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INTER AND INTRA LABORATORY REPRODUCIBILITY

1976 HAT CREEK COAL ANALYSES

by

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INTER AND INTRA LABORATORY REPRODUCIBILITY
1976 HAT CREEK COAL ANALYSES

SUMMARY AND CONCLUSIONS

1. Duplicate samples from the 1976 drilling program on the Hat Creek No. 1 coal deposit, taken to monitor and evaluate analytical quality, were as follows: General Testing--24 sample pairs, Commercial Laboratories--20 sample pairs, and Loring Laboratory--12 sample pairs, General and Commercial--25 sample pairs, and Loring and Commercial--16 sample pairs.
2. In general, precisions of pre-1976 proximate, Btu/# and total sulphur analyses were better or as good as precisions of comparable 1976 variables. The only exception to this is total sulphur by General Testing for which poor pre-1976 precision was improved more-or-less to the level of precision for the other two labs.
3. A general evaluation of the internal precisions of the three labs indicates that Loring and Commercial labs are more-or-less equivalent in terms of numbers of variables for which they show good relative precision and both are substantially better than General Testing. This conclusion assumes equal importance to all variables measured and ignores the possibility of systematic differences among the three laboratories. A different conclusion could well be drawn for a particular subset of variables.
4. A comparison of sample pairs analyzed by Loring and Commercial labs indicates:
 - (a) Commercial analyses are more precise for Btr/#, CO_2 , pyritic sulphur, organic sulphur, CaO , MgO , Na_2O , Mn_3O_4 and V_2O_5 .
 - (b) Loring analyses are more precise for N_2 , $\text{O}_2(\text{diff})$, SiO_2 , Al_2O_3 , TiO_2 and K_2O .
 - (c) Precisions of the two labs cannot be distinguished statistically for ash, fixed carbon, volatile matter, carbon, H_2 , Fe_2O_3 , P_2O_5 and SO_3 .

4. (d) Systematic differences seem to exist between the two labs for fixed carbon, volatile matter, pyritic sulphur, and TiO_2 . Available data do not show which lab is more accurate for any of these variables.
5. A comparison of sample pairs analyzed by General Testing and Commercial labs indicates:
 - (a) Commercial Laboratory analyses are more precise for fixed carbon, volatile matter, pyritic sulphur, organic sulphur, carbon, H_2 , $\text{O}_2(\text{diff})$, Fe_2O_3 , MgO , Na_2O , V_2O_5 and P_2O_5 .
 - (b) General Testing analyses are more precise for ash, N_2 , Cl_2 , SiO_2 , K_2O and Mn_3O_4 .
 - (c) Precisions of the two labs cannot be distinguished for Btu/#, CO_2 , Al_2O_3 , TiO_2 , CaO and SO_3 .
 - (d) Systematic differences seem to exist between the two labs for Btu/#, CO_2 , H_2 , TiO_2 and SO_3 .
6. A comparison of precisions for each of General Testing and Loring Labs indicates:
 - (a) General analyses are more precise for ash, CO_2 , CaO , MgO , Na_2O , Mn_3O_4 and V_2O_5 .
 - (b) Loring analyses are more precise for fixed carbon, volatile matter, pyritic sulphur, carbon, H_2 , N_2 , $\text{O}_2(\text{diff})$, Al_2O_3 , TiO_2 and Fe_2O_3 .
 - (c) Precisions of the two labs cannot be distinguished statistically for Btu/#, organic sulphur, SiO_2 , K_2O , P_2O_5 and SO_3 .
 - (d) No comparison was done for Cl_2 . Systematic differences between the two labs could not be investigated because no samples analyzed were common to both labs.

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INTRODUCTION

As a check on analyses of samples from the 1976 drilling program, sample pairs were analyzed as follows:

<u>Lab(s)</u>	<u>No. of Pairs Analyzed</u>
General	24
Commercial	20
Loring	12
Commercial-General	25
Commercial-Loring	16

The foregoing sample pairs were analyzed for proximate, ultimate and mineral ash data and the analytical results were evaluated using the method described by Garrett (1969) illustrated by the following equation:

$$S_a^2 = \frac{1}{N} \sum_{i=1}^N \frac{(X_{1i} - X_{2i})^2}{2}$$

where S_a^2 is the combined sampling and analytical variance
 X_{1i} is value for a routine sample
 X_{2i} is value for a duplicate sample, and
 N is the number of sample pairs.

This equation was applied to each of the above 5 groups of duplicate samples. Results for both logged (base 10) and raw data are given in Tables I to V inclusive, although discussion here will be confined to the raw results. In the tables analytical (actually analytical plus sampling) precision is given as the 95 percent confidence range quoted as a percentage of the mean value.

$$\text{i.e. Precision} = \frac{1.98 S_a}{\bar{X}} \times 100$$

Precision refers to laboratory reproducibility (consistency). Accuracy used later in this report refers to closeness to true value.

TABLE I
SUMMARY OF RELATIVE PRECISION DATA
COMMERCIAL VS. GENERAL
HAT CREEK COAL REPLICATE ANALYSES-1976

THE TOTAL NUMBER OF SAMPLES IS 50

THE NUMBER OF REPLICATE SAMPLES IS 25

LOGARITHMIC VALUES								
NAME	ANALYTICAL VARIANCE	ANALYTICAL STD.DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA STD.DEV.	SAMP/ANAL VARIANCE
RH2O	0.02	0.13	21.10	22.97	0.84	2.02	0.22	
BIU	0.00	0.02	0.72	27.12	3.88	2.03	0.17	
ASH	0.00	0.01	0.72	35.83	1.43	0.05	0.22	
FIXC	0.00	0.04	4.89	38.59	1.54	0.03	0.17	
VCLM	0.00	0.03	3.03	37.45	1.50	0.01	0.10	
CO2	0.14	0.37	-1329.14	-1.39	-0.06	0.28	0.53	
SPY	0.11	0.33	-43.19	-37.34	-1.49	0.23	0.47	
SORG	0.01	0.09	-32.98	-13.63	-0.55	0.03	0.18	
TALK	0.02	0.14	-66.06	-10.30	-0.41	0.04	0.20	
CAPH	0.00	0.01	1.26	41.48	1.66	0.02	0.16	
H2	0.00	0.07	22.45	14.41	0.58	0.01	0.10	
N2	0.00	0.20	-145.44	-2.16	-0.09	0.03	0.17	
CL2	0.33	0.58	-119.96	-23.75	-0.95	0.04	0.20	

ARITHMETIC VALUES								
RH2O	0.50	0.22	24.29	122.82	7.71	12.85	3.58	
BIU	58698.54	242.28	5.90	203098.00	8123.92	5564608.00	2358.24	
ASH	0.11	0.33	2.14	767.37	30.69	278.03	16.67	
FIXC	5.93	2.43	12.97	929.40	37.18	120.52	10.98	
VCLM	4.99	2.23	13.77	803.23	32.13	35.00	5.92	
CO2	0.86	0.93	123.11	37.36	1.49	1.79	1.34	
SPY	0.01	0.08	192.24	1.96	0.08	0.03	0.17	
SORG	0.00	0.07	44.92	7.78	0.31	0.02	0.15	
TALK	0.03	0.17	78.61	10.84	0.43	0.05	0.23	
CAPH	1.53	1.24	5.10	1201.74	48.07	175.50	13.25	
H2	0.42	0.65	33.05	96.60	3.86	0.61	0.78	
N2	0.01	0.10	22.98	21.85	0.87	0.08	0.28	
CL2	0.01	0.03	125.29	3.05	0.12	0.00	0.05	

EXECUTION TERMINATED

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THE TOTAL NUMBER OF SAMPLES IS 50

THE NUMBER OF REPLICATE SAMPLES IS 25

LOGARITHMIC VALUES

NAME	ANALYTICAL VARIANCE	ANALYTICAL STD. DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA STD. DEV.	SAMP/ANAL. VARIANCE
O2DF	0.00	0.06	10.59	29.93	1.20	0.01	0.08	
SIC2	0.00	0.01	1.47	43.69	1.75	0.00	0.06	
AL20	0.00	0.04	5.42	36.58	1.46	0.00	0.07	
TIC2	0.07	0.26	-169.85	-7.58	-0.30	0.07	0.26	
FE20	0.01	0.09	25.06	17.40	0.70	0.11	0.33	
CAD	0.01	0.09	57.74	7.52	0.30	0.05	0.21	
MGO	0.01	0.09	-927.05	-0.46	-0.02	0.03	0.18	
NA20	0.01	0.09	307.45	1.48	0.06	0.04	0.20	
K2C	0.02	0.13	-55.10	-11.55	-0.46	0.05	0.22	
MN30	0.02	0.12	-18.57	-33.27	-1.33	0.43	0.66	
V205	0.01	0.12	-17.65	-33.71	-1.35	0.01	0.11	
P205	0.25	0.50	-104.05	-23.80	-0.95	0.08	0.29	
S03	0.07	0.27	-1741.01	-0.76	-0.03	0.09	0.30	
UNDT	0.22	0.47	-576.79	-4.07	-0.16	0.22	0.44	

ARITHMETIC VALUES

O2DF	3.14	1.77	21.94	399.64	15.99	6.52	2.55	
SIC2	2.97	1.72	6.05	1411.15	56.45	59.90	7.74	
AL20	6.62	2.57	17.33	734.90	29.40	20.46	4.52	
TIC2	0.10	0.32	109.96	14.25	0.57	0.06	0.24	
FE20	1.23	1.11	32.47	169.07	6.76	39.68	6.30	
CAD	0.13	0.36	32.59	55.29	2.21	0.88	0.94	
MGO	0.02	0.16	29.58	25.96	1.04	0.20	0.45	
NA20	0.12	0.35	55.17	31.10	1.24	0.20	0.44	
K2C	0.01	0.09	43.80	9.83	0.39	0.05	0.23	
MN30	0.00	0.02	22.48	3.55	0.14	0.05	0.23	
V205	0.00	0.01	55.96	1.16	0.05	0.00	0.01	
P205	0.12	0.35	505.02	3.45	0.14	0.01	0.09	
S03	0.70	0.84	145.72	28.43	1.14	0.51	0.71	
UNDT	2.17	1.47	387.01	18.86	0.75	0.50	0.71	

EXECUTION TERMINATED

TABLE II
SUMMARY OF RELATIVE PRECISION DATA
COMMERCIAL VS. LORING
HAT CREEK COAL REPLICATE ANALYSES-1976

THE TOTAL NUMBER OF SAMPLES IS 32

THE NUMBER OF REPLICATE SAMPLES IS 16

LOGARITHMIC VALUES

NAME	ANALYTICAL	ANALYTICAL	ANALYTICAL	REPLICATE	REPLICATE	DATA	DATA	SAMP/ANAL.
	VARIANCE	SID. DEV.	PRECISION	SUMS	MEAN	VARIANCE	SID. DEV.	VARIANCE
PH2C	0.00	0.07	15.04	14.42	0.90	0.10	0.32	
BTU	0.00	0.02	0.94	59.42	3.71	0.07	0.27	
ASH	0.00	0.01	0.65	25.99	1.62	0.03	0.17	
FIXC	0.00	0.07	10.60	20.09	1.25	0.14	0.38	
VOLM	0.00	0.05	7.01	24.23	1.51	0.01	0.10	
CO2	0.10	0.31	236.27	4.22	0.26	0.49	0.70	
SPY	0.01	0.09	-13.89	-14.90	-0.93	0.23	0.48	
SCPG	0.10	0.32	-168.20	-5.95	-0.37	0.04	0.19	
CARB	0.00	0.01	1.21	24.37	1.52	0.03	0.17	
H2	0.00	0.03	12.00	7.10	0.44	0.04	0.20	
N2	0.03	0.18	-192.55	-2.90	-0.18	0.05	0.22	
CL2	0.61	0.78	-512.72	-4.82	-0.30	0.44	0.66	

ARITHMETIC VALUES

RH2C	1.15	1.07	23.14	146.57	9.16	9.79	3.13
BTU	25759.81	160.50	5.37	94674.00	5917.13	699121.00	2644.07
ASH	0.33	0.57	2.51	721.71	45.11	249.93	15.81
FIXC	14.48	3.80	35.09	343.46	21.47	148.21	12.17
VOLM	15.80	3.98	23.55	534.83	33.43	52.95	7.28
CO2	7.71	2.79	108.64	80.97	5.06	69.18	8.32
SPY	0.00	0.03	22.31	3.45	0.22	0.09	0.30
SURG	0.01	0.08	41.77	6.42	0.40	0.03	0.18
CARB	0.47	0.68	3.79	571.06	35.69	171.92	13.11
H2	0.01	0.10	6.79	48.03	3.00	0.98	0.99
N2	0.06	0.24	66.56	11.60	0.72	0.08	0.28
CL2	0.02	0.02	1046.75	0.02	0.01	0.00	0.01

EXECUTION TERMINATED

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THE TOTAL NUMBER OF SAMPLES IS 32

THE NUMBER OF REPLICATE SAMPLES IS 16

LOGARITHMIC VALUES

NAME	ANALYTICAL VARIANCE	ANALYTICAL STD. DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA STD. DEV.	SAMP/ANAL. VARIANCE
O2DF	0.00	0.03	5.30	18.59	1.16	0.01	0.09	
SI02	0.00	0.02	2.23	27.15	1.70	0.03	0.19	
AL2O	0.00	0.05	8.03	21.22	1.33	0.16	0.40	
TIC2	0.11	0.32	1686280.00	0.00	0.00	0.08	0.28	
FE2O	0.00	0.03	7.62	13.53	0.85	0.11	0.33	
CAC	0.01	0.08	35.85	7.15	0.45	0.13	0.37	
MGO	0.01	0.12	146.33	2.53	0.16	0.03	0.16	
NA2O	0.01	0.09	328.52	0.84	0.05	0.02	0.15	
K2O	0.11	0.33	-199.01	-5.22	-0.33	0.27	0.52	
MN3O	0.14	0.38	-71.09	-16.89	-1.06	0.53	0.73	
V2O5	0.17	0.41	-67.79	-18.99	-1.19	0.19	0.43	
P2O5	0.17	0.41	-103.50	-12.48	-0.78	0.34	0.58	
SO3	0.01	0.10	200.51	1.55	0.10	0.07	0.27	
UNDT	0.24	0.49	-1406.73	-1.11	-0.07	0.11	0.33	

ARITHMETIC VALUES

O2DF	1.18	1.09	14.49	237.41	14.84	9.94	3.15	
SI02	2.10	1.45	5.45	842.00	52.66	164.89	12.84	
AL2O	2.95	1.72	13.51	403.03	25.19	56.91	7.54	
TIC2	0.15	0.39	69.39	17.89	1.12	0.12	0.34	
FE2O	0.55	0.74	14.80	159.00	9.94	157.59	12.55	
CAC	0.57	0.76	33.02	72.74	4.55	42.63	6.53	
MGO	0.24	0.49	63.16	24.75	1.55	0.48	0.69	
NA2O	0.03	0.18	30.01	18.93	1.18	0.10	0.32	
K2O	0.03	0.17	49.63	10.59	0.66	0.12	0.35	
MN3O	0.27	0.52	278.50	5.96	0.37	1.31	1.14	
V2O5	0.00	0.02	64.58	0.95	0.06	0.00	0.03	
P2O5	0.02	0.12	128.80	3.02	0.19	0.04	0.20	
SO3	0.10	0.31	41.38	23.36	1.46	0.62	0.79	
UNDT	0.46	0.68	125.23	17.18	1.07	0.40	0.63	

EXECUTION TERMINATED

THE TOTAL NUMBER OF SAMPLES IS 48

THE NUMBER OF REPLICATE SAMPLES IS 24

TABLE III
GENERAL TESTING
INTERNAL LABORATORY PRECISION
BASED ON 1976 HAT CREEK DUPLICATE ANALYSES

LOGARITHMIC VALUES									
NAME	ANALYTICAL VARIANCE	ANALYTICAL STD. DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA STD. DEV.	SAMP/ANAL. VARIANCE	SAMP/ANAL. STD. DEV.
RH2O	0.03	0.17	39.86	20.08	0.84	0.03	0.17		
BTU	0.00	0.01	0.56	93.28	3.89	0.03	0.17		
ASH	0.00	0.00	0.50	34.77	1.45	0.04	0.21		
FIXC	0.00	0.00	7.18	37.46	1.56	0.03	0.16		
VOLM	0.00	0.05	6.64	35.22	1.47	0.01	0.10		
CO2	0.11	0.33	-220.45	-7.13	-0.30	0.17	0.41		
STOT	0.00	0.02	-10.08	-11.54	-0.48	0.05	0.23		
SPY	0.17	0.41	-49.49	-39.44	-1.64	0.32	0.57		
SCRG	0.01	0.09	-32.73	-13.00	-0.54	0.03	0.18		
TALK	0.02	0.13	-60.76	-10.14	-0.42	0.04	0.19		
CARB	0.00	0.01	1.27	39.81	1.66	0.03	0.16		
H2	0.00	0.03	9.32	15.06	0.63	0.01	0.11		
N2	0.00	0.06	-317.02	-0.96	-0.04	0.03	0.17		
CL2	0.06	0.25	-21.06	-38.72	-1.61	0.03	0.16		

ARITHMETIC VALUES									
NAME	ANALYTICAL VARIANCE	ANALYTICAL STD. DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA STD. DEV.	SAMP/ANAL. VARIANCE	SAMP/ANAL. STD. DEV.
RH2O	1.83	1.35	36.34	176.77	7.37	7.70	2.77		
BTU	24196.79	155.55	3.77	156155.00	8173.13	5649574.00	2376.88		
ASH	0.09	0.31	1.93	757.01	31.54	271.30	16.47		
FIXC	13.89	3.73	19.17	923.90	38.50	125.22	11.19		
VOLM	13.09	3.62	23.91	719.09	29.96	30.53	5.53		
CO2	0.22	0.47	117.94	19.10	0.80	0.80	0.89		
STOT	0.00	0.01	7.41	9.49	0.40	0.11	0.34		
SPY	0.01	0.08	208.41	1.86	0.08	0.03	0.17		
SCRG	0.01	0.09	53.47	7.62	0.32	0.03	0.18		
TALK	0.03	0.16	76.50	10.02	0.42	0.04	0.21		
CARB	1.69	1.30	5.34	1154.59	48.11	184.97	13.60		
H2	0.07	0.27	12.27	104.58	4.36	0.85	0.92		
N2	0.01	0.11	23.42	23.29	0.97	0.10	0.31		
CL2	0.00	0.02	175.77	0.64	0.03	0.00	0.02		

EXECUTION TERMINATED

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THE TOTAL NUMBER OF SAMPLES IS 48

THE NUMBER OF REPLICATE SAMPLES IS 24

LOGARITHMIC VALUES

NAME	ANALYTICAL	ANALYTICAL	ANALYTICAL	REPLICATE	REPLICATE	DATA	DATA	SAMP/ANAL.
	VARIANCE	SID.DEV.	PRECISION	SUMS	MEAN	VARIANCE	SID.DEV.	VARIANCE
O2DF	0.00	0.06	9.69	27.83	1.16	0.00	0.07	
SIC2	0.00	0.01	1.09	41.79	1.74	0.00	0.06	
AL2O	0.00	0.03	4.51	34.81	1.45	0.00	0.07	
TIC2	0.01	0.09	-146.42	-2.80	-0.12	0.01	0.07	
FE2O	0.01	0.10	29.98	16.07	0.67	0.12	0.35	
CAO	0.01	0.10	64.27	7.72	0.32	0.05	0.22	
MGO	0.02	0.14	-306.64	-2.17	-0.09	0.04	0.21	
NA2O	0.01	0.09	687.39	0.62	0.03	0.04	0.19	
K2O	0.00	0.05	-18.69	-12.17	-0.51	0.08	0.29	
MN3O	0.01	0.09	-13.26	-33.57	-1.40	0.39	0.63	
V2O5	0.03	0.17	-28.74	-27.69	-1.15	0.03	0.16	
P2O5	0.07	0.26	-62.83	-15.09	-0.63	0.04	0.21	
SC3	0.02	0.16	186.67	4.02	0.17	0.04	0.19	
UNDT	0.10	0.32	476.58	3.21	0.13	0.13	0.36	

ARITHMETIC VALUES

O2DF	2.23	1.49	20.24	350.40	14.60	4.15	2.04	
SIC2	1.40	1.18	4.21	1333.55	55.56	50.10	7.08	
AL2O	4.44	2.11	14.60	685.65	28.57	20.39	4.52	
TIC2	0.03	0.17	44.23	18.60	0.77	0.02	0.14	
FE2O	1.44	1.20	35.65	160.01	6.67	43.42	6.59	
CAC	0.20	0.45	38.48	55.69	2.32	0.88	0.94	
MGO	0.06	0.25	54.90	21.50	0.90	0.15	0.38	
NA2O	0.12	0.34	59.60	27.49	1.15	0.16	0.39	
K2O	0.00	0.04	22.54	9.12	0.38	0.06	0.24	
MN3O	0.00	0.05	85.94	2.76	0.11	0.03	0.18	
V2O5	0.00	0.03	68.27	1.80	0.07	0.00	0.03	
P2O5	0.07	0.26	197.76	6.26	0.26	0.01	0.12	
SC3	0.32	0.56	69.30	38.66	1.61	0.54	0.74	
UNDT	1.22	1.10	133.85	38.91	1.62	0.49	0.70	

EXECUTION TERMINATED

THE TOTAL NUMBER OF SAMPLES IS 42

THE NUMBER OF REPLICATE SAMPLES IS 21

TABLE IV
COMMERCIAL TESTING
INTERNAL LABORATORY PRECISION
BASED ON 1976 HAT CREEK DUPLICATE ANALYSES

LOGARITHMIC VALUES									
NAME	ANALYTICAL VARIANCE	ANALYTICAL SID. DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA SID. DEV.	SAMP/ANAL.	VARIANCE
RH2O	0.00	0.05	10.13	19.91	0.95	0.03	0.18		
BTU	0.00	0.02	1.07	79.49	3.79	0.04	0.19		
ASH	0.00	0.01	0.89	33.44	1.59	0.03	0.18		
FIXC	0.00	0.04	4.92	29.63	1.41	0.06	0.24		
VOLM	0.00	0.02	2.21	30.49	1.45	0.01	0.09		
SPY	0.01	0.07	-15.01	-20.29	-0.97	0.32	0.57		
SORG	0.00	0.06	-25.02	-10.02	-0.48	0.06	0.25		
TALK	0.01	0.07	-47.95	-6.13	-0.29	0.02	0.13		
CARB	0.00	0.01	0.87	32.81	1.56	0.03	0.18		
H2	0.00	0.02	6.90	10.62	0.51	0.02	0.12		
N2	0.01	0.09	-251.97	-1.55	-0.07	0.01	0.08		
CL2	0.26	0.51	-100.10	-21.22	-1.02	0.48	0.62		
CO2	0.02	0.14	130.56	4.12	0.21	0.14	0.38		
ARITHMETIC VALUES									
RH2O	1.54	1.24	25.81	200.03	9.53	11.66	3.41		
BTU	10501.59	102.48	3.07	138683.00	6603.95	5722585.00	2392.19		
ASH	0.43	0.66	3.07	889.17	42.34	273.20	16.53		
FIXC	1.48	1.22	8.36	605.62	28.84	132.10	11.49		
VOLM	1.15	1.07	7.36	605.31	28.82	30.25	5.50		
SPY	0.00	0.01	11.42	5.42	0.26	0.17	0.41		
SORG	0.00	0.05	23.56	8.07	0.38	0.04	0.19		
TALK	0.01	0.09	35.23	11.17	0.53	0.03	0.16		
CARB	0.31	0.56	2.82	824.37	39.26	183.82	13.56		
H2	0.01	0.12	7.25	69.73	3.32	0.72	0.85		
N2	0.04	0.21	47.55	18.00	0.86	0.02	0.16		
CL2	0.00	0.04	160.87	1.16	0.06	0.00	0.00		
CO2	2.12	0.44	40.29	43.05	2.15	2.45	1.50		

(Cont'd on next page)

THE TOTAL NUMBER OF SAMPLES IS 42

THE NUMBER OF REPLICATE SAMPLES IS 21

LOGARITHMIC VALUES

NAME	ANALYTICAL	ANALYTICAL	ANALYTICAL	REPLICATE	REPLICATE	DATA	DATA	SAMP/ANAL.
	VARIANCE	STD.DEV.	PRECISION	SUMS	MEAN	VARIANCE	STD.DEV.	VARIANCE
O2DF	0.00	0.02	4.41	23.55	1.12	0.01	0.09	
SIO2	0.00	0.02	2.20	36.20	1.72	0.00	0.05	
AL2O	0.00	0.02	3.16	31.11	1.48	0.00	0.06	
TIO2	0.01	0.10	-145.76	-2.86	-0.14	0.01	0.08	
FE2O	0.00	0.04	10.81	17.14	0.82	0.05	0.23	
CAO	0.01	0.08	50.39	6.36	0.30	0.05	0.23	
MGO	0.00	0.05	87.12	2.48	0.12	0.02	0.15	
NA2O	0.00	0.05	-329.46	-0.69	-0.03	0.03	0.18	
K2O	0.01	0.10	-65.79	-6.01	-0.29	0.04	0.20	
MN3O	0.06	0.24	-40.62	-24.29	-1.16	0.27	0.52	
V2O5	0.01	0.08	-11.73	-28.58	-1.36	0.01	0.11	
P2O5	0.02	0.15	-43.66	-14.31	-0.68	0.17	0.41	
SO3	0.02	0.15	416.28	1.47	0.07	0.07	0.27	
LNDI	0.18	0.42	-300.09	-5.86	-0.28	0.12	0.35	

ARITHMETIC VALUES

O2DF	0.72	0.85	12.45	283.02	13.48	6.29	2.51	
SIO2	4.77	2.19	8.12	1119.50	53.31	35.24	5.94	
AL2O	2.41	1.55	10.05	642.23	30.58	17.73	4.21	
TIO2	0.03	0.17	46.41	15.61	0.74	0.02	0.13	
FE2O	0.58	0.76	20.02	157.81	7.51	19.00	4.36	
CAO	0.12	0.35	30.12	48.64	2.32	1.81	1.35	
MGO	0.02	0.15	22.07	29.00	1.38	0.18	0.43	
NA2O	0.01	0.11	21.77	21.15	1.01	0.19	0.43	
K2O	0.02	0.14	47.68	11.89	0.57	0.05	0.23	
MN3O	0.02	0.12	189.51	2.74	0.13	0.03	0.18	
V2O5	0.00	0.01	40.95	0.94	0.04	0.00	0.01	
P2O5	0.02	0.15	84.09	7.24	0.34	0.21	0.46	
SO3	0.25	0.50	68.99	30.13	1.43	1.08	1.04	
LNDI	0.84	0.92	292.59	13.04	0.62	0.26	0.51	

EXECUTION TERMINATED

THE TOTAL NUMBER OF SAMPLES IS 24

THE NUMBER OF REPLICATE SAMPLES IS 12

TABLE V
LORING LABORATORY
INTERNAL LABORATORY PRECISION
BASED ON 1976 HAT CREEK DUPLICATE ANALYSES

LOGARITHMIC VALUES									
NAME	ANALYTICAL	ANALYTICAL	ANALYTICAL	REPLICATE	REPLICATE	DATA	DATA	SAMP/ANAL.	S
	VARIANCE	SID. DEV.	PRECISION	SUMS	MEAN	VARIANCE	SID. DEV.	VARIANCE	
RH2O	0.00	0.07	17.22	9.76	0.81	0.09	0.30		
BTU	0.00	0.01	0.68	44.19	3.68	0.08	0.28		
ASH	0.00	0.01	0.61	19.65	1.64	0.02	0.15		
FIXC	0.00	0.03	4.92	15.13	1.26	0.18	0.42		
VCLM	0.00	0.02	2.76	17.93	1.49	0.01	0.10		
CO2	0.06	0.24	481.07	1.18	0.10	0.65	0.81		
STOT	0.01	0.10	-72.02	-3.24	-0.27	0.07	0.26		
SPY	0.01	0.11	-23.71	-10.55	-0.88	0.17	0.41		
SORG	0.18	0.42	-161.82	-6.19	-0.52	0.27	0.52		
CARB	0.00	0.00	0.58	18.24	1.52	0.03	0.16		
H2	0.00	0.02	11.58	4.78	0.40	0.05	0.23		
N2	0.00	0.05	-45.85	-2.14	-0.20	0.07	0.26		

ARITHMETIC VALUES									
NAME	ANALYTICAL	ANALYTICAL	ANALYTICAL	REPLICATE	REPLICATE	DATA	DATA	SAMP/ANAL.	S
	VARIANCE	SID. DEV.	PRECISION	SUMS	MEAN	VARIANCE	SID. DEV.	VARIANCE	
RH2O	1.79	1.34	35.70	89.04	7.42	6.82	2.61		
BTU	48294.91	219.76	7.87	66350.00	5529.16	5550545.00	2355.96		
ASH	0.26	0.51	2.23	547.56	45.63	197.16	14.04		
FIXC	2.26	1.50	13.45	265.27	22.11	149.15	12.21		
VCLM	2.02	1.42	8.78	384.17	32.01	59.13	7.69		
CO2	7.86	2.80	114.38	58.23	4.85	85.07	9.22		
STCT	0.01	0.10	32.25	7.47	0.62	0.10	0.32		
SPY	0.00	0.03	34.00	2.26	0.19	0.02	0.16		
SORG	0.01	0.10	46.77	5.12	0.43	0.05	0.23		
CARB	0.14	0.37	2.12	420.72	35.06	141.39	11.89		
H2	0.02	0.13	9.23	33.02	2.75	0.95	0.98		
N2	0.00	0.05	13.41	8.45	0.70	0.07	0.27		

EXECUTION TERMINATED

(Cont'd on next page)

THE TOTAL NUMBER OF SAMPLES IS 24

THE NUMBER OF REPLICATE SAMPLES IS 12

LOGARITHMIC VALUES

NAME	ANALYTICAL VARIANCE	ANALYTICAL STD. DEV.	ANALYTICAL PRECISION	REPLICATE SUMS	REPLICATE MEAN	DATA VARIANCE	DATA STD. DEV.	SAMP/ANAL.	SAMP VARIANCE
O2CF	0.00	0.01	2.21	14.09	1.17	0.01	0.09		
SI02	0.00	0.01	0.92	20.17	1.68	0.05	0.21		
AL2C	0.00	0.01	1.92	15.48	1.29	0.20	0.45		
TIO2	0.01	0.11	-269.53	-1.00	-0.08	0.21	0.46		
FE2C	0.00	0.04	10.40	9.84	0.82	0.13	0.37		
CAO	0.01	0.10	45.75	5.02	0.42	0.18	0.42		
MGO	0.01	0.12	122.33	2.36	0.20	0.04	0.20		
NA2O	0.06	0.25	132.71	4.49	0.37	0.01	0.11		
K2C	0.02	0.14	-102.33	-3.25	-0.27	0.16	0.40		
MN3O	0.21	0.46	-122.70	-8.85	-0.74	0.44	0.66		
V2O5	0.17	0.41	-110.31	-8.78	-0.73	0.01	0.11		
P2O5	0.43	0.65	-97.20	-15.97	-1.33	0.24	0.49		
SO3	0.01	0.11	141.67	1.87	0.16	0.08	0.28		
UNDT	0.15	0.39	-221.98	-4.14	-0.35	0.22	0.46		

ARITHMETIC VALUES

O2DF	0.19	0.44	5.72	182.76	15.23	9.81	3.13		
SI02	0.88	0.94	3.60	620.00	51.67	208.35	14.43		
AL2O	0.66	0.81	6.61	291.38	24.28	57.19	8.20		
TIC2	0.01	0.09	16.17	12.53	1.04	0.14	0.37		
FE2O	0.39	0.63	12.20	122.39	10.20	198.75	14.10		
CAO	0.72	0.85	36.65	55.19	4.60	42.04	6.48		
MGO	0.22	0.47	53.84	20.82	1.73	0.73	0.85		
NA2O	0.87	0.93	75.81	29.18	2.43	0.27	0.52		
K2C	0.00	0.06	16.40	8.14	0.68	0.11	0.33		
MN3O	0.19	0.44	114.04	9.08	0.76	3.51	1.87		
V2O5	0.01	0.10	103.64	2.28	0.19	0.00	0.04		
P2O5	0.03	0.17	380.36	1.08	0.09	0.01	0.12		
SO3	0.12	0.34	39.50	20.51	1.71	1.02	1.01		
UNDT	0.34	0.58	185.56	7.42	0.62	0.11	0.34		

EXECUTION TERMINATED

- The foregoing methodology has been used to examine
- (1) comparison of pre-1976 precision with 1976 precision,
 - (2) reproducibility of all variables within each of the three labs used, and
 - (3) comparison of values between pairs of labs-- General vs. Commercial and Loring vs. Commercial. No duplicates were analyzed by both General and Loring.

Replicate samples are few in number considering the variability that some variables show (see Sinclair, 1977). Furthermore, most variables do not have normal density distributions. Hence, it is difficult to evaluate results rigorously. In particular, it is unwise to attribute a precise confidence level to statistical tests even though such tests are done at a particular level of confidence. Despite this precautionary statement F- and t-tests provide a useful and convenient framework within which to consider within-lab and between-lab variations.

COMPARISON WITH PREVIOUS PRECISION MEASURES

Only 5 variables were evaluated in an earlier analysis of precision (Sinclair, 1976)--ash, volatile matter, fixed carbon, Btu per pound, and total sulphur. Precision values for the pre-1976 data are compared with those for 1976 by an F-test (Table VI). Calculated F values outside the critical range (for $\alpha = 0.05$) indicate a significant difference in the two precision estimates compared. A low F value indicates that pre-1976 data are more precise, a high F value indicates that 1976 data are more precise. In only one case was there a significant improvement in precision--total sulphur by General. For three other variables (ash, volatile matter and fixed carbon) General had a marked decrease in precision. Commercial showed a significant decrease in precision for volatile matter and fixed carbon (the reader should bear in mind that the variabilities of these two variables are closely tied together). Loring showed a significant change to poorer precision for total sulphur. For proximate variables Loring's precisions were

TABLE VI
F-VALUES COMPARING PRE-1976 ANALYTICAL VARIANCES
WITH 1976 ANALYTICAL VARIANCES

<u>Variable</u>	<u>F-Value</u>		
	<u>General</u>	<u>Commercial</u>	<u>Loring</u>
Ash	0.14*	0.44	1.63
Volatile Matter	0.01*	0.20*	3.12
Fixed Carbon	0.01*	0.20*	1.72
Btu/#	1.44	0.41	0.88
S(total)	38.9 *	-	0.06*
Critical Range**	.23-2.90	.29-2.83	.26-3.60
* Indicates significant differences between pre-1976 and 1976 precisions. A value lower than critical range indicates a decrease in precision; a value greater than critical range indicates increase in precision.			
** Critical range of F-values for $\alpha = 0.05$.			

statistically unchanged but in three cases they were significantly worse than the other two labs for pre-1976 data. In general, the 1976 proximate analytical data for all three labs has poorer overall precision than do earlier data.

Analytical precisions for individual labs are given in Tables III, IV and V for proximate, ultimate and mineral ash raw data (labelled 'Arithmetic' in the Tables). Precisions are quoted as a variance, as a standard error, and as a percentage of the mean value, i.e. as s_a^2 , s_a and precision as described in the two equations in the Introduction.

INTRA LAB PRECISION

To generally evaluate the labs relative to each other let each lab be ranked 1, 2 or 3 depending on whether it has best, middle or worst precision for each variable. Such rankings are listed in Table VII. Sums for individual labs are Loring (46), Commercial (38.5) and General (53.5). In this case the lower score indicates better overall precision. Such an approach assumes that all variables are of equal importance. A comparable summation for a selected group of variables might produce a different ranking. The approach also ignores the possibility of systematic differences between labs. A summary of this approach follows:

<u>Lab.</u>	<u>No. of 1's</u>	<u>No. of 2's</u>	<u>No. of 3's</u>
Loring	8	7	8
Commercial	12	6.5	4.5
General	3	9.5	10.5

Note: the .5's arise because of essentially equal precisions.

By either reckoning (the above summary or Table VII) there is little to choose between Loring and Commercial but both are significantly better than General.

Alternatively, the data can be summarized as in Table VIII which shows by lab the number of variables whose precisions are in specified but arbitrary ranges. The differ-

TABLE VII

RELATIVE RANKINGS (1, 2 or 3) OF EACH LAB FOR
PRECISIONS OF PROXIMATE, ULTIMATE AND MINERAL ASH DATA

Variable	Lab		
	General	Commercial	Loring
Btu/#	2	1	3
Ash	1	3	2
Fixed Carbon	3	1	2
Volatile Matter	3	1	2
CO ₂	2	1	3
S(pyritic)	3	1	2
S(organic)	2	1	3
C	3	2	1
H ₂	3	1	2
N ₂	2	3	1
Cl ₂			
O ₂ (diff)	3	2	1
SiO ₂	2	3	1
Al ₂ O ₃	3	2	1
TiO ₂	2.5	2.5	1
Fe ₂ O ₃	3	2	1
CaO	2	1	3
MgO	2	1	3
Na ₂ O	2	1	3
K ₂ O	1	3	2
Mn ₃ O ₄	1	2	3
V ₂ O ₅	2	1	3
P ₂ O ₅	3	1	2
SO ₃	<u>3</u>	<u>2</u>	<u>1</u>
TOTALS:	53.5	38.5	46.0

Rankings based on standard deviations. Values with .5 indicate essentially equivalent values.

TABLE VIII

NUMBERS OF VARIABLES WITHIN ARBITRARY PRECISION RANGES
FOR EACH OF THREE LABS

Precision**	Lab		
	Commercial	General	Loring*
0-5%	3	3	2
5.1-10.0%	4	2	6
10.1-20%	3	3	5
> 20%	16	18	12

* does not include Cl_2

** 95% confidence interval as percentage of the mean

ences between labs are not quite so apparent as in Table VII but the general ranking from "best" to "worst" is Loring, Commercial, General.

A somewhat more rigid approach to comparing labs utilizes results of statistical comparisons that appear in later sections of this report. The methodology is to compare various reproducibility estimates by F-tests, in this case at the 95 percent confidence level. These data are shown in Tables X to XIV inclusive but the important general results are summarized in Table IX which lists those variables that each lab measures more precisely than both other labs and more precisely than one other lab. By this criterion Commercial shows relatively good precision for the greatest number of variables. However, the question of which lab is best obviously has a different answer for different variables or groups of variables.

TABLE IX

LISTING OF VARIABLES FOR WHICH EACH LAB HAS BETTER PRECISION
THAN ONE OR TWO OTHER LABS*

	Commercial	Loring	General
Better Precision Than Both Other Labs	MgO S(pyritic) S(organic) Na ₂ O V ₂ O ₅	N ₂ O ₂ (diff) Al ₂ O ₃ TiO ₂	Ash Mn ₃ O ₄
Better Precision Than One Other Lab	Btu/# CO ₂ CaO Mn ₃ O ₄ fixed carbon volatile matter carbon H ₂ O ₂ (diff) Fe ₂ O ₃ P ₂ O ₅	SiO ₂ K ₂ O fixed carbon volatile matter S(pyritic) carbon H ₂ Fe ₂ O ₃	N ₂ Cl ₂ SiO ₂ K ₂ O CO ₂ CaO MgO Na ₂ O V ₂ O ₅

* Better precision is defined arbitrarily as a significantly better precision at the 95 percent confidence level based on comparison by an F-test.

COMPARISON OF COMMERCIAL AND LORING LABS

F-tests were used to compare the internal errors of Commercial and Loring Labs as a standardized means of evaluating their relative performances. Of the 23 variables compared (see Table X) significant differences were found in 15 cases. F-values below 0.36 and above 3.23 indicate significant differences. For a given variable low F-values indicate Commercial is more precise, whereas high values indicate that Loring is more precise. By this criterion Commercial measures Btu/#, CO_2 , S(pyritic), S(organic), CaO, MgO, Na_2O , Mn_3O_4 and V_2O_5 with a significantly (95% certainty) lower error than does Loring. On the other hand, Loring measures N_2 , O_2 (diff), SiO_2 , Al_2O_3 , TiO_2 and K_2O with a significantly lower error than does Commercial. Precisions of each of eight variables (Ash, F.C., V.M., C, H_2 , Fe_2O_3 , P_2O_5 and SO_3) cannot be distinguished statistically for the two labs.

Previous analyses indicated that Loring in general measured volatile matter systematically higher than Commercial or General. Using a t-test the writer compared volatile matter data for the 16 samples analyzed by both Loring and Commercial labs and again found a highly significant difference--Loring consistently measures higher volatile matter than does Commercial by about 18 percent of Commercial's values on the average (a calculated t of 10.27 greatly exceeds the critical values of 1.697 for $\alpha = 0.05$ and 30 d.f.). Of course, this results in a comparable systematic difference between the two labs for fixed carbon data. In the case of fixed carbon, Loring measures low relative to Commercial. In one duplicate sample Loring measured -8.7% fixed carbon, the negative sign almost certainly due to an error in reporting volatile matter. No comparison could be made for Cl_2 .

Inter lab precision variances are compared with intra lab precision variances in Table XI as calculated F values. High values of F indicate the between-lab variances are greater than within lab variances. If, for a given variable no sig-

TABLE X

REPRODUCIBILITY BETWEEN AND WITHIN LABS: COMMERCIAL AND LORING

(Precision is 95% confidence range expressed as a percentage of mean value.)

Variable	PRECISION			F *
	Between Lab	Within Lab		
	C O vs. LL (n = 16 prs)	C O (n = 21 prs)	L L (n = 12 prs)	
Btu/#	5.37	3.07	7.87	* 0.22
Ash	2.51	3.07	2.23	1.65
Fix. Carbon	35.09	8.36	13.45	0.65
Vol. Mat.	23.55	7.36	8.78	0.57
CO ₂	108.64	40.29	114.38	* 0.02
S(pyrritic)	22.81	11.42	34.00	* 0.18
S(organic)	41.77	23.56	46.77	* 0.27
Carbon	3.79	2.82	2.12	2.21
H ₂	6.79	7.25	9.23	0.6
N ₂	66.56	47.55	13.41	* 15.3
Cl ₂	1046.75	160.87		
O ₂ (diff)	14.49	12.45	5.72	* 3.79
SiO ₂	5.45	8.12	3.60	* 5.42
Al ₂ O ₃	13.51	10.05	6.62	* 3.71
TiO ₂	69.39	46.41	16.17	* 3.39
Fe ₂ O ₃	14.80	20.02	12.20	1.49
CaO	23.02	30.12	36.68	* 0.17
MgO	63.16	22.07	53.84	* 0.11
Na ₂ O	30.01	21.77	75.81	* 0.02
K ₂ O	49.63	47.68	16.40	* 4.98
Mn ₃ O ₄	278.50	189.51	114.04	* 0.08
V ₂ O ₅	64.58	40.95	103.64	* 0.02
P ₂ O ₅	128.80	84.09	380.36	0.78
SO ₃	41.88	68.99	39.50	2.08

* Data for F test taken from Tables II, IV and V.
 Values in range 0.36 - 3.23 could be same population.
 (95 percent confidence). Outside this range the two
 measures of variability are different.

TABLE XI

F-VALUES COMPARING INTER AND INTRA LAB REPRODUCIBILITIES
COMMERCIAL AND LORING

Variable	Calculated F Values	
	CO vs. LO/CO	CO vs. LO/LO
Btu/#	2.45	0.53
Ash	0.75	1.25
F.C.	33.15 *	6.42 *
V.M.	13.49 *	6.86 *
CO ₂	39.92 *	0.99
S(pyritic)	64.0 *	7.1 *
S(organic)	2.56 *	0.64
C	1.47	3.38 *
H ₂	0.69	0.59
N ₂	1.31	23.04 *
Cl ₂	0.56	-
O ₂ (diff)	0.56	3.73 *
SiO ₂	2.28 *	2.39
Al ₂ O ₃	0.92	4.54 *
TiO ₂	2.84 *	15.00 *
Fe ₂ O ₃	0.95	1.38
CaO	4.72 *	0.80
MgO	10.67 *	1.09
Na ₂ O	2.68 *	0.04
K ₂ O	1.47	8.03 *
Mn ₃ O ₄	18.78 *	1.40
V ₂ O ₅	4.00 *	0.04
P ₂ O ₅	0.64	0.50
SO ₃	0.38	0.83
Degrees of freedom	(15,21)	(15,11)
F(critical) $\alpha=0.05$	2.22	2.73

* Between lab error significantly larger than within lab error.

nificant difference is found in either of the two comparisons then both labs have comparable precisions and no systematic differences can be recognized in results for that variable. If the inter lab variability differs significantly from (i.e. is significantly greater than) both intra lab precisions, a systematic difference in results by the two labs is indicated for the variable(s) in question. By this criterion Commercial and Loring appear to measure fixed carbon, volatile matter, pyritic sulphur, and TiO_2 with systematic differences. It is not possible to say which lab is the more accurate with data available.

COMPARISON OF COMMERCIAL AND GENERAL LABS

Precisions within and between Commercial and General Labs are given in Table XII. F-tests are used to compare these precisions.

Within and between lab precisions of all variables for General and Commercial are given in Table XII along with calculated F values comparing their within lab variances. Calculated F-values in the range 0.41 to 2.35 indicate comparable precisions. Low F-values indicate that Commercial has the better precision whereas high F-values show that General has better precision (at the 95% confidence level). By this measure Commercial is more precise for fixed carbon, volatile matter, pyritic sulphur, organic sulphur, carbon, H_2 , O_2 (diff), Fe_2O_3 , MgO , Na_2O , V_2O_5 and P_2O_5 , a total of 12 variables. General is more precise for Ash, N_2 , Cl_2 , SiO_2 , K_2O and Mn_3O_4 . For 6 other variables ($Btu/\#$, CO_2 , Al_2O_3 , TiO_2 , CaO and SO_3) the two labs cannot be distinguished at the 0.05 level.

Calculated F values comparing within lab and between lab precisions for Commercial vs. General are listed in Table XIII. For any one variable two F-values higher than the

TABLE XII

REPRODUCIBILITY BETWEEN AND WITHIN LABS: COMMERCIAL AND GENERAL
(Precision is 95% confidence range expressed as percentage of mean value.)

Variable	Precision			F *
	Between Lab CO vs. GT (25 pairs)	Within Lab		
		CO (21 pairs)	GT (24 pairs)	
Btu/#	5.90	3.07	3.77	0.43
Ash	2.14	3.07	1.93	* 4.33
Fixed Carbon	12.97	8.36	19.17	* 0.11
Vol. Matter	13.77	7.36	23.91	* 0.09
CO ₂	124.11	40.29	117.94	0.86
S(pyritic)	192.24	11.42	208.41	* 0.03
S(organic)	44.92	23.56	53.47	* 0.34
Carbon	5.10	2.82	5.34	* 0.18
H ₂	33.05	7.25	12.27	* 0.21
N ₂	22.98	47.55	23.42	* 3.50
Cl ₂	125.29	160.87	175.77	* 3.24
O ₂ (diff)	21.94	12.45	20.24	* 0.32
SiO ₂	6.09	8.12	4.21	* 3.41
Al ₂ O ₃	17.33	10.05	14.60	0.54
TiO ₂	109.96	46.41	44.23	1.00
Fe ₂ O ₃	32.47	20.02	35.65	* 0.40
CaO	32.59	30.12	38.48	0.60
MgO	29.58	22.07	54.90	* 0.37
Na ₂ O	55.17	21.77	59.60	* 0.11
K ₂ O	43.80	47.68	22.54	* 10.38
Mn ₃ O ₄	22.48	189.51	85.94	* 5.17
V ₂ O ₅	55.96	40.95	68.27	* 0.18
P ₂ O ₅	505.02	84.09	197.76	* 0.34
SO ₃	145.72	68.99	69.30	0.80

* Values outside the critical range (0.41-2.35) $\alpha = 0.05$

TABLE XIII

F-VALUES COMPARING INTER AND INTRA LAB REPRODUCIBILITIES
GENERAL AND COMMERCIAL

Variable	Calculated F Values	
	CO vs. GT/CO	CO vs. GT/GT
Btu/#	5.59 *	2.43 *
Ash	0.25	1.13
F.C.	3.97 *	0.42
V.M.	4.34 *	0.38
CO ₂	4.47 *	3.92 *
S(pyritic)	9.00 *	0.14
S(organic)	1.96	0.60
C	4.90	0.91
H ₂	29.34 *	5.80 *
N ₂	0.23	100.00 *
Cl ₂	0.56	2.25 *
O ₂ (diff)	4.34 *	1.41
SiO ₂	0.62	2.12 *
Al ₂ O ₃	2.75 *	1.48
TiO ₂	3.54 *	3.54 *
Fe ₂ O ₃	2.13 *	0.86
CaO	1.06	0.64
MgO	1.14	0.41
Na ₂ O	10.12 *	1.06
K ₂ O	0.41	5.06 *
Mn ₃ O ₄	1.00	0.16
V ₂ O ₅	1.00	0.11
P ₂ O ₅	5.44 *	1.81
SO ₃	2.82 *	2.25 *
Degrees of freedom	(24,20)	(24,23)
F(critical) =0.05	2.08	2.01

* Between lab error significantly larger than within lab error.

listed critical values indicate the likelihood of a systematic difference in analytical results. In the case of these two labs, possible systematic differences exist for Btu/#, CO_2 , H_2 , TiO_2 and SO_3 . Which of the two labs is more precise cannot be determined with available data.

COMPARISON OF GENERAL AND LORING

An F-test comparison of individual variables for the two labs (Table XIV) shows that General analyses are more precise for ash, CO_2 , CaO , MgO , Na_2O , Mn_3O_4 and V_2O_5 at the 95 percent confidence level. Loring analyses are more precise for fixed carbon, volatile matter, pyritic sulphur, carbon, H_2 , N_2 , $\text{O}_2(\text{diff})$, Al_2O_3 , TiO_2 and Fe_2O_3 . For other variables (Btu/#, organic sulphur, SiO_2 , K_2O , P_2O_5 and SO_3) precisions of the two labs are indistinguishable at the 95 percent level of confidence.

No evaluation of systematic differences could be done for these two labs because no samples were analyzed by both labs.

TABLE XIV
 WITHIN LAB REPRODUCIBILITY - GENERAL AND LORING
 (Precision is 95% confidence range expressed as
 percentage of mean value.)

Variable	Within Lab Precision		F
	General (24 pairs)	Loring (12 pairs)	
Btu/#	3.77	7.87	0.50
Ash	1.93	2.23	0.37 *
Fixed Carbon	19.17	13.45	6.15 *
Volatile Matter	23.91	8.78	6.48 *
CO ₂	117.94	114.38	0.03 *
S(pyritic)	208.41	34.00	7.11 *
S(organic)	53.47	46.77	0.81
Carbon	5.34	2.12	12.07 *
H ₂	12.27	9.23	4.31 *
N ₂	23.42	13.41	4.84 *
Cl ₂	175.77	-	-
O ₂ (diff)	20.24	5.72	11.47 *
SiO ₂	4.21	5.60	1.59
Al ₂ O ₃	14.60	6.61	6.83 *
TiO ₂	44.23	16.17	3.57 *
Fe ₂ O ₃	35.65	12.20	3.69 *
CaO	38.48	35.68	0.28 *
MgO	54.90	53.34	0.28 *
Na ₂ O	59.60	75.81	0.14 *
K ₂ O	22.54	16.40	0.44
Mn ₃ O ₄	85.94	114.04	0.01 *
V ₂ O ₅	68.27	103.64	0.09 *
P ₂ O ₅	197.76	380.36	2.34
SO ₃	69.30	39.50	2.71
Degrees of freedom	23	11	(23,11)
F(critical) $\alpha=0.05$			0.39-3.19

* Values outside critical range (0.39-3.19) = 0.05

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A handwritten signature in cursive script, reading "A.J. Sinclair". The signature is written in dark ink and is positioned above a horizontal line.

Dr. A.J. Sinclair, P.Eng.

May 25, 1977.