

Speciation and Determination of Tetraalkyllead Compounds in Gasoline by Gas Chromatography-Atomic Absorption Spectrometry

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INTRODUCTION

The selective determination of alkyllead compounds in various matrixes, such as water, biological materials, air, and gasolines, has been successfully carried out by chromatography (1-5), vapor phase sample introduction (6), and flow injection analysis (7) methods using either spectrophotometric or flame and graphite furnace atomic absorption spectrometric detection. A comparison of the various techniques leads to the conclusion that the graphite furnace atomizer offers best sensitivity for the determination of the concentration of tetraalkyllead (TAL) compounds. However, there are usually some difficulties associated with the way in which the chromatograph interfaces with the graphite furnace (2). In this work, an alternative method for interfacing a gas chromatograph with a flame-heated quartz cell and atomic absorption spectrometry (AAS) is described. This procedure allows the introduction of hydrogen into the quartz cell, which is easily demountable. This procedure is simple and used for the separation and determination of TAL compounds in gasoline samples.

EXPERIMENTAL

Figure 1 shows the diagram of the GC-AAS manifold used. The separation of the TAL compounds was achieved by using a Perkin-Elmer[®] F11 gas chromatograph,

ABSTRACT

The use of gas chromatography in combination with atomic absorption spectrometry is described for the speciation and determination of tetraalkyllead (TAL) compounds in gasoline. The effects of various parameters affecting the sensitivity and precision are discussed. Absolute detection limits for Pb ranged between 0.1 and 0.25 ng for the $PbMe_4$ and $PbEt_4$ species, respectively. For all species, the reproducibility is better than 6% (relative standard deviation) at the ng level for Pb. The absolute selectivity is demonstrated by the accurate analysis of standards and gasoline samples.

fitted with a glass column (1.0 m x 0.085 inch i.d. x 1/8 inches o.d.) and packed with 3% OV-101 on Chromosorb W acid-washed DMCS (60-80 mesh). A Varian 1475 atomic absorption spectrometer, equipped with a hollow cathode lamp for Pb and deuterium background correction, was used to carry out the absorbance measurements. The output peaks were displayed in a Cole-Parmer 156 chart recorder. The interface between the gas chromatograph and the atomic absorption spectrometer was achieved using stainless steel tubing (0.43 cm long x 0.5 mm i.d.),

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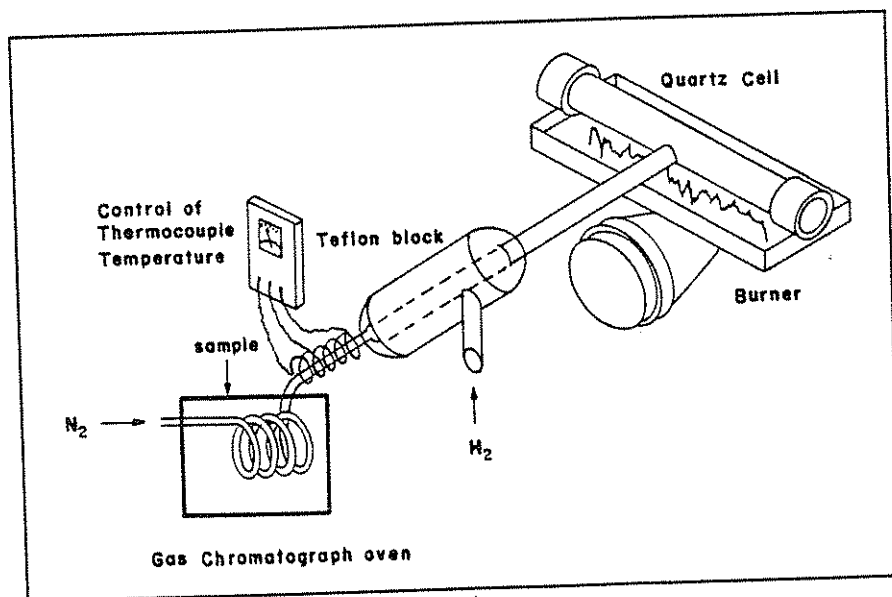


Fig. 1. Schematic diagram of the GC-AAS system.

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wrapped with a heating tape at 150°C, and closely fitted with a cylindrical block made of Teflon (Figure 1). The Teflon block, containing a side tube of 2.0-mm i.d. through which an additional flow of hydrogen can be introduced to improve the sensitivity, was closely fitted to the 3.0-mm o.d. side arm of the silicon absorption cell. Standard working solutions (Associated Octel Co., South Wirral, England) were prepared in diisopropyl ether daily before use, containing 20 mg/mL tetramethyllead (TML), trimethyl-ethyllead (TMEL), dimethyldiethyl-lead (DMDEL), methyltriethyllead (MTEL), and tetraethyllead (TEL) in diisopropyl ether.

An investigation of the optimal GC and AAS working parameters of this procedure was performed by repeated injection of a standard test solution containing a 20- $\mu\text{g/L}$ concentration of the TAL compounds under study in diisopropyl ether. Figure 2 shows that the nitrogen carrier gas flow rate is a rather critical parameter, with an optimum at about 30 mL/min. The decrease in sensitivity at higher flow rates could be attributed to the reduced residence time of the atomic cloud in the light path (4). The sharp decrease for lower flow rates could also be related to excessively long GC elution times and, therefore, to a higher probability of thermal decomposition.

The introduction of hydrogen gas through the Teflon block at the end of the interface increased the sensitivity (Figure 2). Some authors have also described the beneficial effect of hydrogen on the AAS signal (4,8), which is probably the result of the higher temperature developed within the cell due to the burning of the hydrogen gas. A flow rate of 109 mL/min was chosen as the optimal value.

Other optimized instrumental parameters that were found to be a good compromise between the separation of the different

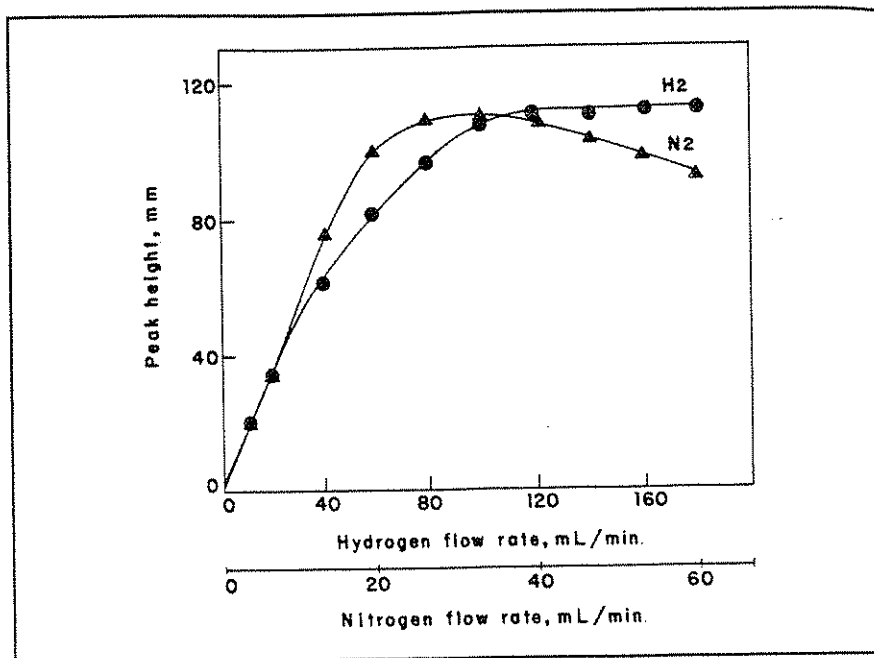


Fig. 2. Effect of nitrogen carrier gas flow rate on the sensitivity (20 $\mu\text{g/L}$ TML; other conditions as specified in Table I).

organolead compounds, sensitivity, and reproducibility are summarized in Table I. Figure 3 is a typical GC-AAS chromatogram using these parameters. The retention times for TML, TMEL, DMDEL, MTEL, and TEL compounds were of 0.9, 1.5, 2.5, 3.4, and 4.3 minutes, respectively.

Calibration graphs were prepared for the five organolead compounds by measuring peak heights and absorbance vs. amount of lead (Figures 4 and 5). These graphs show that the sensitivities obtained by either evaluating peak heights or absorbance are almost identical. Sensitivities increased in the following order: TML > TMEL > DMDEL > MTEL > TEL. Typically, good linearity was obtained from 1–25 ng Pb injected. Other analytical characteristics of the method are presented in Table II. The results show satisfactory precision, good accuracy, and suitable detection limits. These detection limits were superior to those previously reported using a GC-AAS system (4), but lower than those previously obtained using a GC-GFAAS system (2).

A series of normal quality gasolines from Venezuela were analyzed to illustrate the scope of the optimized speciation procedure and to assess the burden of organolead compounds and its species composition in these samples (Table III). All TAL compounds were detected in the various grade gasolines; the highest concentrations were found for TEL and TML. The TEL content decreases as the grade of gasoline decreases, whereas the TML content increases as the grade of gasoline increases. The total alkyllead content increases with the gasoline grade.

CONCLUSION

The GC-AAS system described is a simple, sensitive, precise, and accurate method for the selective determination of TAL compounds in gasolines. The signal is measured in the most useful part of the calibration graph and these measurements can be performed within five minutes using 1- μL sample volumes.

TABLE I
GC-AAS Conditions used for the Speciation and Determination of TAL Compounds

System	Parameter	Condition
GC	Sample volume	1 μ L
	column	
	Packing material	3% OV-101 on chromosorb W (60-80 mesh)
	Dimensions	1.0 m x 0.08 inch. i.d. x 1/8 inch. o.d.
	Temperatures:	
	Column program	50-200°C at 8°C/min
	Injector	180°C
	Detector	150°C interface 150°C
	Gas flow rates:	
	Nitrogen (carrier gas)	30 mL/min
AAS	Hydrogen	109 mL/min
	Light source ^a	Pb hollow cathode lamp
	Lamp current	5 mA
	Slit width	1 nm
	Air/acetylene flow rate	8/2 L/min
	Recorder Range	10 mV full scale
	Speed	1 cm/min

^a With deuterium background correction.

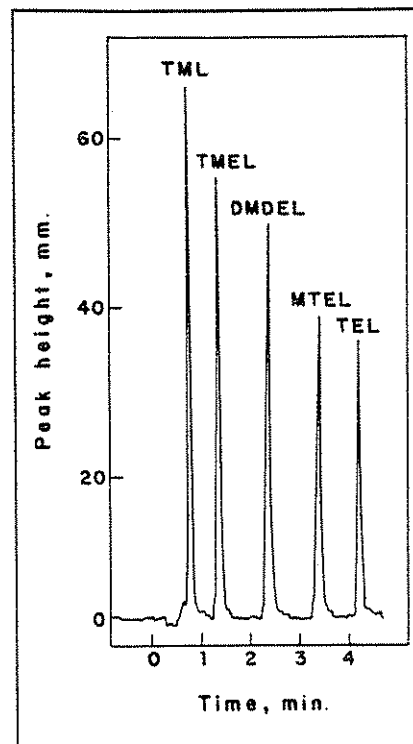


Fig. 3. Effect of hydrogen flow rate on the sensitivity conditions as specified.

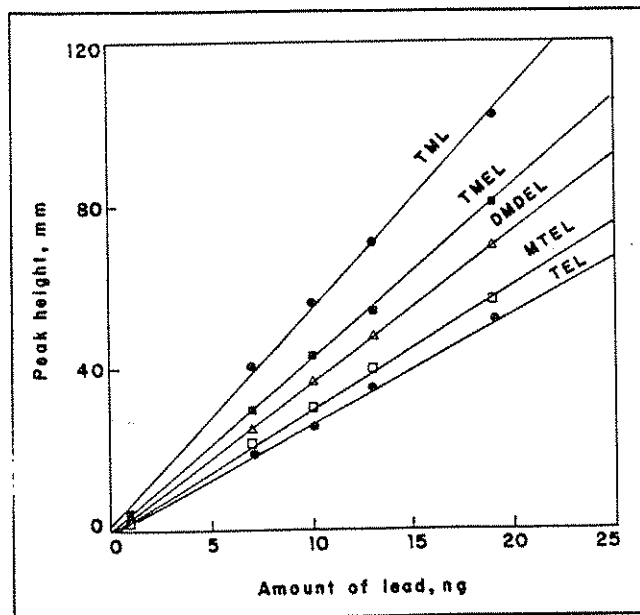


Fig. 4. Typical GC/AAS Chromatogram; 13 μ g/L of each alkyllead compound; conditions as specified in Table I.

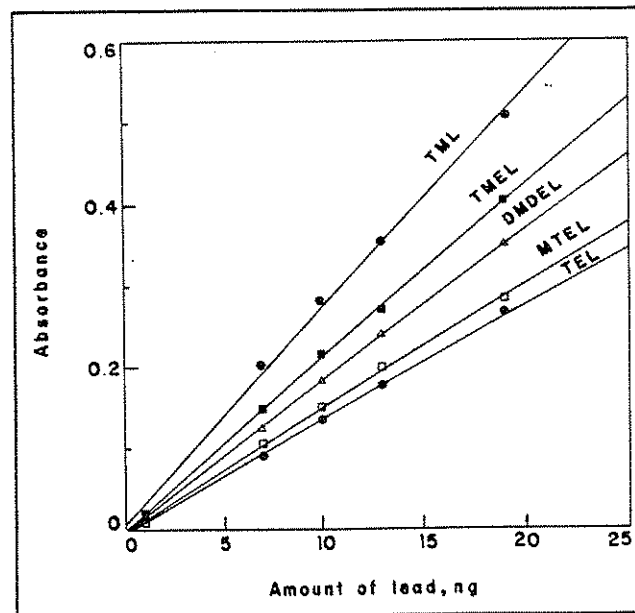


Fig. 5. Calibration graphs obtained by evaluating (a) peak height and (b) absorbance vs. TAL compound concentrations.

TABLE II
Some Analytical Characteristics of the Determination
of TAL Compounds by GC-AAS

Component	Precision ^a (RSD %)	Mean recovery ^b (%)	Absolute detection limit ^c (ng)
TML	2-4	102	0.10
TMEL	3-5	98	0.13
DMDEL	3-6	100	0.13
MTEL	3-5	99	0.20
TEL	4-6	102	0.25

^a Ten measurements of standard (with 10 µg/L of organolead compound) and gasoline samples.

^b Five analyses of gasoline with different amounts of organolead compounds.

^c Detection limit defined as three times the standard deviation of the noise divided by the sensitivity of the five organolead compounds.

TABLE III
Determination of Organolead Compounds in
High Octane Number Venezuelan Gasolines

Octane number	Organolead compounds	Amount (µg/mL)	Total (µg/mL)	Total by digestion (µg/mL)
95	TML	65		
	TMEL	5.1		
	DMDEL	2.2		
	MTEL	5.2		
	TEL	458	536	540
89	TML	110		
	TMEL	3.2		
	DMDEL	2.0		
	MTEL	2.1		
	TEL	360	477	480
87	TML	134		
	TMEL	2.7		
	DMDEL	1.6		
	MTEL	1.3		
	TEL	239	379	380
83	TML	155		
	TMEL	2.1		
	DMDEL	1.7		
	MTEL	1.3		
	TEL	207	367	370

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