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Organic lead compounds in vehicle exhaust

C Nicholas Hewitt and M B Rashed
Department of Environmental Science, University of Lancaster, Lancaster LA1 4YQ, UK

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Species-specific measurements of the five tetra-alkyllead compounds used in gasoline and their intermediate decomposition products, the tri- and di-alkyllead species, have been made in vehicle exhaust fumes. Under normal engine running conditions 0.3–3% of the lead emitted in exhaust is as an organic compound, but cold, choked engines emit proportionally much larger amounts of alkyllead. Alkyllead is emitted in both the gas and the aerosol phases.

Keywords: Organolead emissions, vehicle exhaust

INTRODUCTION

The addition of tetra-alkyllead (TAL) compounds to gasoline to prevent the spontaneous premature combustion of the fuel mixture remains by far the largest industrial use of organic lead compounds, representing about 5% of total lead consumption.[1] Of the alkyllead additive in fuel about 75% is emitted from the exhaust as a complex mixture of inorganic lead salts with the majority of the remainder being deposited in the engine and exhaust system. However, a small fraction of the TAL is emitted into the atmosphere by evaporation from the fuel tank and carburettor and by fuel spillage during transport and handling. The magnitude of these sources is uncertain but possibly amounts to ~1% of the alkyllead in fuel. A further small fraction of alkyllead is emitted into the atmosphere in the exhaust gases, either unchanged as TAL or partially decomposed as the trialkyl (TriAL) or dialkyllead (DiAL) compounds. It is known that TAL decomposes forming these ionic species by gas-phase reactions,[3] in the liquid phase,[4,5] and probably by heterogeneous reactions from the aerosol phase,[6] and it is therefore to be expected that a multiplicity of organic lead compounds will be present in vehicle exhaust in both the gas and aerosol phases.

Various estimates have previously been obtained of the individual concentrations of the five tetra-alkyllead species in vehicle exhaust,[7] and more recently of total gas-phase alkyllead concentrations in exhaust (i.e. the total TAL + TriAL + DiAL concentrations)[8] but prior to this present study no complete speciation and quantification of all these compounds in both the gas and aerosol phases in exhaust had been made. Such data are required as a prerequisite to the complete understanding of the atmospheric sources, chemistry and sinks of organic lead compounds and the role they play in the environmental cycling of the metal.

EXPERIMENTAL

Gas-phase and aerosol-phase lead compounds were collected from the exhaust stream of stationary and moving vehicles at 0, 30, 56 and 70 mph (0, 48, 90 and 113 km h^{-1}) using the sampling arrangement shown in Fig. 1. Ideally the first component in such a sampling train should be a membrane filter to remove the aerosol-phase compounds, followed by separate collection of the gaseous alkyllead species. However, the condensation of water from the exhaust gases resulted in the rapid blockage of the filter when this was attempted. Heating the filter holder and its inlet using electrical heating tape was ineffective in preventing condensation and so an alternative arrangement was devised using a 125 cm^3 gas bubbler immersed in ice as a water trap.

Two parallel sampling trains were employed, one for the inorganic lead aerosol, the other for the organic species. A 0.45 μm Millipore membrane in a stainless-steel holder with a Teflon gasket was used for collection of the lead aerosol. However, some particulate lead will be collected by impingement in the gas bubbler, and so for the determination of inorganic lead aerosol the bubbler was washed twice after sampling with

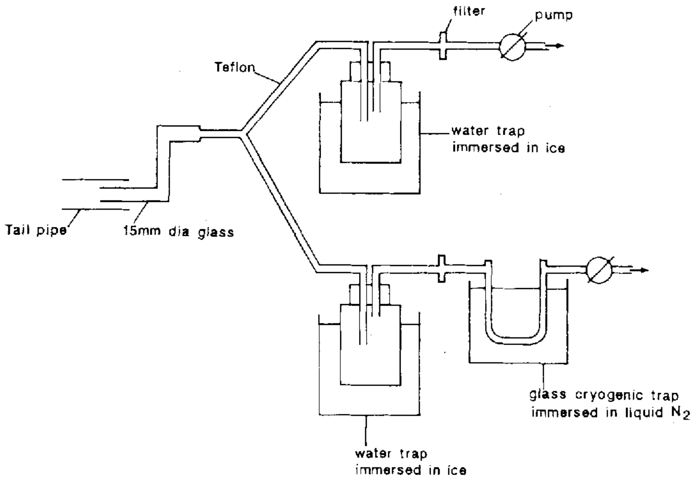

Figure 1 Sampling system for gas- and aerosol-phase alkyllead and inorganic lead compounds

10 cm^3 of 10% Aristar nitric acid. The washings and condensate were added to the membrane filter extract for analysis. Extraction of inorganic lead from the filter was by ultrasonically agitating the membrane in 20 cm^3 of 10% Aristar nitric acid for 1 h and analysis was carried out by graphite furnace atomic absorption spectroscopy (GFAA) using a Perkin–Elmer 2280/HGA 400 and the method of standard additions.[9] Unavoidable collection of gaseous and aerosol-phase organic lead compounds both in the condenser and on the membrane filter, with subsequent oxidation by nitric acid to inorganic lead (Pb^{II}) will give rise to an overestimate in inorganic lead concentrations. This bias has been corrected for by deduction of the organic lead concentrations from the total lead and the resultant inorganic lead concentrations should be in error by less than 1% from this cause.

The parallel sampling train was used for collection of the organic lead species. A 125 cm^3 gas bubbler immersed in ice was again used as a water trap, followed by a 0.45 μm Millipore membrane filter in a stainless-steel holder for collection of the aerosol-phase compounds and a cryogenic trap for collection of the gaseous species. This trap consisted of a glass U-tube, of length 20 cm and diameter 1 cm, containing 2 mm glass beads and immersed in a liquid nitrogen/ethanol slush bath at −130°C. As previously described[3] this quantitatively collects both tetra-alkyllead and any ionic alkyllead compounds present in the gas phase.

After sampling, the lead compounds were extracted from the Millipore membrane using 30 cm^3 water, 5 cm^3 hexane, 1.5 g sodium chloride and 1.5 cm^3 sodium diethyldithiocarbamate (NaDDC, 0.5 mol dm^{-3}).[10] The water trap and condensate were also extracted in the same way and the extracts combined. The contents of the cryogenic trap were similarly extracted. Analysis was by the species-specific method of propylation–gas chromatography–atomic absorption spectroscopy (GC AA).[11,12] There is no interference from the presence of inorganic lead using this technique.

Some loss of alkyllead compounds will occur in the water trap and its condensate. Preliminary experiments indicate that there is little loss of gaseous tetra-alkyllead compounds in a condenser of this type at the flow rates used. Ionic alkyllead compounds in the gas phase also largely pass through such a system. However, compounds in the aerosol phase are removed more efficiently by impaction in this configuration. However, as it was not possible to differentiate between the contributions of gaseous and aerosol-phase compounds to the loss, it was assumed to be all from the aerosol phase. This will lead to a small but unquantifiable error, underestimating the gas-phase organic lead concentrations and overestimating those in the aerosol phase.

A 15 mm diameter glass tube was used as the sampling probe, being inserted 10 cm into the vehicle exhaust pipe. Connections with the water traps and subsequent components of the sampling trains were by 7 mm diameter Teflon tubing. A 12-volt dc pump (Charles Austen Ltd, UK) was used with sampling flow rates of 2 dm^3 min^{-1} measured by a GAP rotameter and with sampling periods of ~10 min.

Inevitably some lead, especially that in the aerosol phase, will be lost in the sampling probe by impaction and deposition. This was minimized by using large-diameter tubing, using the shortest possible tube lengths and by avoiding unnecessary bends. However, deposition will still have occurred and caused an unknown underestimate in lead concentrations. By collecting the inorganic lead fraction in the same position in the sampling train as the organic fraction, it is hoped that the resultant errors in organic to inorganic lead **ratios** will be small. Similarly, problems arising from the use of a non-isokinetic sampling regime remain unquantified.

Two vehicles were used for these determinations, a Ford Transit van of 2.0 dm^3 engine capacity and model year 1982, and a Ford Escort Estate car of 1.1 dm^3 capacity and model year 1983. Both vehicles have been regularly maintained and serviced since new.

For a 20 dm^3 exhaust fume sample and a 50 μl injection into the GC AA system the method gives 3σ detection limits in the range 8–55 ng (Pb) m^{-3} in the exhaust. Sensitivity is greatest for $(CH_4)_4Pb$, progressively decreasing to $(C_2H_5)_2Pb^{2+}$. The propylation method does not allow identification of the counterion associated with the ionic alkyllead species.

RESULTS AND DISCUSSION

Lead in exhaust concentrations

The concentrations of the five individual TAL compounds and four ionic TriAL and DiAL compounds in both the gas and aerosol phases, together with the inorganic lead aerosol concentrations, are shown in Table 1. The data are also summarized in Fig. 2.

For both vehicles TAL concentrations decreased with increasing vehicle speed, with the highest concentrations being emitted when the engines were cold and choked. TAL was predominantly found in the gas phase, with concentrations in the range 0.26–56.2 $\mu g(Pb)\,m^{-3}$ in the gas phase compared with 0.03–0.61 $\mu g(Pb)\,m^{-3}$ in the aerosol phase.

The lead speciation in the gasoline used in these tests is also shown in Table 1, with $(CH_3)_4Pb$, $(CH_3)_3(C_2H_5)Pb$ and $(C_2H_5)_4Pb$ being the dominant species. However, in the exhaust gases $(CH_3)_4Pb$ was the most abundant compound, presumably due to the increasing reactivity and thermal instability of TAL species with increasing molecular weight.[13]

The ionic TriAL and DiAL compounds were, as expected, not found in the liquid gasoline samples. However, in the exhaust gases they were present in both the gas and aerosol phases. In the gas phase total ionic alkyllead concentrations in the range 8.9–46.1 $\mu g(Pb)\,m^{-3}$ were found and in the aerosol phase 1.7–22.9 $\mu g(Pb)\,m^{-3}$. In the exhaust fume of the stationary choked vehicles higher concentrations of TAL than ionic alkyllead were found, but in all other samples concentrations of the ionic species were highest. The higher TAL concentrations in the former case were presumably due to the greater emission of unburnt fuel through the choked engines. In every case more DiAL was emitted than TriAL, but with the relative proportions of $(CH_3)_2Pb^{2+}$ and $(C_2H_5)_2Pb^{2+}$ varying between samples.

Inorganic lead aerosol concentrations in the range 600–11 730 $\mu g\,m^{-3}$ were measured in the vehicle exhaust, with concentrations increasing with vehicle speed. This is consistent with the greater fuel consumption expected at higher engine loads.

The measured alkyllead concentrations may be compared with those previously found in vehicle exhausts. Reamer *et al.*[7] collected TAL compounds on a cooled adsorbent (10% SE-52 on Chromosorb-P in a Teflon tube cooled by a dry ice–methanol slush bath) from which they were removed by freeze-drying and extraction into hexane. Analysis was by gas chromatography–microwave plasma detection. The total TAL concentrations so found were much less than those obtained in the present study, being in the range 0.3–1.0 $\mu g\,m^{-3}$. This is surprising as the lead content of the fuel previously used was approximately four times that used in the present study. Whether their sampling method was not able to collect quantitatively the lead species at the high concentrations expected in vehicle exhausts is not known, and neither is it clear whether samples were obtained from stationary or moving vehicles.

Total gas-phase alkyllead (i.e. TAL + TriAL + DiAL) has recently been determined in vehicle exhaust by collection on activated carbon, conversion to inorganic lead (Pb^{II}) by boiling nitric acid and analysis by conventional AA.[8] Particulate organic lead was excluded from the carbon trap by a membrane filter and any lead collected on this was assumed to be inorganic lead. Using the European Community (EC) vehicle emission standard test cycle, total gas-phase alkyllead concentrations of 3.0–14.4 $\mu g(Pb)\,m^{-3}$ were found. At 50 mph

Table 1 Measurements of alkyllead and inorganic lead in vehicle exhaust fumes [$\mu g(Pb)\,m^{-3}$ unless otherwise indicated]

	Tetra-alkyllead TAL[a]					Ionic alkyllead[b]								TAL	Ionic alkyllead	Alkyllead	
Phase	TML	TMEL	DMDEL	MTEL	TEL	TriML$^+$	TriEL$^+$	DiML^{2+}	DiEL^{2+}	Total TAL	Total ionic alkyllead	Total alkyllead lead	Pb^{2+}	Total lead (%)	Total lead (%)	Total lead (%)	
(A) Ford transit 2.0 dm^3																	
Stationary vehicle (choked)																	
Aerosol	0.45	0.1	0.01	0.02	0.03	0.50	0.29	0.09	8.00	0.61	8.88	9.49	600	<0.1	1.3	1.3	13.1
Gas	25.88	6.35	13.17	5.41	5.40	4.94	0.47	14.35	5.02	56.21	24.33	80.54		8.2	3.5	11.7	
30 mph (48 km h^{-1})																	
Aerosol	0.37	<0.01	<0.01	0.14	<0.02	0.41	0.28	0.23	10.85	0.51	11.77	12.28	1500	<0.1	0.8	0.8	3.2
Gas	4.02	0.86	1.09	0.45	0.25	1.43	1.47	7.00	21.25	6.67	31.15	37.82		0.4	2.0	2.4	
56 mph (90 km h^{-1})																	
Aerosol	0.21	0.04	<0.01	0.06	0.05	0.92	0.35	0.68	7.06	0.37	9.01	9.38	3700	<0.1	0.2	0.3	0.6
Gas	2.70	0.06	0.05	0.09	0.72	0.36	0.10	3.77	4.62	3.62	8.85	12.47		0.1	0.2	0.3	
70 mph (113 km h^{-1})																	
Aerosol	0.09	<0.01	<0.01	0.06	<0.02	0.57	0.32	0.48	21.51	0.15	22.88	23.08	11730	<0.1	0.2	0.2	0.3
Gas	1.04	0.12	0.05	0.16	<0.02	2.46	0.48	2.14	8.57	1.37	13.65	15.02		<0.1	0.1	0.1	
Gasoline Pb (mg dm^{-3})	29.0	9.4	18.3	15.4	33.0	Total = 105 mg dm^{-3}											
(B) Ford Escort 1.1 dm^3																	
Stationary (choked)																	
Aerosol	<0.01	0.07	<0.01	0.24	0.03	0.39	0.16	1.05	1.10	0.34	2.7	3.04	990	<0.1	0.3	0.3	4.4
Gas	8.5	4.73	4.58	2.04	1.82	6.11	3.81	1.67	9.10	21.67	20.69	42.36		2.1	2.0	4.1	
30 mph (48 km h^{-1})																	
Aerosol	<0.01	<0.01	<0.01	0.04	<0.02	0.13	0.16	0.14	1.31	0.04	1.74	1.78	1830	<0.1	<0.1	<0.1	2.5
Gas	0.38	0.37	<0.01	0.46	<0.02	2.44	5.63	16.06	22.00	1.21	46.13	47.34		<0.1	2.5	2.5	
70 mph (113 km h^{-1})																	
Aerosol	<0.01	<0.01	<0.01	0.03	<0.02	0.09	0.05	0.21	5.32	0.03	5.67	5.70	4310	<0.1	0.1	0.1	0.3
Gas	<0.01	<0.01	<0.01	0.26	<0.02	2.77	0.09	5.45	1.6	0.26	9.91	10.17		<0.1	0.2	0.2	
Gasoline Pb (mg dm^{-3})	21.8	12.2	24.6	9.1	21.3	Total = 89 mg dm^{-3}											

[a] TML, $(CH_4)_4Pb$; TMEL, $(CH_4)_3(C_2H_5)Pb$; DMDEL, $(CH_4)_2(C_2H_5)_2Pb$; MTEL, $(CH_4)(C_2H_5)_3Pb$; TEL, $(C_2H_5)_4Pb$. [b] TriML$^+$, $(CH_4)_3Pb^+$; TriEL$^+$, $(C_2H_5)_3Pb^+$; DiML^{2+}, $(CH_4)_2Pb^{2+}$; DiEL^{2+}, $(C_2H_5)_2Pb^{2+}$.

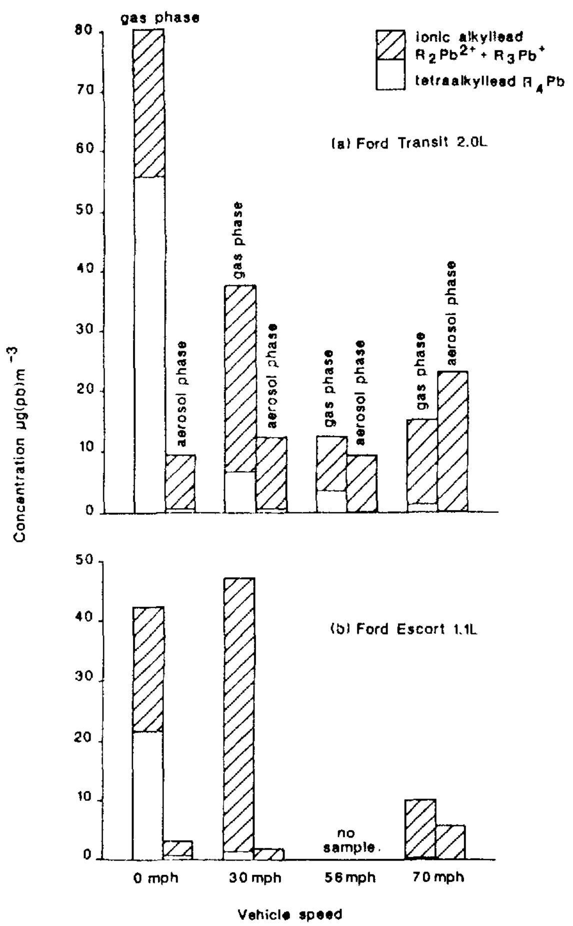

Figure 2 Concentrations of alkyllead in vehicle exhaust.

(80 km h^{-1}) the concentration range was 0.1–2.7 μg(Pb) m^{-3}. In the present study much higher total gas-phase alkyllead concentrations of 10–80 μg(Pb) m^{-3} were found from stationary and moving vehicles. The lead content of the gasoline used by Røyset and Thomassen was 0.4 μg dm^{-3}, and the inorganic lead concentrations measured in the exhaust fumes were in the range 1060–14 300 μg(Pb) m^{-3}, comparable with those found in the present study.

Alkyllead to total lead ratios

Because of the highly variable concentrations of organic lead and inorganic lead found in the atmosphere at different sampling sites and at different sampling times, arising from various site-specific and meteorological parameters, it is most convenient to express organic lead concentrations as a percentage of the total ambient lead. Table 1 shows the data in this form. Total alkyllead represented 0.3–3.2% of the total lead emissions from the hot moving vehicles, and 4.4 and 13.1% from the cold, choked vehicles.

Except when stationary, cold and choked, both vehicles emitted $\ll$1% TAL compared with total lead, and <0.1% TAL at higher speeds. TAL/total lead ratios of 8.2% and 2.1% were found when the engines were cold and choked. These compare with ratios of 2.2 and 1.9% for TAL/total lead previously reported.[7]

Total gas-phase alkyllead/total lead ratios of 0.1–2.4% were found from the hot moving vehicles (and 4.1 and 11.7% from the cold choked engines) compared with 0.002–0.44%.[8]

Comparison with ambient lead in air measurements

Measurements of both gas- and aerosol-phase organic lead compounds in the atmosphere at a variety of sites have been extensively reported and reviewed.[1,6] Because of the considerable variation in reported concentrations, it is often, as noted above, more useful to compare organic lead measurements from different sites in terms of their percentage of the total lead concentrations. In urban air total gas-phase alkyllead to total lead ratios of 5–6%,[14] 3–14%,[9] 2–7%[15] and 3–4%[10] are typical values. These correspond closely to ratios of 0.1–11.7% found in exhaust gases in this study.

Tetra-alkyllead to total lead ratios of 2–3%,[10] 2–7%,[11] and 3%[16] are typical of those reported for urban air. These are much higher than the ratios found from the hot, continuously moving vehicles used in this study, presumably because of the use of the choke and continual acceleration/deceleration during urban driving. The few species-specific measurements of the ionic alkyllead compounds in urban air that have been made indicate TriAL+DiAL/total lead ratios of $\sim$3%,[11] compared with 0.2–3.5% found in vehicle exhaust.

In ambient urban air the quantity of TAL and ionic alkyllead compounds associated with the aerosol phase is small, being $\sim$1% of the gas-phase alkyllead.[10] In the vehicle exhaust aerosol phase TAL was found to be insignificant, whilst aerosol phase ionic alkyllead represented 0.1–1.3% of the total lead.

Possible presence of monoalkyllead in vehicle exhaust

During analysis of most of the vehicle exhaust samples, GC AA peaks which we ascribe to a monoalkyllead species were found. Whether these are due to the presence of such a compound in the exhaust or are an artifact of the propylation technique arising from the rearrangement of other, more stable, ionic alkyllead compounds,[17] or are an artifact of the GC AA system itself,[18] is not clear. These unstable species have not, to date, been unequivocally identified in environmental samples.

CONCLUSIONS

Despite the limitations of our sampling method it is clear that gasoline vehicles directly emit not only TAL but also the ionic TriAL and DiAL species directly into the atmosphere. Under normal engine running conditions probably 0.3–3% of the total lead emitted is as an organic compound. However, cold, choked engines can emit substantially more alkyllead, mainly as unreacted TAL, presumably in unburnt fuel. In contrast to the alkyllead in ambient urban air, where aerosol alkyllead is insignificant compared with that in the gas phase, the ionic species are emitted in both the gas and aerosol phases. This may be due to their solubility and the presence of large amounts of water vapour and droplets and other particulate material in the exhaust fume. The alkyllead species present as these large particles may then be rapidly deposited from the atmosphere or volatilized into the gas phase. The presence of monoalkyllead species in vehicle exhaust is possible, but is not yet confirmed.

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