REPORT ON

THE POTENTIAL HEALTH HAZARD FROM THE USE OF LEADED FUEL IN ARMY FIELD RANGE M-1937

June 1, 1941

The Potential Health Hazard from the Use of Leaded Fuel in Army Field Range M-1937

I. Purpose

To determine the magnitude of the health hazard arising from the use of leaded gasoline for fuel in the fire unit.

II. Conclusions

(1) No health hazard exists from the breathing of lead in air when the stove is operated in rooms or enclosures under normal conditions of ventilation. The small amounts of lead which escape through the burner may deposit upon cool cooking receptacles or the walls of the stove. The deposits are easily removed and under normal housekeeping conditions no hazard should be created by them.

(2) The stove should not be used for the broiling or grilling of foodstuffs that come into direct contact with the flame.

III. Introduction

(1) Design

Complete description of the stove may be obtained from the manual for its use and by reference to reports of the Detroit Laboratory of the Ethyl Gasoline Corporation LTD #41-5, 363-XP-21, 22, and 24-28. Previous experimental work has been carried out on the stove at the Army Medical School and at the Detroit Laboratory of the Ethyl Gasoline Corporation. The tests at the Army Medical School, using gasoline that contained 0.75 ml. of lead tetraethyl (TEL) per gallon, indicated that insignificant amounts of lead escaped into the room air during the operation of the stove. They further found no increase in the lead content

of foodstuffs prepared with the unit. Studies carried out at the Detroit Laboratory indicated that about 70% of the lead input was removed by the filter disc and other parts of the stove. Neither of the above experiments were carried out in such a manner as to account for all of the lead in the gasoline by examination of lead remaining in the stove and analysis of the flue gases. The following experiments were carried out with that objective in view.

IV. Procedure

Following preliminary operation and adjustment of the fire unit, observations were made on the temperatures at various parts of the stove and fire unit. Following this a sheet metal hood was constructed for the purpose of collecting, measuring and sampling the effluent gas from the stove and to provide for temperature determinations upon it. Details of this equipment are given in Figure 1. The drain at the second ell was found unnecessary as no condensate formed. It was not possible to measure the velocity of the effluent in the lead-off duct by mechanical means and volumes were determined by sampling the effluent and analyzing it for carbon dioxide, oxygen, and carbon monoxide, using a Burrell gas testing apparatus. Volumes were computed in terms of cubic feet of effluent per gram of carbon.

The lead content of the effluent was determined by passing the sample through an electric precipitator of the Cottrell type, at known volumes and temperatures for the sampling period. In addition, a portion of the precipitator exhaust was passed through freshly activated charcoal to determine whether any

organic lead vapor was present in the flue gas. All gas volumes were corrected to standard conditions. In computing results, the amounts of carbon monoxide were neglected as the percentages were so small as to have no effect upon the final values.

The fuel used for the first 4 runs was an Ethyl Gasoline base stock of the Standard Oil Company of Ohio, mixed in the laboratory to a concentration of 3 ml. of TEL per U.S. gallon. Samples were analyzed for lead content at an Ethyl Gasoline Corporation Laboratory before use in the stove. At the conclusion of several runs, samples for analysis were removed from the stove reservoir as a check on the original results.

Lead was recovered from the fire unit according to a definite procedure. The unit was dismantled and the parts brushed and scraped into a clean porcelain dish containing a small amount of 20% solution of ammonium acetate, after which each part was bathed with hot 20% ammonium acetate followed by hot 5% nitric acid, then with hot distilled water. This treatment effectively removed all deposits which were then combined and analyzed. The filter disc was carefully removed and steeped in hot nitric acid. This destroyed the structure of the disc and permitted complete solution of all filtered material. Following filtration the residue was boiled with 20% ammonium acetate. The filtrate obtained from this treatment was added to the nitric acid filtrate. Hood and chimney scrapings were also dissolved in nitric acid. Analyses were carried out by the lead sulfate or by spectrographic methods and some samples were analyzed by both methods for check purposes.

In short, therefore, the procedure involved the analysis of gasoline for lead content prior to use, the determination of the lead deposited in various portions of the fire unit, in the filter disc, and on the walls of the hood and chimney as well as that in the effluent, either as vaporized organic or as particulate inorganic lead. The totals of the last sets of analyses should equal the first within the limits of allowable analytical error, duly corrected for the amount of gasoline burned.

Thirty-nine runs of approximately 4 hours each were carried out. Complete analytical data, as indicated above, were obtained on runs 1, 2, and 39. When received by us the stove was new and after the first two sets of observations, it was thought desirable to operate the stove under conditions that would simulate a period of at least a month's use and to recheck the results of the initial experiments. Runs 3 and 4 as described later, were carried out to determine the behavior and efficiency of the filter immediately after the stove was started up and before the generator and filter had reached operating temperatures.

V. Results

(1) Operating temperatures of the stove

Referring to Table 1, the figures for the temperature of the filter case, filter level and at the generator level, are of considerable interest from the point of view of the nature of the deposits on the filter. In certain instances these figures approach the boiling point of the lead halides that may be expected to be present at the filter.

However, the high percentage recovery of lead from the filter, together with the fact, discussed later, that most of the lead escaped from the filter before it reached high temperature, indicates that the vapor pressure of lead halides in the generator tube had no material effect upon the escape of lead through the filter.

(2) Balance Experiments - Runs 1, 2, and 39

Results are given in detail and in summary in the attached tables. The average lead recovery in these three experiments was 98.23%, within the limits of error of the analytical methods employed. Accordingly, no explanation is offered for the unrecovered lead. Amounts of organic lead recovered from the effluent were insignificant and sampling for organic lead in the flue gas was discontinued after the second run. Considering the fact that a perfect balance was not achieved in any experiment, it should be pointed out that the results varied when duplicate samples of the gasoline were analyzed, the maximum discrepancy being from 2.86 to 3.15 ml. TEL per gallon. Depending upon which figure was taken for computation of the balance, recoveries varied from 96 to 112%. In this situation we selected the value for lead in gasoline that most closely corresponded with the amounts that had been carefully measured and added to the fuel. As indicated in the summary, 90 to 96% of the lead which entered in the gasoline was recovered from the stove and filter. Since the results of the Detroit Laboratory, obtained in using a different stove, showed only 70% recovery from these sources, it would appear

that either differences in stoves or differences or imperfections in filter discs may greatly affect the amounts of lead retained by the unit. The total amounts of lead recovered from the flue gas were small, the average being less than 4%. It should be noted however, that a variability of as much as 100% in the amounts of lead recovered in the flue gas occurred on two successive runs. Since the stove was operated under identical conditions each time, the only change being the renewal of the filter disc, it is quite possible that there is significant difference in either the effectiveness or fit of different filter discs. Certainly any channeling, perforation or imperfection of discs would greatly affect the retention of lead. Since there is no way of determining the condition of the disc prior to use other than by inspection, the results of any one run with a bad disc may deviate widely from others. This would however, represent only a maximum 4-hour period of use.

(3) Initial Period of Operation

In runs 3 and 4, the results of which are given in the attached tables, samples of flue gas were taken at frequent intervals as soon as feasible after the stove was put in operation (beginning usually within 1 minute). As might be expected, it was found that the efficiency of the filter was least when the generator tube was cool and the filter disc previously unused. Over 75% of the amounts of lead found in the flue gas in the 4-hour run came over in the first hour and about 70% in the first 30 minutes of operation. From a practical point of view, therefore, it is apparent that if

adequate ventilation is provided in the first 30 minutes of operation of the stove, the hazard from contamination of room air will be greatly reduced, not only in this time, but during the subsequent 3-1/2-hour period of operation. This failure on the part of the stove to retain lead in the first 30 minutes of operation is apparently almost entirely due to the low temperature of the generator tube. The TEL not being broken down, passes the filter as vapor and is burned in the flame. To test this, samples of gasoline vapor were collected at a slow rate from the mixing chamber beneath the burner, the vapors condensed at - 44° C, and analyzed. Because of the length of time necessary to collect sufficient condensate (1 - 3 ml.) for analysis, it was necessary to extend this sampling period over the entire period in which the stove was coming to its operating temperature. Fractional analyses by minutes during the early stages of operation were not feasible. It was found that during this heating up period, the generator was very inefficient as compared to an efficiency of 80 to 85% when the generator tube had become hot and the stove was operating normally. It follows therefore that from 15 to 20% of the TEL in the fuel is not cracked or broken down in the generator tube or filter case, but passes on to the flame where it is decomposed. In view of possible modifications, such as an increase in the length of the generator tube to bring about more complete decomposition of TEL, it should be pointed out that no change in design other than one that would permit starting the stove with a hot generator tube would alter the behavior of the unit in the first 30 minutes of operation.

It is in this period that the greater proportion of the lead in the fuel passes through the filter and into the flue gases.

VI. Hygienic Considerations

As pointed out above, the greatest escape of lead in the flue gas occurs in the first 30 minutes of operation. In Table 2, pertinent data from each of the experimental runs are tabulated and the lead in the flue gas has been computed in terms of mgm. per 10 cu.m. Amounts of 1.5 mgm. of lead per 10 cu.m. of air or less are considered to be allowable. If we assume that only flue gas is respired, under conditions which permit of no ventilation, inspection of the figures in Table 2 is of considerable interest in the light of the behavior of the stove following the first 30 minutes of operation. In runs 1, 2, 3 (after 40 minutes), and 39, amounts of lead in the flue gas were within permissible limits. In run 4, the concentration dropped to allowable limits after the first 30 minutes, but increased significantly in the last 15 minutes of the first hour's run. This tendency to increase may be a joint manifestation of the irregular operation of the stove and the relatively short sampling period. A similar trend operating to a much less marked degree is noted in the results for the fourth hour of run 1. It should be noted, however, that in all instances in which the stove was operated for periods longer than 1 hour, the tendency to decrease is uniform and striking after the first 30 minutes. It follows therefore, that hazardous levels are reached from the flue gas mainly in the first 30 minutes of the run. Since these will be diluted at

once into existing room air, exposure to high levels by the operators of the stove is unlikely. For example, if the stove were started in an enclosure 20' x 20' x 10', the effluent from the stove would be diluted by more than an equal volume of air if the air change in the enclosure is only 1 time in 30 minutes. Furthermore, considering the temperature of the flue gas, as noted on the data sheets for the respective runs, it is likely that sufficient ventilation will of necessity be provided for comfortable and efficient operation of the stove. This would dilute and reduce the lead concentrations in the effluent to safe levels even in the first 30 minutes of operation.

VII. Recommendations

(1) The present stove should be operated only under conditions of good ventilation.

(2) The escape of lead into the air from the stove is a consequence of the failure of degradation of TEL in the generator tube and filter. Any changes in design which would increase the degree of decomposition of TEL should reduce proportionately the amount of lead in the flue gas. If the stove must be operated under conditions of poor ventilation, attempts should be made to increase the efficiency of the generator and filter unit in breaking down the TEL or non-leaded fuel should be used.

(3) Precautionary measures should be taken when the stove is torn down and cleaned. No significant amounts of organic lead were found either in the filter or the stove parts; consequently no hazard from vapor or skin absorption will exist. However, the amounts of lead (in large part as metallic lead and lead oxide) found in the filter disc and stove are of the order

of grams following a 4-hour run and these parts should not be cleaned when dry or in such manner as to evolve dust. Dipping of the parts in kerosene prior to brushing and scraping should safeguard this operation. All cleaning of the fire unit should be carried out in a place other than that in which cooking is done. Used filter discs removed at the time of cleaning, as well as the deposits scraped or cleaned from the stove should be buried or disposed of in the same fashion as other wastes from the kitchen.

(4) Towels or cleansing rags used to remove deposits from the walls of the cabinet or from kettles or pans should not be allowed to come in contact with foodstuffs.

(5) The stove must never be operated without the filter disc.

(6) The potential hazard can be practically eliminated if the fire unit is allowed to operate for 30 minutes after starting outside the cookhouse.

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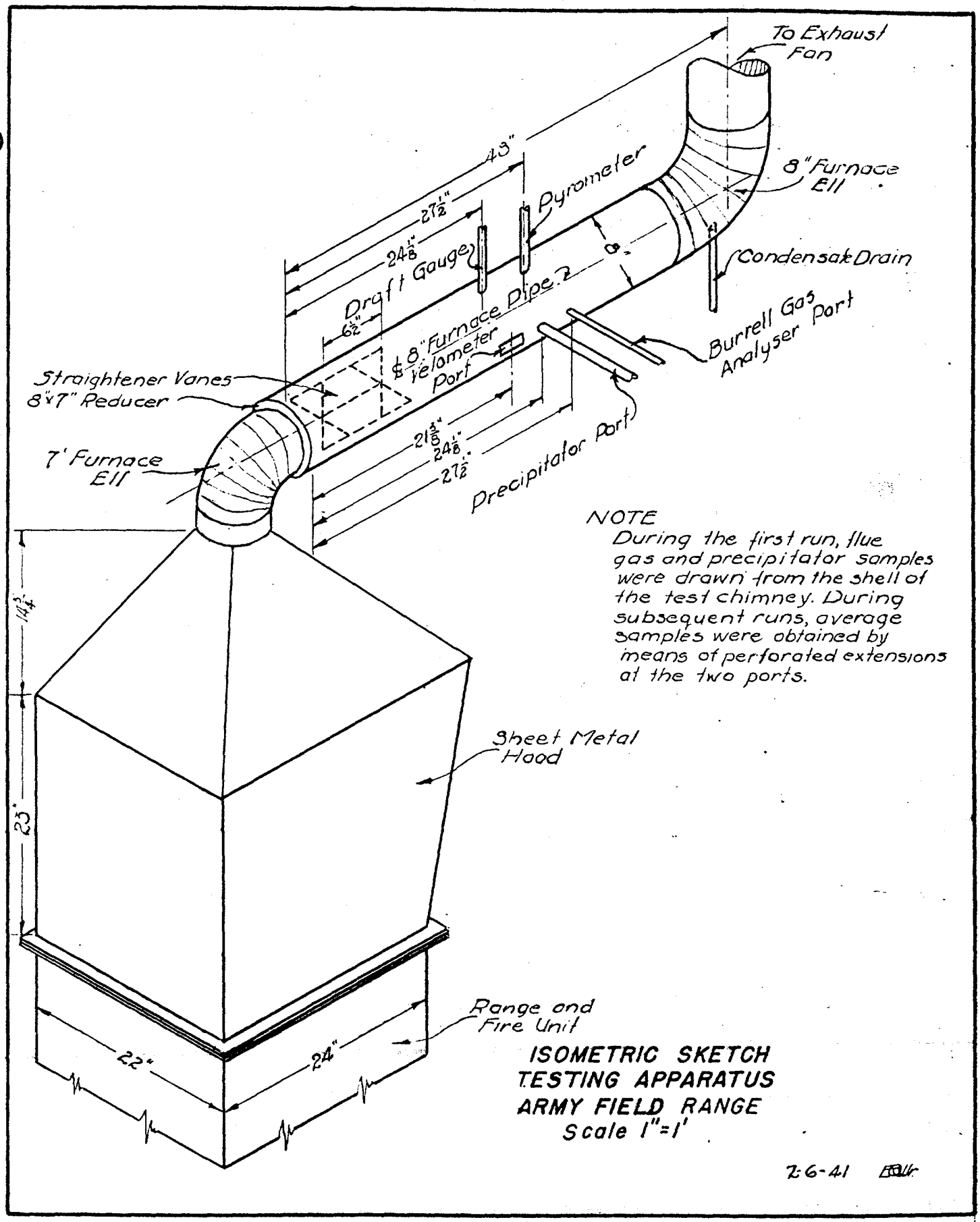
Figure 1



NOTE
During the first run, flue gas and precipitator samples were drawn from the shell of the test chimney. During subsequent runs, average samples were obtained by means of perforated extensions at the two ports.

ISOMETRIC SKETCH
TESTING APPARATUS
ARMY FIELD RANGE
Scale 1"=1'

7-6-41

Table 1

Temperature Determinations

Instrument:

Hoskins Thermo-electric Pyrometer
Type PA - Serial No. 16045
Calibrated with boiling water. Atmospheric pressure not considered.

Burner surface - Pyrometer in contact	
1. Outer end (last slot)	790° C
2. Center	885° C
3. Inner end (last slot)	780° C
"V" Space between burners - at level of burner surface	
1. Periphery of burner circle	90° C
2. Center of "V" - 1/2 distance from apex to periphery	120° C
3. Apex of "V"	240° C
Temperatures at generator level	
A. Directly over burner arm	
1. Outer end	845° C
2. Center	970° C
3. Inside end	890° C
B. Between burner arms (generator level)	
1. Periphery of burner circle	110° C
2. 1/2 distance from apex to periphery	160° C
3. Apex of "V"	750° C
Temperatures at filter level (over burner arm)	
1. Outer end	560° C
2. Center	915° C
3. Inside end	845° C
Temperatures of filter case	
1. At periphery over burner arm	750° C
2. At periphery over apex of "V"	620° C
3. Top center	405° C
4. 6" above center of filter case	535° C
5. 12" above center of filter case	455° C
6. 12" above center of burner arm	450° C
Temperature of inside sheeting	175° C

TABLE OF FLUE GAS LEAD RECOVERIES -- RUN #1

Tube #	Sampling Temp. °C	Corrected Sampling Rate cfm at 25°C	Time Min. Sample	Time Min. Run	Volume of Sample cu.ft.	Lead in Sample mg.	Flue Gas per Gr.Carbon cfm	Gr.Carbon per Minute	Total Volume Flue Gas cu.ft. at 25°C	Sampling Factor	Total Lead in Flue Gas mg.
1	2	3	4a	4b	5	6	7	8	9=4bx7x8	10=9÷5	11=6x10
16	129.5	2.405	30	31	72.15	4.8	5.98	16.18	3000	41.6	199.70
13	125.0	2.431	30	32	72.90	0.16	5.98	16.18	3094	42.4	6.79
14	127.0	2.421	60	62	145.3	0.56	6.25	16.18	6275	43.2	24.15
17	123.0	2.445	60	62	146.3	0.50	6.26	16.18	6280	42.9	21.48
19	127.0	2.421	60	61	145.3	0.65	6.24	16.18	6250	43.0	27.96
Note: Average values of CO_2 and O_2 during Run #1 were used to compute results for Tube #16.								Total Lead Recovered In Effluent			280.08

SUMMARY TABLE OF LEAD RECOVERIES -- RUN #1

Source	Partial Total mg.	Total mg.	% Based on Calculation	% Based on Analysis
Stove				
Filter Disc by $PbSO_4$ Method (Spectrographic 3900 mg)	4228.0			
Flame Valve, Burner, generator, Filter Case and Mixing Chamber (Spectrographic)	720.0			
Air and Fuel Lines	9.0			
Total Stove		4957.00	91.30	92.10
Test Chimney Effluent (Flue Gas)		280.08	5.16	5.20
Chimney and Hood Deposits		1.50	0.00	0.00
Organic Lead from Charcoal Adsorber		10.50	0.02	0.02
Total Lead Recovered		5249.08	96.48	97.32
Total Lead in Fuel (Det. Anal. - 5380 mg)		5434.00		

TABLE OF FLUE GAS LEAD RECOVERIES -- RUN #2

Tube #	% CO_2	% O_2	Sampling Temp. °C	Corrected Sampling Rate cfm at 25°C	Time Min.		Volume of Sample cu.ft.	Lead in Sample mg.	Flue Gas per Gr.Carbon cfm	Gr.Carbon per Minute	Total Volume Flue Gas cu.ft. at 25°C	Sampling Factor	Total Lead in Flue Gas mg.
					Sample	Run							
1	2	3	4	5	6a	6b	7	8	9	10	11=6bx9x10	12=11÷7	13 = 8x12
1	1.2	19.3	125.5	2.453	30	31	73.59	2.9	5.98	14.83	2750	37.4	74.8
2	1.05	19.65	118.7	2.475	30	32	74.25	0.13	6.25	14.83	2965	39.9	5.2
3	1.125	19.575	112.6	2.553	60	62	153.18	0.44	6.39	14.83	5880	38.3	16.9
5	1.115	19.525	124.8	2.438	60	62	146.28	0.26	6.45	14.83	5830	39.8	10.4
6	1.10	19.45	116.3	2.392	53	53	126.78	0.12	6.53	14.83	5130	40.5	4.9
									Total Lead Recovered in Effluent				112.2

SUMMARY TABLE OF LEAD RECOVERIES -- RUN #2

Source	Partial Total mg.	Total mg.	% Based on Calculation	% Based on Analysis
Stove - (Fire Unit)				
Filter Disc by $PbSO_4$ Method (Spectrographic 4000 mg)	4056			
Flame Valve, Burner, Generator, Filter Case and Mixing Chamber	600			
Air and Fuel Lines	7			
Total Stove		4663	96.5	97.60
Test Chimney Effluent (Flue Gas)		112.2	2.3	2.32
Chimney and Hood Deposits (Neglected)		0		0.00
Organic Lead from Charcoal		0		0.00
Total Lead Recovered		4775.2	98.8	99.92
Unaccounted for		56.8	1.2	0.08
Total Lead in Fuel (Det. Anal. - 4780 mg)		4832	100.0	100.00

TABLE OF FLUE GAS LEAD RECOVERIES -- RUN #39

Tube #	% CO_2	% O_2	Sampling Temp. °C	Corrected Sampling Rate cfm at 25°C	Time Min. Sample	Time Min. Run	Volume of Sample cu.ft.	Lead in Sample mg.	Flue Gas per Gr.Carbon cfm	Gr.Carbon per Minute	Total Volume Flue Gas cu.ft. at 25°C	Sampling Factor	Total Lead in Flue Gas mg.
1	2	3	4	5	6a	6b	7	8	9	10	11=6bx9x10	12=11÷7	13=8x12
3	1.10	19.5	131.5	2.280	30	31	68.4	3.50	6.53	14.32	2902	42.5	148.8
8	1.00	19.6	129.3	2.290	30	31	68.6	0.49	7.18	14.32	3190	46.5	22.8
5	0.95	19.65	128.0	2.295	60	61	137.6	0.42	7.56	14.32	6600	48.0	20.2
15	1.10	19.45	117.8	2.355	60	61	141.2	0.11	6.53	14.32	5710	40.4	4.4
13	0.95	19.6	116.9	2.365	60	60	141.8	0.06	7.55	14.32	6490	45.8	2.8
											Total Lead Recovered In Effluent		199.0

SUMMARY TABLE OF LEAD RECOVERIES -- RUN #39

Location of Lead	Partial Total mg.	Total mg.	% Based on Calculation	% Based on Analysis
Stove (Fire Unit)				
Filter Disc ($PbCrO_4$ Method) (Spectrographic 3400 mg)	3776.0			
Burner, Generator, Filter Case and Mixing Chamber	860.0			
Flame Valve, Air and Fuel Lines	26.0			
Total Stove		4662.0	95.3	96.40
Test Chimney Effluent (Flue Gas)		199.0	4.1	4.10
Total Lead Recovered		4861.0	99.4	100.50
Unaccounted for		29.0	0.6	.00
Total Lead in Fuel (Det. Lab. 4840 mg)		4890.0	100.0	100.50

SUMMARY TABLE OF RESULTS
Lead Balance Runs 1, 2 and 39

Distribution	Run #1		Run #2		Run #39		Average
	Mg. of Pb	%	Mg. of Pb	%	Mg. of Pb	%	%
Effluent (Flue Gas)	280.08	5.16	112.2	2.3	199.0	4.1	3.85
Filter Disc	4228.00	77.75	4056.0	84.0	3776.0	77.2	79.66
Stove other than filter disc	741.00	13.57	607.0	12.5	886.0	18.1	14.72
Total Lead Recovered	5249.08	96.48	4775.2	98.8	4861.0	99.4	98.23
Unrecovered Lead	184.92	3.52	56.8	1.2	29.0	0.6	1.77
Total Lead in Fuel Burned	5434.00	100.00	4832.0	100.0	4890.0	100.0	100.00

TABULATION OF RESULTS -- RUNS #3 AND #4

Tube #	Sampling Temp. °C	Corrected Sampling Rate cfm at 25°C	Time Minutes Sample	Time Minutes Run	Air Sampled cu. ft.	Lead in Tube mg.	Flue Gas per Gr.Carbon cfm	Gr.Carbon per Minute	Total Volume Flue Gas cu. ft.	Sampling Factor	To
	RUN #3										
1	120	2.255	10	11	22.55	0.88	2.78	14.33	438.35	19.46	
2	148	2.105	10	11	21.05	0.94	2.78	14.33	438.35	20.83	
3	162.8	2.033	11	12	22.36	0.36	3.63	14.33	624.0	27.95	
4	162.8	2.033	10	11.5	20.33	0.28	3.63	14.33	598.0	29.45	
5	157.5	2.055	10.5	11.5	21.58	0.045	3.63	14.33	598.0	27.76	
6	156.8	2.065	10	10	20.65	0.040	3.63	14.33	520.0	25.18	
							Total Lead in Flue Gas - Run #4				
	RUN #4										
7	111	2.314	15	17	34.67	1.50	5.13	15.28	1330	38.37	
8	125	2.233	15	16	33.50	0.20	5.53	15.28	1351	40.30	
10	122	2.250	15	16	33.77	0.12	5.53	15.28	1351	40.05	
11	130.8	2.202	15	15	33.03	0.50	5.53	15.28	1267	38.35	
							Total Lead in Flue Gas - Run #5				

Table 2

Concentration of Lead in Flue Gas

Time	Mgm. Pb in Flue Gas	Cu. Ft. Flue Gas	Mgm. Pb/10 cu.m. Flue Gas
	Run 1		
1st 30 min.	200.0	3000	23.54
2nd hour	24.2	6275	1.35
4th hour	28.0	6250	1.58
	Run 2		
1st 30 min.	74.8	2750	9.60
2nd hour	16.9	5880	1.01
4th hour	4.9	5130	0.34
	Run 39		
1st 30 min.	148.8	2902	18.11
2nd hour	20.2	6600	1.08
4th hour	2.8	6490	0.15
	Run 3		
1st 10 min.	17.1	438	13.79
2nd 10 min.	19.6	438	15.81
3rd 11 min.	10.0	624	5.66
4th 10 min.	8.3	598	4.84
5th 10.5 min.	1.3	598	0.71
6th 10 min.	1.0	520	0.68
	Run 4		
1st 15 min.	57.5	1330	15.26
2nd 15 min.	8.1	1351	2.11
3rd 15 min.	4.8	1351	1.25
4th 15 min.	19.2	1267	5.35