

# Determination Of Lead In Gasoline By Extraction And Titration At Kurdistan Region – Iraq

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## **Abstract:**

**Introduction:** *A method relates to the determination of lead, tetraethyl lead (TEL) and tetramethyl lead (TML) in commercial gasoline in different places in Kurdistan region – Iraq by dual extraction apparatus and titration was proposed.*

*The lead was extracted by dual extraction apparatus; gasoline, gas oil, iodine monochloride solution and concentrated hydrochloric acid used for extraction. The time required for an extraction is about 45 minutes. The lead content was estimated by titration with the standard EDTA solution at PH 5.*

*The research aimed to determine concentration levels of lead in gasoline available in the local gasoline stations.*

**Material and Methods:** *Ten gasoline samples were gathered from gasoline stations spreading in Erbil, Sulaimania, Koya and Ranya cities.*

**Results:** *The analytical results for various gasoline samples show a lead content within the range (0.016 – 0.18) gm/L, TEL (0.015 – 0.17) gm/ml and TML (0.010 – 0.121) gm/ml. Research octane number(ROn), motor octane number(MON) and anti knocking Index(AKI) were determined for all samples.*

**Conclusion:** *A method for the determination of total lead (such as tetraethyl lead and tetramethyl lead) in commercial gasoline which is used as "anti-knock" additives to gasoline has been proposed.*

**Key Words:** *Gasoline, Lead; Dual extraction apparatus; TEL; TML*

## INTRODUCTION:

Leaded gasoline contains tetraethyl lead and, to some extent, tetramethyl lead which are used as "anti-knock" additives to gasoline<sup>1</sup>. Therefore, leaded gasoline is identified as a source of lead pollution with adverse health effects in humans. Lead exposure in gasoline station occurs from lead fumes generated during filling cars, from cars emissions and from contaminated hands, food, water and clothing<sup>2</sup>.

Many countries were forced to reduce the lead content in the gasoline toward the complete elimination of lead additives in motor gasoline. Leaded gasoline is a major source of human lead exposure. By reducing gasoline lead content, airborne lead emissions and blood lead can be reduced. Evidently, lead is considered as a harmful pollutant.

Gasoline is a complex mixture of light hydrocarbons containing 5 to 11 carbon atoms and having a boiling point range of 15°C to 190°C (60 – 375 °F). In the atmospheric distillation, the fraction identified as light naphtha, medium naphtha and heavy naphtha are the potential components of gasoline<sup>3</sup>.

Gasoline and diesel engines emit a large amount of pollutants and are major sources of urban air pollution<sup>4</sup>. Emissions related to automobile fuel combustion contribute significantly to atmospheric pollution, ultimately reducing air quality and negatively affecting human health. The gasoline used as fuel in automobiles may contain metalloids and metallic elements such as Pb, Cu, Zn, Ni, Fe, As, Cd, Hg, Se and Ti. These elements are derived from the raw product, but can also be introduced as additives during production or contaminants during storage<sup>5</sup>.

Methods involving preconcentration techniques for the quantification of trace elements in different samples, including fuels, are found in the literature<sup>6</sup>. In these methods, different solid phases have been modified with organo functional groups to extract metallic species. Possibly, the main problem related to the development and implementation of these procedures in the analysis of automotive fuel is the difficulty in maintaining the organo functional group attached to the solid phase, due to the leaching action of this type of sample<sup>7,8</sup>.

Flame atomic absorption spectrometry (FAAS) is not sufficiently sensitive for the quantification of trace elements in fuel samples. In addition, the direct introduction of petroleum products may cause instability in the flame<sup>9, 10</sup>. However, in conjunction with a preconcentration step, FAAS methods may prove to be more reliable and accurate for the analysis of fuel samples. One disadvantage of the conventional AAS methods over other techniques, such as ICP OES and ICP-MS, is the longer time required for the determinations, due to their mono-element character<sup>11</sup>.

## MATERIAL AND METHODS:

### *Tested samples*

Ten samples from different fuel stations in (Erbil, Sulaimania, Koya and Ranya) tested to determine the lead concentration (TEL and TML), RON, MON and AKI. Dual extraction apparatus from Linetronic Technologies (Switzerland) and octane meter/ petroleum quality analyzer from Shatox (Russia) were used.

### *Reagents*

Concentrated nitric acid, concentrated hydrochloric acid, ammonia solution (1:1), sodium acetate / acetic acid buffer solution, iodine monochloride solution, EDTA (Na<sub>2</sub>EDTA) solution (0.005 M), gas oil standard and gasoline standard (Rofa – France).

### *Procedure of test:*

Measure the temperature of the sample to the nearest (0.5°C). Using a cylinder, transfer 50 ml of iodine monochloride solution, 50 ml of the gasoline to the flask through the thistle tube of the dual extraction apparatus (ART.LT/EA-244000/M), and add approximately 50 ml of gas oil. Add 50 ml of HCl and reflux the mixture for 45 min. Use the full heat of the heater until boiling has begun (usually 0.5 to 1.0 min); then adjust the rheostat to regulate the heat to maintain boiling at a vigorous rate, but not at such a rate to cause bumping in the flask or to cause the condenser to flood.

After the 30 min reflux period, turn off the heat, allow the sample to cool a few minutes, and drain the acid layer into a 500 ml beaker. Then add 50 ml of water and reflux the water and gasoline for 5 min, using the full heat of the heater.

Drain the water into the 500 ml beaker, and repeat the water extraction<sup>12</sup>.

Add a few glass beads to the beaker, cover it with the watch glass and bring in to low boiling on a hot plate until the volume of the solution is reduced to 15- 20 ml. Without removing the beaker from the hot plate, add 5 ml of nitric acid to run slowly down the sides of the beaker, and then evaporate the contents almost to dryness to oxidize any organic materials present. Repeat the nitric acid treatment until a white residue remains.

Remove the watch glass and evaporate the solution to dryness, then remove the beaker from the hot plate and allow it to cool.

Add 200 ml of distilled water to the beaker and swirl to dissolve the residue. Add several drops of bromothymol blue yellow indicator solution and neutralize with the ammonia solution until the colour just changes from orange to blue, then add 10 ml of sodium acetate and acetic acid buffer solution and 5 drops of the xylenol orange indicator solution. In the presence of lead, the solution shall turn into a plum-red color.

Titrate with standard disodium EDTA solution till the colour of the test solution changes to orange near the end point, at which the colour changes sharply from orange to permanent bright lemon yellow. Record the volume used.

Carry out a blank determination on all reagents without sample and correct the volume use for the test accordingly<sup>13</sup>.

## RESULTS AND DISCUSSION:

Lead is a toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. It is a cumulative toxicant that affects multiple body systems, including the neurological, hematological, gastrointestinal, cardiovascular and renal systems. Children are particularly vulnerable to the neurotoxin effects of lead, and even relatively low levels of exposure can cause serious and, in some cases, irreversible neurological damage<sup>14, 15</sup>. Lead exposure is estimated to account for 0.6% of the global burden of disease, with the highest burden in developing regions. Recent reductions in

the use of lead in petrol (gasoline), paint, plumbing and solder have resulted in substantial reductions in lead levels in the blood<sup>16</sup>. However, significant sources of exposure to lead still remain, particularly in developing countries. Further efforts are required to continue to reduce the use and releases of lead and to reduce environmental and occupational exposures, particularly for children and women of child-bearing age<sup>14</sup>.

Refineries add TEL and TML to gasoline to increase octane. In most stations, adding lead is the least expensive means to providing incremental octane to meet gasoline specifications. At sufficiently high levels, addition of lead can increase octane as much as 10 to 15 control octane numbers.

Octane number is a measure of a gasoline's propensity to knock, the higher a gasoline's octane is, the better is its antiknock performance. Gasoline has two octane ratings. The research octane number (RON) measures antiknock performance at low engine speeds; the motor octane number (MON) measures antiknock performance at high engine speeds. For any gasoline, RON is higher than MON, usually by 8 to 12 numbers. The difference between the two is called octane sensitivity<sup>17</sup>.

The extraction of lead from leaded gasoline is based on the interaction of tetraethyl lead (TEL) and tetramethyl lead (TML) with a solution of iodine monochloride. The lead changes from the tetravalent state to divalent, forming a salt with the inorganic extractant<sup>18</sup>.

Since the reaction of iodine monochloride with the lead alkyl is quantitative, the amount of iodine monochloride can be stoichiometric in relation to the amount of lead alkyl present in gasoline. More usually, however, the amount of iodine monochloride used will be in excess of stoichiometric.

The concentration of iodine monochloride solution used in this method will, of course, vary with the volume of gasoline to be treated. As a matter of convenience the solution used will be in the range (0.1 – 2) molar. Where the petroleum product contains any significant amount of olefin higher amounts of iodine monochloride will be used

because iodine monochloride reacts readily with an olefinic double bond<sup>19</sup>.

This method is based on the discovery that lead alkyls in gasoline will react quantitatively with an aqueous solution of iodine monochloride (to form water soluble dialkyl lead halides), thoroughly mixing the inorganic phase with the organic phase, complete extraction of the lead from the organic phase into the inorganic phase is obtained leaving the gasoline substantially free of lead.

In this work it was found that the content of alkyl lead in some gasoline samples approaches the 0.007 gm/L or the gasoline lead free ( references of this research ) and other samples higher this range, whereas the higher concentration in samples that were subjected to test have been denoted to pollution to the gasoline was occurred from previous additions. Our research references also denoted that concentration of 0.5 gm/L of alkyl lead must be added to the gasoline fuel in order to increase its performance.

Using the procedure that has been used in our work the minimum level of alkyl lead in gasoline samples was found equal to 0.016 gm/L and the maximum value of alkyl lead was found equal to 0.287 gm/L. These levels of alkyl lead found in our research are below the natural additions that give higher performance of gasoline product toward vehicles of gasoline engines.

The results obtained using the commercial gasoline that contains TEL, TML, RON, MON and AKI was employed to determine the content of lead in ten commercial gasoline samples are shown in Table 1. Figure 1, shows lead content (gm/L) in tested samples, and Figure 2, shows (TEL and TML) content (gm/ml) in tested samples.

## CALCULATIONS:

Concentration of lead (gm/L) =  $8.288 (V_1 - V_0) M_1 [1+0.0012 (t-15)]$

Where<sup>20</sup>:

$V_0$  = the volume in milliliters of standard volumetric disodium EDTA solution used for the blank test.

$V_1$  = the volume, in millimeters of standard volumetric disodium EDTA solution used to titrate the test portion.

$M_1$  = the molarity of the standard volumetric disodium EDTA solution.

t = the temperature in °C of gasoline sample.

## CONCLUSION:

A method for the determination of total lead (such as tetraethyl lead and tetramethyl lead) in commercial gasoline which is used as "anti-knock" additives to gasoline has been proposed. Based on the extraction of lead using dual extraction apparatus by iodine monochloride. It is often necessary to determine the lead content of gasoline, because it's direct effects on the performance toward the engines of vehicles and reduce environmental contamination.

## ACKNOWLEDGEMENTS:

Our sincere thanks to Koya technical institute – Oil technology department for providing us with the necessary requirements needed without which this study would not have been possible.

**Table 1: TEL, TML, RON, MON and AKI values for commercial gasoline samples.**

No.	sample	Lead (g/L)	TEL(g/ml)	TML(g/ml)	RON	MON	AKI
1	A	0.01630	0.01541	0.01056	94.3	84.5	98.5
2	B	0.02875	0.02719	0.01863	95.3	85.3	90.3
3	C	0.06194	0.05859	0.04013	94.6	84.7	98.7
4	D	0.04534	0.04289	0.02938	95.3	85.3	90.3
5	E	0.02045	0.01934	0.01325	93.3	83.9	88.6
6	F	0.18641	0.17634	0.12079	95.3	85.3	90.3
7	G	0.10343	0.0978	0.06702	93.5	84.0	88.8
8	H	0.07024	0.06644	0.04551	95.3	85.3	90.3
9	I	0.28598	0.27053	0.18531	93.0	83.7	90.3
10	J	0.02460	0.02327	0.01594	90.5	82.2	86.3

A,G,E ( Erbil) - B,C,D( Koya) – H,F( Ranya) – I,J ( Sulaimania)

**Figure 1: Flow chart shows lead content (gm/L) in tested samples**

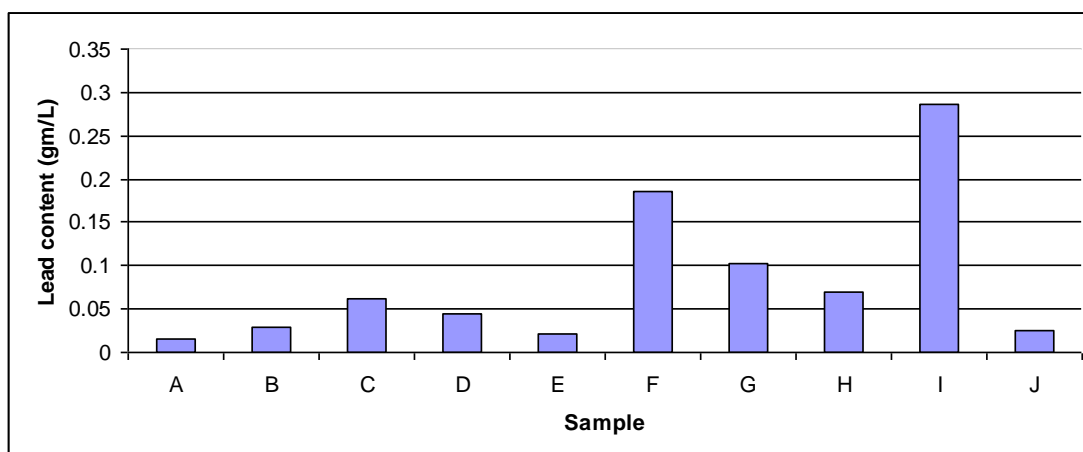
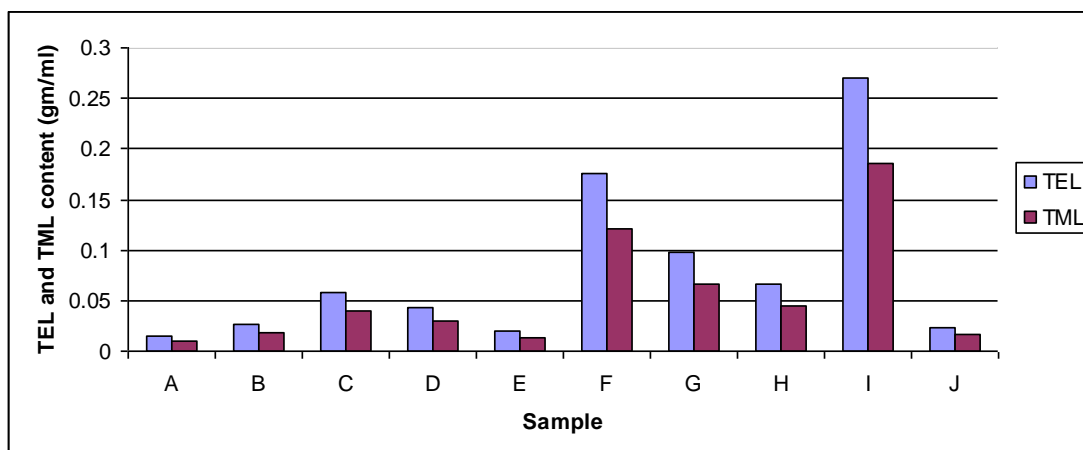


Figure 2: Flow chart shows (TEL and TML)content (gm/ml) in tested samples



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