64	81.20	341.50	2.06	77.22	370.80	2.14
65	31.65	307.27	1.26	31.32	330.25	1.19
66	1.82	41.76	0.80	1.84	42.66	0.74
67	5.58	111.74	1.12	6.45	115.22	1.06
68	30.11	326.22	1.59	22.92	240.38	1.28
69	5.24	5.46	1.20	5.66	5.23	1.15
70	33.93	31.38	1.67	34.70	30.32	1.68
71	28.33	229.32	1.18	25.00	198.85	1.10
72	14.45	2.32	0.62	14.93	2.63	0.59
73	52.72	71.75	1.01	53.55	77.70	0.97
74	48.47	462.67	2.30	49.12	520.09	2.41
75	4.59	100.88	1.62	4.16	100.93	1.59
76	30.94	113.00	1.10	31.75	125.22	1.04
77	37.65	49.76	1.01	38.76	52.70	1.00
78	28.38	411.38	1.21	30.69	270.24	1.19
79	2.16	22.41	0.78	2.02	25.15	0.76
80	4.32	46.47	1.09	5.06	42.71	1.07
81	7.53	218.53	2.51	8.82	265.96	2.55
82	3.97	8.21	1.88	3.97	15.71	1.81
83	17.33	102.08	2.31	16.63	103.38	2.35

Table 2

Scatter Plot of 83 Point HC Data Field

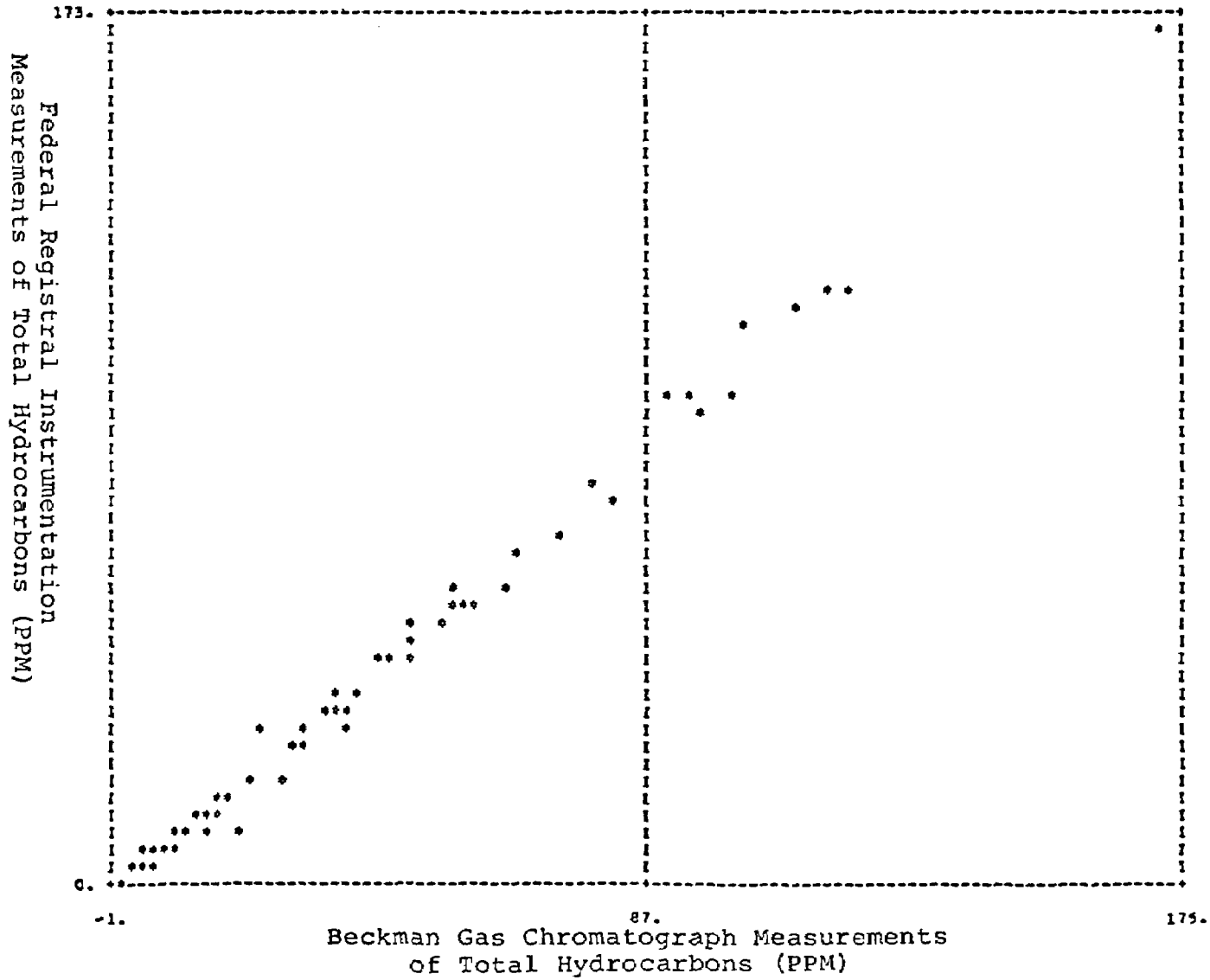

Table 3
Scatter Plot of 83 Point CO Data Field

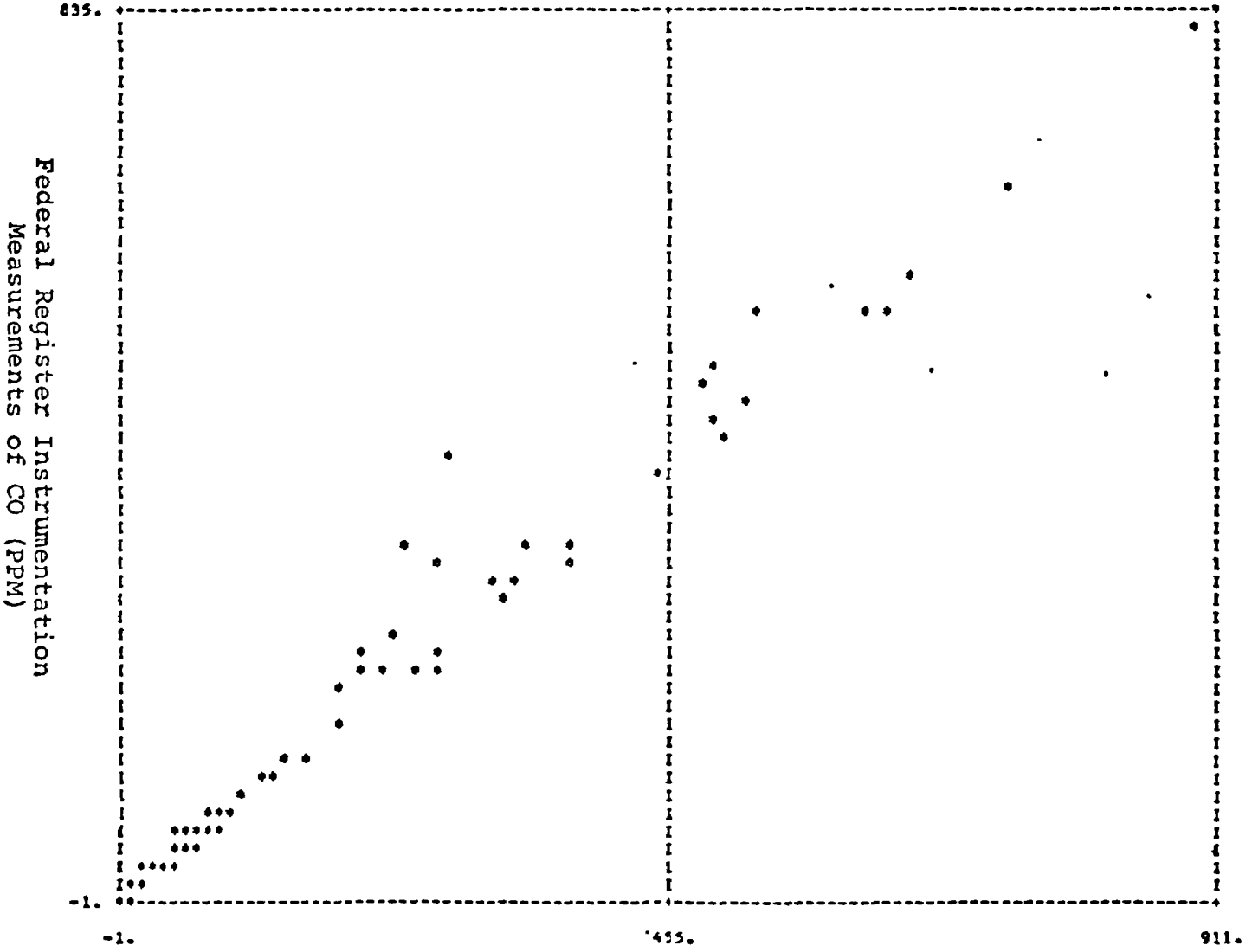

Table 4
Scatter Plot of 83 Point CO_2 Data Field

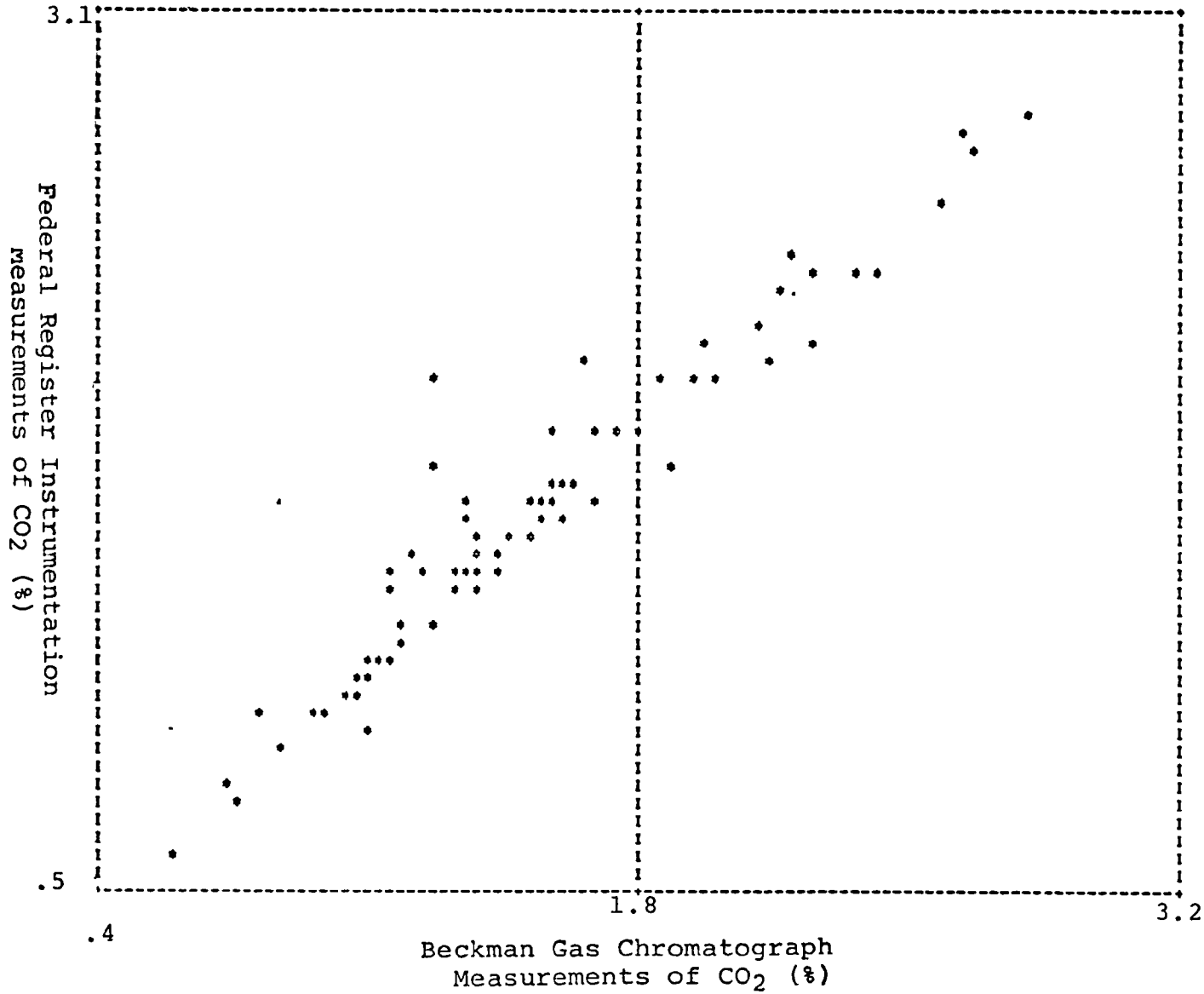

Table 5
Correlation Coefficient Matrix
83 Point Data Field

		Federal Register Instrumentation Measurements			Beckman Gas Chromatograph Measurements		
		HC	CO	CO_2	HC	CO	CO_2
Federal Register Instrumentation Measurements	HC	1.000	0.7519	0.2660	0.5975	0.7587	0.2596
	CO	0.7519	1.000	0.4306	0.7534	0.9909	0.4310
	CO_2	0.2660	0.4306	1.000	0.2693	0.4291	0.9650
Beckman Gas Chromatograph Measurements	HC	0.5975	0.7534	0.2693	1.000	0.7618	0.2675
	CO	0.7587	0.9909	0.4291	0.7618	1.000	0.4404
	CO_2	0.2596	0.4310	0.9650	0.2675	0.4404	1.000

Table 6

Calculated t Values
For 83 Point Data Field

	Hypothesis Intercept = 0	Hypothesis Slope = 1
HC	2.035	0.039
CO	2.174	6.217
CO_2	3.868	2.040

Summary of Testing
At 95% Confidence Level

	Hypothesis Intercept = 0	Hypothesis Slope = 1
HC	reject	accept
CO	reject	reject
CO_2	reject	reject

The t statistic for 95% confidence level for a sample of 83 is 1.989.

APPENDIX II

(76 Point Data Field)

Table 1
(76 Data Points)

	Federal Register Instrumentation			Beckman Gas Chromatograph		
No.	HC PPM	CO PPM	CO_2 %	HC PPM	CO PPM	CO_2 %
1	97.01	558.58	1.71	101.25	637.84	1.62
2	4.45	12.33	1.13	3.81	10.00	1.08
3	10.31	62.21	1.48	11.62	60.00	1.39
4	43.55	168.09	1.65	48.46	182.50	1.56
5	10.28	61.43	1.41	11.80	72.50	1.39
6	117.69	436.39	1.70	117.14	497.84	1.64
7	12.17	40.18	1.13	14.16	42.50	1.11
8	54.26	94.76	1.41	58.89	100.00	1.33
9	53.95	246.25	1.69	54.52	227.50	1.61
10	3.64	1.64	1.13	3.89	2.72	1.08
11	8.04	80.41	1.46	9.04	77.50	1.37
12	96.50	445.14	1.71	93.45	495.00	1.61
13	4.25	11.11	1.14	4.55	7.50	1.08
14	8.94	55.52	1.49	9.72	57.50	1.39
15	14.61	47.58	1.27	16.14	52.50	1.18
16	92.04	94.05	1.43	96.40	100.00	1.34
17	165.75	831.40	1.60	172.07	908.48	1.61
18	10.07	75.09	1.46	15.90	90.00	1.39
19	117.11	464.14	1.55	119.58	450.31	1.51
20	3.38	0.33	1.14	3.95	2.50	1.10
21	4.25	56.24	1.45	7.04	55.00	1.33
22	53.01	578.68	1.83	98.22	657.50	1.75
23	16.64	93.19	1.30	18.52	100.00	1.28
24	44.14	134.37	1.55	44.90	140.00	1.45
25	64.11	235.62	1.63	65.26	265.00	1.56
26	2.92	3.60	1.04	3.29	2.50	0.83
27	7.55	51.50	1.46	8.77	55.00	1.44
28	113.71	666.32	1.63	110.87	737.50	1.57
29	3.98	13.02	1.11	2.37	12.50	1.08
30	9.39	57.07	1.39	10.29	60.00	1.16
31	15.79	312.06	2.76	17.52	375.00	2.80
32	33.25	215.11	2.29	35.29	215.00	2.25
33	56.86	813.06	1.51	58.01	890.00	1.43
34	50.88	284.83	1.59	48.82	320.61	2.00
35	1.11	1.77	1.19	0.86	0.93	1.14
36	10.55	63.55	1.62	10.80	56.88	1.36
37	32.45	479.69	2.66	37.05	478.02	2.67
38	5.13	22.33	1.40	5.32	17.77	1.37
39	19.74	43.52	1.59	22.15	45.38	1.93
40	19.27	295.26	2.10	21.49	307.50	2.24
41	5.62	3.31	1.76	6.93	2.50	1.88
42	60.34	548.77	1.85	63.66	616.47	1.58
43	13.17	81.33	1.49	12.49	68.09	1.21
44	21.28	340.48	2.16	22.15	335.00	2.12
45	2.63	10.71	0.94	2.67	7.50	0.68
46	3.25	9.17	1.50	4.12	5.00	1.38
47	11.90	51.90	2.03	14.58	47.50	1.87
48	67.51	195.17	2.27	72.57	180.00	2.16
49	2.65	2.52	1.53	3.69	2.50	1.39
50	21.30	57.01	1.98	26.65	47.50	1.65
51	55.67	222.70	1.71	90.94	247.50	1.57
52	14.61	68.24	1.43	15.76	45.55	1.15
53	36.04	282.67	2.74	38.32	317.50	2.64
54	5.57	3.85	1.59	5.91	2.50	1.36
55	58.51	293.01	1.64	55.96	312.50	1.53
56	54.65	210.11	1.41	56.53	200.00	1.24
57	38.53	500.63	2.35	36.51	443.85	2.20
58	5.45	126.41	1.60	6.28	157.58	1.56
59	81.20	341.57	2.06	77.72	370.80	2.14
60	31.55	307.27	1.26	31.32	330.25	1.19
61	1.82	41.76	0.80	1.84	42.66	0.74
62	5.51	111.74	1.12	6.45	115.22	1.06
63	5.24	5.46	1.20	5.66	5.23	1.15
64	33.53	31.38	1.67	34.70	30.32	1.68
65	28.37	229.32	1.16	29.00	198.65	1.10
66	14.45	2.32	0.62	14.93	2.63	0.59
67	52.72	71.75	1.01	53.55	77.70	0.97
68	46.47	462.67	2.30	49.12	520.89	2.41
69	4.59	100.68	1.62	4.16	100.93	1.59
70	30.54	113.00	1.10	31.25	125.22	1.04
71	37.85	49.76	1.01	38.76	52.70	1.00
72	2.16	27.61	0.78	2.02	29.15	0.76
73	4.32	46.47	1.09	5.08	42.71	1.07
74	7.53	218.53	2.51	8.82	265.96	2.59
75	3.97	8.21	1.66	3.97	15.71	1.81
76	17.33	102.09	2.31	16.83	103.38	2.35

Table 2
Scatter Plot of 76 Point HC Data Field

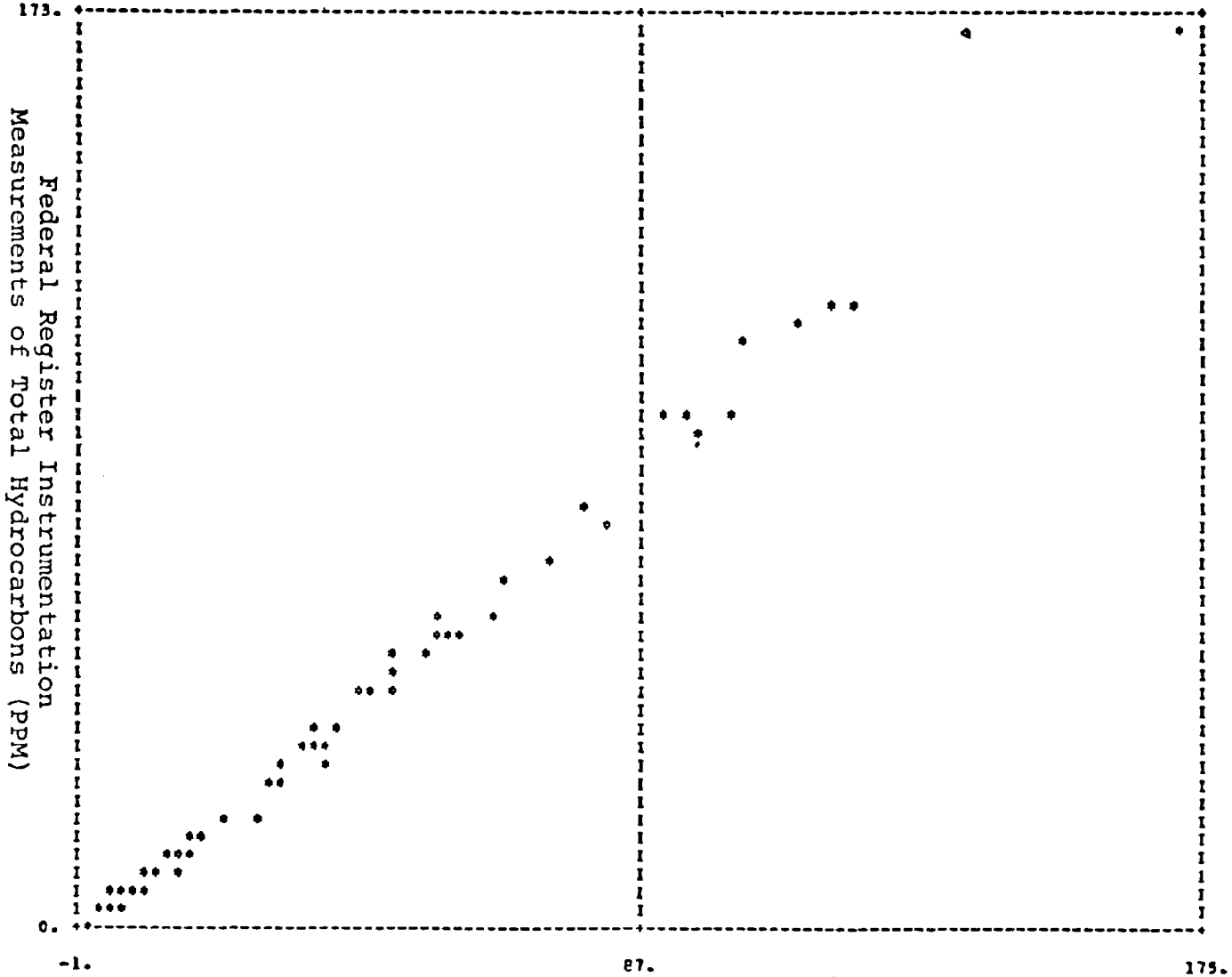

Table 3
Scatter Plot of 76 Point CO Data Field

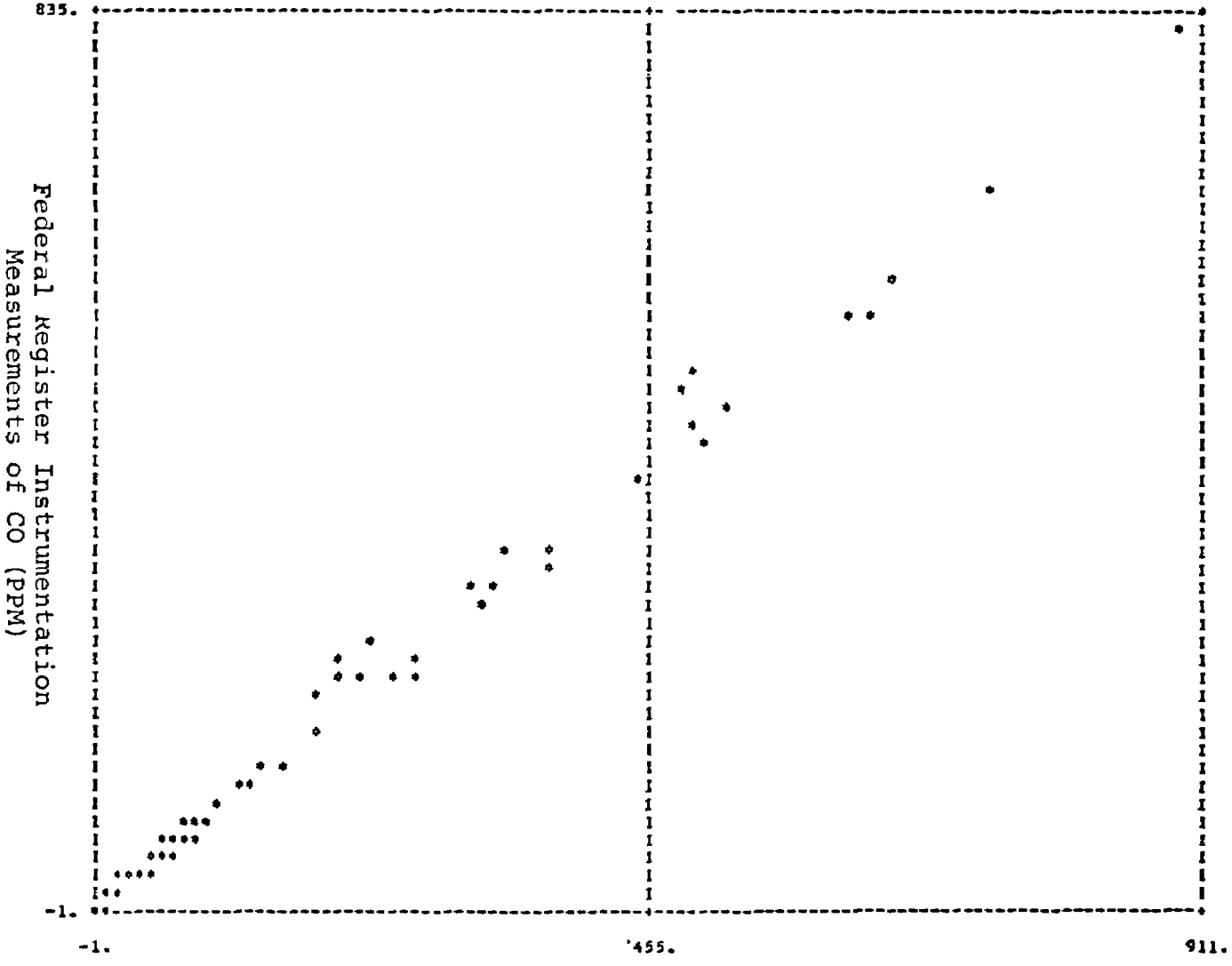

Table 4
Scatter Plot of 76 Point CO_2 Data Field

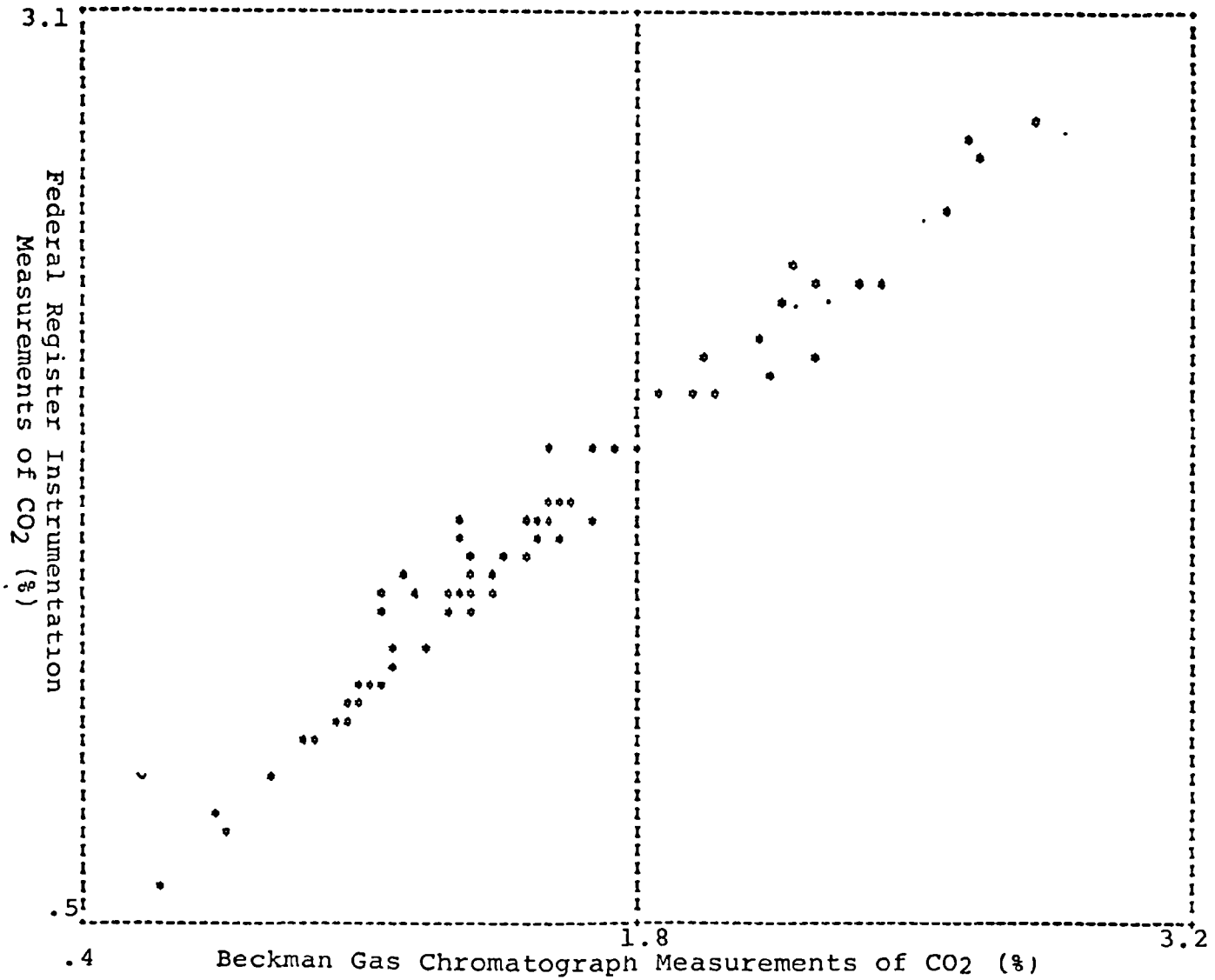

Table 5
Correlation Coefficient Matrix
76 Point Data Field

		Federal Register Instrumentation Measurements			Beckman Gas Chromatograph Measurements		
		HC	CO	CO_2	HC	CO	CO_2
Federal Register Instrumentation Measurements	HC	1.000	0.7663	0.2311	0.9981	0.7713	0.2261
	CO	0.7663	1.000	0.4498	0.7653	0.9973	0.4461
	CO_2	0.2311	0.4498	1.000	0.2400	0.4436	0.9848
Beckman Gas Chromatograph Measurements	HC	0.9981	0.7653	0.2400	1.000	0.7702	0.2343
	CO	0.7713	0.9973	0.4436	0.7702	1.000	0.4429
	CO_2	0.2261	0.4461	0.9848	0.2343	0.4429	1.000

Table 6

Calculated t Values
For 76 Point Data Field

	Hypothesis Intercept = 0	Hypothesis Slope = 1
HC	2.647	0.371
CO	2.630	12.536
CO_2	5.175	3.010

Summary of Testing
At 95% Confidence Level

	Hypothesis Intercept = 0	Hypothesis Slope = 1
HC	reject	accept
CO	reject	reject
CO_2	reject	reject

The t statistic for 95% confidence level for a sample of 76 is 1.992.