CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA

LEAD-IN-AIR ANALYSIS
COMPARISON OF TML AND TEL

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Introduction

There is considerable interest in studying the concentrations of alkyl lead compounds in gasoline vapors under exposure conditions typical of service. Current interest in TML, which is more volatile than TEL, stems from its superior antiknock performance in certain applications. Since TEL has been shown to be nontoxic under the conditions of exposure associated with handling gasoline, a direct comparison of the two alkyl lead compounds under a variety of conditions is pertinent in assessing any increased health hazard.

Analytical Method

The analyses were performed by the method in general use for the field analysis of lead in air.* In principle the analysis consists of drawing an air sample which contains lead compounds through an iodine solution, thus converting the lead alkyls quantitatively to lead iodide. The lead iodide is then complexed and extracted into chloroform with dithizone reagent. The resulting colored solution is compared with standards in a color comparator and the lead concentration of the air sample is read directly. It was found necessary to heat the iodine solutions after collecting the air samples to assure complete conversion of the trapped alkyl lead compounds to lead iodide. It was also necessary to filter the solutions to remove solid colored material which presumably resulted from reaction of the iodine with hydrocarbon components of the sample. These solids were soluble in chloroform and interfered with the color comparisons. With these modifications, highly reproducible results were obtained under a variety of conditions. We believe this method is suitable for making comparisons between TEL and TML under the conditions of a field survey.

Discussion

The molar ratio of TML to TEL above gasoline under equilibrium conditions, calculated from vapor pressure data, is 87:1 at 70°F (see Table I). On the other hand, whenever

*L. J. Snyder, W. R. Barnes, and J. V. Tokos, Anal. Chem. 20, 772 (1948).

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gasoline is spilled or poured from one container to another, a certain part of the whole gasoline, including the lead compound, evaporates. This situation is entirely different from an equilibrium evaporation. To the extent that whole gasoline evaporates, two lead alkyls of different vapor pressure will be vaporized in equal amounts. An effect intermediate between these two situations is to be expected whenever a draft of air removes gasoline vapors at such a rate that equilibrium evaporation cannot be established. In such a process the rapid loss of gasoline by evaporation causes entrainment of heavier gasoline components, including the lead alkyls. The higher boiling components show up in the vapor in greater concentration than would be predicted from equilibrium considerations. We have termed this phenomenon the "spewing effect."

Table I

The Effect of Temperature on Vapor Pressure

Temperature °F	Vapor Pressure (mm Hg) TML	Vapor Pressure (mm Hg) TEL	Mole Ratio TML/TEL
50	13	0.11	118
60	18	0.18	100
70	24	0.28	86
80	32	0.43	74
90	43	0.67	64
100	58	1.0	58

Experimental

In experiments designed to check the equilibrium calculations, solutions of lead alkyls in hydrocarbons were shaken in a separatory funnel with air until equilibrium was established. These vapors were then displaced by gasoline and passed through a scrubber containing the iodine solution which was then analyzed for lead. The results are shown in Table II.

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Table II

Lead-in-Air Measurements
Equilibrium Studies

	Lead Concentration (Micrograms/Cu Ft)		Mole Ratio TML/TEL
	TML	TEL	
Isooctane, Calc*	4200	48	87
Found	5000	50	100
Toluene, Calc	3300	38	87
Found	4400	50	88
Gasoline, Calc	3500	40	87
Found	3300	100**	31
Estimated Experimental Error	±200	±20	

*Gasolines contained 3.18 grams lead per gallon.

**Equilibrium not attained.

In solvents such as isooctane and toluene, the lead concentrations predicted for equilibrium conditions were closely approached for both TML and TEL.

On the other hand, the amount of TEL in gasoline vapor is much larger than calculated. We attribute this to the fact that equilibration of the gasoline samples in the test apparatus was incomplete because of the high vapor pressure of the gasoline. This large, positive deviation is associated with the "spewing effect." The effect is not noted for TML, probably because of the relatively small effect it would have on the total compared to the size of the experimental error associated with the measurements. From these studies with gasoline vapors, it is concluded that the extreme ratio of 87 moles of TML to 1 mole of TEL will not be achieved under ordinary circumstances, but ratios of less than 50:1 will occur in situations which approach the equilibrium case.

Measurements of the lead in gasoline vapors inside automobile tanks and barrels are given in Table III. TML to TEL ratios of 25 to 40 were found under normal conditions. Two extreme examples of the "spewing effect" were measured.

Gasoline from a barrel which had been standing in the sun was pumped into an automobile gas tank which was considerably colder. The mole ratio of TML to TEL in the vapors expelled from the gas tank was about 11.

Table III

	Lead Concentration (Micrograms/Cu Ft)		Mole Ratio
	TML	TEL	TML/TEL
From Auto Fill Pipe			
During Filling*, 86°F	2000	50	40
During Filling, 60°F	1400	40	35
Filling Warm Gasoline into Cool Gasoline	950	90	11
From Half-Full Barrels			
At "Equilibrium," 60°F	1400	40	35
At "Equilibrium," 80°F	1600	60	27
Emptied of Vapors before Sampling	200**	90	2.2
Estimated Error	±200	±20	

*Gasolines contained 3.18 g Pb per gallon

**Estimated error ±40

In a second experiment, gasoline vapors sampled immediately after removing the existing (equilibrium) vapors showed a molar ratio of about 2, as might be expected from the rapid nonequilibrium evaporation of gasoline.

A marked effect of temperature on vapor pressure of lead alkyls is shown in Table I. The mole ratio of TML to TEL at 100°F is half that at 50°F. Although this is undoubtedly an important effect, it was not detected in the "field" studies reported in Table III. The "spewing effect" and experimental error combine to wash out any observable temperature effect over the 20-30°F temperature range of the study.

Lead in the vapors from spilled gasoline and from gasoline allowed to evaporate in open vessels probably constitutes the most serious health hazard associated with the marketing of alkyl lead compounds. Lead analyses of vapors above gasolines evaporating in open beakers are reported in Table IV. These low ratios of TML to TEL which result from the

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"spewing effect" confirm preliminary data reported by another laboratory. It appears that in cases representative of the most flagrant types of gasoline misuse, the difference between TML and TEL is minimized to the extreme.

Table IV

Lead-in-Air Above Gasoline in Open Vessels

Sampling Distance Above Gasoline, Inches	Lead Concentration (Micrograms/Cu Ft) TML	TEL	Mole Ratio TML/TEL
3	60	20	3.0
5	40	15	2.7
7	20	10	2.0
10	3	3	1.0
13	3	3	1.0

Summary

A comparison was made of the amount of lead in vapors above gasolines containing TML and TEL. The calculated ratio of 87 moles of TML to 1 mole of TEL was not achieved over gasoline but was approached with the less volatile fuels, isooctane and toluene.

Vapors collected from automobile gas tanks and barrels contained 25 to 40 times more lead as TML than as TEL. Under conditions which involve a rapid evolution of gasoline vapors, such as pouring a warm gasoline into cold gasoline, or drawing air across gasoline to cause rapid evaporation, the TML to TEL ratio is markedly reduced and approaches unity.

The "spewing effect" is here defined as the rapid evolution of gasoline vapors which takes place whenever the vapors are not in equilibrium with the liquid. This effect accounts for the much smaller ratios of TML to TEL found by experiment than are calculated from vapor pressure considerations. In cases of flagrant misuse of leaded gasolines involving spills or rapid evaporation from open containers, TEL closely approaches the same concentration as TML in the vapors.

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These studies show that the ratio of TML to TEL above gasolines compounded to the same lead level is considerably lower than anticipated. Field sampling data and information on the relative toxicities of TEL and TML will be required to reach a decision on the relative exposure hazards associated with replacing TEL with TML in gasoline.

W. L. RICHARDSON

R. E. NOBLE

G. J. KAUTSKY

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