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COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES
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The determination of lead in gasoline vehicle exhaust using Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

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A Thesis submitted to the Department of Chemistry in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

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This is to certify that the thesis prepared by Amare Mitiku entitled the determination of the level of lead in gasoline vehicle exhaust using Microwave Plasma Atomic Emission spectroscopy (MP-AES) and submitted to the department of chemistry in partial fulfillment of the requirements for the degree of master of science in chemistry complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

Approved by Examining board:

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List of Abbreviations

EGCM	External Gas Control Model
EPA	Environmental Protection Agency
EU	European Union
FAAS	Flame Atomic Absorption Spectroscopy
IARC	International Agency for research on cancer
kICP	Inductively coupled argon Plasma
ICP-MS	Inductively coupled argon Plasma Mass Spectrometry
IDL	Instrumental Detection Limit
IJEAB	International Journal of Environment Agriculture and Biotechnology
LOD	Limit of Detection
MP-AES	Micro Plasma Atomic Emission Spectroscopy
TEL	Tetra Ethyl Lead
USSR	Union of Soviet Socialist Republics
WHO	World Health Organization

Abstract

In recent times, the skyrocketing vehicular population has been accompanied by a decreasing level of vehicle maintenance, aging of vehicle, and increasing inclusion of metal-based additives in fuel. Lead has deleterious health implications ascribed to their tendency to displace the functional groups of enzymes there by modifying physiological and biochemical processes within the body. With the aid of a plastic spatula, accumulated soot particles were scrapped and collected from the inner surface of the tailpipe of vehicles located at *Piyasa* and *Megenagna* garage sites in Addis Ababa Ethiopia. Samples were analyzed for the presence of Pb via microwave plasma atomic emission spectroscopy. The results showed that Pb occurred in concentrations of 444.89±33.69 mg/kg for (corolla), 587.55±10.07 mg/kg for (lada taxi) and for minibus 700.4±5.83 mg/kg. The results from the three soot samples which found are leaded. It is therefore inferred that soot's from the exhaust tail pipes of gasoline vehicles are a major source of toxic lead metal which are capable of affecting physiological health conditions.

Keywords: - Heavy Metals, Physiology, Vehicle Exhaust and Gasoline soot.

1. Introduction

1.1. Background of the study

Transportation is an authoritative component for comfortable human existence. The liberty to travel small and stretched distances creates the prospect for individual progress and professional activities, increases the alternative for leisure and holidays, and allows better contact and understanding with people. The economic expansion of whole regions depends on the effortless contact to citizens and goods ensured by modern transport machinery. Due to its flexibility, road transport is a major transport means, and cars are substance of aspiration and pride in various societies. These positive aspects are very much related with the hazards to the surroundings and human health caused by transport, chiefly road transport [1]. This has resulted in the rising transport volume, associated risk of harm to air quality and health, and an increased threat to the guiding principles of many countries, as affirmed by the European Union (EU) in its 6th Environment Action Program; to realize pollution levels that do not give rise to damaging effects on human health and the environment [2]. Transportations by means of gasoline engine vehicles, have received growing consideration as a cause of air contamination at both local and international scales [2]. Greater than 95% of mechanical transport relies on gasoline and accounts for nearly 50% of world use of gasoline [3]. There is a substantial increase in the number of vehicles [4]. At the moment there are more than 700 million vehicles on roads, and this numeral figure is projected to double in 30 years to come [5]. This significant contribution led to findings of Vehicular exhaust emission as a primary source apportionment of particulate matter which performed using positive matrix factorization (PMF) [6]. Heavy metals, such as Ni, Cd, Pb, Zn, Cu, Hg, Cr and others refer to metals with densities greater than 5 g/cm^3 [7]. Inappropriate disposal of engine oil, brake fluid, and leaded gasoline in the surrounding region of fuel contributes to the heavy metals load [8]. Heavy metals can be able to affect human health when exposed by means of ingestion, inhalation and dermal contact [9].

1.2. Leaded gasoline versus unleaded gasoline

Different types of gasoline can be bought at the pump. The main difference between leaded gasoline and unleaded gasoline is the additive tetraethyl lead. Leaded gasoline contains lead additives while unleaded gasoline does not. Leaded gasoline creates more pollution than unleaded gasoline. Leaded gasoline poses more of a health risk than unleaded gasoline. Unleaded gasoline is available for public consumption while leaded gasoline is banned. “Tetraethyl lead” was used in early model cars to help reduce engine knocking, boost octane ratings, and help with wear and tear on valve seats within the motor Gasoline was added until engines started having higher compression rates and they started to auto ignite, commonly referred to as knocking or sounding. Gasoline companies discovered that adding a lead-based additive eliminated the knocking, thus giving rise to leaded gasoline much later it was discovered that lead had some undesirable side effects, and governments started to discourage the use of leaded gasoline and urged companies to develop unleaded gasoline as an alternative [10]. The combustion of leaded gasoline causes the lead to be released into the air. Lead is a heavy pollutant that does damage not only to the environment but also to the people who are exposed to it [11]. The prevalent use of leaded gasoline saw a steady rise in the lead levels of people residing in populated areas where vehicles were prevalent. Prolonged exposure to large amounts of lead can eventually cause lead poisoning, which can be fatal. Due to concerns over air pollution and health risks, this type of gas was slowly phased out starting in the late 1970’s and banned altogether in all on road vehicles in the U.S. in 1995 [12]. Gasoline itself is a product of crude oil that is made of carbon atoms joined together into carbon chains. The different length of the chains creates different fuels. For example, methane has one carbon atom, propane has three, and octane has eight carbon atoms chained together. These chains have characteristics that behave differently under various circumstances; characteristics like boiling point and explosion temperature, for instance, can vary greatly between them. As fuel is compressed in a motor’s cylinder, it heats up. Should the fuel reach its ignition temperature during compression, it will auto ignite at the wrong time. This causes loss of power and damage to the engine. Fuels such as heptane (which has 7 carbon atoms chained together) can ignite under very little compression. Octane, however, tends to handle compression extremely well. The higher the compression in the cylinders a car’s motor can produce, the greater the power it can get out of each stroke of the piston. This makes it necessary to have fuels that can handle higher compression without auto-igniting. The higher the octane rating, the more compression the fuel can handle. An octane rating of 87 means the fuel is a mixture of 87% octane and 13% heptane, or any mixture of fuels or additives that have the same performance of 87/13.

1.3. Objectives

1.3.1. General Objective

The general objective of this study was to quantify lead in vehicular exhaust in Addis Ababa.

1.3.2. Specific Objectives

To assess the level of contamination of the environment by lead from automobile exhaust in Addis Ababa.

To propose appropriate management systems for controlling the sources of lead pollution of air in automobile exhaust in Addis Ababa.

1.4. Significance of the Study

The significance of the study will be very important in informing the decision makers, the government bodies, health professionals, AAEPA, environmentalists, other scholars and the society concerning the concentration of lead in gasoline. It will help the decision makers or the government regulatory bodies together with the federal EPA to set monitory systems in banning lead gasoline of the nationwide. It also initiates the health professionals, environmentalists and other scholars with related professions to study both the human (especially children) health and environmental vulnerability due to the lead contamination caused by variety of sources and informs the usefulness of remediation measures in minimizing lead pollution.

2. Review of Related Literature

2.1. Chemical identity of gasoline

Gasoline is a refined product of petroleum consisting of a mixture of hydrocarbons, additives, and blending agents. The composition of gasoline varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of gasoline hydrocarbons (% volume) is as follows: 4-8% alkanes; 2-5% $^{\text{alkenes}}$; 25-40% iso-alkanes; 3-7% cycloalkanes; l-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene) [5]. Additives and blending agents are added to the hydrocarbon mixture to improve the performance and stability of gasoline. These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes [5].

2.2. Physical properties of Lead

Lead (atomic number, 82; relative atomic mass, 207.2) has a valence +2 or +4. The alchemists believed lead to be the oldest metal and associated it with the planet Saturn. Lead is a bluish-white metal of bright luster, is very soft, highly malleable, ductile and a poor conductor of electricity. It is very resistant to corrosion; lead pipes bearing the insignia of Roman emperors, used as drains from the baths, are still in service. Natural lead is a mixture of four stable isotopes: ^{204}Pb (1.4%), ^{206}Pb (25.2%), ^{207}Pb (21.7%) and ^{208}Pb (51.7%). Lead isotopes are the end-products of each of the three series of naturally occurring radioactive elements: ^{206}Pb for the uranium series, ^{207}Pb for the actinium series and ^{208}Pb for the thorium series [13].

2.3. Chemical properties of Lead

2.3.1. Reaction with air

Lead is unaffected by dry air but in moist air a layer of lead carbonate or lead hydroxide is deposited on its surface which protects it from further reaction of air. When heated in air or oxygen, lead is oxidized to give (PbO) and red lead (Pb_3O_4)

$2Pb + O_2 \rightarrow 2PbO$

$3Pb + 2O_2 \rightarrow Pb_3O_4$

2.3.2. Reaction with water

Lead is not attacked by pure water in the absence of air, but water containing dissolved air has a solvent action on it due to the formation of lead hydroxide (a poisonous substance).

$2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2$

2.3.3. Reaction with acids

Dilute H_2SO_4 and HCl have no reaction on lead. Hot Conc. H_2SO_4 liberates SO_2 but the reaction is retarded by the formation of an insoluble layer of lead sulphate.

$Pb + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + SO_2.$

2.4. Health effects of lead

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes. Lead fulfills no essential function in the human body, it can merely do harm after uptake from food, air or water. Lead can cause several unwanted effects, such as disruption of the biosynthesis of hemoglobin and anemia, arise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of nervous systems, brain damage, declined fertility of men through sperm damage, diminished learning abilities of children and behavioral disruptions of children, such as, aggression, impulsive behavior and hyperactivity Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children [10].

2.5. Environmental effects of lead

Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only convert to other forms. Lead accumulates in the bodies of water organisms and soil organisms. These will experience health effects from lead poisoning [14]. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. That is why we now begin to wonder whether lead pollution can influence global balances. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present.

2.6. Source of lead

The sources of lead exposure include mainly industrial processes, food and smoking, drinking water and domestic sources. The sources of lead were gasoline and house paint, which has been extended to lead bullets, plumbing pipes, pewter pitchers, storage batteries, toys and faucets [15]. In the US, more than 100 to 200,000 tons of lead per year is being released from vehicle exhausts. Some is taken up by plants, fixation to soil and flow into water bodies, hence human exposure of lead in the general population is either due to food or drinking water [16].

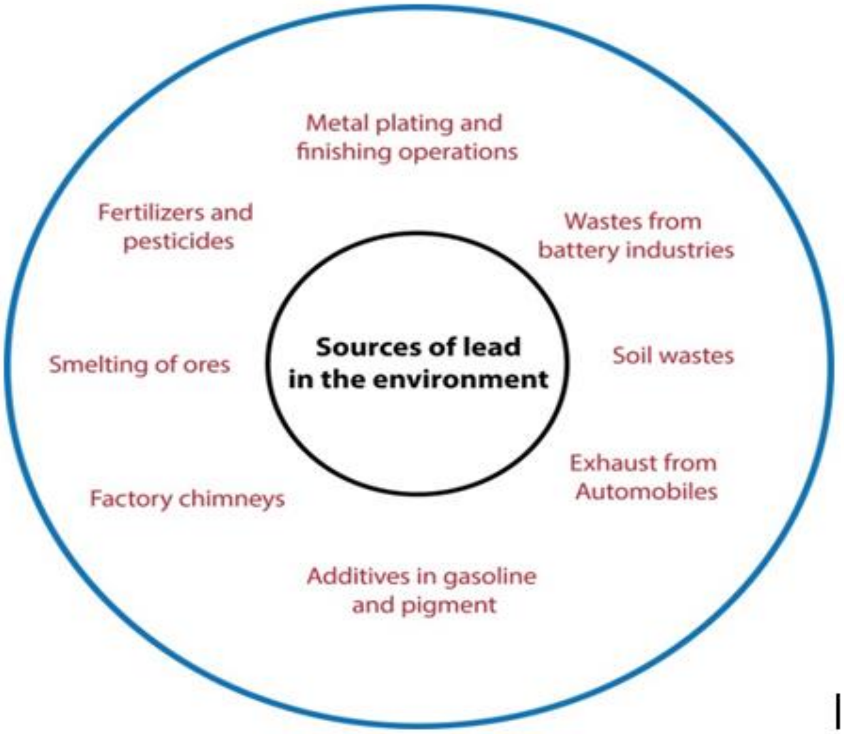


Figure-1: Various sources of lead pollution in the environment [17]

2.7. Importance of lead

Lead is used in the production of batteries, ammunition metal products (solder, pipes, fishing weights, electronics and alloy with other metal) and device to shield x-rays. Tetraethyl lead is used to make other lead compounds (tetra-alkyl lead) and was used in lead fuels. Lead compounds are used in the manufacturing of electronic parts, plastics, rubbers and metals. Lead is used in pigments, dyes paints and coatings. Lead compounds are used in the manufacture of matches, ammunition reworks, explosives, pottery glazes, ceramics, and brake shoes, (Australian Government, Department of the Environment and energy). Over the centuries the unique properties of lead have resulted in its use in many different applications. These properties are mainly its high resistance to corrosion, its softness and low melting-point, its high density and its relatively low conductivity (Lead Development Association International, 2003) [8]. Large quantities of lead, both as the metal and as the dioxide, are used in storage batteries. Lead is also used for cable covering, plumbing and ammunition. The metal is very effective as a sound absorber and as a radiation shield around X-ray equipment and nuclear reactors. It is also used to absorb vibration. Lead, alloyed with tin, is used in making organ pipes. Lead carbonate ($PbCO_3$), lead sulfate ($PbSO_4$), lead chromate ($PbCrO_4$), lead tetra oxide (Pb_3O_4) and other lead compounds have been applied extensively in paints.

2.8. Status of the use of leaded gasoline

As of 1993, an estimated 70,000 tons per year of lead were added to gasoline worldwide [18]. As shown in Table1, about half of the worldwide total of lead used in gasoline is used in the former USSR, Eastern Europe, and the Far East. The remainder is used, in approximately equal amounts, in Western Europe, Africa, the Middle East, and the Americas. In many countries, unleaded gasoline is unavailable. Ethyl Corporation, until recently the other major producer, stopped production of these additives in 1994. However, Ethyl continues to sell and buy lead additives [19]. The other producers are facilities in Germany (less than 4000 tons lead per year) [20] and in Russia (about 5000 tons lead per year). Total annual sales of lead additives are on the order of $1 billion. The antiknock properties of tetra-ethyl lead (TEL) were discovered in the United States by Thomas Midgley and colleagues at the General Motors Research Laboratory in 1921 [21]. Commercially introduced in the United States in the 1920s, leaded gasoline soon became standard [22]. Owing to the introduction of catalytic converters and a better understanding of the risks of lead exposure, leaded gasoline was phased out in the United States.

Table-1: Estimated use of leaded gasoline in Western Europe

Country	Motor gasoline consumption (ton/year) 10^9	Lead content of leaded gasoline g/l	Total added lead (ton/year)	Leaded gasoline percent share. [17,19,23]
France	27	0.15	2,400	59 (1993)
Italy	19	0.15	2,200	76 (1993)
Uk	33	0.15	2,300	47 (1993)
Spain	11	0.15	1,600	94 (1992)
Germany	42	0.15	690	11 (1993)
Turkey	4.4	0.15	650	90 (1994)
Portugal	1.9	0.40	600	79 (1993)
Greece	3.3	0.40	380	77 (1993)

Table-2: Estimated use of leaded gasoline in Middle East

Country	Motor gasoline consumption (ton/year) 10^9	Lead content of leaded gasoline g/l	Total added lead (ton/year)	Leaded gasoline percent share in 1992. [24,25,26]
Saudi Arabia	9.3	0.4	3,700	100
Iraq	4.4	0.4	1,700	100
Iran	8.1	0.19	1,500	100
Kuwait	1.2	0.53	620	100
UAR	1.3	0.4	530	100
Syria	1.5	0.24	360	100
Israel	2.1	0.15	310	<100
Quatar	0.4	0.4	75	47

The use of leaded gasoline for highway vehicles was banned in the United States as of January 1, 1996. In Japan, reduction of lead in gasoline began in the 1970s, after reports of high blood lead concentrations in Tokyo [27], [28]. More recently, leaded gasoline was eliminated in Canada, Brazil, Colombia, Austria, South Korea, and Sweden. In the European Union, the lead content of gasoline is limited to 0.15 g/L, and all new cars are required to have catalytic converters, which require the use of unleaded gasoline [29]. The Soviet Union was the first country to restrict use of lead in gasoline: By 1967. This action was apparently prompted by Soviet research on the effects of low-level lead exposure [30]. The introduction of unleaded gasoline and catalyst-equipped vehicles required numerous changes in U.S. transportation and energy systems. Major changes (and investments) had to be made in oil refinery and storage facilities; transportation technologies had to be modified to separate unleaded gasoline from leaded gasoline; vehicle manufacturers had to invest in the development of new engine systems and retooling of existing factories; and a network of retail fuel outlets had to be established to serve the new single-fuel unleaded vehicles. The introduction of unleaded gasoline and catalytic converters required simultaneous technological and operational changes in fuel production, distribution, and end-use systems, and faced numerous economic and political barriers. Introduction of unleaded gasoline and catalytic converters faced the same type of obstacles as would any other new fuel, dissimilar to petroleum such as alcohols, gaseous hydrocarbons, and hydrogen [12].

2.9. Micro Plasma Atomic Emission Spectroscopy

Micro Plasma Atomic Emission Spectroscopy (MP-AES) consists of microwave induced plasma interfaced to an atomic emission spectrophotometer (AES). It is used for simultaneous multi analytic determination of major and minor elements. MP-AES employs microwave energy to produce a plasma discharge using nitrogen supplied from a gas cylinder or extracted from ambient air, which eliminates the need for sourcing gases in remote locations or foreign countries. Samples are typically prior to interact with the plasma in MP-AES measurements. The atomized sample passes through the plasma and electrons are promoted to the excited state. The light emitted electrons return to the ground state light is separated into a spectrum and the intensity of each emission line measured at the detector. Most commonly determined elements can be measured with a working range of low part per million (ppm) to weight percent (wt. %). MP-AES is a technique comparable to traditional AA and AES but with several potential advantages including lower cost of operation and elimination of the requirement for flammable gasses [4]. MP-AES instruments are bench top instruments. Because the technique is matured, there are a limited number of manufacturers supplying commercial MP-AES instruments.

2.9.1. How Microwave Plasma – Atomic Emission Spectroscopy works

Atomic excitation Microwave plasma atomic emission spectroscopy is an atomic emission technique. It uses the fact that once an atom of a specific element is excited, it emits light in a characteristic pattern of wavelengths and emission spectrum, as it returns to the ground state. Sources for atomic emission include the microwave plasma (MP) and the inductively coupled argon plasma (ICP) both of which are high temperature sources, and therefore excellent excitation sources for atomic emission spectroscopy. The nitrogen fuelled microwave plasma reaches temperatures about 5,000 K. At these temperatures, atomic emission is strong, producing excellent detection limits and linear dynamic range for most elements. Inside a MP-AES instrument, microwave energy from an industrial magnetron is used to form plasma from nitrogen that has been extracted from compressed air by Agilent's Nitrogen Generator (Figure 1). Effectively, the MP-AES runs on air [31].

Figure-2: Instrument of MP-AES

2.9.2. The benefits of MP-AES

The MP-AES runs on air, it vastly reduces the cost of ownership and eliminates the need for ongoing supply of flammable or expensive gases. There are no gas cylinders or lamps to buy and no standby operating costs. When a MP-AES is off, no gas or power is used. Simply it is switched on again when needed for analysis. It removes the requirement for flammable gases means no gas leaks and no ordering and transporting of cylinders. Removing all of these risks makes the laboratory a safer workplace. It handles difficult matrices with ease, including fuels and organic solvents, geochemical samples, fertilizers and foods. A vertically positioned torch gives the best performance with difficult samples, and features end-on axial viewing for excellent detection limits. Requires only electricity, an MP-AES can be located at a sampling point, instead of in a lab. This allows measurement turn around to be much quicker, delivering timely data that could deliver huge benefits, such as preventing environmental spills or incorrectly manufactured products. It features easy-to-use, application-specific software applets that automatically load a pre-set method so you can start analysis immediately without method development or alignment, and with minimal training. The instrument´s torch loader automatically aligns the torch and connects gases for fast start up and reproducible performance [4].

3. Experimental

3.1. Instrumentation

All measurements were performed using an Agilent 4200 Microwave Plasma Atomic Emission Spectroscopy (MP-AES) with nitrogen supply from an Agilent 4107 nitrogen generator. The sample introduction system consisted of a micro mist nebulizer and double pass glass cyclonic spray chamber. An external gas control model (EGCM) accessory and auto sampler were used.

3.2. Apparatus

The apparatus used in the laboratory were sample preparation utilized polyethylene conical flask, 50 ml volumetric beaker for sample and solution preparation, round bottom flask, filter paper ceramic mortar and pestle, digital analytical balance (four digits) and Kjeldahl apparatus for the purpose of digestion. All the glassware used were first kept overnight in 10% HCl solution and then repeatedly washed with distilled water and dried in an oven for 24 hrs before use.

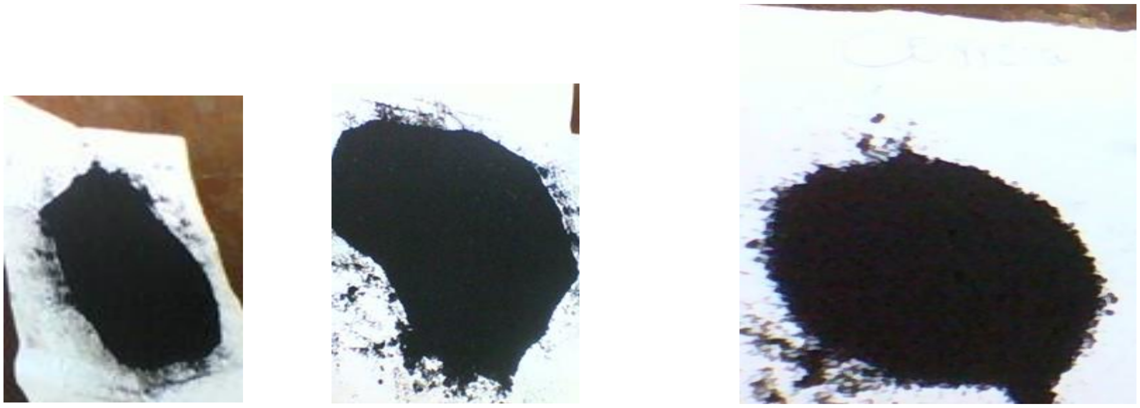
3.3. Study area

This study was undertaken in Addis Ababa metropolis which lies `at latitude 9^{o} 1' N and at longitude 38^{o} 44' E. It is currently one of the major cities in Ethiopia. The mean annual rainfall is 1089 mm per year and annual temperature varies between 12 to 22^{o}C. It occupies an area of approximately 527 square kilometers and the population density is estimated to be near 5,165 individuals per square kilo meter available. According to the 2007 E.C census it had a population of 3,384569. But approximately it estimate about 6,000,000 now.

3.4. Samples collection and preparation

Soot particles were collected from the inner surface of the tailpipe of the vehicles and were considered to have similar characteristics as that of those emitted into the atmosphere. Soot particles were collected by scraping using plastic spatula. Soot samples were collected from various sources; the soot samples of gasoline vehicle were obtained from *Megenagna* and *Piyasa*. The collected soot samples were transported to the laboratory and soot samples were then air- dried for three to four days to remove moisture. Some unwanted materials in the samples were clarified or filtered and were stored in a pre-washed plastic sample bottle until the time of digestion. The respective samples collected from the two sites and the three vehicles are shown in Figure -3.

Sample identity: Sample C: - Corolla, Sample L: - Lada, Sample M: - Mini-bus



C L M

Figure-3: Sample of corolla, lada and minibus (Hiace) respectively**.**

3.5. Reagents and chemicals

Reagents and chemicals used in the experiments were Aqua regia (prepared from 3:1 ratio of 37% Hydrochloric acid, 70% nitric acid respectively) and deionized water.

3.6. Optimization of digestion procedure

Wet acid digestion is one of the methods used to get free metal ions from dissolved complex organic matrix based on changing different digestions parameters like volume ratio of reagents added, digestion temperature and duration of time. One of the wet acid digestions can be carried out by kjeldahl apparatus in which organic components are assumed to be decomposed in the form of different gaseous forms. Moreover it is assumed that digestion is to be complete if the solution is clear and colorless. Different digestion procedures were carried out for the gasoline soot samples using aquaregia (HCl: HNO_3 = 3:1) by varying volume of aquaregia, digestion time and digestion temperature [32]. Optimized procedures were selected based on the usage of lesser reagent volume, shorter digestion time and reasonable mild temperature for obtaining clear and colorless solution of the resulting digests. Based on this fact, the optimized digestion condition for the gasoline soot samples in this study were 3 ml of aquaregia (HCl: HNO_3 = 3:1), 300 ^{0}C digestion temperature and 4:30 hrs digestion time. The optimization conditions for digestion of gasoline soot samples in this study are shown in table 3, 4 and 5.

Table-3: Optimization of volume for digestion of 1.0 g of soot samples at 300 ^{0}C for 5 hrs

	Parameters			Observation
	Volume (ml)	Temperature (^{0}C)	Time (hrs)	
1	**3**	**300**	**5**	**Clear colorless solution**
2	4	300	5	Clear solution
3	5	300	5	Bright yellow
4	6	300	5	Bright yellow
5	7	300	5	Yellow
6	8	300	5	Yellow

The bold font shows the optimization of digestion volume, v = 3 ml

Table-4: Optimization of temperature for digestion of 1.0 g of soot sample on 3 ml for 5hrs.

	Parameters			Observation
	Volume (ml)	Temperature (^{0}C)	Time (hrs)	
1	3	150	5	Deep yellow
2	3	180	5	Deep Yellow
3	3	210	5	Yellow
4	3	240	5	Bright yellow
5	3	270	5	Clear solution
6	**3**	**300**	**5**	**colorless clear solution**

The bold font indicates optimum of digestion temperature, T =300 ^{0}C

Table.5. Optimization of time for digestion of 1.0 g of soot samples on 3 ml at 300 ^{0}C

	Parameters			Observation
	Volume (ml)	Temperature (^{0}C)	Time (hrs)	
1	3	300	2:30	Deep yellow
2	3	300	3:00	Deep yellow
3	3	300	3:30	Yellow
4	3	300	4 :00	Slightly clear solution
5	**3**	**300**	**4:30**	**clear colorless solution**
6	3	300	5 :00	Clear colorless solution

The bold font shows the optimization of digestion time, t = 4:30 hrs.

3.7. Sample digestion

1.0 g of each pretreated sample was weighed and placed in 50 ml round bottomed flask, after which 3 ml of freshly prepared aquaregia (HCl : HNO_3 = 3:1) was added and the mixture was digested on a kjeldahl digestion apparatus fitted with a reflux condenser by setting the parameters temperature and time as shown Figure-4. The digest was allowed to cool at room temperature for 10 min without dismantling the condenser and 10 min after removing the condenser and distilled water was added to the cooled solution to dissolve the precipitate formed on cooling and to minimize dissolution of filter paper by the digest residue while filtering with filter paper in to 50 ml volumetric flask. The round bottom flask was raised subsequently with around 5 ml distilled water until the total volume reached around 40 ml. Then finally the solution was filled to the mark 50 ml using distilled water. The digestion was carried out in triplicate for each sample. Digestion of the blank was also performed in parallel with the gasoline soot samples keeping all digestion parameters the same. Then the metal concentration in the digested sample solutions was determined by using MP-AES.

Figure-4: Digestion process

3.8. Method validation and Measuring of performance

In order to validate the efficiency of digestion procedure MP-AES methods were used for the analysis of lead in the digested samples by performing the following validation parameters such as limit of detection (LOD), limit of quantification (LOQ)**,** precision and accuracy studies were carried out [33,34].

3.8.1. Limit of Detection (LOD)

Limit of detection (LOD) is the minimum concentration of analytes that can be detected. In other words, it is the lowest concentration that can be determined to be statistically different from a blank solution which detected by the analytical method with a given confidence limit [35]. The triplicate blank samples were digested following the same procedures utilized for digesting the soot samples. The SD of the triplicate blanks was calculated to determine the LOD [36]. Limit of detection (LOD) was calculated according to the equation indicated below.

LOD = 3SD, Where: SD = Standard deviation of blank

3.8.2. Limit of quantification (LOQ)

Limit of quantification is the lowest concentration of an analyte in the soot samples which can be quantitatively determined with acceptable uncertainty. LOQ was obtained from triplicate analysis method of blanks which were digested in the same digestion procedure as the actual samples.

The LOQ was calculated according to the equation indicated below.

LOQ = 10xSD, Where SD is the standard deviation of the method blank.

4. Results and discussion

4.1. Calibration of the instrument

The calibration curve was drawn to determine the concentration of lead metal in soot sample solutions. The instrument was calibrated using calibration blank solution and the working standard solutions. Concentration of the working standard, calibration curve and value of correlation coefficient (R^2) of the Calibration graph for lead metal was provided (table-10 & fig-5). The correlation coefficient (R^2) of the calibration curves of lead metal was determined by plotting working standard concentration (mg/L) versus their corresponding absorbance as shown below in table 10.

Table-6: Intensity and working standard concentration

Standards	Intensity	Calibration concentration	measured concentration
S_1	1323.9760	0.50	0.486
S_2	2734.1895	1.0	0.999
S_3	3851.4687	2.00	2.040
S_4	5088.1311	4.00	3.980

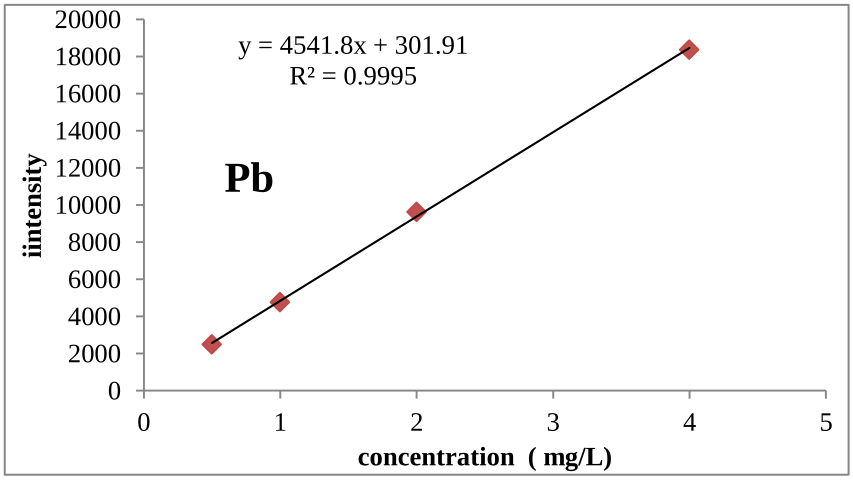


Figure-5: Calibration curve for lead.

4.2. The results showing the concentration of lead for each vehicle

Table-7: Lead concentration of gasoline in corolla

Metal	Unit	C1	C2	C3	Mean	SD	%RSD
Pb	mg/kg	410.26	446.27	478.15	444.89±33.97	33.97	7.6

Where: - C is corolla and Sd- Standard deviation, RSD -Relative standard deviation.

Table-8: Lead concentration of gasoline in lada taxi (L)

Metal	Unit	L1	L2	L3	Mean	SD	%RSD
Lead (Pb)	mg/kg	600.40	586.50	575.80	587.57±10.07	10.07	1.71

Where: - L is lada

Table-9: Lead concentration of gasoline in minibus (Haice) (M)

Metal	Unit	M1	M2	M3	Mean	SD	%RSD
Lead (Pb)	mg/kg	704.86	704.76	692.45	700.69±5.83	5.83	0.831

Where: - M is minibus

Table-10: Results showing the mean concentration of lead in gasoline for each vehicle (corolla (C), lada (L) and minibus (M))

Metal	Unit	C	L	M	Mean
Pb	mg/kg	444.89±33.69	587.57±10.07	700.69±5.83	577.72±16.53

Where: - C = for corolla, L = for lada and M = minibus

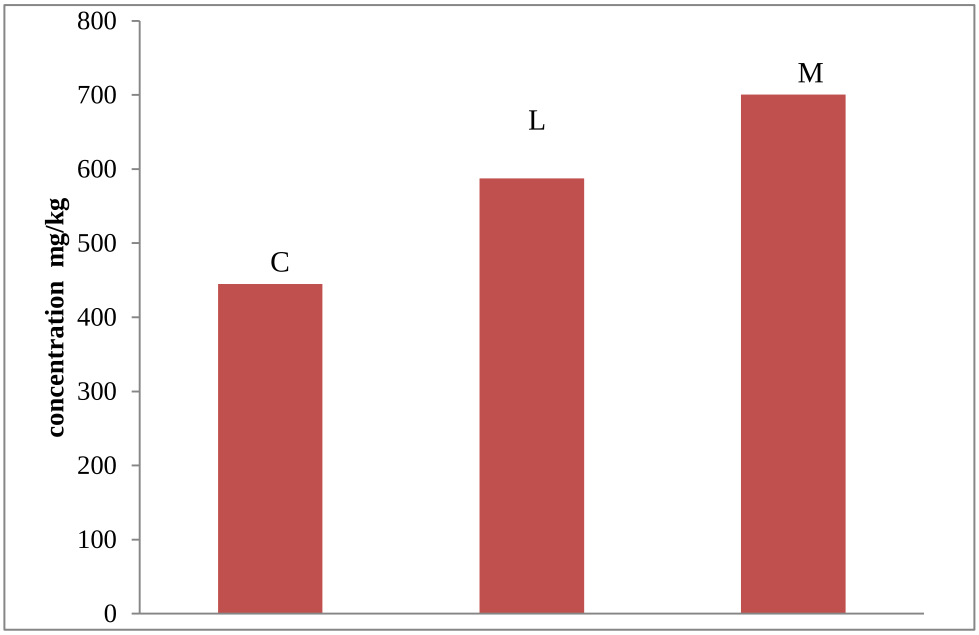


Figure-6: The graphs of concentration of lead metal in gasoline for each vehicle (corolla (C), lada (L) and minibus (M).)

The increased lead contamination in soot sample M, (700.69±5.83 mg/kg), and sample lada,(587.57 ±10.07 mg/kg), and sample C 444.69 mg/kg can be credited to the use of metal lead-based additives that was used as an anti-knock or alkyl-lead contamination compounds [40]. Automobile corolla having less lead concentration /content, why because it releases low content of lead as compared automobile lada taxi and minibus. This indicates motor of corolla is latest and recycle the exhaust gasoline. The use of gasoline with lead was banned a decade ago; lead was the second most commonly detected heavy metal. Pb is found as a trace element in diverse fuels, though is not allowed as additive constituent in petrol fuels [41]. In addition to this, it could not identify the source of Pb in a soot sample whose reference gasoline was absent [32]. Combustion of all kinds of gasoline leads to emission of lead to the ambiance [42]. In the US, more than 100 to 200,000 tons of lead per year is being released from vehicle exhausts. Some is taken up by plants, fixation to soil and flow into water bodies, hence human exposure of lead in the general population is either due to food or drinking water [43].

4.3. Regression analysis and detection limits

As can be seen from figure-5 given above, the calibration curve for lead showed that a good linearity with coefficient of determination (R^2) was 0.9995 that is greater than the acceptable limit (0.9990) for the linearity of the regression line [37]. This showed that there is a good correlation between concentration and absorbance indicating good calibration of the instrument. The instrumental detection limit was 0.36 mg/Kg which is below the limit of detection, which indicating good sensitivity of the measuring instrument for analysis. The limits of detection & quantification limit values are 1.93 & 12.5 mg/kg respectively. The result showed both the LOD and LOQ values are greater than the IDL; hence, the result of the analysis could be reliable.

Table-11: The value of limit of detection (LOD) and limit of quantification

Metal	IDL (mg/Kg)	LOD (mg/Kg)	LOQ (mg/Kg)	Coefficient of determination (r^2)	Regression equation
Pb	0.36	1.93	12.5	0.9995	Y= 4541.8x + 301.91

4.4. Method Validation

In order to check the validity of the optimized & digestion procedure, precision and accuracy of MP-AES were checked by performing spiking the soot samples with standard of solutions. The spiked and non-spiked samples were digested and analyzed in similar conditions using optimized procedure for sample analysis. The percentage recoveries of the analytes were calculated to evaluate the accuracy of the analytical procedures. Then, the percentage recoveries of the analytes were calculated by using the following equation:

$$\%\ \text{recovery}\ (R) = \frac{(C_{Pb}\ \text{in the spiked sample}) - (C_{Pb}\ \text{in the non-spiked sample}) \times 100\ \%}{C_{Pb}\ \text{added for spiking}}$$

Where: C_{Pb} is concentration of lead metal.

Table-12: Recovery and precision test result of lead metal for the spiking soot sample

Metal	conc. of non-spiked (mg/kg)	Amount added (mg/Kg)	Conc. in spiked Sample a (mg/kg)	Recovery (%)	RSD (%)
Pb	444.89	88	526.03	92.20	3.77

4.4.1. Accuracy and precisions

Precision and accuracy of the results were assessed by determining recovery and repeatability of the analysis of matrix spike, matrix spike duplicate and laboratory control samples. The spiked sample were digested and analyzed following the same analytical procedure as the soot samples. Precision was expressed as relative standard deviation (RSD) of triplicate results. The relative standard deviations of the sample were obtained as:

$$\%RSD = \frac{\text{Standard deviation}}{\text{Mean value}} \times 100$$

The mean percent recovery for the studied metal in the spiked sample was 92.20% which is found within the acceptable range of 80–120% for metal analysis [38]. The precision of the method was expressed in terms of % RSD of the triplicate readings. So, the %RSD value obtained for spiked soot sample is 3.7%, which was under the required control limits ≤15% [39]. These results indicate that the proposed method was precise and accurate.

4.5. Comparison of lead content in gasoline vehicle exhaust between Addis Ababa, Ethiopia and Kaduna metropolis, Nigeria.

Table-13: Lead content in gasoline vehicle soot in Nigeria (Kaduna metropolis)

S/No	Metal	Unit	Golf vehicle	Honda vehicle	Benz vehicle	Average
1	Pb	Mg/kg	0.444±0.022	1.277±0.074	40.571±1.837	14.097±0.644

Table-14: Lead content in gasoline vehicle soot in Addis Ababa Ethiopia

S/No	Metal	Unit	Corolla	Lada taxi	Minibus	Average
1	Pb	mg/kg	444.89±33.69	587.57±10.07	700.69±5.83	577.71±16.53

The mean concentration of lead in gasoline vehicle soot sample in Addis Ababa is 577.71±16.53 and the concentration range of lead metal is observed 444.89 ±33.69-700.69±5.83 mg/kg. The mean concentration of lead found in this study for Addis Ababa is higher than that of the cities from Nigeria which is 14.097mg/kg with the range of mean concentration 0.444±0.022 mg/kg-40.571±1.837mg/kg [19]. It can be inferred that more lead gasoline is used in Ethiopia than in Nigeria.

4.6. Statistical analysis

One way ANOVA has been used in this study to determine the significance of variation with in the same and different soot samples. The computation was done by means of detail calculations based on formula using computer with excel and Minitab (FNB, 2002). Minitab was used to find out significance differences in the mean values of the concentrations of the metal. No significance difference ($p > 0.05$) at 95% confidence interval was determined for some soot samples within the same or different sites. Significance difference ($p < 0.05$) at 95% confidence interval was also determined for the mean concentrations of the metal.

Table-15: determination of significance difference between samples

Metal	F calculated	F critical	P value	Remark
Pb	130.736	9.552	0.001	have significant difference between samples

The cause for the significance difference may be: the sample was collected from different vehicles, it may be contamination of sample (duration of sample before collected)

5. Conclusion

In general, minibus gasoline engine vehicle has proven to be more hazardous to health than corolla gasoline engine vehicle when exposure to the same quantity of the soot or its particulate matter in terms of metal concentrations. This study has highlighted the concentrations of heavy metal lead in the environment. Concentrations of lead metal are above the permissible maximum limit for air quality [44, 45]. This cause increases the presence of this metal in air and water bodies. Therefore, the consequent health effect becomes harmful to persons living around the study area. The consequent risk factor of injecting this metal into the body that causes various associated illness has been discussed, varying from stroke, cardiovascular diseases, death, genetic disorder, skeletal damage (osteoporosis), sleep disorder, memory loss, and convulsion etcetera. There is a need to identify strategies to limit vehicular emissions of this harmful metal in addition to seeking for alternative fuels that are safer for our health and ecosystem.

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