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Method for Measuring Tetraethyl Lead and Total Lead in Organic Solvents

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Lead (Pb) contamination is a nationwide public health problem which is prevalent among children in urban metropolitan areas (Mielke et al. 1983). Pb in the bloodstream has been shown to produce toxic effects in children such as lowered intelligence and behavioral dysfunctions. In senior adults, Pb exposure causes high blood pressure, which is associated with increased risks of heart attacks, strokes, and death (Driscoll et al. 1992). The source of Pb contamination is due mostly to emissions from vehicular traffic using leaded gasoline (Adriano 1986). Other sources of Pb contamination include the production of Pb-acid storage batteries and lead-based paint on houses (Mielke et al. 1983; Rhue et al. 1992).

Pb alkyl species used by automobile-related industries include tetraethyl Pb (TEL), tetramethyl Pb, triethylmethyl Pb, dimethyldiethyl Pb, and trimethylethyl Pb compounds. All of these compounds have been used as antiknock agents and have provided a convenient and inexpensive means to enhance octane rating for gasoline (Caplun et al. 1984). Use of leaded gasoline was almost global for more than 50 years during 1925 to 1975. The amount of Pb released in automobile exhaust during that time accounted for more than a half of the total yearly Pb pollution of the entire earth (Settle and Patterson 1980; Caplun et al. 1984). Production of leaded gasoline in the US peaked in early 1970 and steadily declined after 1975 (Grandjean and Nielsen 1979). Although only Pb-free gasoline may now be used as an automobile fuel in the US, leaded gasoline is still used as both an aviation and automobile fuel in many countries in the world (Driscoll et al. 1992; Rhue et al. 1992). Extensive use of Pb antiknock additives in gasoline has made Pb perhaps the most widely distributed toxic heavy metal in the urban environment (Brown and Hem 1984).

The public health concern about Pb content in the subsurface environment requires a method to determine Pb contents (both organic and inorganic species) that is both accurate and not demanding of time, technique, or special equipments. Currently, the American Society for Testing Materials (ASTM) Standard Method D3237 is used to measure the total Pb content in leaded gasoline (Kashiki et al. 1971; ASTM 1982). This method is time consuming, expensive, and tedious as

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compared to the method presented in this article.

Newman et al. (1974) reported that TEL in aviation leaded gasoline can be determined by the iodimetric method. The chemical reaction for the procedure was expressed as:

$$Pb(C_2H_5)_4 + I_2 - Pb(C_2H_5)_3I + C_2H_5I . \quad (1)$$

An excess of iodine was first added to a measured volume of gasoline. After complete reaction the unreacted iodine was titrated with sodium thiosulfate. The authors concluded that the method was applicable to all aviation gasoline and had a maximum deviation of ± 0.05 mL of TEL per gallon when compared with ASTM results.

Conversions of TEL and triethyl lead (TREL) to diethyl lead (DEL) using iodine monochloride (ICl) solution has been reported by Hancock and Slater (1975), Chau et al. (1979), and Noden (1980). However, degradation of TEL occurs through a series of sequential dealkylation steps and eventually to Pb^{+2} (Rhue et al. 1992). That is, TEL was first degraded to TREL which in turn degraded to DEL, and finally to inorganic Pb^{+2}. Since the ICl solution can be used to convert TEL and TREL to DEL, TEL may possibly be converted directly to Pb^{+2} using the ICl solution. If this is the case, TEL and total Pb contents in organic solvents can be easily determined. That is, TEL can first be converted to Pb^{+2} which can be measured by atomic absorption spectrophotometry (AAS). Then, TEL content can be estimated using a back calculation according to the molecular fraction of Pb present in TEL. The objective of this study was to develop a simple method to measure TEL as well as total Pb contents in organic solvents using a ICl digestion method. Two types of samples were used: (1) TEL in gasoline, and (2) TEL in hexane. In additional, an experiment was also conducted to verify that conversion of TEL by ICl with the above procedures is actually to inorganic Pb^{+2} and not to a mixture of the intermediate TREL and DEL species which are highly water soluble.

MATERIALS AND METHODS

Analytical grade TEL and Pb standard solution were purchased from All-Chemie LTD (Ft. Lee, NJ) and Fisher Scientific (Orlando, FL), respectively. Unleaded gasoline was obtained at a local gasoline station in Gainesville, FL. All other chemicals such as concentrated HCl, n-hexane, KI, and KIO_3, EDTA, and NaDDTC were analytical grade. 0.1 M ICl aqueous solution was prepared by mixing 40 mL deionized water (DI), 44.5 mL concentrated HCl, 11.0 g KI, and 7.5 g KIO_3. This solution was used to convert the TEL to Pb^{+2}. Solvent for extracting TREL and DEL from aqueous solution was prepared by mixing 2 g EDTA disodium salt and 2 mL of 0.25 M $NaDDTC.3H_2O$ into a 100 mL volumetric flask and adjusted to pH = 9 with NH_4OH and diluted with DI water.

Leaded gasoline samples were prepared by spiking a known amount of TEL into the unleaded gasoline. Two leaded gasoline concentrations used in this study were 5 and 10 mg TEL L^{-1}. Hexane samples were prepared by dissolving TEL in n-hexane solution in volumetric flasks wrapped with aluminum foil at concentrations of 5 and 10 mg TEL L^{-1}. Standard Pb solution was made by adding analytical grade Pb standard solution in 3:1 DI water:0.1 M ICl solution at concentrations of 1, 10, and 20 mg Pb L^{-1}. All of the samples were prepared in a semi-dark condition to avoid photo-degradation of TEL under the light.

Triplicate 3 mL aliquots of these samples and 1 mL of 0.1 M ICl solution were added to test tubes and shaken for 30 minutes. After TEL had been converted to Pb^{+2}, 3 mL of DI water was added to the test tubes, and the test tubes were mechanically shaken for another 30 minutes. This allowed Pb^{+2} to dissolve in the water phase since Pb^{+2} is insoluble in organic solvent, but is highly soluble in water. Then, the samples were transferred to separatory funnels for phase separation. The contents of Pb^{+2} in the water was analyzed by AAS. Blank samples were prepared by mixing 3 mL of DI water and 1 mL of 0.1 M ICl solution.

An additional experiment was conducted to verify that conversion of TEL by ICl with the above procedures is actually to inorganic Pb^{+2} and not to a mixture of the intermediate TREL and DEL species which are highly water soluble. Triplication 10 mL of TEL with a concentration of 40 mg L^{-1} and 3.3 mL of 0.1 M ICl solution were added to test tubes and shaken for 30 minutes. Then, 10 mL of DI water was added to the test tubes and shaken for another 30 minutes. The samples were transferred to separatory funnels for phase separation. Three mL aliquots of water samples were used to analyze the contents of Pb^{+2} using AAS. For verifying the possible existence of TREL and DEL species during the conversion of TEL to Pb^{+2} by the ICl digestion method, triplicate 5 mL aliquots of the water samples and 20 mL solvent made of a mixture of EDTA, NaDDTC, and DI water were added to test tubes and shaken for 10 minutes. Then, 10 mL of n-hexane was added the test tubes and shaken for another 10 minutes. This allowed removal of TREL and DEL from the water phase (Blais and Marshall 1986). Finally, the samples were transferred into separatary funnel for phase separation. The water samples were used to measure the Pb^{+2} contents by AAS.

RESULTS AND DISCUSSION

TEL is a hydrophobic compound with a very low water solubility (< 0.1 mg L^{-1}), but is highly soluble in hydrophobic solvents such as gasoline and hexane (Feldhake and Steven 1963). To measure the TEL content in organic solvents indirectly, TEL was converted to Pb^{+2} by ICl solution, and then the Pb^{+2} content was measured by AAS. Therefore, TEL content in organic solvent can be calculated as follows

$$C_{TEL} = \frac{W_{TEL} \; x \; C_{Pb}}{W_{Pb}} , \qquad (2)$$

where C_{TEL} is the concentration of TEL (mg L^{-1}), W_{TEL} is the molecular weight of TEL (323.4), C_{Pb} is the concentration of Pb^{+2} in the samples (mg L^{-1}), and W_{Pb} is the molecular weight of Pb^{+2} (207.2).

A comparison of theoretical values and experimental measurements of TEL in leaded gasoline and hexane using the ICl digestion method is shown in Table 1.

Table 1. Theoretical values of TEL and experimental measurements of TEL and total Pb by ICl method.

Replication No.	Theoretical Conc.	Measured Conc.	Average Conc.	CV	Recovery Rate	Total Pb Conc
	(mg TEL L^{-1})				(%)	(mg L^{-1})
			Leaded Gasoline Samples			
1	5.0	4.74	4.64	1.90	92.7	3.04
2	5.0	4.64				2.97
3	5.0	4.53				2.90
1	10.0	9.71	9.67	1.34	96.7	6.22
2	10.0	9.81				6.29
3	10.0	9.49				6.08
			Hexane Samples			
1	5.0	5.08	5.01	2.07	100.2	3.26
2	5.0	4.86				3.11
3	5.0	5.08				3.26
1	10.0	10.15	10.23	1.02	102.3	6.50
2	10.0	10.15				6.50
3	10.0	10.37				6.64

Each type of sample has two treatments with triplication. Concentrations of TEL for samples in Table 1 were obtained by using Eq. (2) to convert the concentrations of Pb^{+2} measured from AAS into TEL. Average recovery rates of

TEL in leaded gasoline samples at concentrations of 5 and 10 mg L^{-1} were 96.7 and 92.7, respectively. Coefficient of variability (CV) among the triplication ranged from 1.34 to 1.90%. Such high TEL recovery rates and low CV values suggest that ICl digestion is a successful method in measuring the TEL contents in leaded gasoline samples.

Similar results were obtained for TEL in hexane solutions. Average recovery rates of TEL at concentrations of 5 and 10 mg L^{-1} were 100.2 and 102.3 %, respectively. The CV values ranged from 1.02 to 2.07%. The TEL contents observed from this experiment slightly overestimated the theoretical values for the hexane samples, but slightly underestimated the theoretical values for the leaded gasoline samples.

No concentration difference in Pb^{+2} was observed in the water samples before and after the extraction of TREL and DEL by the solvent made of a mixture of EDTA, NaDDTC, and DI water. This result indicates that no TREL and DEL existed in the water samples and thereby all the TEL was converted to inorganic Pb^{+2} by the ICl digestion method.

This investigation shows that TEL not only can be converted to TREL (Newman et al., 1947) and DEL (Hancock and Slater 1975), but also can be converted to total Pb^{+2}. The chemical reaction for the process may be expressed as

$$Pb(C_2H_5)_4 + 4I^{+1} = Pb^{+2} + 4(C_2H_5)I \,. \qquad (3)$$

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