Determination of Tetraethyl Lead in Gasoline fuel

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Abstract

Tetraethyl lead TEL is an organometallic component that is added to gasoline to improve engine performance. This material is also called an anti-knock because it reduces the knocking of the engine. The engine starts to throttle if the oil in its pistons burns quickly or after a short period of time from entering it. In this study, a sensitive, simple, economical, fast and accurate, an indirect spectral analytical method has been developed using Eriochrome Black T as chelating agent without use of separation and isolation to estimate the amount of lead in the gasoline by using UV-Visible spectrophotometer instrument. The accuracy and sensitivity of the method were 99.9067 ± 0.09 and 0.0338 while the limits of detection (LOD) and qualification (LOQ) were 0.0721 and 0.2186 μg ml^{-1} respectively. The developed method can be applied to water, biological, environmental and fuel sample.

Keyword: Tetraethyl, Gasoline fuel, UV, LOD

1. Introduction

The manufacture and use of tetraethyl lead began in the thirties of the last century to improve the performance of internal combustion machines(The, 1939). Tetraethyl lead is added in minute proportions to gasoline in order to improve the quality of its combustion and prevent cracking in internal combustion machines. In view of the toxicity of lead compounds, it is necessary to control its addition and identify appropriate methods for quantifying the added quantities and protecting humans and the environment from its harmful effects. differential pulse polarography and differential pulse anodic- stripping voltammetry were used to estimate lead in gasolines(Polak, 1991). There is a study that presented modern methods for determining metals by atomic absorption in aviation and automotive gasolines(Balak, Volgin and Privalenko, 2021). For the analysis of tetraethyllead in gasoline (leaded and unleaded) and water, a new approach based on solid phase microextraction (SPME) and detection by quartz furnace atomic absorption spectrometry after thermal desorption from the microextraction fiber has been presented(Fragueiro *et al.*, 2000; Crnoja *et al.*, 2001; Fragueiro, Lavilla and Bendicho, 2004). After in situ hydride production and headspace solid phase microextraction, capillary gas chromatography on-line coupled with atomic. absorption spectrometry was used to analyze organomercuric species in soils from orchards and wheat fields(Jiang, 1999; Yu and Pawliszyn, 2000). Polarography is the most used electrochemical technique for determining Pb 2+ in leaded gasoline(Zhang *et al.*, 2021). In our study has been developed an indirect spectral method which has high sensitivity and great accuracy to estimate the tetraethyllead in gasoline fuel.

2. Experimental

2.1. Preparation solutions of standards, working, sample and reagent

All solutions were prepared with analytical grade reagents and freshly deionized water DIW. Stock solution (I) µg/µl of Pb(II) was prepared by dissolving (0.1598 g) of lead nitrate in DIW and made up to 100-ml volumetric flask, and stock solution (II) µg/µl of TEL was prepared by dissolving (0.100 g) of tetraethyl lead in isooctane and made up to 100-ml volumetric flask. Working solution (reference solution) was prepared by diluting 50 ml of stock solution (II) to 500-ml volumetric flask by isooctane. The reference solution (III) has been used to create optimal conditions for maximum reliability and accuracy of the new method. In a 500-ml flat bottom flask equipped with a magnetic bar and attached to a reflux condenser, 20 ml concentrated nitric acid was poured to 200 ml of solution (III) and heated to 40-50 $^\circ$C on a hot plate stirrer for 30 minutes. The liquid mixture was cooled to room temperature and transferred to a 500-ml stoppered-glass separator funnel, where it was mixed with DIW used to clean the decomposition flask. The stopper was loosen carefully and let the separator to stand 2 minutes. The acid layer readily separates at the bottom of the funnel. The acid layer was drawn into a 100-ml volumetric flask, a 20 ml of DIW was added to the funnel and shaken 15 minutes and let stand 2 minutes and draw off the lower water layer into the volumetric flask containing the acid solution. The collected acid and water portions, which should amount to about 80 ml and completed to the mark with DIW. The sample solution was prepared by the same procedure as described above except that solution (III) was replaced with gasoline fuel.

Buffer solution pH 9 was prepared by mixing 0.2M ammonia and 0.2M NH_4NO_3 solutions in suitable proportion and the pH was adjusted by a pH meter. Stock standard solution µg/µl of Eriochrome Black T (EBT) was prepared by transferring a (0.1 g) of (EBT) to a 100 ml volumetric flask by means of small portions of DIW. The total volume of water used was about 10 ml. Two milliliters of pH 9 buffer solution were added and the solution was diluted to 100 ml with absolute ethanol.

2.2. Procedure

To each flask in a set 50 ml volumetric flasks, 1 ml of digested reference solution by nitric acid was added except the first flask, a variable volume of solution 50 µg/ml Pb(II) which prepared from solution (I) was added except the first flask and second flask, 2 ml of solution (20% w/v) NaCN, 15ml of triethanol amine, 3ml hydroxyl amine, 5 ml of the buffer solution pH 9 and 10 ml of solution µg/µl (EBT) were added. Then all of the volumetric flasks were supplemented by deionized water to the marks. The blank solution was prepared at the same procedure without addition solutions of EBT and lead. The absorbance of these solutions was measured at 531 nm. A straight line is obtained which corresponded to the equation ($A_{531}= 0.0169$ C + 0.169. C is the amount of lead in µg ml^{-1}). The developed method was applied to a live sample of gasoline by using 1ml of sample solution in place of reference solution to estimate lead in the fuel.

3. Results and Discussion

Eriochrome black T (EBT) is amongst the most significant azo indicators used in complexion titration of numerous metals: Ca, Mg, Mn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and the Pt metals. Therefore, the formation constants of complexes for those ions with EBT were studied(Mamdouh S Masoud, Hammud and Beidas, 2002). Studies referred to the high sensitivity of the EBT reagent to react with lead ions in a 1:1 molar ratio, which helped us to find the new indirect method of estimating lead in gasoline fuel (Szabó *et al.*, 2011; Wang *et al.*, 2018).

The maximum wavelength of the absorption of the EBT reagent changes according to the change in the acidity of the medium that is chosen to form the complex with an ion to be studied and to estimate its quantity(Pysarevska *et al.*, 2013). In this study the spectra of the EBT and Pb(II)-EBT showed a maximum absorption peak at 531and 407 nm in an acidity solution equals to 9 as in Figure 1and 2 respectively.
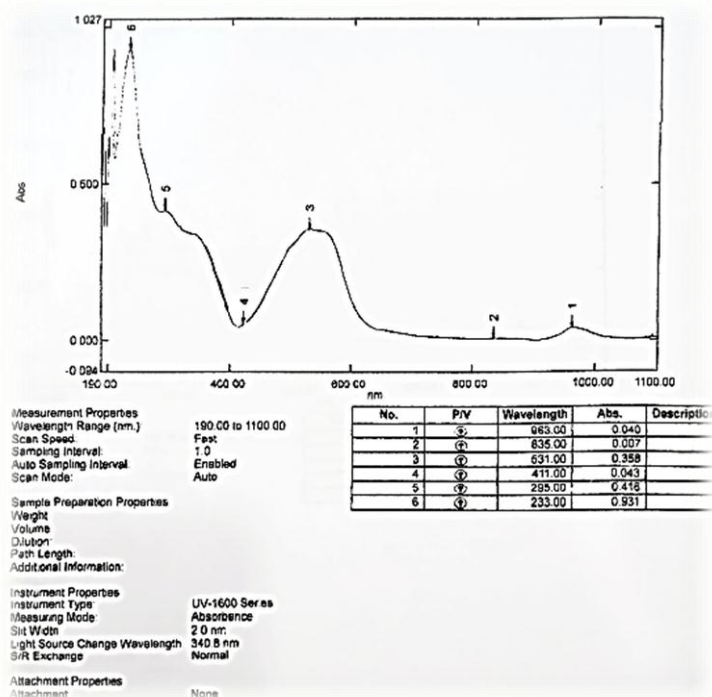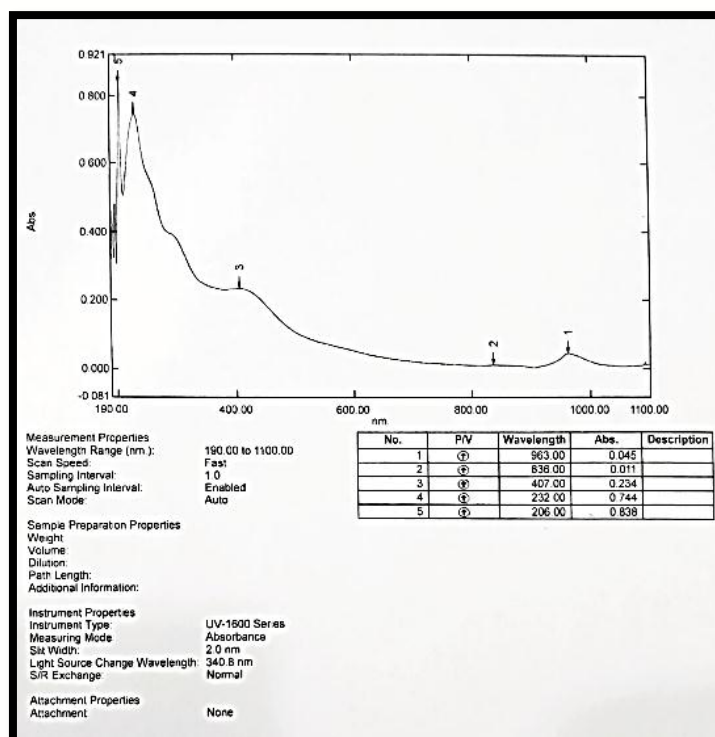

Figure 1. Spectrum of EBT at pH 9.

Figure 2. Spectrum of Pb(II)-EBTcomplex at PH equals 9.

3.1. Interferences study

The interference effect of the Al, Zn, and other ions on the determination of Pb was eliminated by using sodium cyanide, triethanol amine and hydroxyl amine as masking agents and wavelengths of the maximum absorbance for Al and Zn ions complexes were far from the wavelength of maximum absorbance for EBT as shown in table 1.

Table 1. wavelengths of the maximum absorbance for EBT and other compounds

Compound	λ_{max} nm
EBT	531
Al(III)-ethanolamine complex	412
Pb(II)-EBT complex	407
Zn(II)-cyanide complex	320

To ensure that there is no interference between the signal of reagent EBT and signals of Al(III) and Zn(II) cyanide complexes and Pb(II)-EBT complex, the

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absorption   spectrum was recorded for a solution containing a 1 ml of reference solution, 2 ml solution (20% w/v) of NaCN, 15ml of triethanol amine, 3ml solution (10% v/v) hydroxyl amine, 5 ml of buffer solution pH 9, 10 ml of solution μg/μl of the (EBT) and diluted to 50 ml with deionized distilled water by using a UV-1600 Series by Shimadzu Scientific Instruments Inc. The blank solution was prepared at the same procedure without addition solutions of EBT and lead. Where the wavelengths of greatest absorption of EBT and Pd(II)-EBT complex are 531 and 407 nm respectively as shown in fig.1and fig.2 in this study. And the wavelengths of greatest absorption of complexes Al(III) ethanolamine and Zn(II) cyanide are 412 and 300 nm respectively(Serih, 2020).

3.2. Quantitative study

Quantitative analysis of lead in leaded aluminum alloy is performed by measuring the decrease in the absorbance of the EBT by the new developed method based on the calculation of the difference between the absorbance of EBT at its initial concentration (A_{L_o}) and its absorbance at residual concentration (A_{Lr}) as a result of its reaction with lead ions in the sample solution by using standard addition method and application of the following equation:

Absorbance of lead $A_{ML} = A_{L_o} - A_{Lr}$

Where $A_{L_o} = K\,C_{L_o}$

$\quad\quad A_{Lr} = K\,C_{Lr}$

C_{L_o} and C_{Lr} represent the initial and residual concentrations of EBT respectively.

The absorbance of 0.1 μg/μl EBT at λ_{max} (531 nm) is (0.358) as shown in fig.1. And the decrease in EBT concentrations illustrated in fig.3.
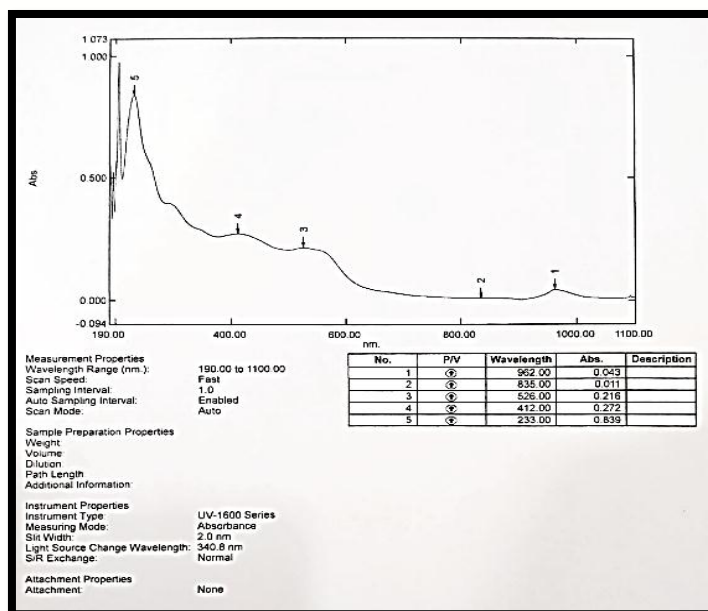

Figure 3. Absorption spectrum of the decrease in EBT concentration and increase in lead ions concentration.

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Studies indicated that (Wang *et al.*, 2018; Serih, 2020) the molar ratio of Pb(II):EBT is 1:1. They contributed to the development of our new method for determining lead in the leaded aluminum alloy as shown in table 2 and figure 4.

Table 2. Data were used to obtain absorbance of Pb (II) as $A_{ML} = A_{L_o} - A_{Lr}$

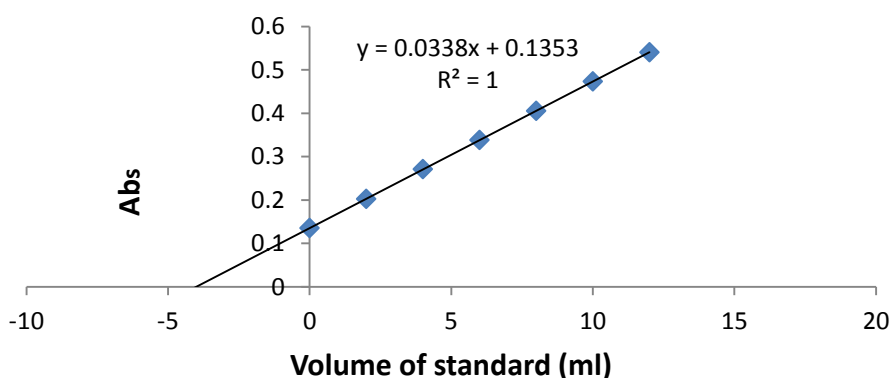| No.	Volume of sample ml	Volume of standard ml	Volume of EBT ml	A_{L_o}	A_{Lr}	A_{ML}
1.	0	0	10	0.715	0.715	0
2.	1	0	10		0.5798	0.1352
3.	1	2	10		0.5124	0.2026
4.	1	4	10		0.4441	0.2709
5.	1	6	10		0.3772	0.3378
6.	1	8	10		0.3097	0.4053
7.	1	10	10		0.2420	0.4730
8.	1	12	10		0.1745	0.5405

Figure 4. Standard additions curve to determine the lead in the preparative gasoline fuel using the new developed spectral method.

In general(Serih, 2020): $S = K * C_a$

Where: C_a = concentration of analyte = $(C_x \cdot V_x + C_s \cdot V_s) / V_t$

K = constant

S = instrument response (signal) = $K \cdot (C_x \cdot V_x + C_s \cdot V_s) / V_t$

V_x = volume of the sample aliquot

C_x = concentration of the sample

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V_s = volume of standard
C_s = concentration of the standard

$$S = K . C_s . V_s / V_t + K . C_x . V_x / V_t$$

From the linear regression: $y = m . x + b$

$y = S$
m = slope = $K . C_s / V_t$
$V_s = x$
b = intercept = $K . C_x . V_x / V_t$

The concentration of analyte can be calculated by applying one of the two equation :

$$C_x = b . C_s / m . V_x \text{ or } C = (V_s)_0 . C_s / V_x$$

Where $(V_s)_0$ is the volume of standard when the device response is zero.
Then the percentage of analyte in the sample is calculated by the following equation :
Al % = $C_x . V . D.F . 100 / W$
Where C_x = Concentration of lead (µg/ml).
V = Markup volume (ml)
D.F = dilution factor
W = weight of sample

3.3. Calculation the accuracy and precision of developed method

In order to validate the developed analytical method, a series of standard solutions were prepared and their absorption measured according to the above procedure and the accuracy of the method was estimated from the calculation of percentage recovery and its standard deviation. The standards error and deviation of intercept and the limits of detection (LOD) and quantification (LOQ) were also calculated from Fig. 5 as shown in Table 3.
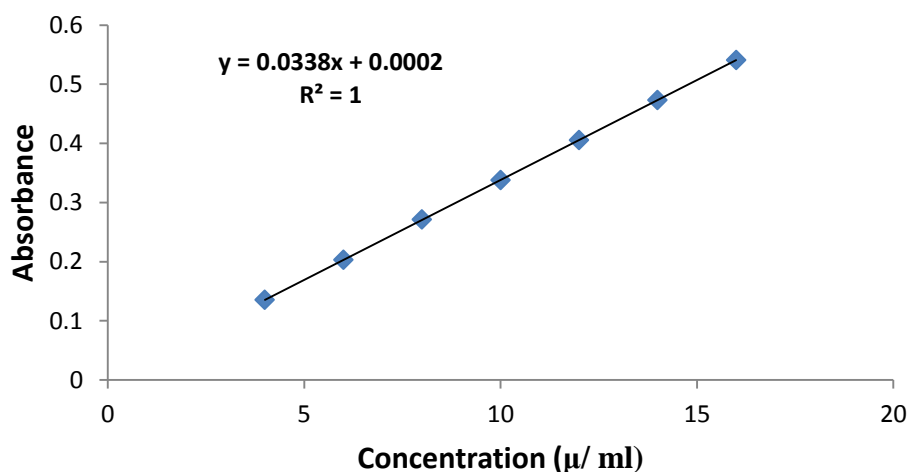

y = 0.0338x + 0.0002
R² = 1

Figure 5. Calibration curve of the validation developed spectrophotometric analytical method

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Table 3. Results of calibration curve analysis

| Parameters	Value
Accuracy	99.9067 ± 0.09
Slope	0.0338
Intercept	0.0002
Linear range	$0.1 - 40\ \mu g\ ml^{-1}$
Correlation coefficient	1.00
SE of intercept	0.0002
SD of intercept	0.0007
LOD	0.0721
LOQ	0.2186

4. Environmental study

One of several low cost adsorbents, PFAC displayed decent adsorptive features. PFAC material as an adsorbent is active for EBT elimination from dye solution. The adsorption of EBT was reliant on pH, original dye concentration, adsorbent amount as well as interaction time which were improved. The action of EBT is possible between pH of 4 and 6 whereas the maximum color removal was achieved at pH 6. The removal rate increased with the increase in adsorbent dosage and contact time while the rate decreased with the increase in EBT concentration and pH. The present study concluded that the Parthenium flowers activated carbon material as an adsorbent can be effectively utilized for the removal of EBT from aqueous environment(Mahadevaswamy *et al.*, 2016). Several studies indicate that although legislation in many countries prohibits the use of tetraethyl lead in gasoline, the effects of accumulated lead are still felt in those countries, including the United States of America. Nothing is a safe amount of lead in the body, and even low levels can cause cognitive and developmental problems such as learning delays and disabilities, low IQ, and attention-deficit/hyperactivity disorder. A BLL level of 5 g/dL or greater, according to the CDC, is considered the basis for an environmental and educational intervention. According to the Environmental Protection Agency, there are approximately 24 million housing units at severe lead hazards today, 4 million of which include children. Minorities and low-income families make up a significant proportion of families exposed to lead hazards in their homes. Temporary lead risk controls may be necessary to reduce lead levels in the home in a simple and cost-effective way to help families with suspected lead hazards in the home (16). Studies have shown that the continuous use of gasoline containing tetraethyl lead is harmful to the environment, in particular to human health(Dioka *et al.*, 2004; Tuakuila *et al.*, 2012, 2013).

5. Structure of complex

The structure of complex that was produced by reaction between Pb(II) and eriochrome black t as follows(Mamdouh S. Masoud, Hammud and Beidas, 2002):
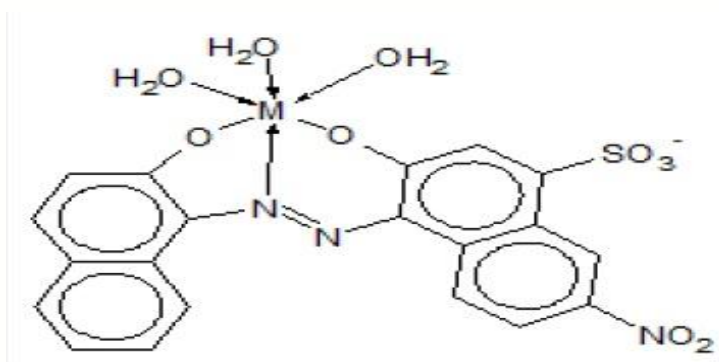
6. Conclusion

The our newly developed study is a non-polluting method for the environment, so that the EBT reagent can be recovered from the solutions through the process of adsorption on activated carbon and reused again in the laboratory analyzes and the lead ions are precipitated by sodium carbonate and its separation and isolation without going to water.

7. Acknowledgement

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