United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EMB Report 81-BYC-12
January 1982

Air

EPA

Benzene Fugitive Leaks Coke Oven By-Product Plants

Leak Frequency And Emission Factors For Fittings In Coke Oven By-Product Plants

DCN 82-222-018-01-26 EMB Report No. 81-BYC-12

FINAL REPORT
LEAK FREQUENCY AND EMISSION FACTORS FOR FITTINGS IN COKE OVEN BY-PRODUCT PLANTS

Prepared by:

D.P. Wiesenborn, J.I. Steinmetz, and G.E. Harris
RADIAN CORPORATION
8501 Mo-Pac Boulevard
Austin, Texas 78759

Prepared for:

Dan Bivins
U.S. Environmental Protection Agency
ESED/EMB (MD-13)
Research Triangle Park, North Carolina 27711

EPA Contract No. 68-02-3542
Work Assignment No. 1
ESED No. 74/4j

8 February 1982

CONTENTS

TABLES

Tables Continued

FIGURES

Figures Continued

Figures Continued

SECTION 1

INTRODUCTION AND SUMMARY

This report presents a statistical analysis of test data for fugitive nonmethane hydrocarbon and benzene emissions from coke by-product plants. Test results have been previously presented in reports entitled, "Benzene Fugitive Leaks; Coke Oven By-Product Plants; Emission Test Report" for the following plants:

Plant	EMB Report No.
Bethlehem Steel Corporation, Bethlehem, PA.	80-BYC-9
Republic Steel Corporation, Gadsden, AL.	80-BYC-10
Wheeling-Pittsburgh Steel Corporation, Monessen, PA.	80-BYC-11

This work was funded and administered by the Emission Measurement Branch of the U.S. Environmental Protection Agency under Contract No. 68-02-3542. The results of this study may be used in support of a National Emission Standard for Hazardous Air Pollutants for benzene from coke oven by-product recovery plants.

The purpose of this study can best be described by discussing the field testing phase and the data analysis phase separately. Two objectives of the field testing were as follows:

1) to count and screen all valves and pump seals and one-third of all flanges, on process lines containing at least 4 weight percent benzene; also to screen all exhauster seals and to determine the percentage of benzene in each process line surveyed,

2) to measure the mass emission rate of benzene and of nonmethane hydrocarbons at each leaking source identified during the screening.

The objectives of the data analysis were as follows:

1) to compile leak frequency distributions for different benzene service populations (all sources screened, all sources on lines with at least 4 weight percent benzene, and all sources on lines with at least 10 weight percent benzene),

2) to compare the percentage of benzene in the line to the estimated percentage of benzene in the leak to determine if the benzene concentration in the line is an adequate identifier of potentially significant sources,

3) to prepare benzene and nonmethane hydrocarbon emission factors for all sources and for sources on lines with at least 10 percent benzene,

4) to compare the coke oven by-product recovery emission factors with emission factors for petroleum refineries.

The objectives of testing were met, and the results published in the Emission Test Reports. The analysis objectives are met by results given in Section 2 and briefly summarized in the following paragraphs. The methodology used in estimating emission factors is discussed in Section 3, and the results of the quality control practices are given in Section 4.

An examination of the population data indicates that no sources were found in the 4 to 10 percent benzene service range. The contribution of sources below 4 percent benzene service to total benzene fugitive emissions was found to be quite small. These data indicate that the bulk of benzene fugitive emissions can be attributed to sources on lines containing at least 10 percent benzene. Usually, only the light oil product lines contain 10 percent or more benzene.

The percentage of benzene in the line is generally a good indicator of the percentage of benzene in the leak. The test results indicate, however, that there are two exceptions. If benzene is, by far, one of the most volatile components in the line, then there may be a higher percentage of benzene in the leak than in the line. The second exception involves very small leaks, where the benzene concentration in the sample gas may be only slightly higher than ambient. In these cases, the sampling and analytical precision is not sufficient to resolve the benzene concentration accurately. This results in a lack of correlation between sample and line benzene concentrations.

This program was not designed to produce an extensive data base from which firm emission factors could be developed. A previous study of fugitive emissions from petroleum refining, however, developed emission factors for similar equipment types. Table 1-1 presents nonmethane hydrocarbon emission factors for comparable sources in coke by-product plants and refineries. The mean emission factors are reasonably close, especially for the important valve category, and the confidence intervals for all categories show a significant degree of overlap. Therefore, the use of refinery data to characterize the coke by-products fugitive emissions is reasonable.

TABLE 1-1. COMPARISON OF EMISSION FACTORS (KG/DAY) FOR SOURCES IN COKE BY-PRODUCT PLANTS AND REFINERIES

	Coke By-Product Plants		Refineries	
Source Type	Emission Factor (Confidence Interval)	Service	Emission Factor (Confidence Interval)	Service
Valves	0.36 (0.03 - 3.3)	> 10% Benzene	0.26 (0.19 - 0.39)	Light Liquid
Pump Seals	5.2 (1.3 - 18)	> 10% Benzene	2.7 (1.7 - 4.0)	Light Liquid
Exhausters (Compressors)	0.37 (0.006 - 10)	All	1.2 (0.54 - 2.5)	Hydrogen
Connections	---	---	0.007 (0.002 - 0.027)	All

SECTION 2

DETAILED RESULTS

This section presents a detailed summary of all of the fugitive emission data gathered at the:

- Wheeling-Pittsburgh Steel Plant on November 24 to December 5, 1980,
- Republic Steel Plant on December 8 to 12, 1980, and
- Bethlehem Steel Plant on January 20 to 28, 1981.

Fugitive emissions testing was performed on fittings on process lines containing at least 4 weight percent benzene. Benzene is concentrated in the light oil recovery section, and therefore almost all of the testing was performed in this area. All three plants have light oil recovery units that operate by the absorption/stripping method of light oil recovery. At two of three plants, the light oil is further fractionated. Light oil production at the facilities ranges from 2,730 to 12,678 gallons per day and coke oven gas production from 8.27 to 67.4 MMSCFD. A detailed description of each process and the lines screened is included in Appendix C.

The fugitive emissions testing at each of these plants included both "screening" and "bagging" procedures. Screening is a generic term covering any quick portable method of detecting fugitive emissions. The initial screening in this study was performed with a Century Systems Organic Vapor Analyzer (OVA) Model 108. Bagging is a technique for measuring fugitive emissions by enclosing the source in Mylar® and analyzing an equilibrium flow of air through the enclosure. The screening and bagging procedures are described in more detail in Section 4 of the individual test reports.

2.1 SCREENING VALUE DISTRIBUTIONS

Screening value distributions are presented in Table 2-1 for all plants combined and in Table B-1 to B-3 for individual plants. These distributions are reported by type of fitting and by the concentration of benzene in the line. Three subcategories for the amount of benzene in the line were considered:

- All service (that is, all sources screened)
- Sources on lines with at least 4 weight percent benzene
- Sources on lines with at least 10 weight percent benzene

There were, however, very few sources found with benzene between 4 and 10 weight percent.

Sources with less than 4 weight percent benzene, other than exhausters, were not intentionally screened. But at the Wheeling-Pittsburgh Steel and Bethlehem Steel plants, it was not immediately known that the wash oil from the light oil absorbers contained less than 4 weight percent benzene. Hence, these wash oil lines were screened, even though subsequent analysis of samples from these lines showed that the benzene concentration was less than 4 weight percent.

Exhauster seals were also tested, even though these are in the service of coke oven gas with less than 4 weight percent benzene, because testing in petroleum refineries indicated that this type of fitting can be a major source of emissions. The exhausters are located on the coke oven gas line upstream from the light oil recovery unit. The distribution of screening values for exhausters is also presented in Table 2-1.

TABLE 2-1. SCREENING RESULT FREQUENCY DISTRIBUTION BY SOURCE TYPE AND BENZENE SERVICE FOR ALL UNITS

Benzene Service	Screening Value (PPMV)	Flanges		Threaded Fittings		Valves		Pump Seals		Exhausters		Total	
		#	%	#	%	#	%	#	%	#	%	#	%
All Service[a]	0 to 199	223	100.0	70	100.0	226	91.5	18	56.3	27	79.4	564	93.1
	200 to 9,999	0	0.0	0	0.0	13	5.3	5	15.6	4	11.8	22	3.6
	≥ 10,000	0	0.0	0	0.0	8	3.2	9	28.1	3	8.8	20	3.3
	Total Sources Screened	223	100.0	70	100.0	247	100.0	32	100.0	34	100.0	606	100.0
≥ 4% Benzene	0 to 199	66	100.0	59	100.0	117	86.7	6	30.0	4	100.0	252	88.7
	200 to 9,999	0	0.0	0	0.0	10	7.4	5	25.0	0	0.0	15	5.3
	≥ 10,000	0	0.0	0	0.0	8	5.9	9	45.0	0	0.0	17	6.0
	Total Sources Screened	66	100.0	59	100.0	135	100.0	20	100.0	4	100.0	284	100.0
≥ 10% Benzene	0 to 199	66	100.0	59	100.0	117	86.7	6	30.0	0	--	248	88.6
	200 to 9,999	0	0.0	0	0.0	10	7.4	5	25.0	0	--	15	5.4
	≥ 10,000	0	0.0	0	0.0	8	5.9	9	45.0	0	--	17	6.1
	Total Sources Screened	66	100.0	59	100.0	135	100.0	20	100.0	0	100.0	280	100.0

\# = Number of sources in each category

% = Percent of total sources screened

a All service category includes all sources screened except exhausters, regardless of the percent benzene in the line. No attempt was made to screen all sources with less than 4% benzene, however, so these figures do not represent a complete unit inventory.

2.2 BENZENE AND NONMETHANE HYDROCARBON LEAK RATES

Table 2-2 summarizes the benzene and nonmethane hydrocarbon leak rates in kilograms per day. All valves, pump seals, and exhausters that caused an OVA reading greater than the ambient reading or that had a visible liquid leak were sampled. Vapor phase leak rates were measured using the bagging technique. Liquid leak rates were measured directly by timed collection in a graduated cylinder, and a sample of the collected liquid was analyzed for benzene. Each sampled source was screened immediately before sampling with an OVA and with a J.W. Bacharach Instrument Company "TLV Sniffer." These screening values are shown in Table 2-2 along with the weight percent benzene in the line.

2.3 COMPARISON OF BENZENE IN LEAK AND IN LINE

Table 2-3 provides a comparison of the weight percent benzene in the vapor, liquid, and total leak with the weight percent benzene in the line. The weight percent benzene in the vapor sample is not directly comparable to benzene in the line, because the sample is diluted with air. These values for percent benzene are calculated as the ratio of benzene to nonmethane hydrocarbon in the sample. This method is probably accurate unless the leak is small. Those values of benzene in the leak that are much less than the benzene in the line represent samples that had only slightly more benzene and nonmethane hydrocarbon than the ambient air samples. The weight percent benzene in the line is plotted against the weight percent benzene in the total and vapor leak in Figure B-1 (a & b).

2.4 EMISSION FACTORS

Benzene and nonmethane hydrocarbon emission factors were calculated according to type of fitting. These factors are summarized in Table 2-4a for sources with at least 10 percent benzene and in Table 2-4b for all sources

TABLE 2-2. BENZENE AND NONMETHANE LEAK RATES (KG/DAY) FROM SAMPLED SOURCES

	Plant[a]	Source ID[b]	Before Tenting OVA Screening Value (ppmv)	Before Tenting TLV Screening Value (ppmv)	Weight Percent Benzene In Line	Benzene Leak Rates			Nonmethane Leak Rates		
						Vapor	Liquid	Total	Vapor	Liquid	Total
Valves	1	18	1500	400	39.00	0.0002	0.0000	0.0002	0.0015	0.0000	0.0015
	2	23	0	No Data	71.50	No Data	3.2639	No Data	No Data	4.7578	No Data
	2	32	70000	8700	71.50	4.7389	0.0000	4.7389	5.1927	0.0000	5.1927
	2	73	2200	500	71.50	0.0102	0.0000	0.0102	0.0162	0.0000	0.0162
	2	121	10000	4200	71.50	0.0028	0.0000	0.0028	0.0100	0.0000	0.0100
	2	122	100001	10001	71.50	0.4868	0.4389	0.9257	0.4929	0.6029	1.0958
	2	123	3600	0	71.50	0.0172	0.0000	0.0172	0.0267	0.0000	0.0267
	2	124	100001	10001	71.50	1.4287	0.0000	1.4287[e]	1.2395	0.0000	1.2395[e]
	2	125	100000	600	71.50	0.0147	0.0000	0.0147	0.0159	0.0000	0.0159
	2	129	10000	800	71.50	0.0742	0.0000	0.0742[e]	0.0701	0.0000	0.0701[e]
	3	40	500	2000	ND[c]	0.0000	0.0000	0.0000	0.0001	0.0000	0.0001
	3	84	50	50	ND	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	3	87	600	2600	NA[c]	0.0014	0.0000	0.0014	0.0043	0.0000	0.0043
	3	91	800	1800	ND	0.0260	0.0000	0.0260	0.0339	0.0000	0.0339
	3	103	300	400	NA	0.0015	0.0000	0.0015	0.0029	0.0000	0.0029
	3	104	35	80	NA	0.0032	0.0000	0.0032	0.0050	0.0000	0.0050
	3	108	'50	540	63.00	0.0000	0.0000	0.0000	No Data[f]	0.0000	No Data
	3	114	2000	900	63.00	0.0215	0.0000	0.0215	0.0263	0.0000	0.0263
	3	115	350	300	63.00	0.0031	0.0000	0.0031	0.0071	0.0000	0.0071
	3	116	350	200	63.00	0.0000	0.0000	0.0000	0.0034	0.0000	0.0034
	3	120	29000	10001	63.00	0.3511	1.1425	1.4936	No Data	2.0401	No Data
	3	121	5000	2000	63.00	0.0302	0.0000	0.0302	0.0386	0.0000	0.0386
	3	124	65	28	63.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	3	129	110	100	63.00	0.0001	0.0000	0.0001	0.0005	0.0000	0.0005
	3	139	140	60	63.00	0.0006	0.0000	0.0006	0.0013	0.0000	0.0013
	3	141	30000	10001	63.00	0.2382	0.0000	0.2382	0.3488	0.0000	0.3488
Pump Seals	1	98-I	1000	4200	85.00	0.5953	0.0000	0.5953	0.7093	0.0000	0.7093
	1	98-Ø	45000	10001	85.00	1.6684	1.3995	3.0679	1.7137	1.7860	3.4996
	1	117-Ø	15000	10001	77.00	0.4086	0.0000	0.4086	0.4333	0.0000	0.4333
	1	131-Ø	6000	6500	77.00	1.1581	1.7736	2.9318	1.2764	2.2610	3.5374
	1	139-I	40000	7500	39.00	No Data	6.1584	No Data	1.5555	15.3825	16.9380
	1	139-I[d]	5000	5400	39.00	0.9945	6.1330	7.1275	0.9069	15.3172	16.2241
	1	139-Ø	7000	4000	39.00	No Data	0.0000	No Data	1.0155	0.0000	1.0155
	1	139-Ø[d]	1000	1100	39.00	0.6272	0.0000	0.6272	0.8073	0.0000	0.8073
	1	141-I	500	700	0.97	0.0095	0.0000	0.0095	0.0106	0.0000	0.0106
	2	21-S	50000	8200	71.50	3.1515	0.0000	3.1515	4.0297	0.0000	4.0297
	2	28-S	100001	10001	71.50	1.3240	5.2077	6.5317	1.4234	7.8666	9.2900
	2	119-S	60000	8000	71.50	4.8617	13.1965	18.0582	5.2887	17.2277	22.5164
	2	120-S	24000	10001	71.50	6.8238	27.6367	34.4604	7.9808	36.0792	44.0599

(Continued)

TABLE 2-2. Continued

	Plant	Source ID[b]	Before Tenting OVA Screening Value (ppmv)	Before Tenting TLV Screening Value (ppmv)	Weight Percent Benzene In Line[c]	Benzene Leak Rates Vapor	Benzene Leak Rates Liquid	Benzene Leak Rates Total	Nonmethane Leak Rates Vapor	Nonmethane Leak Rates Liquid	Nonmethane Leak Rates Total
Pump Seals	3	26-I	140	700	ND	0.0257	0.0000	0.0257	0.0354	1.2716	1.3070
	3	27-Ø	25	35	ND	0.0013	0.0000	0.0013	0.0028	0.0000	0.0028
	3	66-I	30	35	ND	0.0081	0.0000	0.0081	0.0111	0.4187	0.4298
	3	68-I	15	14	ND	0.0017	0.0000	0.0017	0.0026	0.1821	0.1848
	3	98-Ø	20000	10001	63.00	0.8473	0.0000	0.8473	No Data	0.0000	No Data
	3	98-Ø[d]	15000	7600	63.00	0.6937	0.0000	0.6937	1.0233	0.0000	1.0233
	3	109-I	6000	8000	63.00	0.8701	0.0000	0.8701	No Data	0.0000	No Data
	3	109-I[d]	15000	8000	63.00	0.7878	0.0000	0.7878	1.2266	0.0000	1.2266
	3	333-Ø	3200	10001	63.00	3.0992	4.4133	7.5125	3.1692	6.8424	10.0115
	3	334-I	75000	10001	63.00	2.2132	96.2911	98.5043	1.8661	149.289	151.155
Exhausters	2	2	2000	1300	3.10	0.0207	0.0000	0.0207	0.1248	0.0000	0.1248
	2	4	500	1100	3.10	0.0082	0.0000	0.0082	0.0598	0.0000	0.0598
	3	18	75000	10001	2.10	2.1791	0.0000	2.1791	5.3717	0.0000	5.3717
	3	19	100001	10001	2.10	1.6867	0.0000	1.6867	4.1286	0.0000	4.1286
	3	20	40000	10001	2.10	1.8928	0.0000	1.8928	No Data	0.0000	No Data
	3	20[d]	65000	10001	2.10	0.2317	0.0000	0.2317	0.5790	0.0000	0.5790
	3	23	15000	10001	2.10	0.0071	0.0000	0.0071	0.0303	0.0000	0.0303

[a] Plant codes are as follows:
1) Wheeling-Pittsburgh Steel
2) Republic Steel
3) Bethlehem Steel

[b] I denotes inboard seal and Ø denotes outboard seal of a pump with two seals. S denotes a single seal pump.

[c] NA= Stream was not sampled and there was not sufficient data to make an estimate.
ND= No benzene detected (Benzene < 1 weight percent).

[d] These sources were sampled twice because problems occurred during initial sampling (leaky ambient air bag, THC not operating).

[e] The benzene analyses and the nonmethane hydrocarbon analyses were performed on two different instruments. The vapor sample for these two sources was approximately 100% benzene, and normal experimental error between the two analyses resulted in the anomalous results of the benzene leak rates being larger than the nonmethane leak rates.

[f] No data = No data was collected because vapor leak stopped before fitting could be sampled, THC was not operating, or sample bag leaked.

TABLE 2-3. COMPARISON OF PERCENT BENZENE IN LINE TO PERCENT BENZENE IN EQUIPMENT LEAKS FOR COKE OVEN BY-PRODUCT PLANTS

Equipment Type	Plant[a]	Source ID[b]	Before Tenting Screening Value (ppmv)	Nonmethane Leak Rate (kg/Day)	Weight Percent Benzene In Line[c]	Weight Percent Benzene In Total Leak[d]	Weight Percent Benzene In Vapor Leak[d]	Weight Percent Benzene In Liquid Leak	Other Major Chemicals In Line
Block Valves	1	18	1500	0.00147	39.00 (M)	15.83	15.83	--[e]	Light Oil
	2	23	0	No Data	71.50 (M)	--	--	68.60	Toluene, Xylene
		73	2200	0.01622	71.50 (E)	63.15	63.15	--	Toluene, Xylene
		121	10000	0.00996	71.50 (M)	28.48	28.48	--	Toluene, Xylene
		122	100001	1.09578	71.50 (M)	84.48	98.76	72.80	Toluene, Xylene
		123	3600	0.02665	71.50 (M)	64.38	64.38	--	Toluene, Xylene
		124	100001	1.23947	71.50 (M)	115.26[f]	115.26[f]	--	Toluene, Xylene
		125	100000	0.01590	71.50 (M)	92.21	92.21	--	Toluene, Xylene
		129	10000	0.07013	71.50 (M)	105.78[f]	105.78[f]	--	Toluene, Xylene
	3	40	500	0.00011	(ND) (M)	0.00	0.00	--	Wash Oil
		84	50	0.00000	(ND) (M)	--	--	--	Wash Oil
		87	600	0.00432	(NA)	32.61	32.61	--	Water, Heavy Organics
		91	800	0.03388	(ND) (M)	76.77	76.77	--	Wash Oil
		103	300	0.00286	(NA)	53.57	53.57	--	Water
		104	35	0.00503	(NA)	62.74	62.74	--	Water
		108	160	No Data	63.00 (M)	--	--	--	Toluene, Xylene
		114	2000	0.02634	63.00 (M)	81.62	81.62	--	Toluene, Xylene
		116	350	0.00336	63.00 (M)	0.00	0.00	--	Toluene, Xylene
		120	29000	No Data	63.00 (M)	--	--	56.00	Toluene, Xylene
		124	65	0.00000	63.00 (M)	--	--	--	Toluene, Xylene
		129	170	0.00050	63.00 (M)	20.00	20.00	--	Toluene, Xylene
		139	140	0.00129	63.00 (M)	46.83	46.83	--	Toluene, Xylene
		141	30000	0.34882	63.00 (M)	68.30	68.30	--	Toluene, Xylene
Control Valves	2	32	70000	5.19267	71.50 (M)	91.26	91.26	--	Toluene, Xylene
	3	115	350	0.00714	63.00 (M)	43.65	43.65	--	Toluene, Xylene
		121	5000	0.03857	63.00 (M)	78.30	78.30	--	Toluene, Xylene
On-Line Pump Seals	1	98-I	1000	0.70926	85.00 (M)	83.93	83.93	--	Toluene, Xylene
		98-Ø	45000	3.49964	85.00 (M)	87.66	97.36	78.36	Toluene, Xylene
		117-Ø	15000	0.43330	77.00 (M)	94.30	94.30	--	Toluene, Xylene
		131-Ø	6000	3.53743	77.00 (M)	82.88	90.73	78.44	Toluene, Xylene
		139-I	40000	16.93801	39.00 (M)	--	--	40.04	Wash Oil
		139-I[g]	5000	16.22410	39.00 (M)	43.93	109.66[f]	40.04	Wash Oil
		139-Ø	7000	1.01553	39.00 (M)	--	--	--	Wash Oil
		139-Ø	1000	0.80732	39.00 (M)	77.69	77.69	--	Wash Oil
		141-I	500	0.01057	0.97 (M)	90.02	90.02	--	Wash Oil

(Continued)

TABLE 2-3. Continued

Equipment Type	Plant[a]	Source ID[b]	Before Tenting Screening Value (ppmv)	Nonmethane Leak Rate (kg/Day)	Weight Percent Benzene In Line[c]	Weight Percent Benzene In Total Leak[d]	Weight Percent Benzene In Vapor Leak[d]	Weight Percent Benzene In Liquid Leak	Other Major Chemicals In Line
On-Line Pump Seals	2	21-S	50000	4.02973	71.50 (M)	78.21	78.21	--[e]	Toluene, Xylene
		119-S	60000	22.51639	71.50 (M)	80.20	91.93	76.60	Toluene, Xylene
		120-S	24000	44.05992	71.50 (M)	78.21	85.50	76.60	Toluene, Xylene
	3	26-I	140	1.30700	(ND) (M)	1.97	72.64	0.00	Wash Oil
		27-Ø	25	0.00282	(ND) (M)	46.15	46.15	--	Wash Oil
		66-I	30	0.42978	(ND) (M)	1.87	72.80	0.00	Wash Oil
		68-I	15	0.18475	(ND) (M)	0.90	63.33	0.00	Wash Oil
		98-Ø	20000	No Data	63.00 (M)	--	--	--	Toluene, Xylene
		98-Ø[g]	15000	1.02333	63.00 (M)	67.79	67.79	--	Toluene, Xylene
		109-I	6000	No Data	63.00 (M)	--	--	--	Toluene, Xylene
		109-I[g]	15000	1.22656	63.00 (M)	64.23	64.23	--	Toluene, Xylene
		333-Ø	3200	10.01154	63.00 (M)	75.04	97.79	64.50	Toluene, Xylene
		334-I	75000	151.155	63.00 (M)	65.17	118.60[f]	64.50	Toluene, Xylene
Off-Line Pump Seals	2	28-S	100001	9.29001	71.50 (M)	70.31	93.02	66.20	Toluene, Xylene
Exhausters	2	2	2000	0.12483	3.10 (E)	16.58	16.58	--	Coke Oven Gas
		4	500	0.05975	3.10 (E)	13.76	13.76	--	Coke Oven Gas
	3	18	75000	5.37174	2.10 (E)	40.57	40.57	--	Coke Oven Gas
		19	100001	4.12858	2.10 (E)	40.85	40.85	--	Coke Oven Gas
		20	40000	No Data	2.10 (E)	--	--	--	Coke Oven Gas
		20[g]	65000	0.57896	2.10 (E)	40.02	40.02	--	Coke Oven Gas
		23	15000	0.03030	2.10 (E)	23.28	23.28	--	Coke Oven Gas

[a] Plant codes are as follows:
1) Wheeling-Pittsburgh Steel
2) Republic Steel
3) Bethlehem Steel

[b] I denotes inboard seal and Ø denotes outboard seal of a pump with 2 seals, S denotes a single seal pump.

[c] M = Measured , E = Estimated , NA = Stream was not sampled and there was not sufficient data to make an estimate
ND = No benzene detected, Benzene < 1 weight percent.

[d] $\text{Weight percent benzene} = \frac{\text{mass emissions of benzene}}{\text{mass emissions of NMHC}} \times 100$ Where the weight percent benzene in the vapor leak is much less than the weight percent benzene in the line, note that these sources generally have low leak rates and are difficult to sample and analyze accurately.

[e] Insufficient data or no liquid leak present.

[f] Analyses for benzene and NMHC were performed on different instruments - probably almost all of the NMHC in this sample is benzene.

[g] These sources were sampled twice because problems occurred during initial sampling (leaky ambient air bag, THC not operating).

No data = No data collected because vapor leak stopped before fitting could be sampled, THC was not operating, or sample bag leaked.

TABLE 2-4a. EMISSION FACTORS FOR SOURCES WITH ≥ 10% BENZENE IN LINE ACCORDING TO SOURCE

		NONMETHANE				BENZENE			
				Emission Factor				Emission Factor	
Source Type	Number Screened[1]	Number Emitting[2]	Number Liquid Emitters[3]	Estimate (kg/day/source)	95% Confidence Interval	Number Emitting[2]	Number Liquid Emitters[3]	Estimate (kg/day/source)	95% Confidence Interval
Valves	135	21	3	0.36	(0.03,3.3)	20	3	0.21	(0.02,1.7)
Pump Seals	20	15	8	5.2	(1.3,18)	15	8	4.0	(1.1,13)

[1] Sources were screened using instrument screening and inspection for visible leakage.

[2] Emitting Sources were those releasing emissions detectable by the screening method (excluding those sources with measured leak rate of zero).

[3] Liquid emitting sources were those releasing liquid leakage detectable by visual inspection.

TABLE 2-4b. EMISSION FACTORS FOR ALL SOURCES SCREENED ACCORDING TO SOURCE

		NONMETHANE				BENZENE			
				Emission Factor				Emission Factor	
Source Type	Number Screened[1]	Number Emitting[2]	Number Liquid Emitters[3]	Estimate (kg/day/source)	95% Confidence Interval	Number Emitting[2]	Number Liquid Emitters[3]	Estimate (kg/day/source)	95% Confidence Interval
Valves	247	29	3	0.19	(0.02,1.4)	27	3	0.11	(0.01,0.71)
Pump Seals	32	20	11	6.3	(1.3,28)	20	8	2.6	(0.56,11)
Exhausters	34	7	0	0.37	(0.006,10)	7	0	0.087	(0.002,1.4)

[1] Sources were screened using instrument screening and inspection for visible leakage.

[2] Emitting sources were those releasing emissions detectable by the screening method (excluding those sources with measured leak rate of zero).

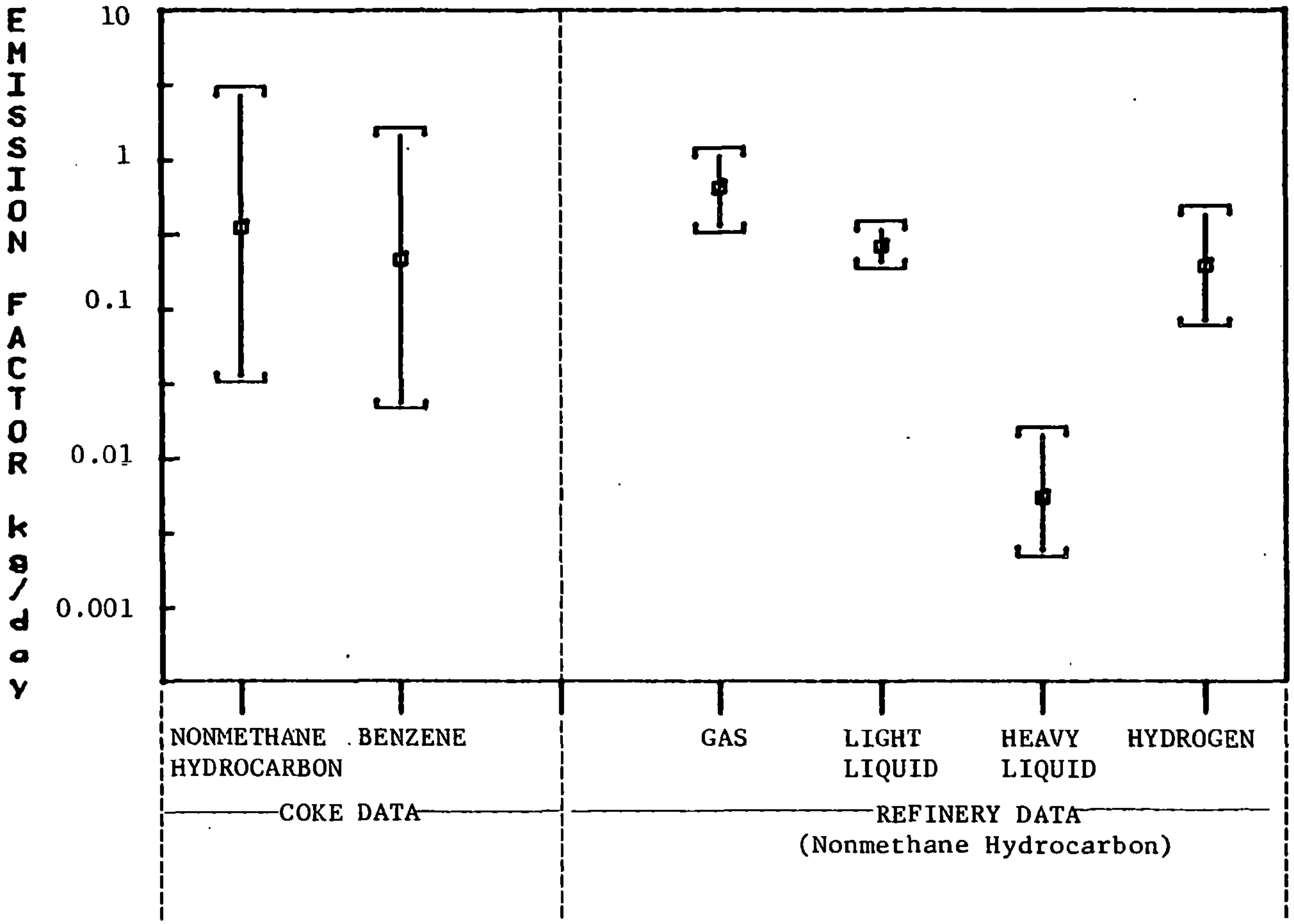
[3] Liquid emitting sources were those releasing liquid leakage detectable by visual inspection.

screened. In Figures 2-1 to 2-5, these factors are compared with emission factors developed during the refinery program and published in "Assessment of Atmospheric Emissions from Petroleum Refining," EPA Report No. 600/2-80-075 (Vol. a-e), Radian Corporation, Austin, Texas, July 1980.

2.5 RELATIONSHIPS BETWEEN SCREENING VALUES AND LEAK RATES

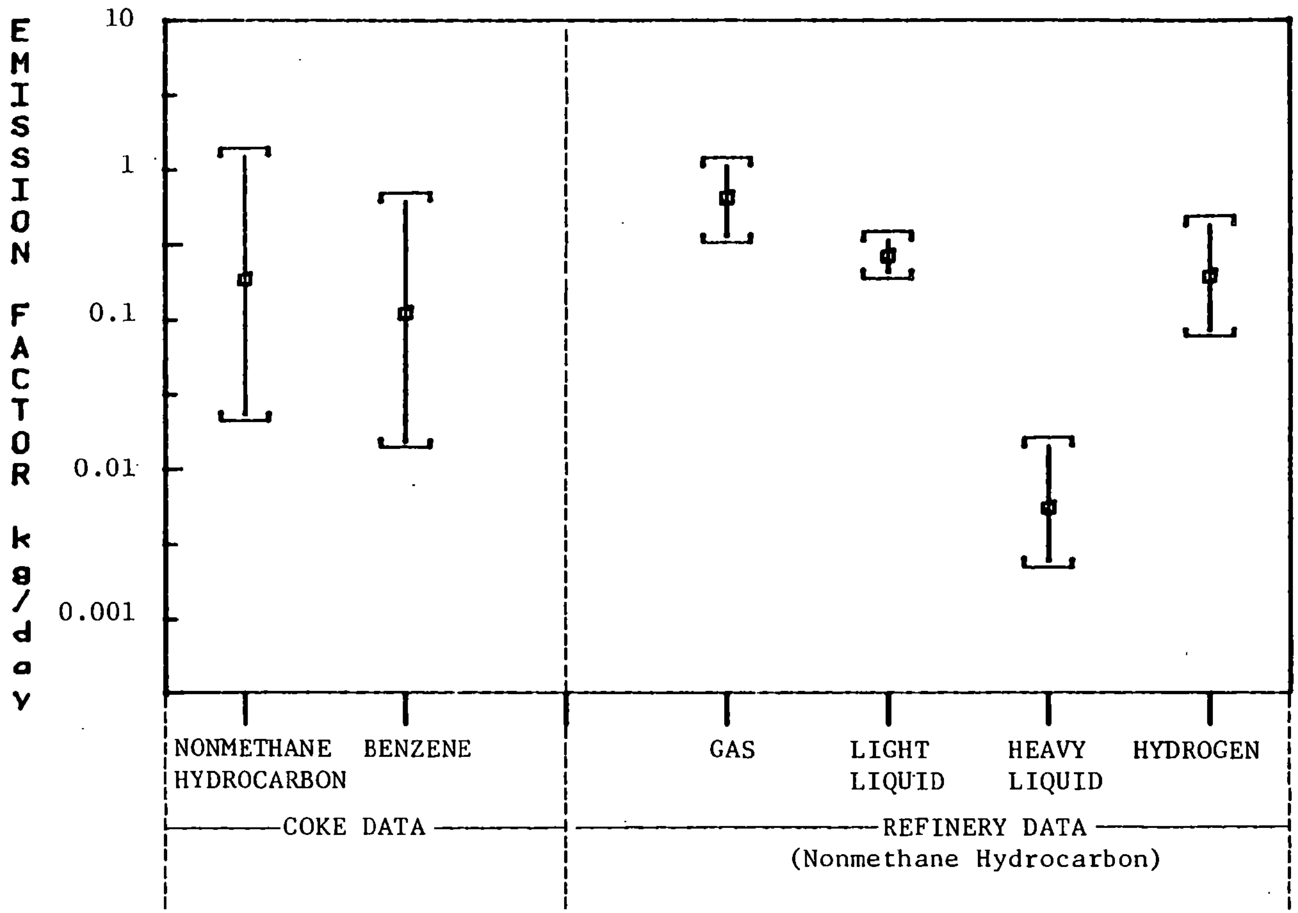
Empirical relationships between instrument screening value and total (vapor plus liquid) leak rate were developed from the data for valves, exhausters and pump seals. The relationships for total nonmethane leak rate are presented graphically on arithmetic scales in Figures 2-6 through 2-12 for both OVA and TLV Sniffer instrument screening values. The same relationships are presented on logarithmic scales in Appendix B. Similar graphs for total benzene leak rate are given in Figures 2-13 through 2-19 and in Appendix B. Each figure also gives the parameters of the fitted equation used to develop the plot. Ninety-five percent confidence intervals for the predicted mean leak rate bound each curve. Sources screening at greater than or equal to 100,000 ppmv for the OVA instrument or greater than 10,000 ppmv for the TLV Sniffer were not included in developing the graphs (these values are the instrument scale maximum). Insufficient data were available to develop relationships for flanges and threaded fittings.

The relationship of total leak rate to instrument screening value are presented in tabular form in Appendix B. These tables also include individual leak rate confidence intervals. The mean leak rate confidence intervals, which are presented in Figures 2-6 through 2-19, apply to the estimated mean leak rate. There is 95 percent confidence that the actual mean leak rate for a particular screening value falls between the mean leak rate confidence limits. However, if a single source is to be screened and measured, the measured leak rate should fall within the broader individual leak rate confidence limits with 95 percent confidence.



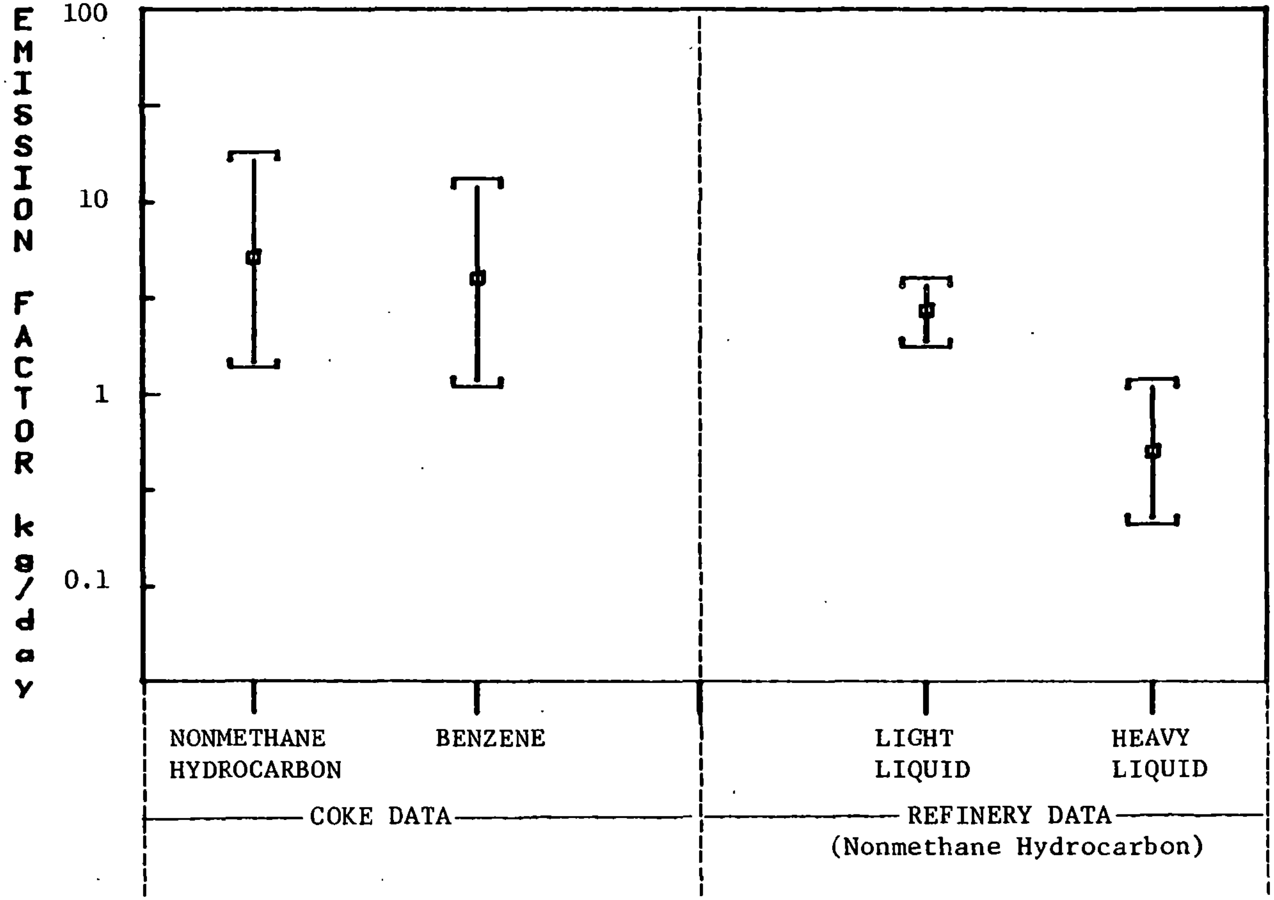
Bracketed intervals are 95% confidence intervals.

Figure 2-1. Emission factor comparison - coke (sources with ⩾ 10% benzene service) and refinery (all sources) -- Valves.



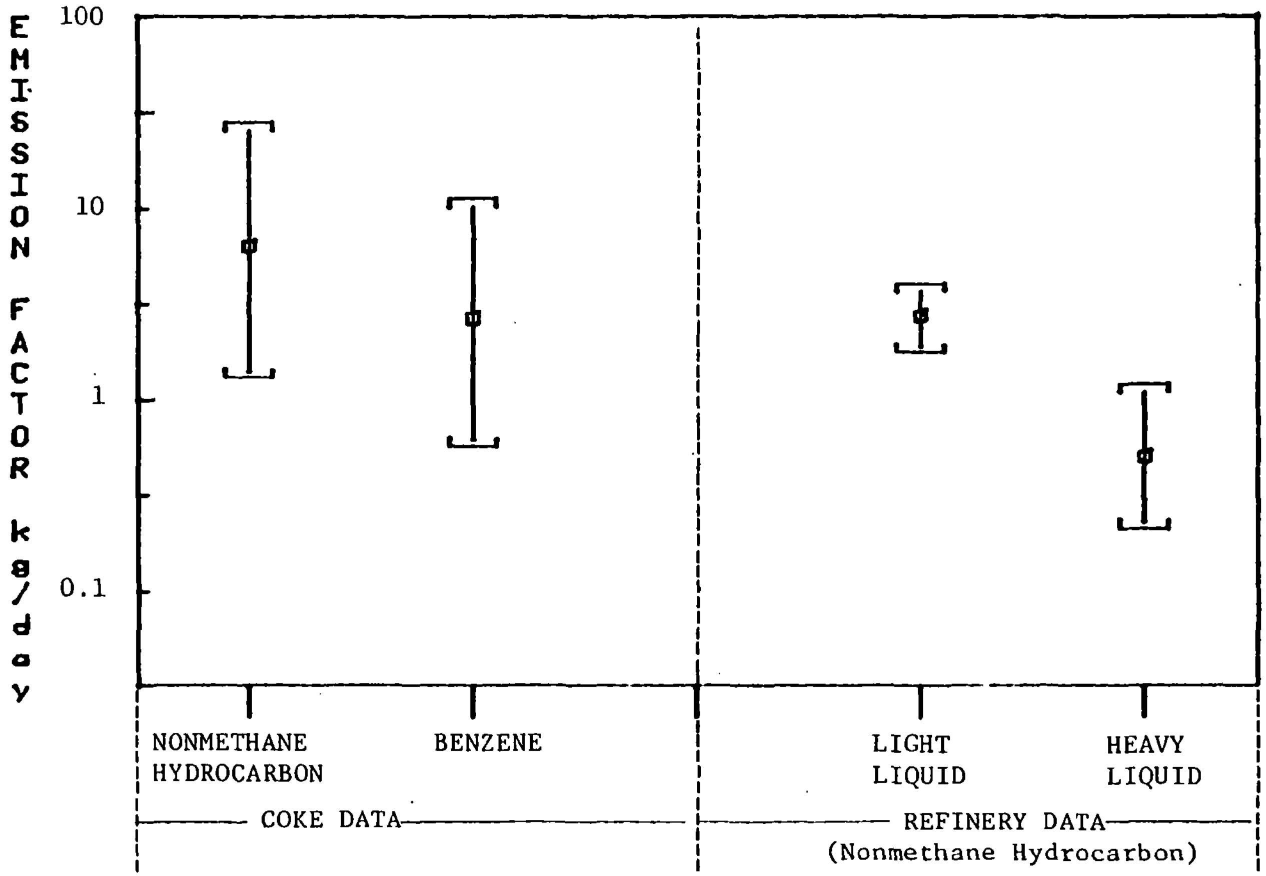
Bracketed intervals are 95% confidence intervals.

Figure 2-2. Emission factor comparison - coke (all sources) and refinery (all sources) -- Valves.



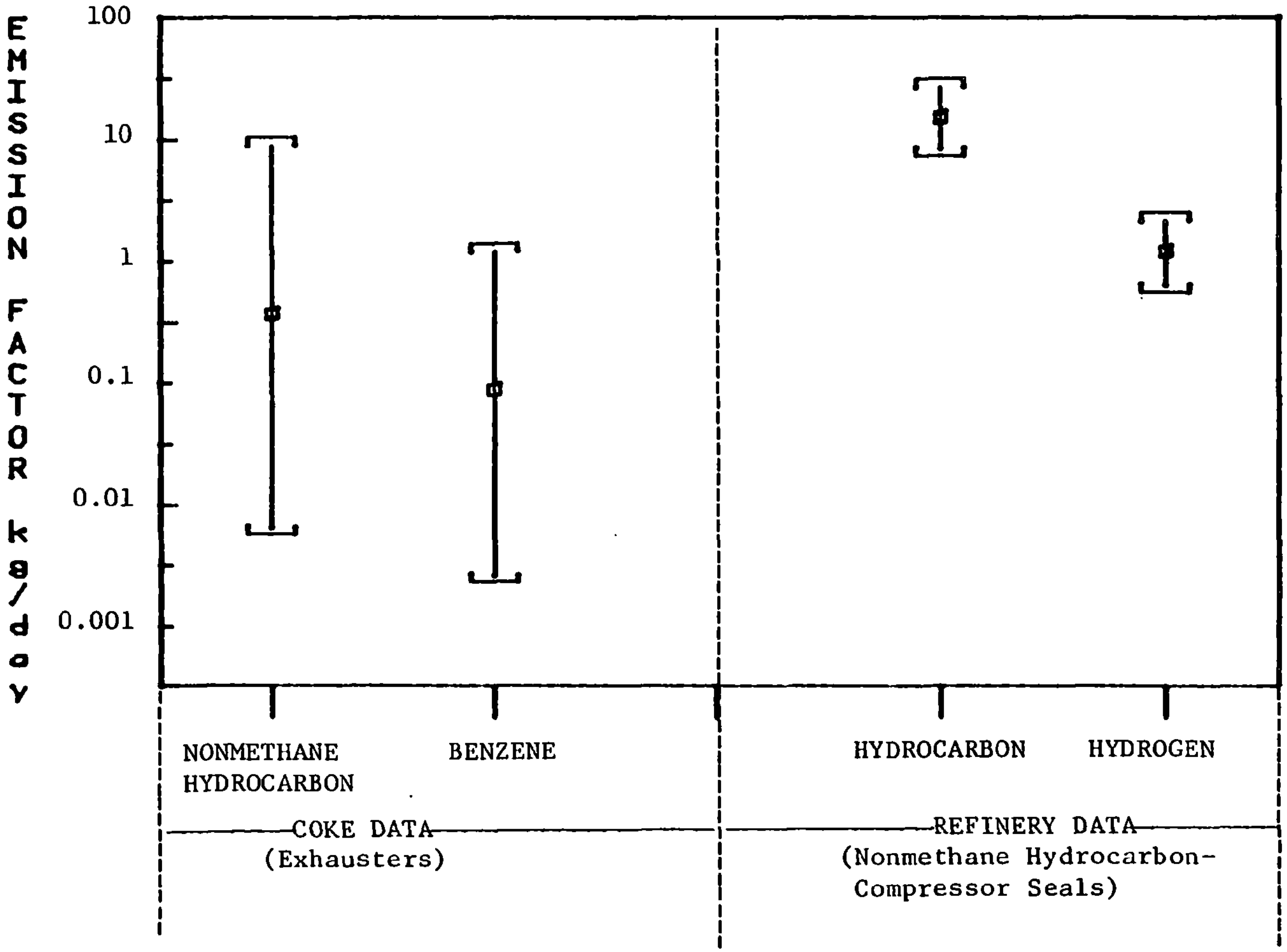
Bracketed intervals are 95% confidence intervals.

Figure 2-3. Emission factor comparison - coke (sources with ≥ 10% benzene service) and refinery (all sources) -- pump seals.



Bracketed intervals are 95% confidence intervals.

Figure 2-4. Emission factor comparison - coke (all sources) and refinery (all sources) -- pump seals.



Bracketed intervals are 95% confidence intervals.

Figure 2-5. Emission factor comparison - coke (exhausters) and refinery (compressor seals).

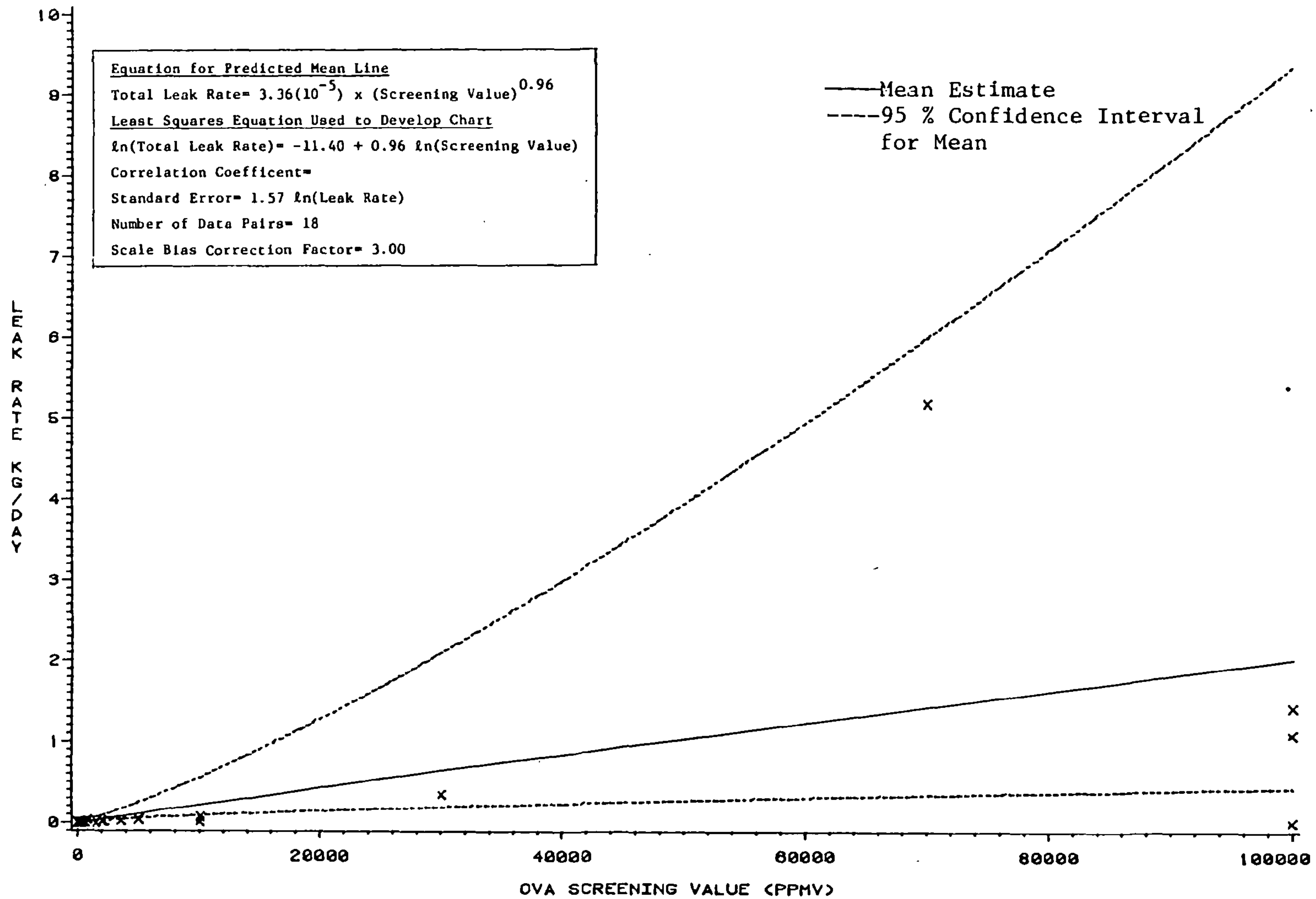


Figure 2-6. Nonmethane leak rate to OVA screening valve relationship - valves.

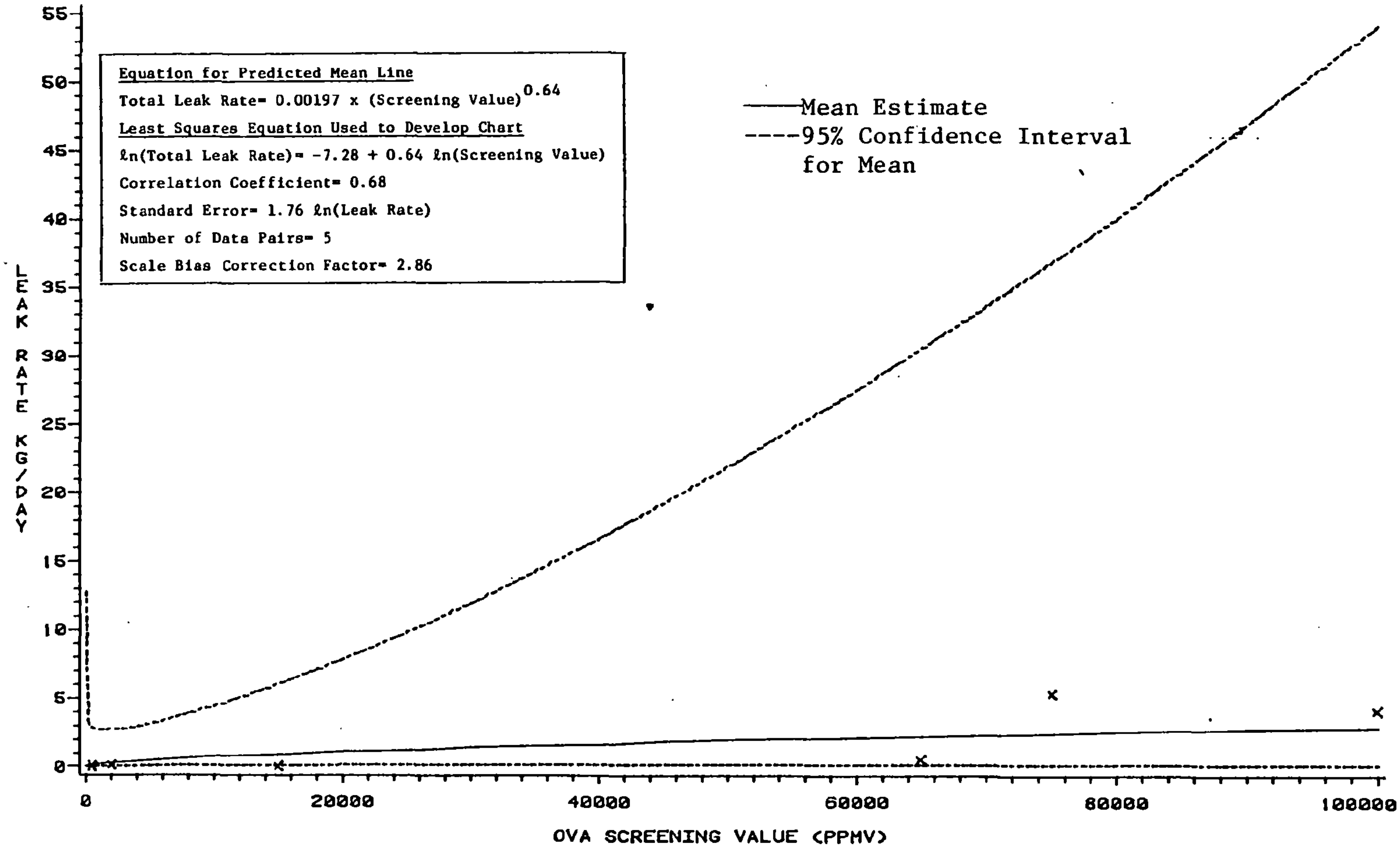


Figure 2-7. Nonmethane leak rate to OVA screening value - exhausters.

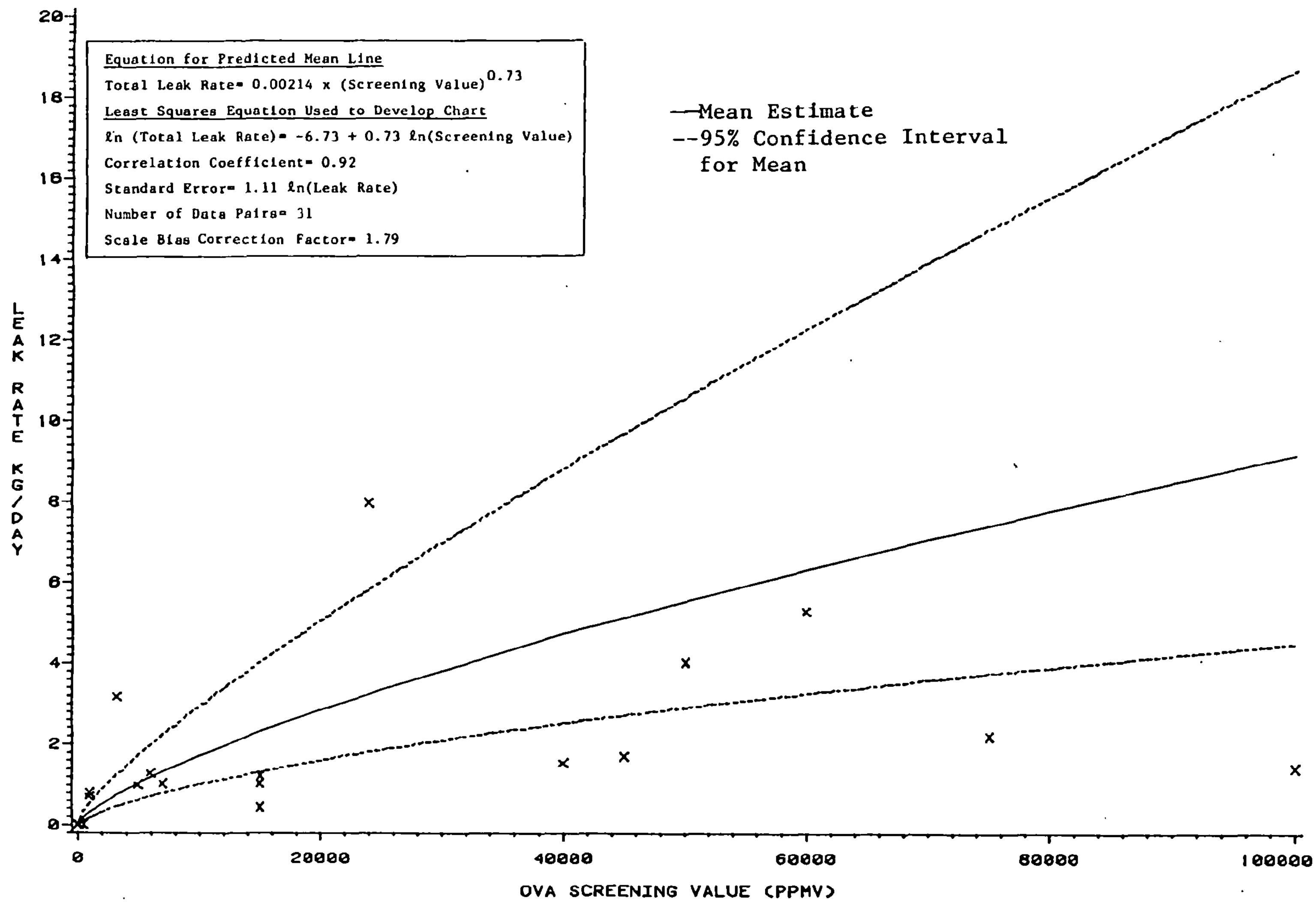


Figure 2-8. Nonmethane leak rate to OVA screening value relationship - pump seals (without liquid leakage).

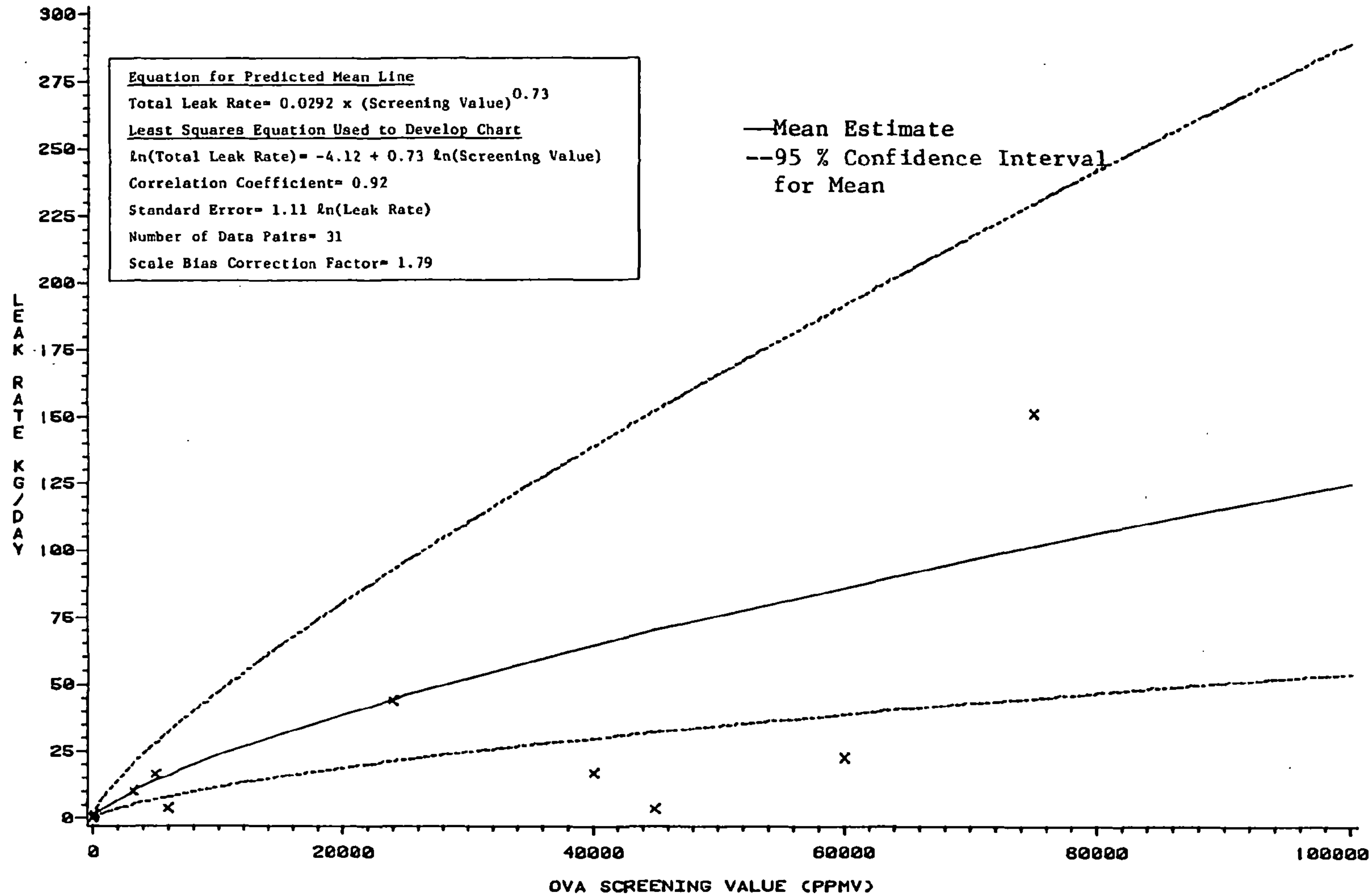


Figure 2-9. Nonmethane leak rate to OVA screening value relationship - pump seals (with liquid leakage).

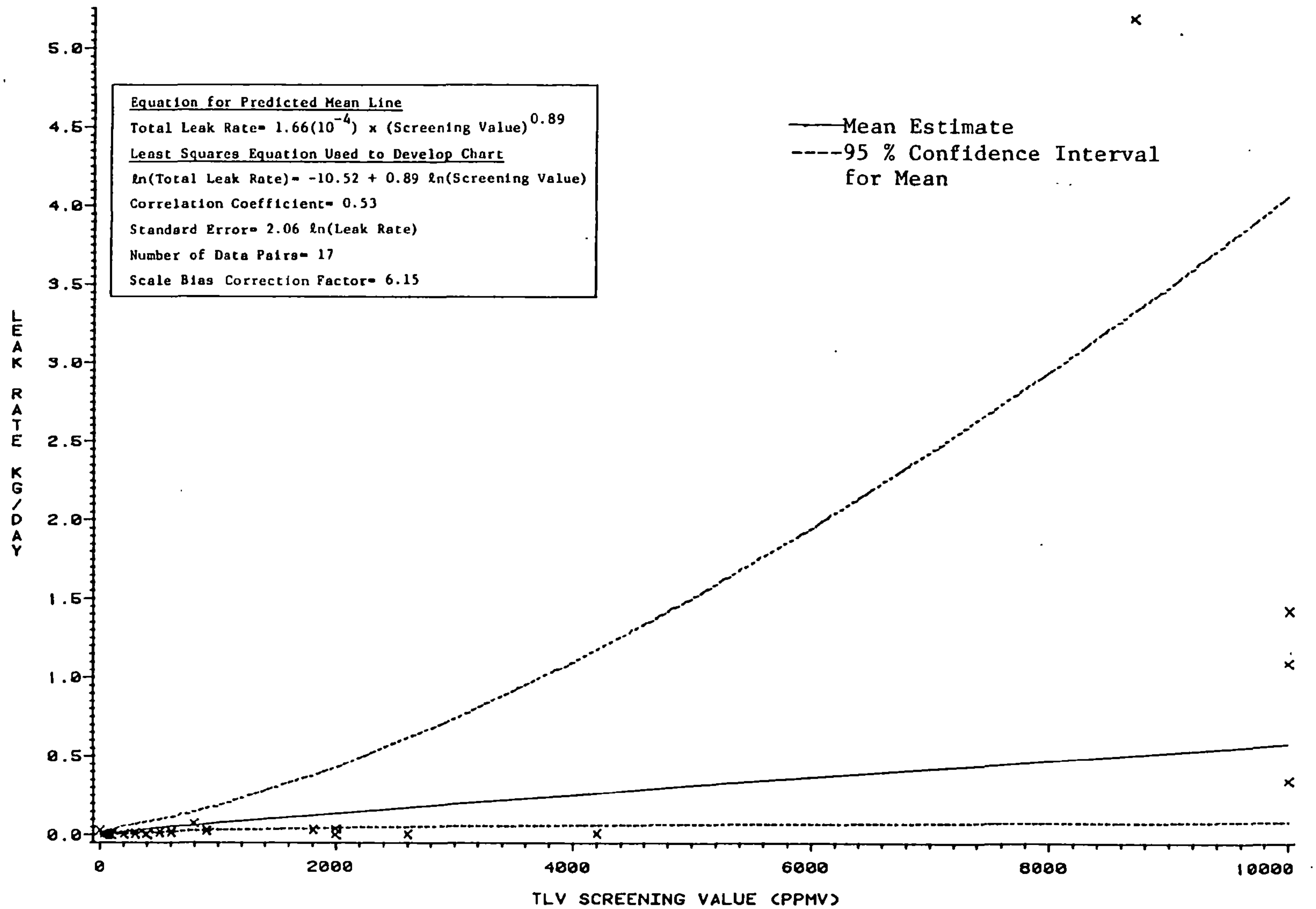


Figure 2-10. Nonmethane leak rate to TLV screening value relationship - valves.

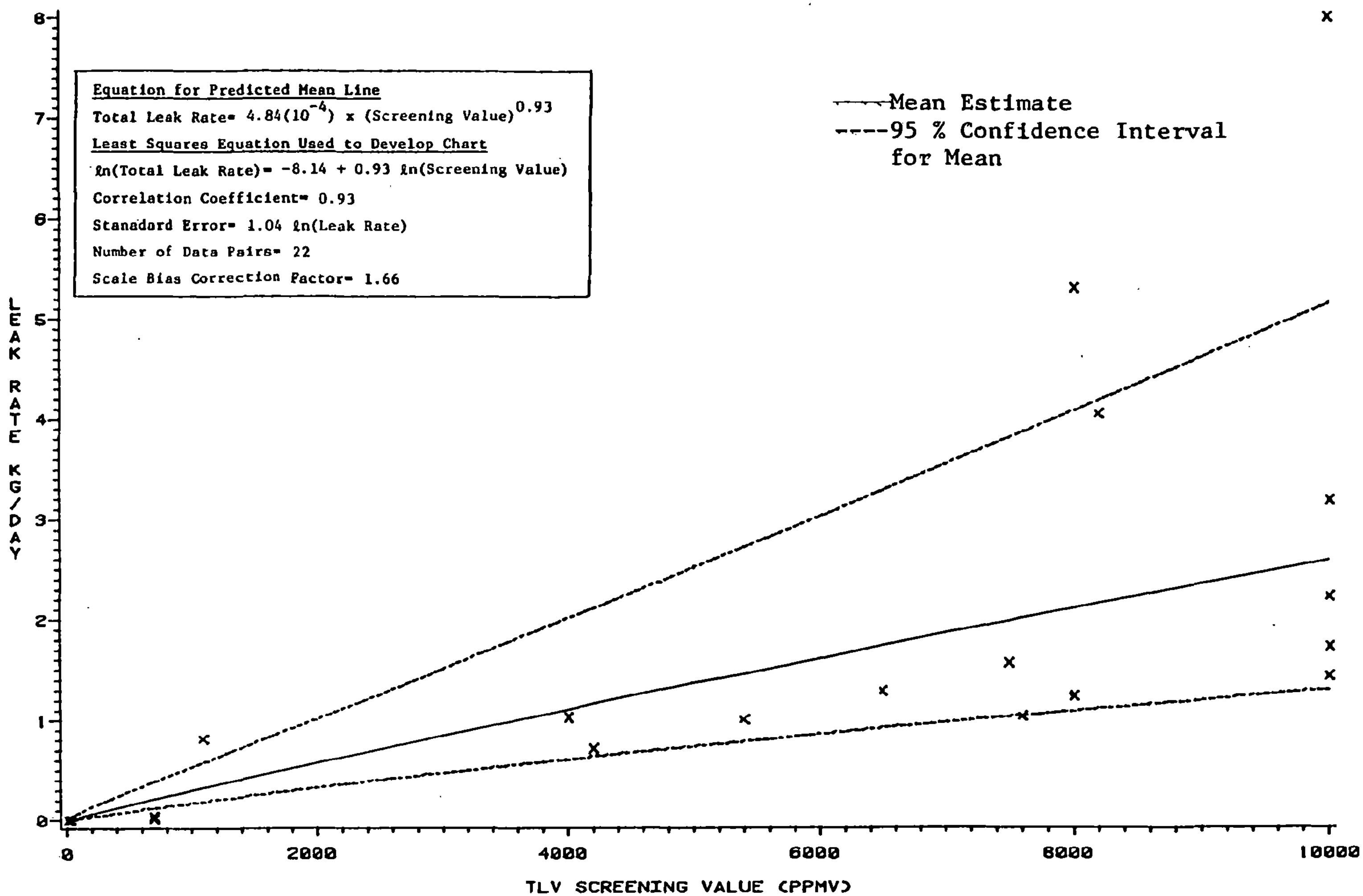


Figure 2-11. Nonmethane leak rate to TLV screening value relationship - pump seals (without liquid leakage).

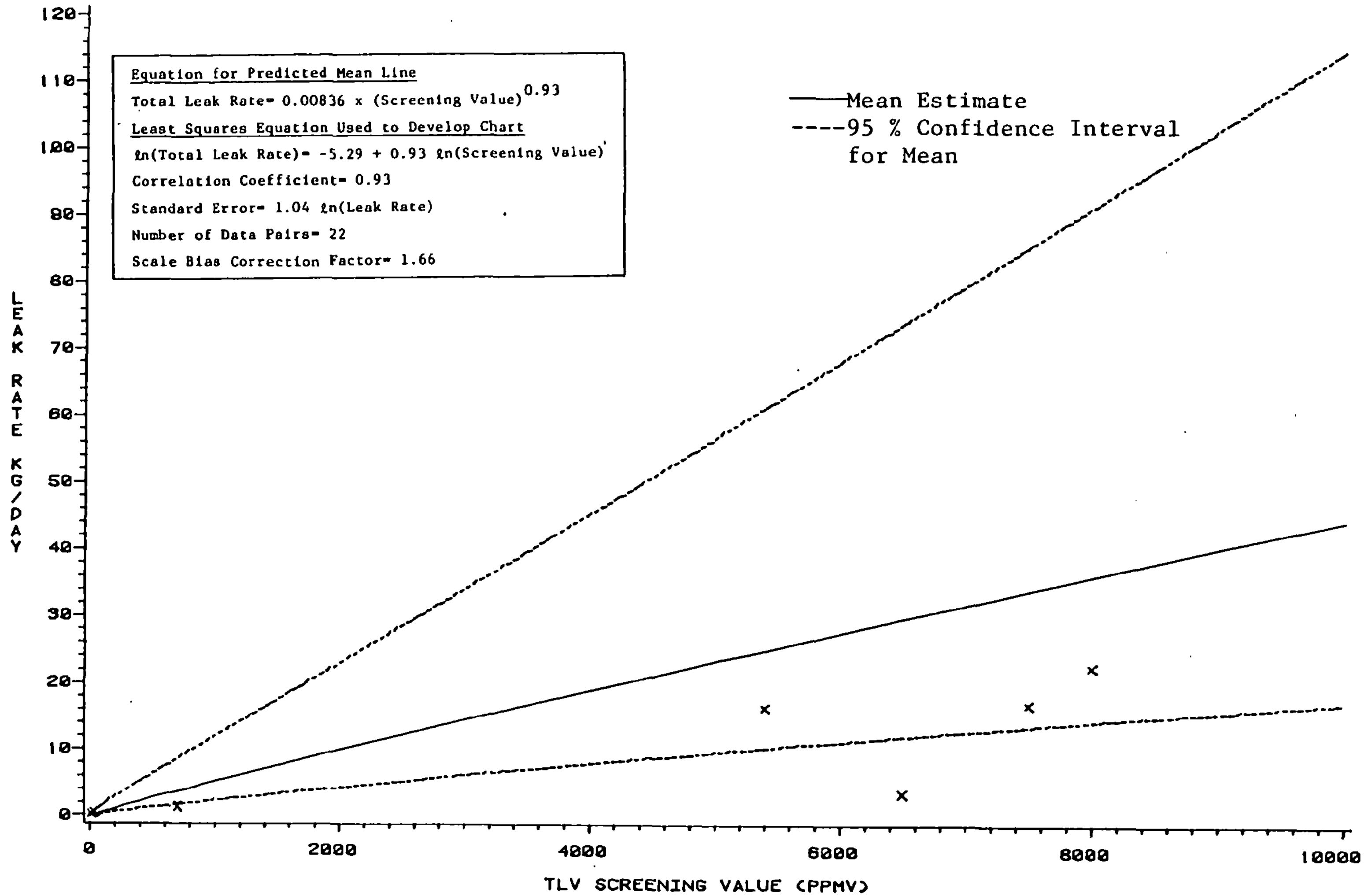


Figure 2-12. Nonmethane leak rate to TLV screening value relationship - pump seals (with liquid leakage).

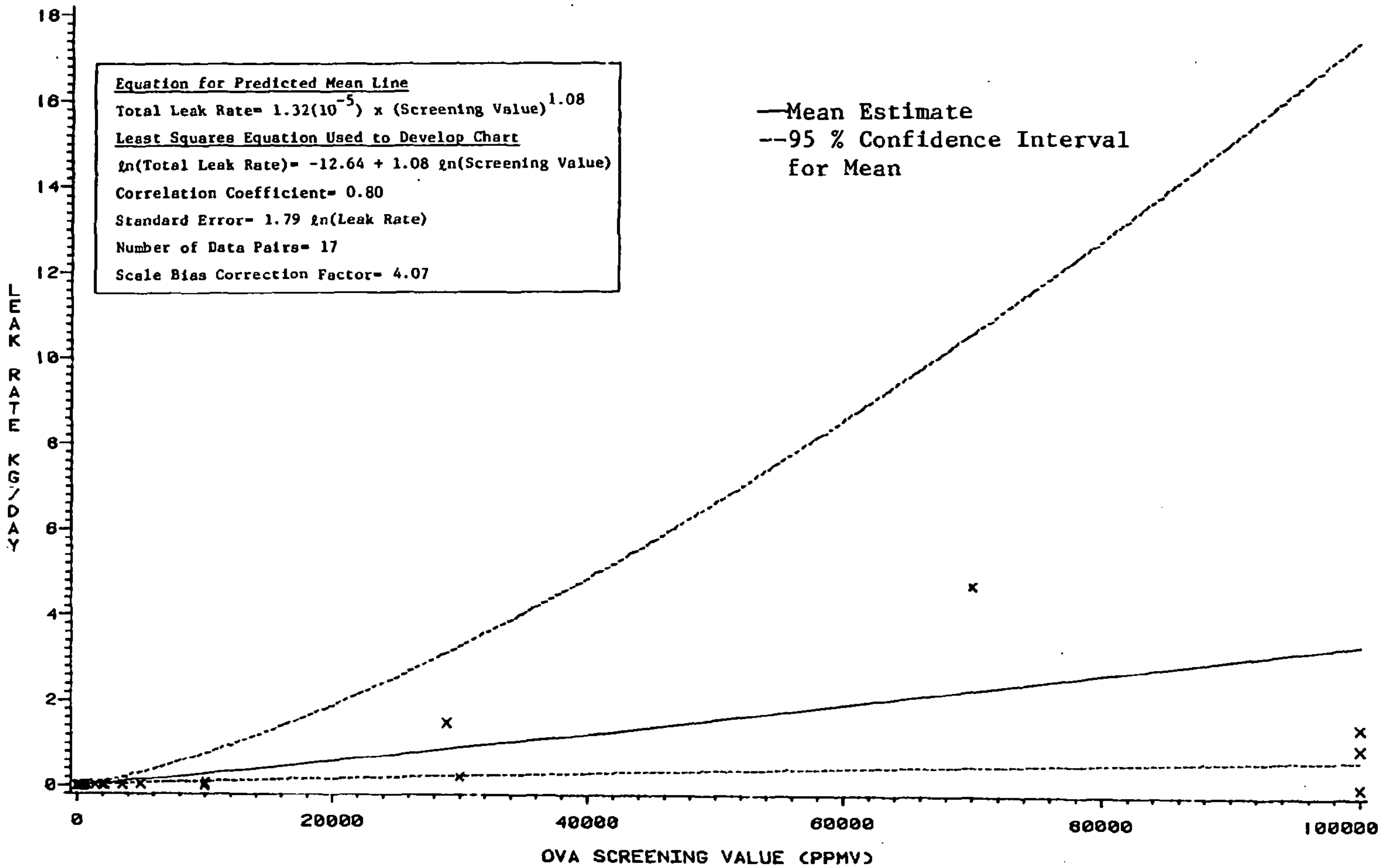


Figure 2-13. Benzene leak rate to OVA screening value relationship - valves.

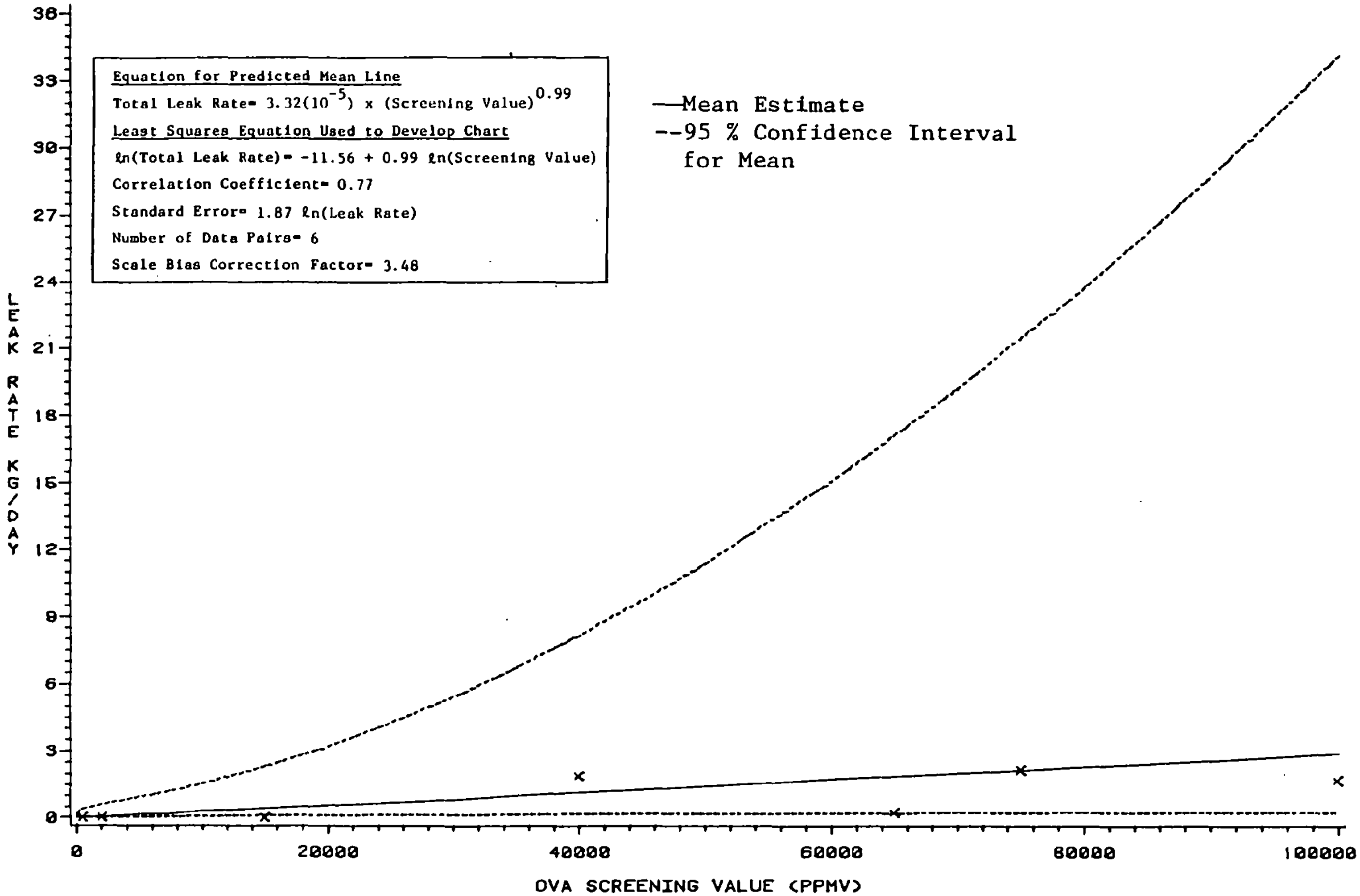


Figure 2-14. Benzene leak rate to OVA screening value relationship - exhausters.

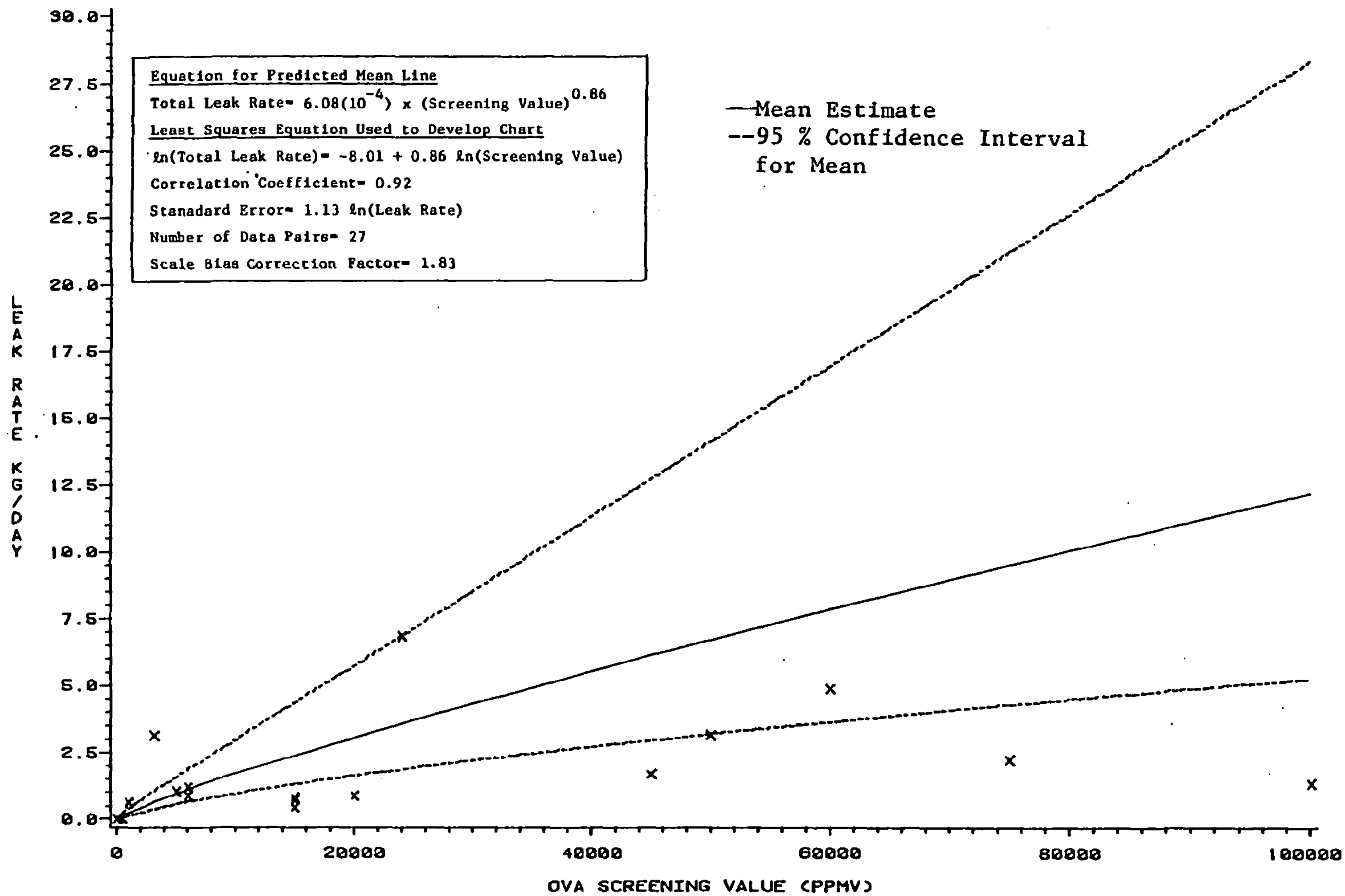


Figure 2-15. Benzene leak rate to OVA screening value relationship - pump seals (without liquid leakage).

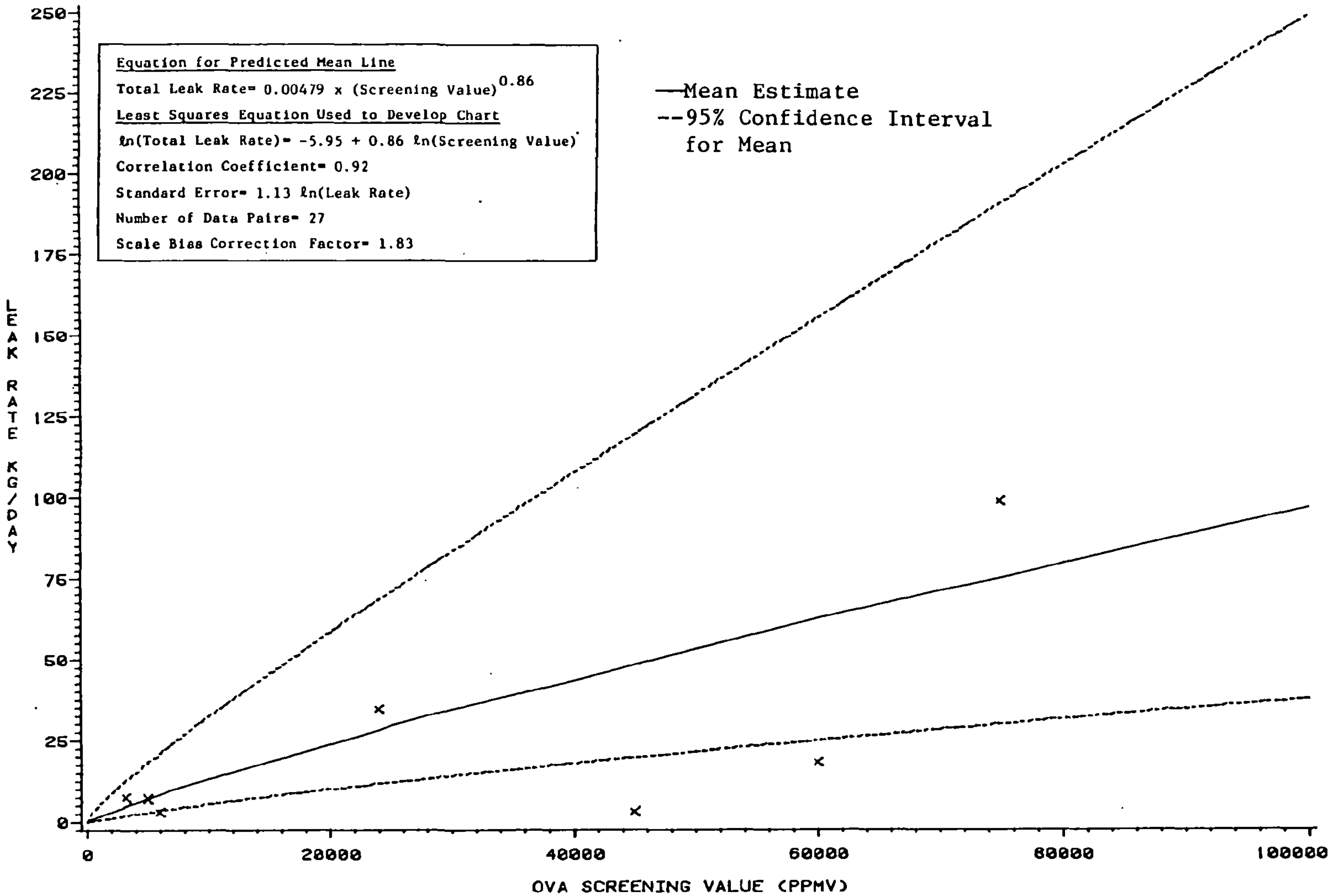


Figure 2-16. Benzene leak rate of OVA screening value relationship - pump seals (with liquid leakage).

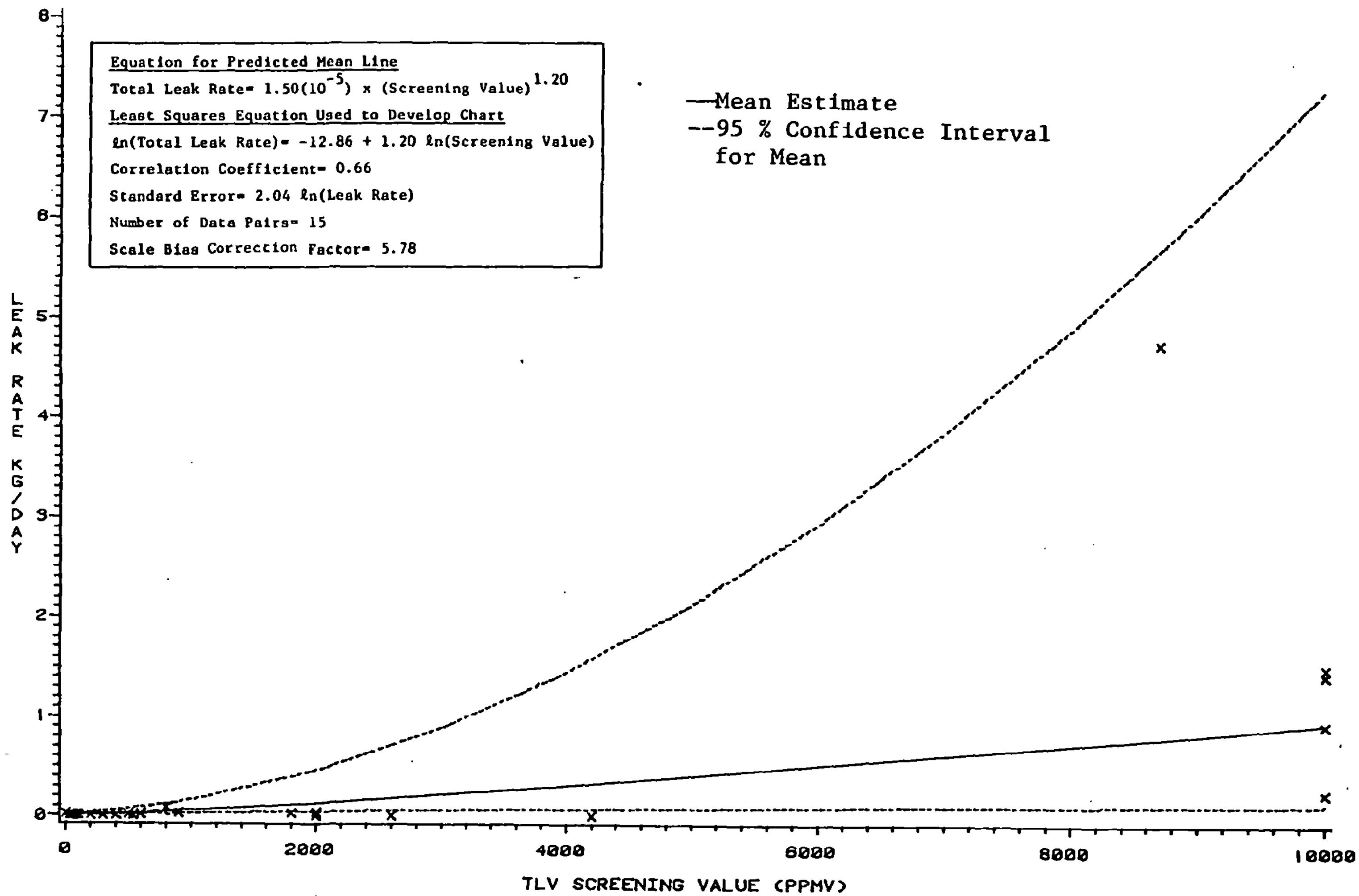


Figure 2-17. Benzene leak rate to TLV screening value relationship - valves.

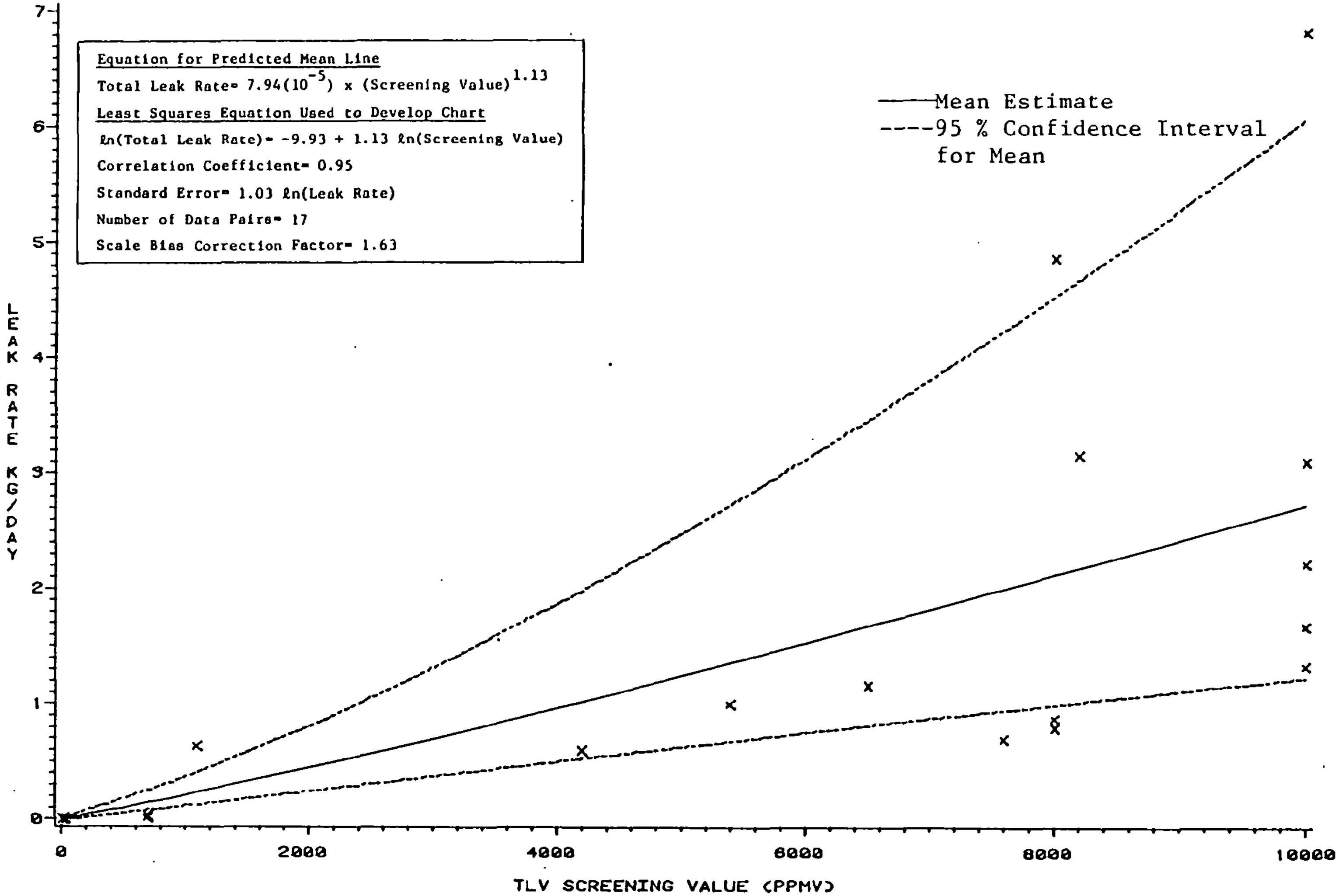


Figure 2-18. Benzene leak rate to TLV screening value relationship - pump seals (without liquid leakage).

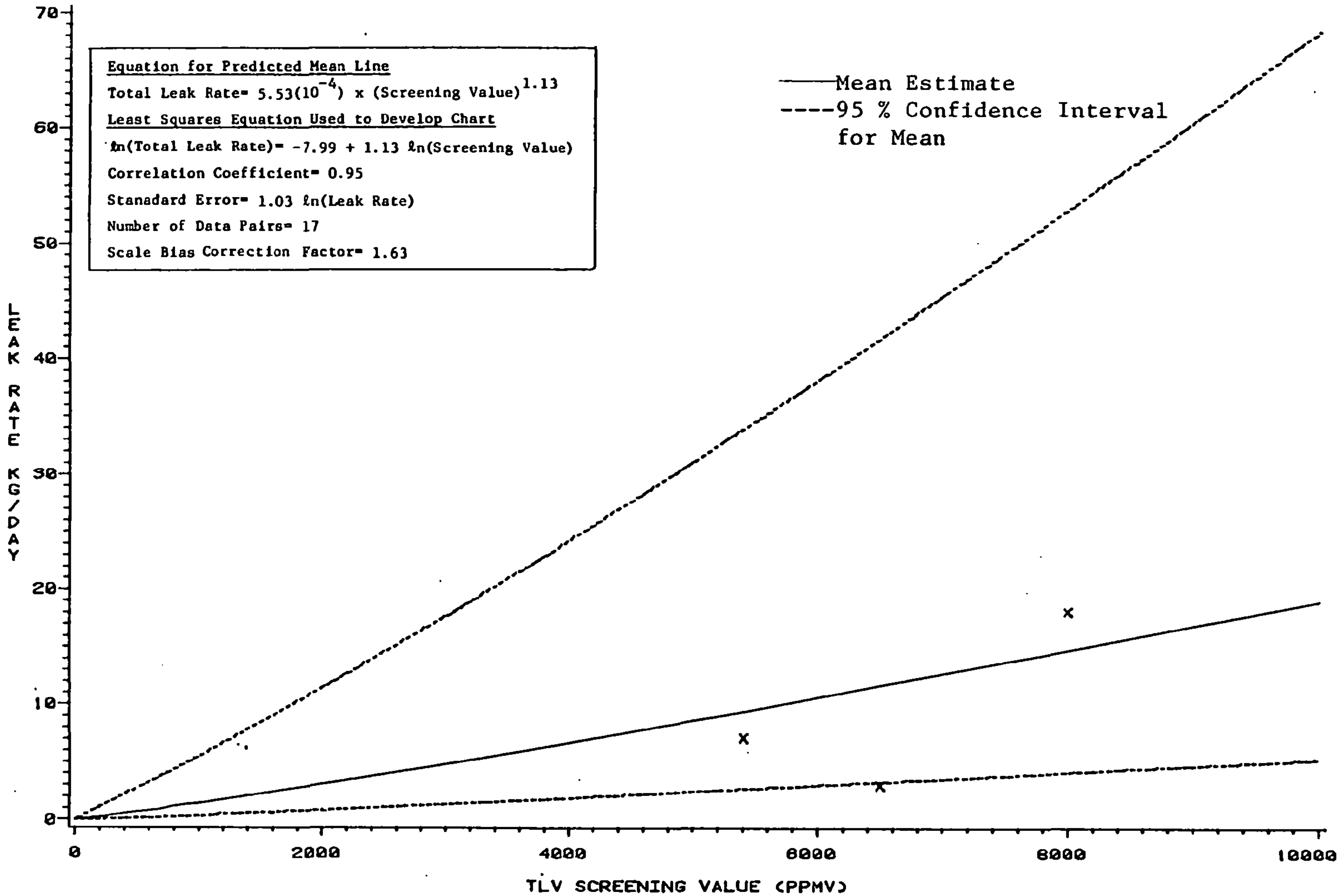


Figure 2-19. Benzene leak rate to TLV screening value relationship - pump seals (with liquid leakage).

SECTION 3

ESTIMATION METHODOLOGY

This section summarizes the methods used to compute the emission factors and prediction equations presented in Section 2. The mathematical details and background are discussed in Appendix A.

3.1 EMISSION FACTORS

In developing emission factors, sources were divided into three groups: sources identified as not emitting, emitting sources which were not measured,[1] and emitting sources that were measured. The emissions were detected with instrument screening and/or visual inspection. The data from measured sources was used to develop an empirical relationship between the screening valve and the nonmethane vapor leak rate. This relationship was then used to predict the nonmethane vapor leak rate for the unmeasured valves, pump seals and exhausters. Separate relationships were developed for the different source types.

After nonmethane vapor leak rates were predicted for the unmeasured sources, as described above, the benzene vapor leak rate was predicted using the relationship between nonmethane vapor leak rate and benzene vapor leak rate. For the several cases in which only the benzene vapor leak rate was measured, the nonmethane vapor leak rate was predicted using the relationship between benzene leak rate and nonmethane leak rate. One relationship was found to

[1] Almost all emitting sources were measured; however, the analysis of a few samples was incomplete or erroneous and emission rates for these sources were estimated.

adequately describe the emissions from all source types, but a second relationship was required for sources in coke oven gas service (see Table A-3).

Emission factors for total (vapor plus liquid) nonmethane hydrocarbon and benzene emissions were estimated from the combined measured and predicted leak rates. Because of the high degree of skewness in the distribution of total leak rates, a lognormal distribution was used to model the distribution of leaking sources. An evaluation of the transformed data based on tests of normality indicates that the data for most sources appeared to approximate a normal distribution.

The emission factor computed from emitting sources was adjusted to account for the non-emitting sources. This adjustment was made as a weighted average with the weights being the frequency of emitting and non-emitting sources. An "emitting" source is defined here as any source with a screening value greater than zero.

As described earlier, fitted regression equations were developed to estimate nonmethane vapor leak rate from instrument screening value for unmeasured valves, pump seals, and exhausters. Regression relationships between nonmethane vapor leak rate and instrument screening value were developed from measured sources. The equations were fitted to the data on a logarithmic scale. No relationship between instrument screening value and nonmethane vapor leak rate could be developed for flanges and threaded fittings due to insufficient data. Sources with instrument screening values of zero or measured leak rates of zero were treated as having zero emissions.

If the nonmethane vapor leak rate was not measured, but the benzene vapor leak rate was measured, then the nonmethane rate was estimated from the benzene rate using regression equations. Conversely, the benzene rate was estimated from the nonmethane rate, if measurements were available for the nonmethane but not the benzene. The regression equations were fitted on a logarithmic scale using measured source data using two product groupings.

Total (vapor plus liquid) emission factors were estimated from the combined measured (vapor and liquid) and estimated (vapor) leak rates. The estimated mean total leak rate for emitting sources was first computed (leak rates being averaged on a logarithmic scale). The average was converted to the arithmetic scale by exponentiation and multiplication by a transformation bias correction factor appropriate for the lognormal distribution. The estimated mean total leak rate for emitters was combined with the zero leak rate for nonemitters by a weighted average using the proportion of emitters and nonemitters respectively as weights. This final weighted average is the estimated emission factor per source.

3.2 SERVICE FACTORS

Four of the pump seals tested (sources 119-S and 120-S at Republic Steel and 333-Ø and 334-I at Bethlehem Steel) were on loading pumps that only operated intermittently, for an average of about one hour per day. These pump seals were tested while in operation, and the measured leak rates presented in Tables 2-2 and 2-3 are representative of the higher emissions during loading. Screening of the pumps during their idle periods indicated that the vapor leak rate was comparable to that under operating conditions. There was, however, significant liquid leakage during pump operation that stopped completely when it was idle. In computing the average daily emission factors for Table 2-4, the measured vapor leak rate was assumed to be constant, but the measured liquid leak rate was multiplied by a service factor of 0.042 (one hour of operation per 24 hour day) to account for the reduced emissions during the idle period.

3.3 RELATION OF TOTAL LEAK RATE TO INSTRUMENT SCREENING VALUE

The presented relationships between total (vapor plus liquid) leak rate and instrument screening value (Figures 2-6 through 2-19, Figures and Tables in Appendix B) were developed using regressing techniques on a logarithmic scale.

To investigate the relationship between instrument screening value and leak rate, a representative screening value was first chosen. Rescreening values for both the OVA and TLV Sniffer were taken before and after each source was sampled. In several cases the before and after leak measurement screening value was found to be significantly different. Since the effect (if any) of sampling a source immediately before taking an instrument screening reading is unknown, the screening reading before leak measurement was chosen as the representative instrument screening value and was used in the model development.

The logarithm of the total (vapor plus liquid) leak rate (nonmethane and benzene) was regressed on the logarithm of the instrument screening value (OVA and TLV Sniffer) for valves and exhausters -- a relationship between TLV instrument screening value and total leak rate could not be developed for exhausters due to insufficient data.

In order to model the relationship between total leak rate and instrument screening value for pump seals, an additional independent variable (indicating whether or not the source released liquid leakage) was included in the above-described regression equation. No relationship between instrument screening value and total leak rate could be developed for flanges and threaded fittings due to insufficient data.

Details of the model and the above described techniques are included in Appendix A.

SECTION 4

QUALITY CONTROL/QUALITY ASSURANCE

Quality control procedures were implemented to insure accurate, consistent, and unbiased techniques during the testing. These procedures included:

- calibration checks on screening instruments
- repeated screening of fittings
- analysis of blind gas and liquid standards
- accuracy checks on leak rate measurement
- analysis for interfering compounds.

The results for each of these are summarized in Table 4.1. The results are described more fully in Section 5 of each of the individual test reports.

An analysis of quality control data indicates that some error is introduced through screening, sampling, and analysis procedures. However, the cumulative error from sampling and analysis procedures is not the limiting factor with respect to the confidence intervals of emission factors. The variance component due to variations in sampling and analysis procedures is small compared to the variance component associated with variation between individual sources and day-to-day variation within one source. Based on this, it can be said that the precision of the sampling and analytical techniques is adequate to support the emission factors and other analyses.

TABLE 4-1. SUMMARY OF ACCURACY AND PRECISION OF SAMPLING AND ANALYSIS TECHNIQUES

	Screening
Accuracy	More than 50 percent of calibration checks were within ± 30 percent of the standard; however, approximately 20 percent of the differences found were greater than ± 100 percent of the known concentration. Consistent negative drifts were noted at the high level for both OVA devices.
Repeatability	Screening value for a given source with an average screening value of x can be expected to vary from x/7.4 to 7.4x within a short time period.
Percent of Variation in Data Attributable to Measurement	About 11 percent of the variability in the screening values from the selected sources with multiple readings can be attributed to the screening devices. More than 86 percent of the variation is attributable to differences between the sources.
	Sampling/Analysis
Accuracy	
Vapor Analysis	The average percent difference from standards for the two analytical systems used is -1.1 percent, indicating no significant bias in the analysis.
Liquid Analysis	The average percent difference from liquid standards for the analytical system used is 1.6 percent, indicating no significant bias in the analysis.
Sampling and Analysis	Average recovery for the benzene and hexane standards were 109 and 93 percent, respectively, indicating slight biases in the total sampling/analysis system.
Interfering Compounds	No compounds were found with the same retention time in the gas chromatograph as benzene.

4.1 CALIBRATION CHECKS ON SCREENING INSTRUMENTS

The OVA and TLV instruments were calibrated in the morning each day before they were used. The instruments were first tested on gas standards to check the calibration drift. These checks indicate that some significant drift did occur; however, other studies have shown that such drift often occurs after a prolonged shut-down. Thus, the over-night drift does not necessarily indicate that the previous day's screening results were inaccurate.

4.2 REPEATED SCREENING OF FITTINGS

Two valves and one pump seal were screened once in the morning and once in the afternoon for five days to determine the reproducibility of screening results. The variation in screening values was analyzed statistically to identify the most significant sources of variation. Table 4-2 summarizes the results of this variance analysis. About 87 percent of the variation is attributed to differences between sources, 11 percent to the screening devices and procedures, and 2.5 percent to the day-to-day variation in the source itself.

The variation from replicate screenings (variation in the screening value due to such factors as screening instruments and procedures) can be used to define the repeatability of the screening measurement. The variance component for replicate readings is 0.189 log $(ppmv)^2$, and this determines that the standard deviation between replicate readings of one source is 0.435 log (ppmv). This standard deviation means that a source with a mean screening value of x may have screening values ranging from x/7.4 to 7.4x with 95 percent confidence. For example, screening values from a source which has an average screening value of 8000 ppmv could be between 1081 ppmv and 59,200 ppmv, 95 percent of the time.

TABLE 4-2. VARIANCE COMPONENT ESTIMATES FOR OVA SCREENING MEASUREMENTS ON SOURCES

	Log_{10} (Screening Value)		
Source of Variation	Degrees of Freedom	Variance Component Estimate $Log_{10}(ppmv)^2$	Percent Of Total Variation In Screening Values
Total Variation	29	1.778	100
Variation Between Individual Sources	2	1.544	86.9
Day-to-Day Variation (within a source)	12	0.045	2.5
Variation From Replicate Screenings	15	0.189	10.6

4.3 ANALYSIS OF BLIND GAS AND LIQUID STANDARDS

Gas and liquid standards were prepared and submitted to the analysts, without divulging the composition, to evaluate the quality of the analytical data. Gaseous hexane standards were used to evaluate the precision of the data for nonmethane hydrocarbons as determined by a Total Hydrocarbon Analyzer. Similarly, gaseous and liquid benzene standards were used to check the precision of the benzene analysis of gas and liquid samples by gas chromatograph. The results of the analyses were an average of -1.1 percent different from the standards for vapor analysis, and 1.6 percent different from the standards for liquid analysis.

4.4 ACCURACY CHECKS

Accuracy checks were used to evaluate the overall accuracy of the sampling and analysis techniques. The checks basically involve inducing a known flow rate of a concentrated calibration gas, and then measuring this simulated leak rate by the same techniques used to measure the leak rates from fittings. Comparison of the measured leak rate with the known leak rate indicates that the average recovery of the benzene and hexane standards were 109 and 93 percent, respectively. These values indicate an acceptable accuracy level for the overall sampling and analysis effort.

4.5 INTERFERING COMPOUNDS

Liquid samples were selected from each plant for analysis by gas chromatograph/mass spectrometer (GC/MS). GC/MS would detect any compounds with the same retention time on gas chromatograph as benzene, that might interfere with the benzene analysis. No such compounds were detected in the samples from coke by-products plants.