COMPARISON BETWEEN AIR POLLUTION LEVELS CAUSED BY CARS OPERATING ON TML AND TEL GASOLINES

by

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1. Summary

As part of the over-all evaluation of tetramethyl lead as a gasoline antiknock additive (TML), the lead content of the air in and around foreign-make cars operating on fuels containing identical quantities of lead as TML or TEL was measured.

The data were obtained simultaneously on the same makes and models of cars during the same driving cycle thus permitting a direct comparison to be made between TML- and TEL-induced lead contamination in the air. Results represent lead in air values inside the car, under the hood, general area behind the car and the exhaust gases. Statistical treatment of the data showed no significant difference between the atmospheric lead levels obtained from the combustion of TML- or TEL-containing gasoline.

2. Introduction

The health aspects of exposures to tetraethyl lead (TEL) have been studied in considerable detail over the years in which this compound has been used extensively as an antiknock additive in gasoline. These studies have shown that no hazards to health need exist where recommended control procedures are conscientiously observed. However, all alkyl lead compounds are generally accorded a high degree of toxicity, so the proposed use of the more highly volatile tetramethyl lead (TML) as a substitute for or in addition to TEL in gasolines necessitated a study of potential health implications that might be associated with it.

One important factor that needed to be determined was the quantitative difference, if any, between the lead content found in the atmosphere in and around automobiles burning fuel containing TML and that released into the air by automobiles operating on fuel containing TEL.

The following atmospheres were sampled: (1) exhaust gases, (2) air directly above the engine with the hood closed, (3) in-car air at the driver's seat at breathing zone height, and (4) air in the general area, four feet behind the car at breathing zone height.

3. Methods

Four pairs of foreign cars were used in the test which was conducted during the period February through March 1960. The vehicles are listed in Table 1

Table 1

Make	Model	Engine Location	Manufactured In
English Ford	Anglia	front	England
Volkswagen	Sedan	rear	Germany
Renault	Dauphine	rear	France
Fiat	1200	front	Italy

The cars were operated on the Mileage Accumulation Dynamometers (MAD) at the Esso Research Center in accordance with a schedule which simulated as closely as possible actual driving conditions in Europe. Some compromises were made because, due to the manual transmission in each car, low engine speed operation had to be manually controlled (idle and 1000 rpm). For the greater part of the test, cars were operated automatically in high gear by electronic programming on the MAD unit. This operation permits frequent changes in throttle position in high gear to simulate changes of speed on the road. For the manually controlled part of the test, mileage was accumulated at constant engine speed. Table 2 outlines the car operation schedule.

Table 2

Car Operation Schedule

Schedule Length - 8 Hours (5 Cycles)

		Total Time Per Cycle - Minutes			
Cycle Number:		1, 2, and 3	4	5	Car Operation
Engine RPM	Gear				
500	Neutral	10	5	Shut	Manual
1000	Top less 1	20	10	Down	Manual
2000	Top	20(1)	10	One	Tape
3000	Top	40(1)	20	Hour	Tape
3500	Top	30(1)	15		Tape

(1) Car operation in top gear controlled by electronic tape. RPM will cycle between indicated speeds during the test with time at each rpm totaling indicated time.

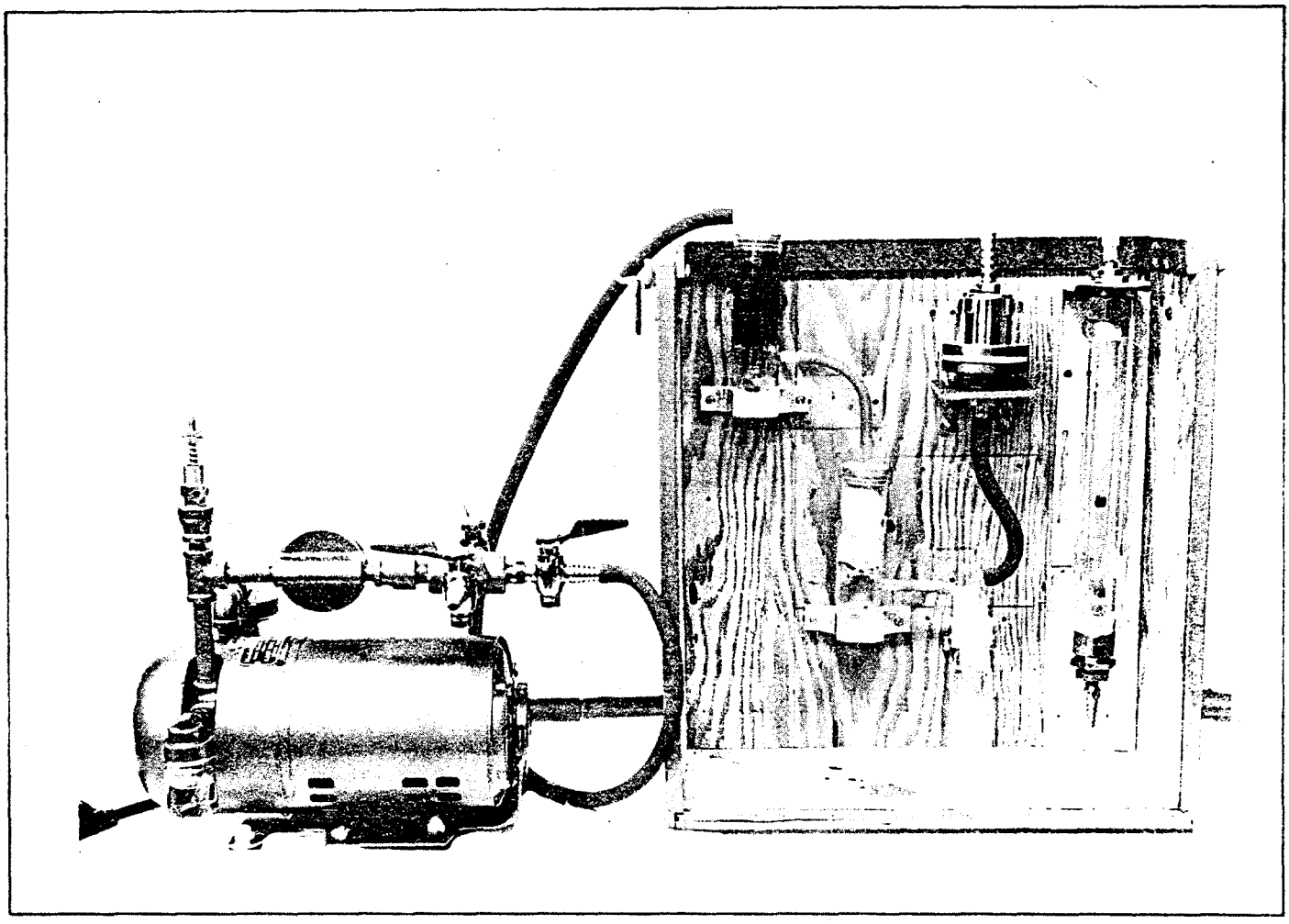
A. Sampling Procedure

The sampler was designed to separate organic from inorganic lead, thus permitting the determination of both forms of lead in the air sampled. This equipment is shown in Figure 1.

The sampling scheme is simply to meter the total flow with some suitable device, like the rotameter shown. The particulate matter in the air containing inorganic lead is filtered on molecular sieve filter paper in a filter holder assembly. The air then bubbles through a collecting solution in an impinger designed for a maximum flow of 14 liters per minute. This impinger contains a solution of KI-I_2 which is a highly efficient medium for capturing organic lead vapor. The air stream is then passed through

Figure 1

SAMPLING EQUIPMENT



THE VACUUM PUMP DRAWS A SAMPLE THROUGH A ROTAMETER, A FILTER ASSEMBLY TO COLLECT INORGANIC LEAD, AN ABSORPTION BUBBLER TO COLLECT ORGANIC LEAD, AND A DISENGAGING TRAP AND CHARCOAL ABSORBER TO PROTECT THE PUMP FROM CORROSIVE VAPOR.

glasswool and activated charcoal in separate traps to protect the pump from the corrosive effects of iondine vapor carryover.

In practice, when sampling the exhaust gases, condensation in the rotameter made accurate flow measurement difficult. In its place, a 10 liter per minute critical nozzle was placed between the collection devices and the pump. Sample times were varied from ten minutes to over two hours, primarily to collect enough organic lead for accurate analysis. For high flow rates, or where condensation is not a problem, the rotameter is more desirable than the critical orifice, mainly because of its lower pressure loss.

The exhaust samples were obtained from stacks located near the cars. The exhaust from each car was directed into an oversized flexible duct which was connected to the base of a stack. Lead contents found in the stack may not truly represent lead concentration in the exhaust gas because of deposition and dilution in the connecting system, but they serve as good approximations for the purpose of this study.

B. Analytical Procedure

Inorganic lead on the filter paper was analyzed by a procedure developed at Esso Research and Engineering Company.[1] The principle of this method involves heating the sample with nitric and sulfuric acids to destroy all organics and changing the metallic elements to the corresponding sulfates. Lead is then extracted with a chloroform solution of dithizone forming the color complex, lead dithizonate. By comparing the color intensity of the sample with that of the series of standards, the lead content of the sample can be determined. The precision of the method is of the order of $\pm$ 0.4 micrograms of lead.

Organic lead collected in the KI-I_2 bubblers was analyzed by a colorimetric procedure developed by Snyder.[2] The bubbler solution pH is adjusted to 11.0 and the unreacted iodine is reduced with 30 ml of an ammoniacal solution containing 10 gms potassium cyanide, 100 gms sodium sulfite, 20 gms ammonium citrate, 550 ml distilled water, and 1,950 ml ammonium hydroxide. The lead is then extracted with a chloroform solution of dithizone forming the color complex, lead dithizonate. The color developed (varies from colorless to cherry red) is compared with previously developed color standards to indicate the total quantity of organic lead collected. The precision of the method is reported to be $\pm$ 0.5 micrograms of lead in low concentrations and $\pm$ 10% for high concentrations.

4. Observations

Samples were taken at random intervals during the car operation cycle. In Tables 3, 4, and 5, adjacent data in the TEL and TML columns, under each sample location heading, were obtained simultaneously.

Table 3

ORGANIC LEAD, microg/cu.m

Engine Location		Exhaust Gas TML	Exhaust Gas TEL	Air Under Hood TML	Air Under Hood TEL	Breathing Zone: Drivers Seat TML	Drivers Seat TEL	Breathing Zone: 4' Behind Car TML	4' Behind Car TEL
	Front	-	480	27	80	11	6		
		80*	80	31	21	4	7		
		80	60	9	15	2	4		
		920	1540					9	93
								8	8
	Rear	430	57	27	40			6	6
		670	100	31	120				
		530	530	13	27				

*Estimated

Table 4

INORGANIC LEAD, microg/cu.m.

Engine Location		Exhaust Gas TML	Exhaust Gas TEL	Air Under Hood TML	Air Under Hood TEL	Breathing Zone: Drivers Seat TML	Drivers Seat TEL	Breathing Zone: 4' Behind Car TML	4' Behind Car TEL
	Front	-	1720	3	7	96	6		
		1870	2670	8	13	22	7		
		4270	4130	6	3	6	3		
		2400	6620					35	20
								12	14
	Rear	8190	3980	20	17			10	6
		3440	1330	90	18				
		4300	3100	50	57				

Table 5

TOTAL LEAD, microg/cu.m

Engine Location		Exhaust Gas TML	Exhaust Gas TEL	Air Under Hood TML	Air Under Hood TEL	Breathing Zone: Drivers Seat TML	Drivers Seat TEL	Breathing Zone: 4' Behind Car TML	4' Behind Car TEL
	Front	-	2200	30	87	107	12		
		1950	2750	39	34	26	14		
		4350	4190	15	18	8	7		
		3320	8160					44	113
								20	22
	Rear	8620	4037	47	57			16	12
		4110	1430	121	138				
		4830	3630	63	84				

Comparison of absolute levels obtained within each sub-grouping (e.g., exhaust-front engine) was not possible because of (1) the wide difference in variance between the TML and TEL data within each sub-grouping, and (2) the limited number of data points. It is believed that high levels obtained within each sub-group cannot be discounted in an attempt to normalize the data. Culling of these peaks might lead to erroneous conclusions. Many more test points would be necessary to define the model accurately, if in fact this is felt to be necessary.

Grouping of all the data for testing as a population of TML or TEL values was then done. The frequency distribution of the aggregate data for both TML and TEL gasolines was highly skewed toward the higher concentrations. This is to be expected since no concentration can fall below 0 and much of the data is near this lower limit.

The data from Tables 3 and 4 were plotted on logarithmic frequency distribution paper as shown in Figures 2 and 3. The similarity of the distributions obtained for both TEL- and TML-fueled cars is easily seen. To compare the curves shown in these figures, the lead concentrations at the deciles were plotted against statistical deviation expected from a normal distribution at the deciles. The comparison curves are shown in Figure 4. The two curves have a maximum spread of only about 0.1 standard deviations. With such similarity in the distribution of the aggregate data, it is appropriate to use nonparametric evaluations for further comparison testing.

The sampling design and technique employed tended to eliminate car operation as a variable because of the fact that samples were taken during identical operating cycles for both cars. With this approach in mind, the best measure of whether or not the TML-fueled cars were producing more air pollution would be a differential analysis of Tables 3, 4 and 5. That is, one should consider the differences between TML-produced values and the TEL levels, and not the absolute values obtained. The composite Table 6 shows these differential levels:

Table 6

DIFFERENTIAL LEAD, microg/cu.m
(Lead in Air from TML Fuel Minus that from TEL Fuel)

		Exhaust Gas			Under Hood			Breathing Zone: Drivers Seat			Breathing Zone: 4' Behind Car		
		Org.	Inorg.	Total	Org.	Inorg.	Total	Org.	Inorg.	Total	Org.	Inorg.	Total
Engine Location	Front	0*	- 800	- 800	-53	-4	-57	5	90	95			
		20	140	160	10	-5	5	-3	15	12			
		-620	-4220	-4840	- 6	3	- 3	-2	3	1	-84	15	-69
											0	- 2	- 2
	Rear	373	4210	4583	-13	3	-10				0	4	4
		570	2110	2680	-89	72	-17						
		0	1200	1200	-14	-7	-21						

*Estimated

Figure 2

FREQUENCY DISTRIBUTION OF ORGANIC AND INORGANIC LEAD IN AIR FROM TML-FUELED CARS

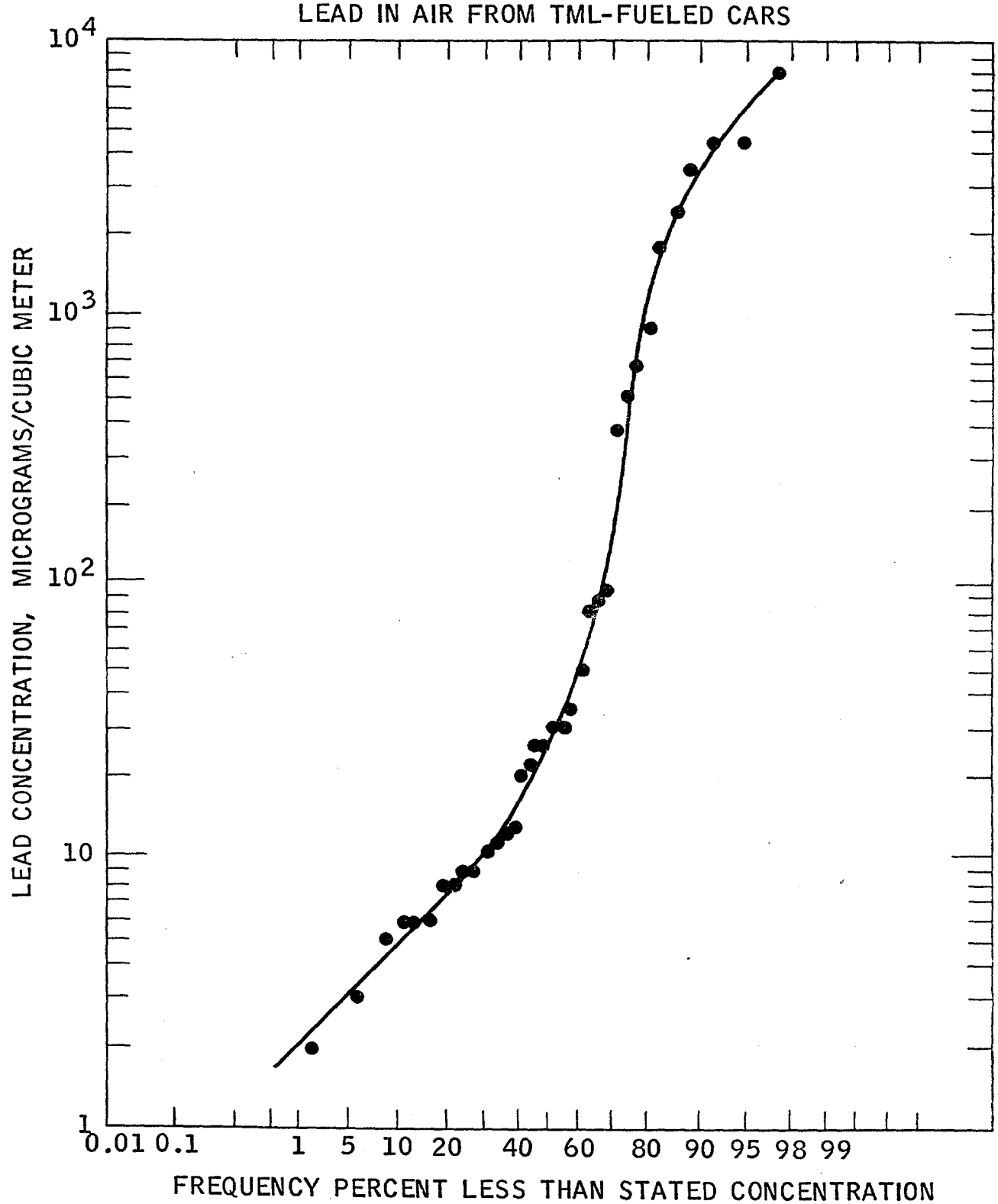


Figure 3

FREQUENCY DISTRIBUTION OF ORGANIC AND INORGANIC LEAD IN AIR FROM TEL-FUELED CARS

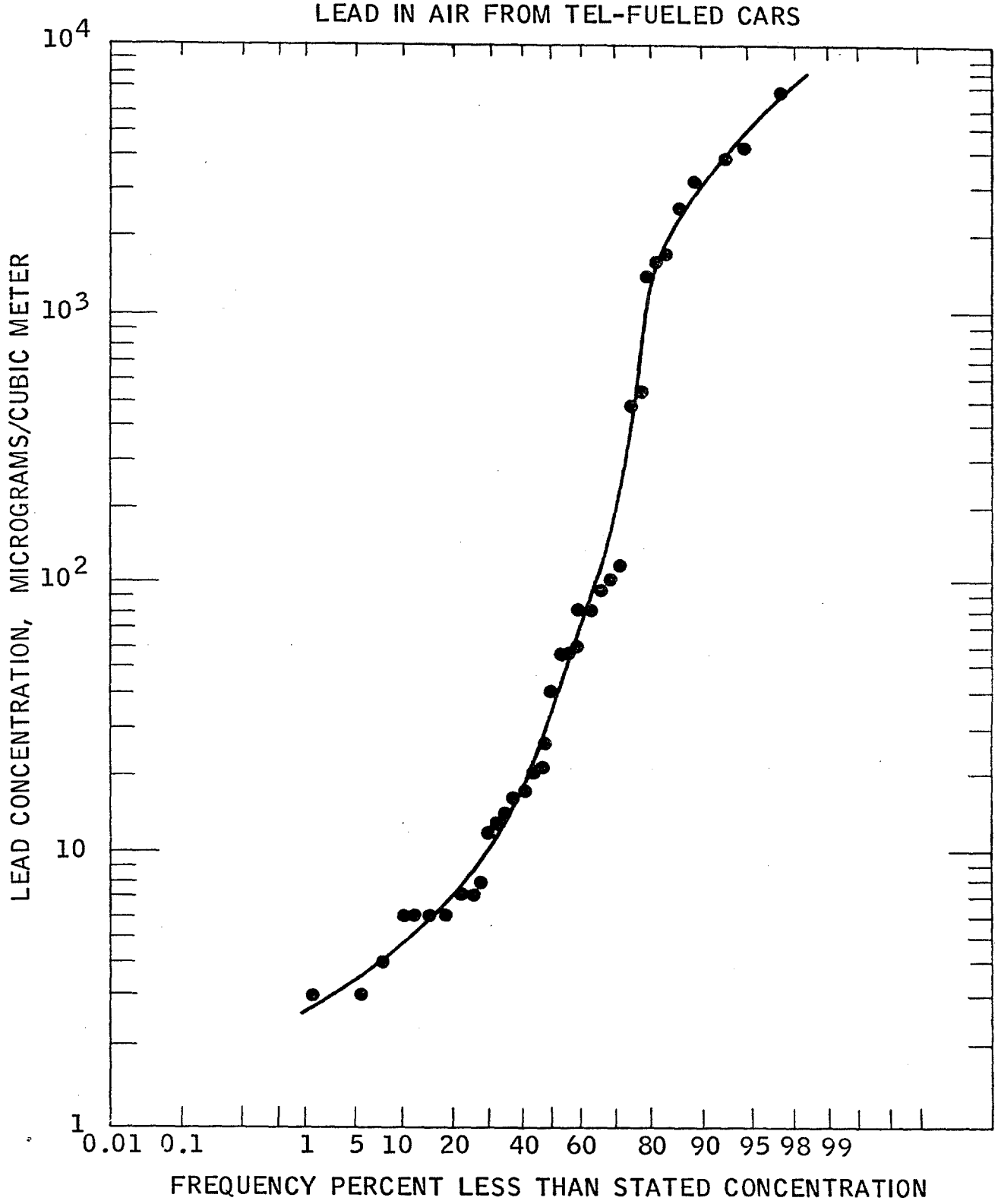
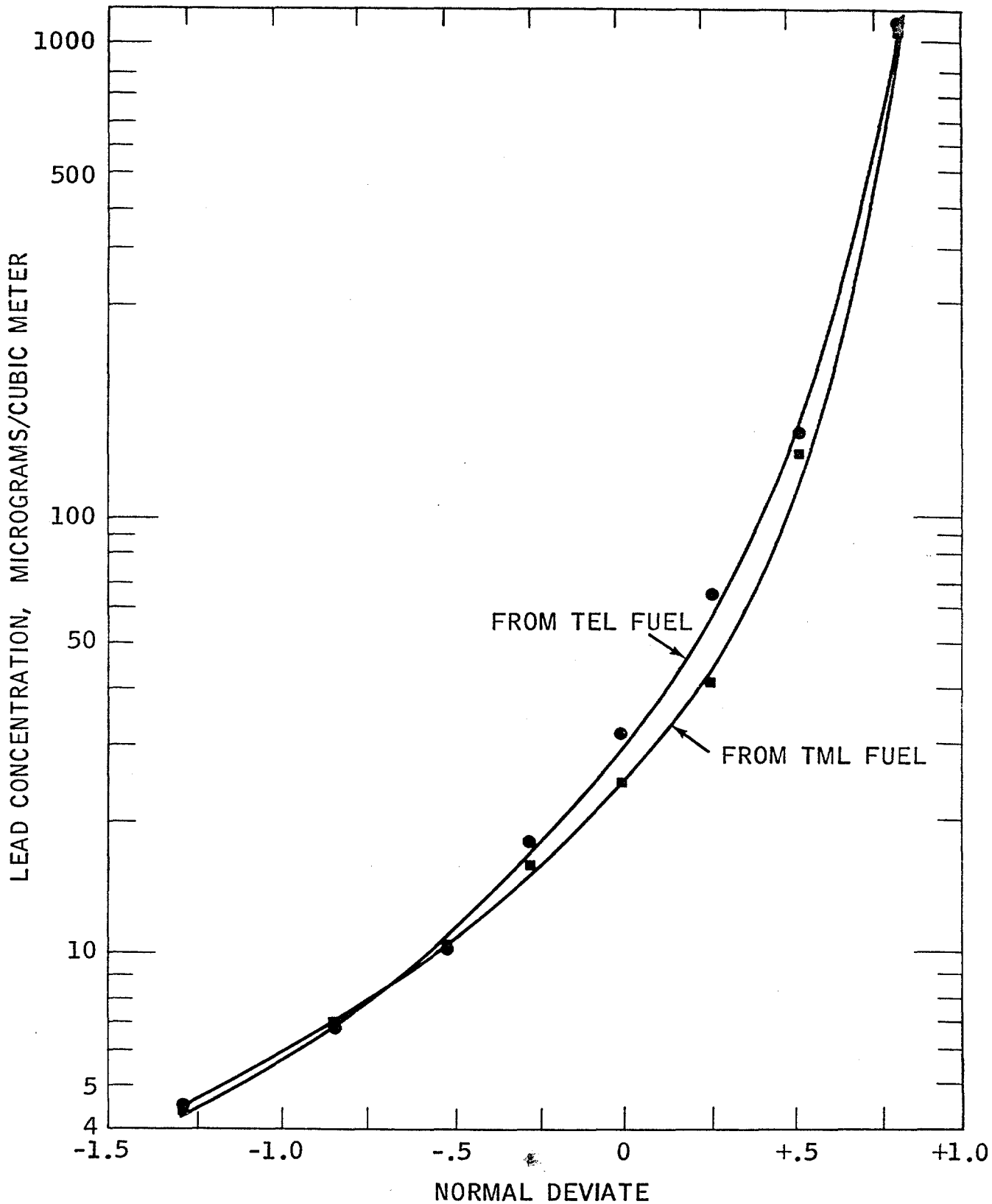


Figure 4

COMPARISON OF FREQUENCY DISTRIBUTIONS
OF LEAD IN AIR FROM TEL- AND TML-FUELED CARS



Nonparametric rank[3] and sign tests[4] of the differential lead generated for organic, inorganic and total lead concentration in the air were done. These tests showed no significant increase in the air pollution caused by TML-leaded gasoline over that from TEL-leaded gasoline.

5. Discussion

The fact that no significant difference appears between the atmospheric concentrations from TML and TEL gasolines is not surprising in view of the experimental set-up at the Mileage Accumulation Dynamometers. The fuel is piped directly to the cars on the unit eliminating tank-filling loss and possible spillage. Blowby, discharged unburned fuel and carburetor loss are other possible means by which lead can be released into the air. These are not believed to be significant, however, for the reasons given below. As a result, it is to be expected that the lead in the fuel supplied will be exhausted on the basis of lead content in the fuel and not on the lead volatility.

In blowby some of the lead in the gasoline dissolves in the crankcase oil. With the more volatile TML more of this lead could escape by subsequent evaporation. Tests done in conjunction with this study have borne this out. Crankcase oil from TML-fueled cars had lower lead content than oil from TEL-fueled cars. In terms of air pollution, however, the difference in lead discharged should be small.

The unburned fuel in the blowby and in the exhaust should approximate the composition of the fuel fed.

Carburetor evaporation loss should be small inthe foreign cars tested. These cars have small carburetor bowls and at the low ambient temperatures existing during the test program little evaporation should occur.

Thus the quantitative lead emissions from cars studied in this program should be quite similar for both TML and TEL fuels. This has been confirmed by the data collected in the study.

In areas where gasoline can evaporate and the vapors can concentrate in the air, like a fueling garage, the higher volatility of the TML gasoline will probably produce higher levels of organic lead in the air. This, in fact, has been proven to be true by Cholak[5] in studies in a California garage where the taxi fleet using the garage was serviced alternately with the same leaded quantities of TEL and then TML gasolines. The particulate lead concentration remained about the same while the organic lead in the air increased about three times.

In conclusion, the general atmosphere should show little or no significant difference in the lead levels created by TML and TEL gasolines. However, occupational exposure should be checked in locations where the higher volatility of TML could increase the organic lead concentration in air. This would include garages, gasoline storage tank cleaning operations, gasoline loading racks, service stations, and areas of congested traffic.

6. References

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5. Cholak, J. and Kehoe, R. A.: A Report of an Investigation of the Potential Hazards of Exposures to Lead Associated with the Handling and Use of Gasoline Containing an Antiknock Fluid in which Tetramethyl Lead is Substituted for Tetraethyl Lead. The Kettering Laboratory, Cincinnati, Ohio (November 10, 1959) Confidential Report.

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