

**ASSESSMENT OF GASOLINE ADULTERATION IN
NAIROBI, KENYA**

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MASTER OF SCIENCE

(Chemistry)

**JOMO KENYATTA UNIVERSITY OF
AGRICULTURE AND TECHNOLOGY**

2010

Assessment of Gasoline Adulteration in Nairobi, Kenya

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**A Thesis submitted in partial fulfillment for the Degree of Master of
Science in Chemistry in the Jomo Kenyatta University of Agriculture
and Technology**

2010

DECLARATION

This Thesis is my original work and has not been presented for a degree in any
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DEDICATION

This work is dedicated to my dear parents Mr. and Mrs. Mwangi Murago, my sister and brothers, and to my loving Fiancé Simon. Thank you for all the support you have given to me. Dad and mum you have laid in me a good foundation that has seen me through to this level of education. May God forever bless you.

ACKNOWLEDGEMENT

I acknowledge my supervisors Dr. Oyaro, Dr. Onditi and Dr. Kiptoo for their guidance, assistance, encouragement and support throughout my study period. I would like to thank the Department of Chemistry academic and technical staff especially Mr. Mawili, Mr. Nderitu, Ms Waithera and Rose the secretary for their support during my research work.

Heartfelt thanks to Jomo Kenyatta University of Agriculture and Technology for funding this Project and for giving me an opportunity to pursue further studies through the staff development program.

I am greatly indebted to Kenya Pipeline Company for waiving the laboratory fee charges. Special thanks go to Head of the Quality Control Laboratory Mr. Mugambi, for allowing me to use their equipments. Special thanks to the KPC laboratory personnel especially Mr. Chege, Mr. Kariuki, Mr. Kiptoo, Ms. Raburu, Ms Gituru, Ms Ngotho and Ms Nzioki for assisting me in gasoline analysis. My gratitude also goes to the Head of SGS laboratory Mr. Kabbis for allowing me to use their equipments.

Special appreciation goes to my dad, mum, sister, brothers, fiancé Simon and my uncle Mr Kirichu of Kenya pipeline company for being an encouragement and a blessing to me. I would also like to thank my best friend Caroline Chege for being an encouragement to me. Lastly I thank all my friends and my classmates for their moral support and prayers. May God bless you all.

Above all I express my sincere thanks to God who has always been my fortress.

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LIST OF ABBREVIATIONS

ASTM	American Standard Testing Method
CO	Carbon monoxide
EDXRF	Energy Dispersive X-ray Fluorescence Spectrometry
ETBE	Ethyl Tertiary Butyl Ether
FAAS	Flame Atomic Absorption Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
GC-FID	Gas Chromatography Flame ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
HC	Hydrocarbon
HPLC	High Pressure Liquid Chromatography
KEBS	Kenya bureau of standards
KPC	Kenya Pipeline Company
MIBK	Methyl Isobutyl Ketone
MON	Motor Octane Number
MTBE	Methyl Tertiary Butyl Ether
NO_x	Oxides of Nitrogen
PAHs	Polyaromatic Hydrocarbons
PPM	Parts Per Million
PM	Particulate Matter
RON	Research Octane Number

SGS	Société Générale de Surveillance
STD	Standard
TAME	Tertiary Amyl Methyl Ether
VOC'S	Volatile Organic Compounds
1a	Represents 0 ppm an indication that no sulphur was present, hence sample is within the specifications set by the American standard testing method (ASTM D130)
1b	Represents 0.25 ppm an indication that sulphur was present, but within the specifications set by the American standard testing method (ASTM D130)

ABSTRACT

Adulteration of automotive gasoline is widespread throughout the world and Kenya is no exception. Adulteration takes its toll both in terms of the air pollution and loss in tax revenue. Increase in prices of fuels and fuel intermediates is often cited as a cause for adulteration. Adulterated fuels deprive the consumers of assured quality fuels thus leads to increased tail pipe emissions of hydrocarbons (HCs), carbon monoxide (CO), oxides of nitrogen (NO_x), particulate matter (PM) and emissions of air toxins such as benzene, methylbenzene and polyaromatic hydrocarbons which are well known carcinogenic compounds. Many conventional methods have been used to test for adulteration such as use of the fuel marker, which has not been effective in cases where visible dyes are used. This study set out to assess the adulteration of automotive gasoline in Nairobi, Kenya using FTIR spectroscopy. The results obtained by FTIR showed that the adulteration ranged from 7.825 ± 1.275 % to 17.464 ± 0.574 % and the results suggested that adulteration was done at central areas like in the storage tanks before distribution to retailers or at retailer points. The results obtained for sulphur for a few samples showed that there was a possibility of adulteration with solvents with high level of sulphur like kerosene and diesel. A few samples of unleaded gasoline were analyzed for the presence of lead. The results obtained indicated that there was lead present in the gasoline but did not surpass the level set by the Kenya bureau of standards an indication that the effect of lead to the environment is far from addressed. From this study, a new

method was developed that was rapid, had high sample through put requiring minimal time and a small amount of sample for analysis.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 General introduction

Crude oil is a complex mixture containing many different hydrocarbons that vary in appearance and composition from one oil field to another (Schremp, 2005). It is found in large quantities below the surface of Earth and is used as a fuel and as a raw material in the chemical industry (Schremp, 2005). Crude oil is formed under Earth's surface by the decomposition of marine organisms. The remains of tiny organisms that live in the sea and those of land are carried down to the sea by rivers (Cedre, 2006). Plants that grow on the ocean bottoms are immersed by fine sands and silts that settle to the bottom in sea basins. As additional deposits pile up, the pressure and temperature rises enormously (Manning *et al.*, 1991). The mud and sand harden into shale and sandstone, carbonate precipitates and skeletal shells harden into limestone. The remains of the dead organisms are transformed into crude oil and natural gas (Speight, 2002). The deposits which are rich in organic materials become the source rocks for the generation of crude oil. This process began millions of years ago and it continues to this day. Crude oils are generally classified as paraffinic, naphthenic, or aromatic, based on the predominant proportion of similar hydrocarbon molecules (Cranmore *et al.*, 2000).

1.1.1 Refinery operations

Petroleum refining is the process of separating the many compounds present in crude petroleum (Potter, 1987). The basic refinery operations include; distillation process,

thermal cracking, catalytic process, treatment, formulation and blending (OTM, 2003). The major refinery products are;

1.1.1.1 Gasoline

Gasoline is a mixture of hundreds of hydrocarbons many of which have different boiling points. Gasoline boils and distills over a range of temperatures, unlike a pure compound, water, for instance, that boils at a single temperature. Gasoline boils between 30°C and 202°C for one to obtain a distillation curve (Speight, 2002). A gasoline distillation curve is the set of increasing temperatures at which it evaporates for a fixed series of increasing volume percentages 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 and 98.5-99% as the final endpoint (Al-Ghouti et al., 2008).

Gasoline also referred to as motor spirit premium contains many substances, such as antiknock agents, antioxidants, metal deactivators, antirust additives, anti-icing agents, preignition additives, upper cylinder lubricants and dyes (ASTM., 1983). The major hydrocarbon components in gasoline include alkanes, isoalkanes, cycloalkanes, alkenes and aromatics (MacFarland *et al.*, 1984). Commercial gasoline contains mainly C₅ to C₈ paraffins (60 to 80%), with much smaller quantities of aromatic compounds (14 to 33%) and olefins (6.4 to 13%) (ASTM., 1983). The density of gasoline is reported to be about 0.700-0.740 Kg/l at 20°C, and its vapour pressure is estimated to be 93.3 kPa at 25°C (MacFarland *et al.*, 1984). Gasoline is highly flammable with a flash point of -45°C and minimum and maximum explosion limits in air of 1.3 and 6% by volume respectively (Cesars., 1984). The important qualities for gasoline are motor octane number (MON),

research octane number (RON), volatility (starting and vapor lock), and vapor pressure (environmental control) and copper corrosion test. Additives such as ethyl tertiary butyl ether (ETBE), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), and other oxygenates improve gasoline octane ratings as well as enhance performance, provide protection against oxidation and rust formation and reduce carbon monoxide emissions (Larissa *et al.*, 2005).

Gasoline is classified as a spirit and finds its most important use as a fuel for internal combustion engines, principally automobile. It has also been used as a solvent for rubber adhesives and as a finishing agent for artificial leathers (Jeltes *et al.*, 1967).

1. 1.1.2 Kerosene

Kerosene is the name for the lighter end of a group of petroleum streams known as the middle distillates (Klimisch *et al.*, 1997). Kerosene is known as dual purpose kerosene which may be obtained either from the distillation of crude oil under atmospheric pressure known as the straight-run kerosene or from catalytic, thermal or steam cracking of heavier petroleum streams which is referred to as cracked kerosene (Klimisch *et al.*, 1997). Kerosene is further treated by a variety of processes including hydrogenation to remove or reduce the level of sulfur, nitrogen or olefinic materials. The precise composition of kerosene will depend on the crude oil from which it was derived and on the refinery processes used for its production (API, 1997). Irrespective of this, kerosene consists predominantly of C₉ to C₁₆ hydrocarbons and boils in the range 145°C to 300°C (API, 1997). The density of dual purpose kerosene is reported to be about 0.760-0.800Kg/l at

20°C. The major components of dual purpose kerosene are branched and straight chain paraffins and naphthenes and these normally account for 70% of the material. Aromatic hydrocarbon, mainly alkyl benzenes and alkylnaphthalenes do not normally exceed 25 % of kerosene streams. Olefins do not normally account for more than 5% of the kerosene (API, 1997).

Kerosene finds considerable use as a jet fuel and as a domestic heating fuel (Klimisch *et al.*, 1997). When used as an ingredient in jet fuel, some of the critical qualities such as freeze point, flash point, and smoke point are monitored (OTM, 2003). Commercial jet fuel has a boiling point range of about 190°C-273.5°C, and military jet fuel 54.4°C-287.8°C. Kerosene, with less-critical specifications, is used for lighting, heating and as a solvent (OTM, 2003).

1.1.1.3 Diesel

Known as automotive gas oil, is produced from petroleum, and is usually referred to as petro diesel to distinguish it from diesel obtained from other sources such as biodiesel (Cedre, 2006). Automotive gas oil is classified under distillates and is a hydrocarbon mixture obtained from fractional distillation of crude oil between 250°C-350°C. Diesel has a density of about 0.820-0.850 kg/l (Cedre, 2006). Petroleum-derived diesel is composed of about 75% saturated hydrocarbons which are primarily paraffins and 25% aromatic hydrocarbons which includes naphthalenes and alkylbenzenes (Cooke *et al.*, 1985). The average chemical formula for common diesel fuel is $C_{12}H_{26}$, ranging from approximately $C_{10}H_{22}$ to $C_{15}H_{32}$ (Cooke *et al.*, 1985). The desirable qualities required for diesel fuels

include controlled flash and pour points, clean burning, no deposit formation in storage tanks, and a proper diesel fuel cetane rating for good starting and combustion. Other types of diesel fuels known are synthetic diesel obtained from wood, hemp, straw, corn, garbage, food scraps, and sewage-sludge through the Fischer-Tropsch process. Synthetic diesel may also be produced out of natural gas in the gas-to-liquid process or out of coal in the coal-to-liquid process. Such synthetic diesel has 30% less particulate emissions than conventional diesel. Biodiesel is another example obtained from vegetable oil or animal fats. Biodiesel is a non-fossil fuel alternative to petro diesel.

Diesel fuel is important as a transportation fuel because it offers a wide range of performance, efficiency and safety features. Diesel fuel contains between 18 and 30 percent more energy per gallon than gasoline. Diesel technology also offers a greater power density than other fuels. In agriculture, diesel fuels are used in more than two-thirds of all farm equipment in the Kenya, because diesel engines can perform demanding work. In addition, it is the most widely used fuel for public buses and school buses. Diesel fuels are however not used for private vehicles due to high costs required for the maintenance of the engines.

1.1.1.4 Other Refinery Products

Other refinery products are residual fuels, asphaltines, resins, solvents, petrochemicals and lubricants.

1.2 Adulteration

Adulteration can be defined as the introduction of a foreign substance into gasoline or diesel, illegally or unauthorized with the result that the product does not conform to the

requirements and specifications of the product (OTM, 2003). The foreign substances are called adulterants which when introduced alter and degrade the quality of the fuels (Kulathunga *et al.*, 2004).

1.2.1 Types of adulteration

Blending or mixing of adulterants into the fuels exists in various forms and both the type and quantity of adulterants vary from place to place. Moreover, profitability, availability and blendability are the prominent factors governing the choice of adulterants (Dutta, 2003). Specific types of adulteration may be broadly classified as follows:

- i. Blending kerosene into petrol
- ii. Blending kerosene into diesel
- iii. Blending variable amounts of gasoline boiling range hydrocarbons such as industrial solvents into automotive gasoline
- iv. Blending small amounts of spent waste industrial solvents such as used lubricants into gasoline and diesel
- v. Blending small amounts of heavier fuel oils into diesel fuels

1.2.2 Characteristics of the adulterants added

Adulterants added must;

- i. Ensure higher financial gains
- ii. Be easily available
- iii. Be easily blended
- iv. Be physically similar in appearance, colour, taste and smell.

1.2.3 Causes of adulteration of fuels

The primary factors encouraging the practice of adulteration are as follows:

- i. Existence of differential tax levels amongst the fuels, intermediate products and byproducts. The adulterants being taxed lower than the fuels give monetary benefits when mixed hence replacing a proportion of the fuels.
- ii. Fluctuation in pricing mechanism of fuels and the easy availability of adulterants in the market.
- iii. Lack of monitoring and consumers awareness.
- iv. Lack of transparency and uncontrolled regulations in the production-supply and marketing chain for intermediates and byproducts of refineries.
- v. The mechanism and instruments for spot-checking the quality of fuels are poor hence their effectiveness is not very high.

1.2.4 Effects of adulteration of fuels

Some adulterants increase emissions of harmful pollutants and thus lead to an indirect adverse effect on society through the loss of tax revenue (Kulathunga *et al.*, 2004). A good example is by large scale diversion of kerosene designated for household use is deviated and used for adulteration in petrol and diesel. Though it does not increase emissions from diesel vehicles, it deprives people kerosene that can be used for cooking. When the impact of fuel adulteration is taken into consideration, the main focus is on the effects on emissions of the basic engine design and maintenance which usually outweigh those of changes in fuel composition (Kulathunga *et al.*, 2004). Fuel adulteration can increase the tail pipe emissions of hydrocarbons (HC), carbon monoxide (CO) due to incomplete

combustion, oxides of nitrogen (NO_x) and particulate matter (PM). Emissions which fall into the category of unregulated emissions are benzene and polyaromatic hydrocarbons (PAHs), which are known carcinogens (Ashworth, 2000). Benzene depends mostly on fuel composition and catalyst performance. PAHs in the exhaust are due to the presence of PAHs in the fuel and in part due to PAH formation by fuel combustion in the engine in the case of gasoline. Amounts of pollutants emitted also depend on parameters such as air-to-fuel ratio, engine speed, engine load, operating temperatures, whether the vehicle is equipped with a catalytic converter and the condition of the catalyst (Kulathunga *et al.*, 2004).

1.2.5 Gasoline adulteration

Gasoline may be adulterated with kerosene, diesel fuels, industrial solvents, gasoline boiling range products such as toluene, xylenes and aromatics or light materials such as pentanes and hexanes (Masami and Robert, 2001). Addition of kerosene into gasoline results in higher levels of HCs, CO and PM emissions even from catalyst equipped cars. This is because kerosene is more difficult to burn than gasoline. The higher sulphur level of kerosene can deactivate catalyst and lower the conversion of pollutants emitted by the engine (Masami and Robert, 2001). If too much kerosene is added then the octane quality falls below the octane requirement of the engine leading to engine knock and hence an increase in HCs, Volatile organic compounds (VOC'S) well known ozone precursors and NO_x emissions (Ashworth, 2000). When gasoline is adulterated with diesel fuels, same effects occur as those when kerosene is added but usually noticed at lower levels of added diesel fuel. Addition of both diesel and kerosene to gasoline increases engine deposit

formation including in fuel injectors, potentially leading to an increase in emission of PM, HC and CO (Kulathunga *et al.*, 2004). Addition of small amounts of toluene and xylene in gasoline would not exhibit drivability problems in motor vehicles. Larger amounts of toluene and /or mixed with xylene cause some increase in HC, CO, NO_x emissions, and significant increase in the level of air toxins which are carcinogenic in the tailpipe exhaust (Kulathunga *et al.*, 2004). The adulterated gasoline has increased potential human toxicity if frequent skin contact is allowed. Extremely high levels of toluene (45 % or higher) could cause premature failure of neoprene, styrene butadiene rubber and butyl rubber components in the fuel system hence increase the maintenance cost of the vehicles and sometimes it has caused vehicle fires in some cases, especially in older vehicles (Bjorklund and Kushida, 2001). Adulteration of gasoline by waste industrial solvents is especially problematic as the adulterants are so varied in composition. They will cause increased emissions, may even cause vehicle breakdown. Even low levels of these adulterants can be injurious and costly to vehicle operation (Kulathunga *et al.*, 2004). For gasoline, any adulterant that changes its volatility can affect drivability. High volatility (resulting from addition of light hydrocarbons) in hot weathers can cause vapour lock and stalling. Low volatility in cold weather can cause starting problems and poor warm-up (Masami and Robert, 2001). Changes in the physical and chemical properties of gasoline are caused by solvent addition. Addition of kerosene into unadulterated gasoline changes the original composition of the fuel thus causing the detection of adulteration to be difficult especially if adulteration involves the addition of a hydrocarbon or their mixtures, normally present in the

composition of gasoline. Density and distillation temperatures are properties closely related to the fuel composition and the characteristic of its components (Al-Ghouti *et al.*, 2008).

1.2.6 Diesel adulteration

The blending of kerosene with automotive diesel is generally practiced by oil industry worldwide as a means of adjusting the low temperature operability of the fuel (Dutta, 2003). This practice is not harmful or detrimental to tailpipe emissions, provided the resulting fuel continues to meet engine manufacturer's specifications, especially for viscosity and cetane number (Dutta, 2003). However, high-level adulteration of low sulphur diesel fuel with high -level sulphur kerosene can cause the fuel to exceed the sulphur maximum (Masami and Robert, 2001). The addition of heavier fuel oils to diesel is usually easy to detect because the resultant fuel will be darker than normal (Masami and Robert, 2001). Depending on the nature of these heavier fuel oils and the possible presence of additional PAHs, there could be some increase in both exhaust PM and PAH emissions (Masami and Robert, 2001).

1.3 Literature Review

As early as 14th century, some surface deposits were being distilled to obtain lubricants and medicinal products, but the real exploitation of crude oil did not begin until the 19th century (Manning *et al.*, 1991). (Speight, 2002), reported that in 1852 Canadian physician and geologist Abraham Gessner obtained a patent for producing clean-burning, affordable lamp fuel called kerosene from crude oil. In 1855 an American chemist, Benjamin Silliman, published a report indicating the wide range of useful products that could be derived through the distillation of crude oil (Manning *et al.*, 1991). The petroleum industry began

with the successful drilling of the first commercial oil well in 1859 by Colonel Edwin L. Drake who drilled an oil well near Oil Creek, Pennsylvania (Manning *et al.*, 1991). Drake's success marked the beginning of the rapid growth of the modern petroleum industry (Manning *et al.*, 1991). This was followed by the opening of the first refinery two years later to process the crude into kerosene (Potter, 1987). The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. The first refinery, opened in 1861, produced kerosene by simple atmospheric distillation. Its by-products included tar and naphtha (Potter, 1987). It was soon discovered that high-quality lubricating oils could be produced by distilling petroleum under vacuum. However, for the next 30 years kerosene was the product consumers wanted. Two significant events changed this situation which was the invention of the electric light which decreased the demand for kerosene and the invention and development of the internal combustion engine which created a demand for diesel fuel and gasoline (Kovarik *et al.*, 2005). Since 19th century, when automobiles were invented, diesel and gasoline have been used as the primary source of energy for the vehicles though many alternate fuels like compressed natural gas, Liquefied Petroleum Gas, methanol, ethanol, dimethylether and biodiesel fuel are emerging in the market (Dutta, 2003). Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. Automobile engines demand for larger amounts of petroleum led to the discovery of better processes in the late 1930's and early 1940's in order to produce higher-octane gasoline with better antiknock characteristics that were required by higher-compression gasoline engines (Kovarik *et al.*, 2005). Following the Second World War, various reforming processes improved gasoline

quality, yield and produced higher-quality products. (Kovarik *et al.*, 2005). Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry (Dutta, 2003).

A variety of products from the refineries are being used by a few people in the society for selfish interests hence tampering with the quality of the fuels. Cases of places where this practice has been carried out are Kenya where Kenya broadcasting cooperation (KBC Business, 2006) published a document on adulteration of fuel highlighting on the increase of cases of adulteration of petroleum products since the liberalization of the petroleum sub-sector in 1994. The Government of Kenya, according to this document was concerned that adulteration of either gasoline or diesel by kerosene was wreaking automobile engines apart from denying it the much needed revenue. In Tanzania adulteration of fuels has been reported to be increasing to alarming proportions. The problem is mostly due to mixing of petrol or diesel with kerosene (Charles, 2007).

In New Zealand, unscrupulous firms exceeded “acceptable” limits when they added too much of the off specification toluene to gasoline as a cheap source of octane and caused many car fires (Chang, 2001). The centre for science and environment (CSE, 2002) reported that in south Asia adulteration of automotive gasoline and diesel fuels was wide spread. A report prepared by CSE on gasoline and adulteration in Delhi has provided a good overview of the scope of the problem and some technical and economic data on the subject. In Uttar Pradesh in the city of Meerut in India, an authorized transport company was caught with adulterated stock. This transport agency had the authority to transport both

petrol and diesel to retail outlets and solvents for industrial use. The agency was supposedly using its workplace for adulterating diesel with kerosene (Dutta, 2003).

The Kenya bureau of standards (KEBS) specifications for gasoline, kerosene and diesel is shown in table 1

Table 1: Kenya Bureau of Standards Specifications for Gasoline (KEBS, 2007), Kerosene (KEBS, 1996) and Diesel (KEBS, 2006).

Characteristics	Requirements for gasoline		Requirements for diesel		Requirements for kerosene	
	Max	Min	Max	Min	Max	Min
Lead content (ppm)	15	-	-	-	-	-
Density (Kg/l)	0.75	0.70	0.80	0.76	0.85	0.80
Sulphur content (ppm)	1500	-	5000	-	1500	-
Flash point °C	-45	-	60	-	39	-
Distillation °C	210	-	400	-	300	-

KEY:

- Data not available

Adulteration of fuels has been monitored using various analytical techniques. These include; Standard test method for distillation of petroleum products (ASTM D 86), gas chromatography mass spectrometry (GC-MS) (Barbeira, 2002), Fourier transform infrared spectroscopy (FTIR) (Al-Ghouti *et al.*, 2008) and multivariate data analysis, ultraviolet (UV) (Narasimham, 2008), gas chromatography flame ionization detection (GC-FID) (Pedroso *et al.*, 2008), high pressure liquid chromatography (HPLC) Ghosal and Dholev, 1995) and fluorescence spectroscopy (Kulathunga *et al.*, 2004). Detection and identification of gasoline adulteration is not an ordinary task, as solvents usually employed for this

purpose are mixtures of hundreds of different compounds and some of them are even found in unadulterated gasoline (Leonardo *et al.*, 2008).

Statistical techniques along with infrared spectroscopy have been used to obtain accurate and simple calibration data to dictate chemical composition and physical properties of different samples. Examples of fields where infrared spectroscopy in association with statistical techniques have been used are in food (Moussa and Hamed, 2007), pharmaceutical (Bunaciu *et al.*, 2006), petrochemical industries and also in monitoring quality of fuel (Al-Ghouti *et al.*, 2008), (Leonardo *et al.*, 2008) (Rita *et al.*, 2006). In gasoline Al-Ghouti *et al.* (2008) recorded 10 peaks of absorbance at wave numbers: 432, 694.3, 732.9, 1033.8, 1458.1, 1604.7, 2869.9, 2923.9, 2954.7 and 3024.2cm^{-1} on the gasoline standard spectrum.

In this research FTIR, distillation, density, copper corrosion, fast sequential atomic absorption spectroscopy and energy dispersive X-ray fluorescence spectroscopy methods will be employed.

The FTIR method to be employed will differ from other methods previously used as only a single peak characteristic to kerosene at 1380.9 cm^{-1} is will be used to identify adulteration whereas in previous studies a multiple number of peaks have been used and the above mentioned peak has not been cited.

1.4 THEORY

1.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Principle

It involves the absorption of electromagnetic radiation in the infrared region of the spectrum which results in changes in the vibrational energy of molecule. Usually molecules have vibrations in the form of stretching and bending and the absorbed energy is utilized in changing the energy levels associated with them. It is a valuable tool in identifying organic compounds which have polar chemical bonds such as OH, NH, CH, -C=C-, aromatics with good charge separation (strong dipoles) (Colthup *et al.*, 1990).

Instrumentation

This technique utilizes a single beam of un-dispersed light and has the following components; a double beam spectrophotometer comprising IR source, grating monochromator, thermocouple detector, cells made of either sodium chloride or potassium bromide materials. In FT-IR, the un-dispersed light beam is passed through the sample and the absorbances at all wavelengths are received at the detector simultaneously (Ingle and Crouch, 1988). Spectra are obtained by screening wavelength from 4000cm^{-1} to 400cm^{-1} . A computerized mathematical manipulation known as “Fourier Transform” is performed on the data to obtain absorption data for each and every wavelength. In this type of calculations interference of light pattern is required for which the FTIR instrumentation contains two mirrors, one fixed and one moveable with a beam splitter in between them. Before scanning the sample a reference or a blank scanning is required (Ingle and Crouch,

1988). The diagram shown in figure 1 is a simplified design of Fourier Transform Infrared Spectrometer.

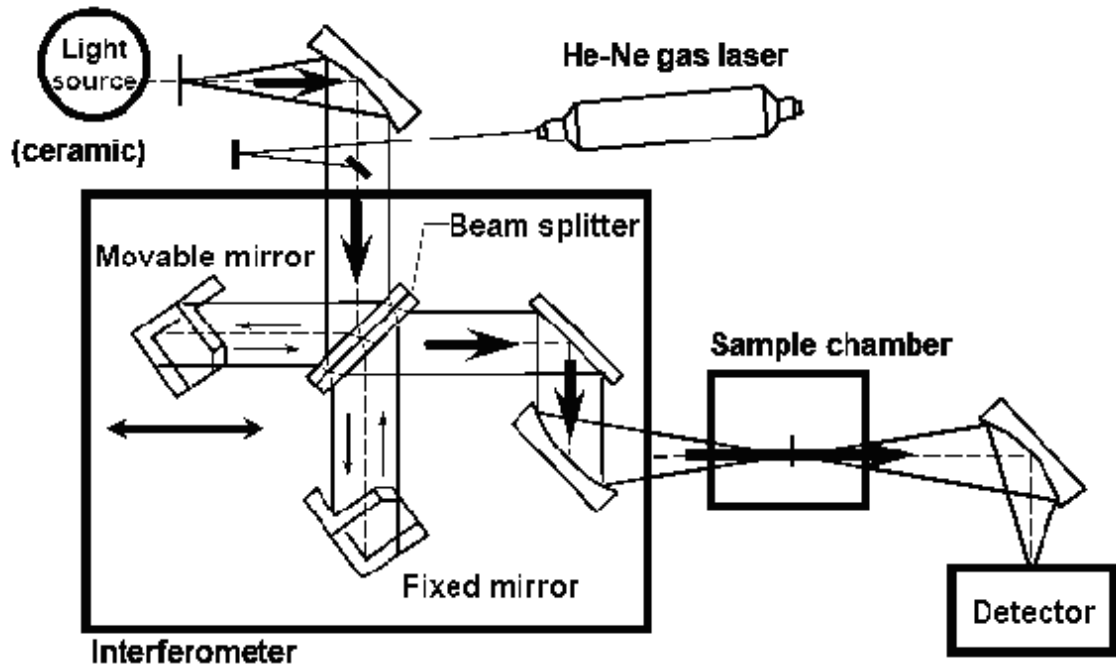


Figure 1: Simplified design of the FTIR instrument (Jasco, 2007)

1.4.2 Determination of boiling point range characteristics of gasoline by distillation (ASTM D 86)

One of the most important features of gasoline is the volatility that is measured by a distillation experiment. In this method the determination of volatility of petroleum products is done using a laboratory batch distillation unit to determine quantitatively the boiling range characteristics of products such as gasoline, light and middle distillates, aviation turbine fuels, low sulfur diesel fuels, special petroleum spirits, naphtha, white spirits and kerosene. Distillation is based on the composition, vapor pressure, expected initial boiling

point, expected final end point, and combustion of the sample. Both automated and manual equipments may be used (ASTM D 86., 2006).

Significance of distillation

The distillation characteristics of hydrocarbons have an important effect on their safety and performance. The various ranges of a distillation profile have been correlated with specific aspect of gasoline performance. Front-end volatility is adjusted to provide: (a) easy cold starting, (b) easy hot starting, (c) freedom from vapour lock, and (d) low evaporation and running-loss emissions. Mid-range volatility is adjusted to provide: (a) rapid warm-up and smooth running, (b) good short-trip fuel economy, (c) good power and acceleration, and (d) protection against carburetor icing and hot stalling. Tail-end volatility is adjusted to provide: (a) good fuel economy after engine warm-up, (b) freedom from engine deposits, (c) minimal fuel dilution of crankcase oil, and (d) minimal volatile organic compound (VOC) exhaust emission (Al-Ghouti *et al.*, 2008).

1.4.3 Determination of density using the hydrometer method (ASTM D 1298)

This method covers the laboratory determination of density petroleum products normally handled as liquids using a glass hydrometer. The values are measured on a hydrometer at either the reference temperature or at another convenient temperature, and readings corrected to the reference temperature by means of the petroleum measurement tables (ASTM D 1298., 2006).

Significance of density

Accurate determination of the density, of petroleum products is necessary for the conversion of measured volumes to volumes or masses at the standard reference

temperatures during storage. This method can also be used for viscous liquids by allowing sufficient time for the hydrometer to reach equilibrium, and for opaque liquids by employing a suitable meniscus correction. Density is an important quality indicator for automotive, aviation and marine fuels, where it affects storage, handling and combustion (ASTM D 1298., 2006).

1.4.4 Detection of copper corrosion by the copper strip tarnish Test (ASTM D 130)

This method covers the detection of the corrosiveness of sulphur compounds to copper of automotive gasoline, aviation gasoline and aviation turbine fuel (ASTM D 130., 2006).

Significance of copper strip tarnish Test

Crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur compounds remaining in the petroleum product, some can have a corroding action on various metals. The effect can vary according to the chemical types of sulfur compounds present. The copper strip corrosion test is designed to assess the relative degree of corrosivity of a petroleum product (ASTM D 130., 2006).

1.4.5 Determination of lead in gasoline by Flame Atomic Absorption Spectroscopy (FAAS)

Principle of FAAS

FAAS is used to determine trace levels of metals in samples. In this technique, a fine spray of the analyte is passed into a suitable flame such as air-acetylene, oxygen-acetylene or nitrous oxide acetylene, which converts the element to atomic vapor. Through this vapour, a radiation is passed from hollow cathode lamp at the right wavelength to excite the atoms

at ground state to their first excitation electron levels. The amount of radiation absorbed can then be measured and directly related to the atom concentrations. A hollow cathode lamp is used to emit light with characteristic narrow line spectrum of the analyte element.

Its main advantages are high specificity since the lining of hollow cathode lamp is made of the element similar to the one being determined in the sample, high sensitivity, minimum interference from other elements and very hot flame is not necessary because the atoms are used at ground state (Ewing, 1985).

1.4.6 Determination of Sulphur in gasoline by Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF)

This method covers the measurement of sulfur in hydrocarbons, such as diesel, naphtha, kerosene, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded), and other distillates. The applicable concentration range is 0.0150 to 5.00 mass percentage of sulfur and a typical analysis time is 2 to 4 min per sample (ASTM D 4294., 2008).

Significance of the Energy Dispersive X-ray Fluorescence Spectrometry

determination of sulphur

The quality of many petroleum products is related to the amount of sulfur present (ASTM D 4294., 2008). The method provides rapid and precise measurement of total sulfur in petroleum products with a minimum of sample preparation. Compared to other test methods for sulfur determination, this method has high throughput, minimal sample preparation, good precision, and is capable of determining sulfur over a wide range of concentrations (ASTM D 4294., 2008).

1.5 Statement of the problem

Since the year 2000, there has been an increase of vehicles on the Kenyan roads most of which are second hand vehicles and have lead to an increase of vehicular density in major towns in Kenya especially Nairobi where traffic jams are the norm of the day. As vehicles move at a slow speed, the combustion of the fuel is not complete in most cases and hence tail pipe emissions increase. In recent times there have been increased reports on complications related to breathing as well as complaints on reduced engine spans by vehicle owners and loss of government revenue. All these have been attributed to the quality of fuel dispensed in the fuel outlets hence there is need to assess the quality of fuels dispensed in the fuel outlets.

1.6 Objectives

1.6.1 General objective

To assess the quality of gasoline dispensed in the Kenyan market.

1.6.2 Specific objective

- To develop and validate FTIR method for assessment of the adulteration of gasoline
- To quantify the levels of kerosene at the point of sale
- To determine the levels of lead in gasoline in selected samples
- To determine the levels of sulphur in gasoline in selected samples

1.7 Justification of the study

Environmentally friendly fuels are sought after all over the world hence there is need to have gasoline with fewer pollutants. Kenya as a country is not left behind, hence there is need to have fuels with little emissions. Gasoline and diesel are the major transport fuels in our country. Gasoline carries a much higher tax than diesel, which in turn is taxed more than kerosene. Industrial solvents and recycled lubricants are other materials with little or no tax. Previous studies have indicated that more than 30% of Kerosene distribution intended for household consumption flowed back to the motor industry. As the cost of living increases, fuel prices increase too, and it is due to this price disparity and significant price difference between these products and the adulterants that unscrupulous businessmen have resorted to adulterating fuels so as to make quick money and enrich themselves at the expense of innocent consumers. Adulteration made at selling points or during transportation has led to financial loss by the government in terms of tax, increase in the emission of harmful pollutants and reduced life span of the engine. Hence there is need to assess the quality of fuels to reduce risks of harmful emissions to humans, loss of revenue to the government and decrease in life span of the engine.

CHAPTER TWO

2.0 METHODOLOGY

2.1.0 Reagents

The following reagents were used; Aliquat 336 (tricapryl methyl ammonium chloride), Methyl isobutyl ketone (MIBK), Aliquat 336/MIBK (10%v/v), Aliquat 336/MIBK (1%v/v), Iodine, Methyl benzene (AR), Lead chloride, Conostan sulphur standards, Conostan gasoline standards, Conostan Kerosene standards, Conostan lead standards.

2.1.1 Apparatus

KBr disks

KBr disk holder

Syringe

Distillation flasks

Thermometers

Hydrometers

Volumetric flasks 100ml (Class A)

Conical Flasks 100ml (Class A)

Measuring cylinder 5ml, 10ml, 20ml, 100ml (Volac type, Class A)

Sample cells

Polycarbonate high performance XRF sample film

Pipets

2.1.2 Equipment

Fourier Transform Infrared Spectrometer (Shimadzu 8400)

Manual distillation unit (Seta still)

XRF analyser (Oxford -X³⁰⁰⁰)

Fast sequential atomic absorption spectrometer (AA 240 FS Varian)

2.1.3 Cleaning of glassware

All glassware which included measuring cylinders, pipettes, distillation flasks, beakers, boiling tubes, glass bottles were thoroughly cleaned with tap water and detergent. They were then rinsed with water and finally with distilled deionised water. The glassware was then dried in the oven at 100⁰C.

2.2.0 Experimental procedure

2.2.1 Gasoline standards and reference material collection and labeling

The gasoline samples were obtained from various petrol stations in Nairobi Kenya. Dark glass bottles were used for collecting the samples since light degrades the samples. A representative sample was drawn directly from the pump into the bottle and well corked in order to prevent loss of light hydrocarbons that may affect the test results. The glass bottle was labeled immediately after the sample was obtained. Kerosene, sulphur, lead standards and certified reference materials were obtained from Conostan oil analysis standards.

2.2.2 Gasoline storage

The gasoline samples were then transported to JKUAT chemistry laboratory, where a small quantity of sample was transferred into a smaller glass bottle and stored in a cool dry place

awaiting analysis whereas the remainder of the sample was transported to the Kenya pipeline company for analysis.

2.3 Experimental

The chemical and physical parameters analysed were based on the standardized analytical methods to provide an overall indication of the status of fuel. American Standards for Test and Materials (ASTM) chemical methods such as the determination of distillation (ASTM D 86), density (ASTM D 1298), copper corrosion (ASTM D 130), Lead in gasoline (ASTM D 3237), sulphur in gasoline (ASTM D 4294) were carried out. FTIR spectroscopy method was also used.

2.3.1 Determination of boiling range characteristics of gasoline by distillation (ASTM D 86)

A 100ml of the sample was distilled in a laboratory batch distillation unit at ambient pressure under conditions that are designed to provide approximately one theoretical plate fractionation. Systematic observations of temperature readings and volumes of condensate were made and the observed temperatures were corrected for barometric pressure. The volumes of the residue and the losses were also recorded (ASTM D 86., 2006).

2.3.2 Determination of density using hydrometer method (ASTM D 1298)

The sample was brought to prescribed temperature and transferred to a cylinder at approximately the same temperature. The appropriate hydrometer was then lowered slowly into the sample and allowed to settle. After temperature equilibrium had been reached, the hydrometer scale was read and the temperature of sample noted. The observed hydrometer

reading was reduced to the reference temperature of 20⁰C by means of the petroleum measurement tables (ASTM D 1298., 2006).

2.3.3 Standard test method for copper corrosion (ASTM D 130)

A copper strip was polished and immersed in 30ml of test sample placed in heated bath at a temperature of 50⁰C for 3 hours. The copper strip was then removed and compared with ASTM copper strip corrosion standards (ASTM D 130., 2006).

2.3.4 Determination of gasoline adulteration by Fourier Transform Infrared (FTIR)

Various concentrations of gasoline-kerosene v/v were prepared from the gasoline standard and kerosene standard. A background spectrum of an empty liquid cell was run and saved. 2 μ l of gasoline standard was transferred with the use of a syringe on to the two well polished KBr disks, it was then spread creating a thin film. A normal resolution of 16cm⁻¹ was used and a 100 scans were run and triplicate run were obtained for each. This was followed by running different concentrations of 0-12% v/v of gasoline intentionally adulterated with kerosene. Peak area at 1380.9cm⁻¹ was recorded for each concentration. A calibration graph of peak area against percentage contamination was plotted and the best line of fit obtained. 2 μ l of each sample was collected carefully and homogenously spread between two well polished KBr disks of fixed weight, creating a thin film. The spectra were obtained in triplicate for each sample. The peak area for each sample was recorded and from the regression equation of the standards the percentage contamination of each sample was obtained.

2.3.5 Determination of lead in gasoline by atomic absorption spectroscopy (ASTM D 3237)

5.0 ml of gasoline sample was added and mixed to a 50 ml volumetric flask containing 30 ml methyl isobutyl ketone (MIBK). 1.0 ml of iodine solution was added to the mixture and allowed to react for about one minute. This was followed by the addition of 5.0ml of 1% aliquat 336 / MIBK solution and mixed. The solution was then diluted to volume with MIBK and mixed. The working standards and samples were aspirated and the absorbance values recorded (ASTM D 3237., 2008).

2.3.6 Determination of Sulphur in gasoline by energy dispersive X-ray fluorescence spectrometry (ASTM D 4294)

The gasoline samples were first preconditioned by placing them in a refrigerator at temperatures below 10⁰C. A certified reference material was placed in the beam emitted from an X-ray tube and the resultant excited characteristic X radiation measured as counts for a period of 90 seconds was recorded. This was followed by a known volume of sample which was put in a sample cell and placed in the beam emitted from an X-ray tube and the resultant excited characteristic X radiation was measured. (ASTM D 4294., 2008).

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

3.1 Gasoline standard spectrum by FTIR method

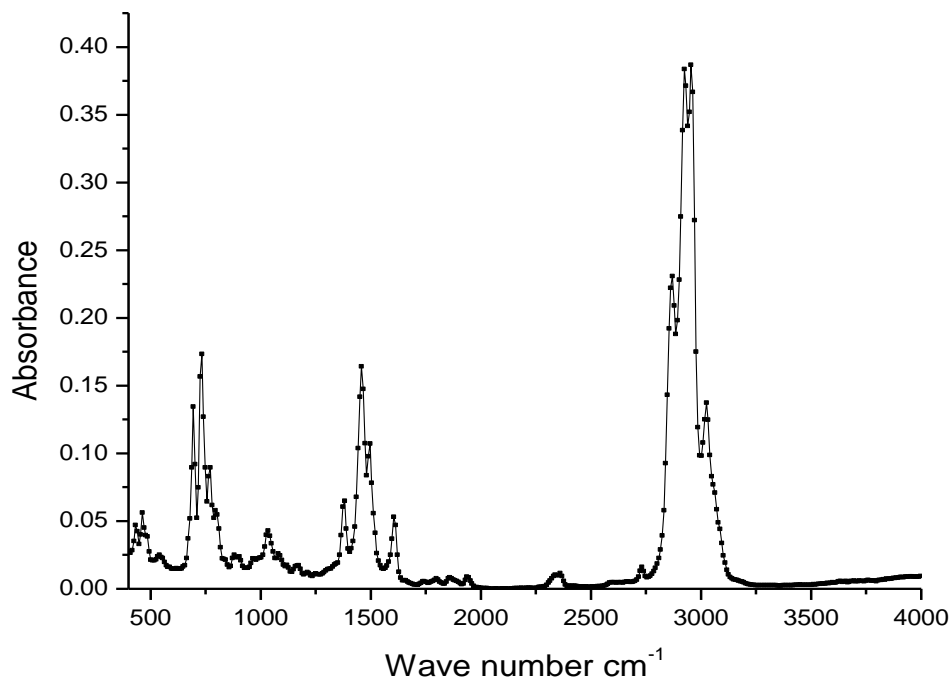


Figure 2: A spectrum of gasoline standard using FTIR spectroscopy

The gasoline standard spectrum figure 2 was obtained using FTIR instrument. The FTIR spectrum of gasoline standard was recorded over the range (400-4000cm⁻¹) as illustrated in figure 2. The spectrum was divided into five regions from 400-500cm⁻¹, 600-800cm⁻¹, 1000-1200cm⁻¹, 1300-1600 cm⁻¹ and 2750 –3250cm⁻¹.

The peak of gasoline standard was strongly overlapping within the entire spectrum region as shown on figure 3.

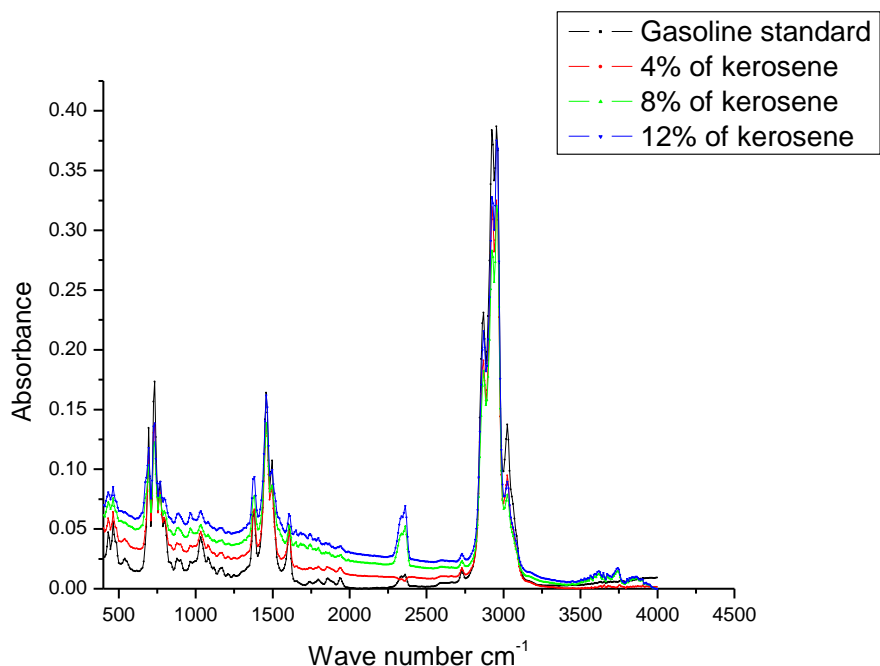


Figure 3: FTIR spectra (400-4000 cm^{-1}) of, gasoline standard, gasoline with 4% of kerosene, gasoline with 8% of kerosene, gasoline with 12% of kerosene using the FTIR spectrometer.

Figure 3, shows FTIR spectra of adulterated and unadulterated gasoline. It can be seen that they coincide, and it is not possible to distinguish each one of them by just visual examination of the whole spectra whether gasoline is adulterated or not.

However, a careful investigation of the fingerprint region specifically the spectral region (1320-1420 cm^{-1}), revealed that there are visual differences in the peak areas at absorption band at 1380.9 cm^{-1} which was responding with the amount of the adulterant as shown on figure 4. The absorption band at 1380.9 cm^{-1} was the only absorption peak that increased with increase of the amount of kerosene adulterant added to gasoline. This indicates that convectional calibration procedures would have a role in quantitative determination.

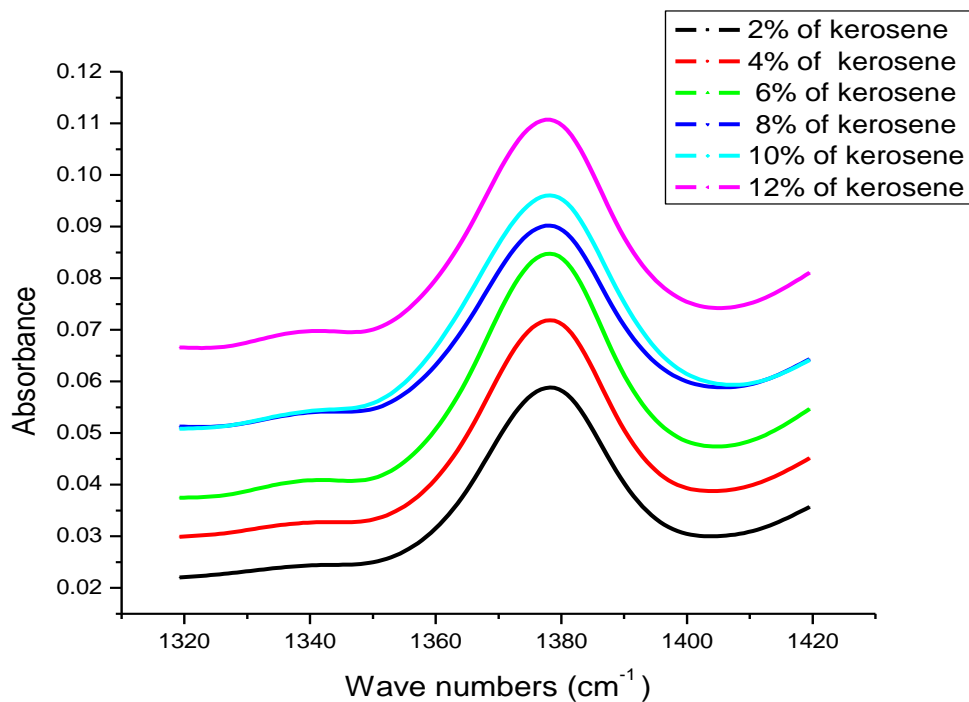


Figure 4: Fourier transform infrared spectra of standards scanned from 1320 to 1420 cm-1

The peak in figure 4 represents CH₃ asymmetric bending, which is possibly due to the heavy hydrocarbons found in kerosene with C₁₂ to C₁₅. These hydrocarbons are n-dodecane, n-tridecane, n-tetradecane and n-pentadecane. The gasoline standard was adulterated using 2-12% of kerosene as shown in figure 3. The area for each peak was determined and a calibration graph of peak area versus percentage adulteration of kerosene was drawn as shown in figure 5.

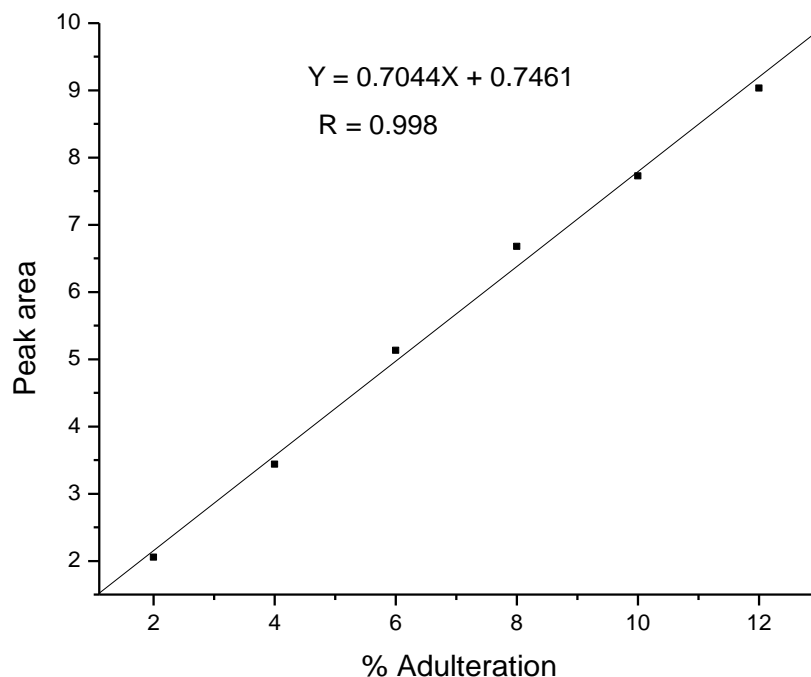


Figure 5: Calibration curve of peak area against % adulteration of gasoline standard with kerosene.

The percentage adulteration of the gasoline samples from the FTIR method was obtained from the calibration graph in figure 5 by interpolation of peak area against the calibration graph. These values are shown in table 3.

3.2 Percentage contamination levels obtained by FTIR and distillation methods

The values indicated in table 2 and figure 6, represent percentage contamination levels obtained by FTIR and distillation, density, copper corrosion values and distillation final end points are also shown on table 2 respectively.

Table 2: Comparison of the effect of kerosene adulteration of gasoline using FTIR, distillation (ASTM D86), density and copper corrosion methods

Samples	FTIR (% adulteration)	Distillation (ASTM-D 86) (% adulteration)	Distillation (Final end point)	Density (Kg/L @ 20 ^o C)	Copper corrosion
Std			186.00 ± 0.29	0.7300	1a
1	17.312 ± 0.729	20.00 ± 0.58	259.50 ± 1.00	0.7536	1b
2	12.336 ± 0.606	11.50 ± 1.16	207.50 ± 1.00	0.7433	1b
3	11.861 ± 0.469	11.00 ± 0.58	202.50 ± 1.00	0.7433	1b
4	11.277 ± 0.515	10.00 ± 1.00	205.50 ± 1.00	0.7452	1a
5	10.111 ± 1.952	10.00 ± 0.58	205.83 ± 0.58	0.7468	1b
6	9.431 ± 0.446	10.50 ± 0.58	206.17 ± 0.58	0.7472	1b
7	15.608 ± 1.063	15.50 ± 0.58	252.00 ± 1.00	0.7580	1b
8	11.302 ± 0.090	12.50 ± 1.00	207.50 ± 1.00	0.7423	1a
9	10.908 ± 0.586	10.50 ± 1.00	213.50 ± 1.00	0.7665	1b
10	11.781 ± 2.114	10.00 ± 1.00	208.50 ± 1.00	0.7493	1b
11	17.749 ± 0.513	16.00 ± 1.00	304.50 ± 1.00	0.7665	1b
12	13.155 ± 1.522	15.00 ± 0.58	242.67 ± 0.58	0.7560	1b
13	11.317 ± 2.700	10.00 ± 1.00	206.17 ± 0.58	0.7670	1b
14	12.810 ± 0.818	10.00 ± 1.00	212.17 ± 0.58	0.7680	1b
15	11.871 ± 0.280	10.00 ± 0.58	207.17 ± 0.58	0.7685	1b
16	10.682 ± 1.481	10.00 ± 0.58	205.83 ± 0.58	0.7670	1b
17	12.878 ± 0.607	10.50 ± 0.58	211.83 ± 0.29	0.7550	1b
18	13.230 ± 0.322	10.00 ± 1.00	200.33 ± 0.29	0.7504	1b
19	11.037 ± 0.749	10.00 ± 0.58	205.17 ± 0.58	0.7508	1a
20	10.486 ± 0.455	9.00 ± 0.58	198.67 ± 0.29	0.7498	1b
21	10.871 ± 0.642	9.50 ± 0.58	197.83 ± 0.29	0.7445	1a
22	10.400 ± 0.706	9.50 ± 0.58	200.67 ± 0.29	0.7485	1b
23	11.341 ± 0.741	9.50 ± 0.58	203.17 ± 0.58	0.7455	1b

Table 2 Continuation

Samples	FTIR (% adulteration)	Distillation (ASTM-D 86) (% adulteration)	Distillation (Final end point)	Density (Kg/L @ 20 ⁰ C)	Copper corrosion
24	10.086 ± 0.949	10.00 ± 0.58	198.33 ± 0.29	0.7405	1b
25	9.505 ± 0.377	10.00 ± 0.58	200.83 ± 0.29	0.7420	1a
26	12.187 ± 0.042	15.00 ± 0.58	267.17 ± 0.57	0.7475	1b
27	10.220 ± 0.558	10.00 ± 0.58	206.50 ± 0.50	0.7450	1b
28	7.829 ± 1.278	10.00 ± 0.58	202.33 ± 0.29	0.7460	1b
29	9.556 ± 0.561	10.00 ± 0.58	202.17 ± 0.58	0.7465	1b
30	9.990 ± 1.087	10.00 ± 0.58	206.17 ± 0.58	0.7450	1b
31	12.280 ± 0.098	11.00 ± 0.58	210.17 ± 0.58	0.7560	1b
32	15.680 ± 0.534	14.50 ± 0.58	238.67 ± 0.58	0.7565	1b
33	13.550 ± 0.667	12.00 ± 0.58	210.00 ± 0.50	0.7550	1b
34	12.490 ± 0.471	10.50 ± 0.58	208.33 ± 0.29	0.7530	1b
35	11.380 ± 0.549	10.50 ± 0.58	207.83 ± 0.29	0.7525	1b
36	10.720 ± 0.549	10.00 ± 0.58	205.83 ± 0.58	0.7435	1b
37	10.040 ± 0.682	10.50 ± 0.58	204.67 ± 0.29	0.7355	1b
38	9.620 ± 0.659	10.00 ± 0.58	206.17 ± 0.58	0.7410	1b
39	10.376 ± 0.258	9.50 ± 0.58	201.83 ± 0.58	0.7355	1b
40	11.273 ± 0.317	10.50 ± 0.58	204.17 ± 0.58	0.7360	1b
41	12.010 ± 0.514	12.20 ± 0.58	227.83 ± 0.58	0.7515	1b
42	8.050 ± 0.186	9.00 ± 0.58	200.17 ± 0.58	0.7515	1b
43	9.359 ± 0.665	11.00 ± 0.58	204.33 ± 0.29	0.7517	1b
44	11.806 ± 0.653	12.00 ± 0.58	207.17 ± 0.29	0.7521	1b
45	9.518 ± 0.826	10.00 ± 0.58	205.83 ± 0.58	0.7432	1b
46	8.662 ± 0.484	10.00 ± 0.58	203.67 ± 0.29	0.7471	1a
47	14.602 ± 0.321	15.50 ± 0.58	231.00 ± 0.50	0.7544	1b
48	10.985 ± 0.696	12.00 ± 0.58	206.67 ± 0.29	0.7475	1b
49	13.728 ± 0.757	14.00 ± 0.58	258.17 ± 0.29	0.7530	1b
50	12.451 ± 1.110	13.50 ± 0.58	261.83 ± 0.29	0.7565	1b
51	13.567 ± 0.904	14.00 ± 0.58	227.67 ± 0.29	0.7540	1b
52	8.520 ± 0.461	10.50 ± 0.29	200.67 ± 0.29	0.7512	1a

Table 2 Continuation

Samples	FTIR adulteration) (%)	Distillation (ASTM-D 86) (%) adulteration)	Distillation (Final end point)	Density (Kg/L @ 200C)	Copper corrosion
53	10.595 ± 0.927	11.00 ± 0.87	200.67 ± 0.29	0.7510	1a
54	8.998 ± 0.500	11.00 ± 0.58	204.67 ± 0.29	0.7514	1b
55	10.678 ± 0.348	12.50 ± 0.29	214.17 ± 0.58	0.7522	1b
56	9.489 ± 0.428	10.50 ± 0.58	202.83 ± 0.58	0.7522	1a
57	11.635 ± 0.535	12.00 ± 0.58	204.33 ± 0.29	0.7512	1b
58	9.259 ± 0.249	11.50 ± 0.58	206.83 ± 0.58	0.7510	1b
59	11.339 ± 0.200	10.50 ± 0.29	202.67 ± 0.29	0.7517	1a
60	17.464 ± 0.574	22.00 ± 0.58	245.17 ± 0.29	0.7601	1a
61	10.831 ± 1.112	10.50 ± 0.50	206.00 ± 0.50	0.7515	1b
62	11.849 ± 0.641	12.00 ± 0.58	200.83 ± 0.58	0.7522	1a
63	11.716 ± 0.824	12.00 ± 0.58	206.00 ± 0.50	0.7513	1b
64	11.596 ± 0.225	13.00 ± 0.58	205.00 ± 0.50	0.7481	1b
65	10.014 ± 1.006	12.00 ± 0.58	204.00 ± 0.50	0.7484	1b
66	12.007 ± 0.706	11.50 ± 0.58	204.67 ± 0.29	0.7478	1b
67	12.257 ± 0.491	13.50 ± 0.58	204.67 ± 0.29	0.7480	1b
68	11.073 ± 1.162	12.00 ± 0.58	205.67 ± 0.29	0.7476	1b
69	12.119 ± 1.381	11.00 ± 0.58	206.17 ± 0.29	0.7477	1b
70	12.596 ± 0.432	12.00 ± 0.58	204.67 ± 0.29	0.7484	1b

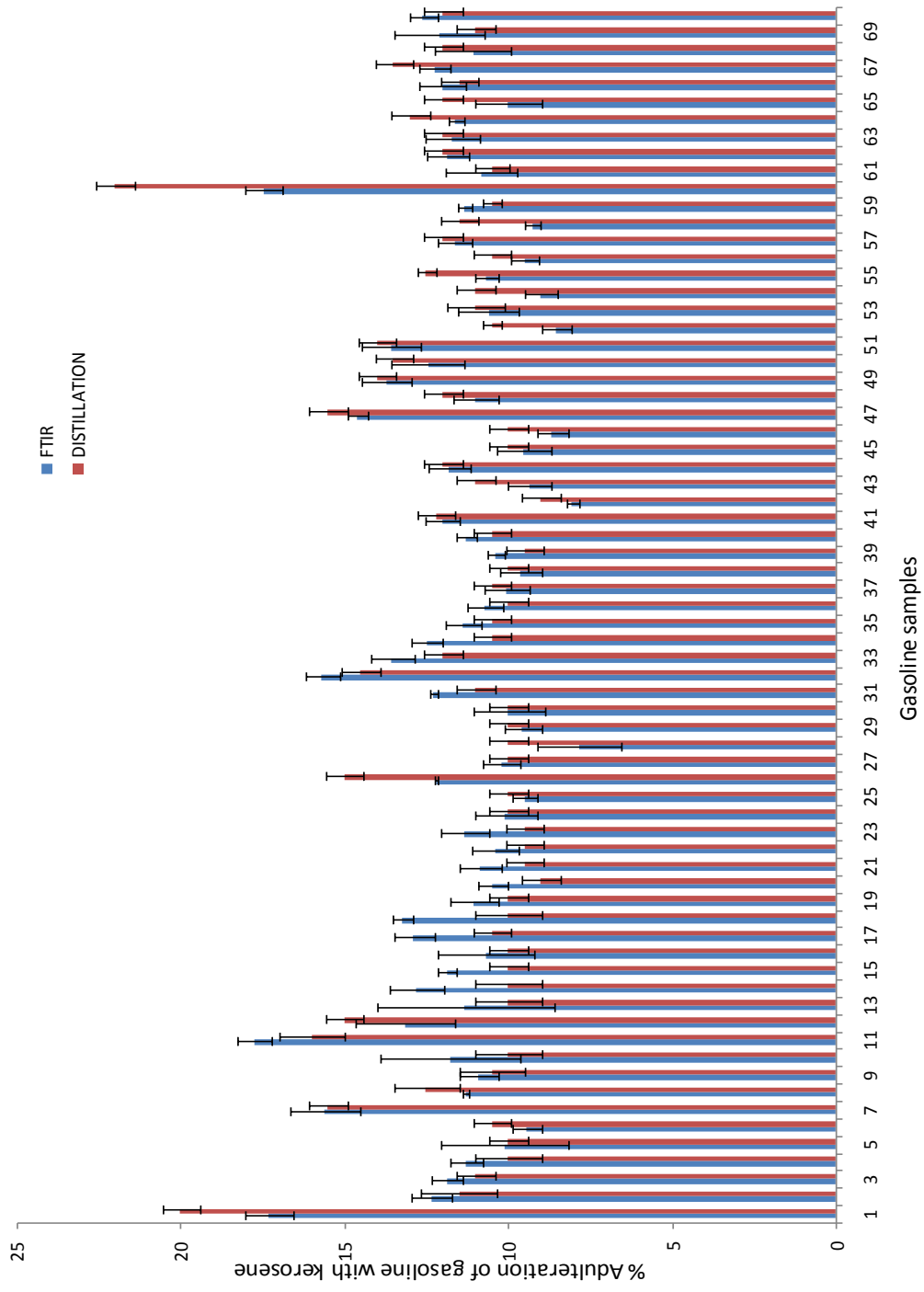


Figure 6: Percentage adulteration of gasoline by FTIR and distillation methods

The mean percentage adulteration for all 70 samples was found to be $11.50 \pm 2.035 \%$ ($11.55 \pm 2.34 \%$) for FTIR and distillation respectively. The highest adulteration of gasoline was found in sample 60 (Along Langata road) which had a mean value of $17.464 \pm 0.574 \%$ ($22.00 \pm 0.58 \%$) while the lowest was found in sample 28 (Thika-along Garissa highway) with a mean value of $7.829 \pm 1.278 \%$ ($10.00 \pm 0.58 \%$) for FTIR and distillation respectively as shown in figure 6 and table 2. The paired t test for all the 70 samples with degree of freedom of 69 at 95% confidence level gave a p-value of 0.7853. This value was found to be greater than the α -value 0.05, hence this suggests that the values of FTIR are not statistically different from those obtained by distillation (ASTM D 86). From the wilcoxon sign ranked test with continuity correlation for the 70 samples gave a p-value of 0.8744. This value was found to be greater than the α -value 0.05, hence this suggests that the experimental values obtained by FTIR are not statistically different from those obtained by distillation (ASTM D 86).

3.2.1 Multinational fuel stations

The values in table 2 as indicated in figure 7 represents a comparison of percentage contamination of gasoline obtained by both FTIR and distillation methods for the multinational fuel stations.

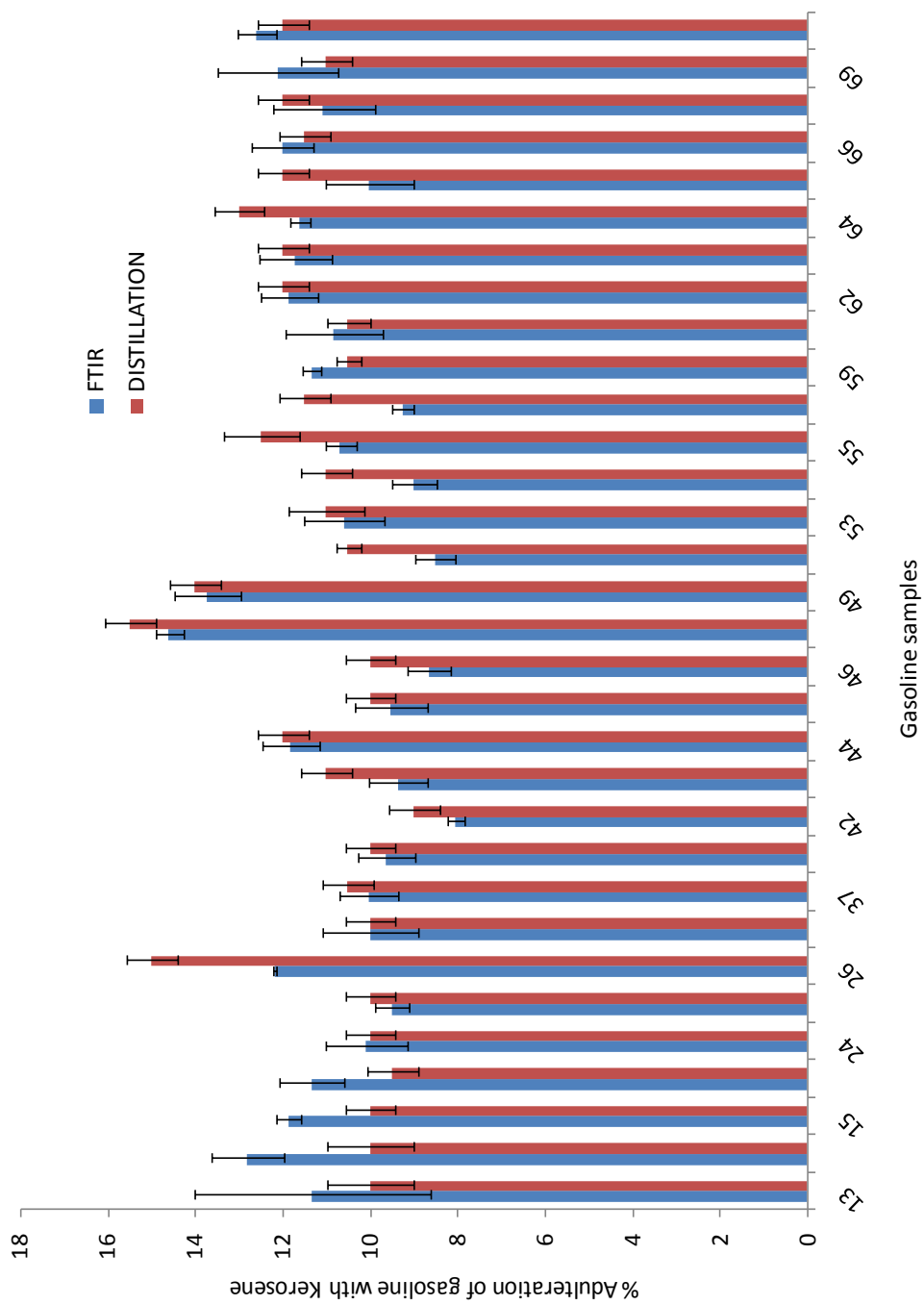


Figure 7: Percentage adulteration of gasoline samples by FTIR and distillation methods collected from multinational fuel stations

The mean adulteration for multinational Fuel stations samples was found to be 10.87 ± 1.54 % (11.23 ± 1.53 %) for FTIR and distillation respectively as shown in table 3 and figure 13. The highest adulteration of super among the multinationals was found in sample 47 (Along Ngong Road) which had a mean value of 14.602 ± 0.321 % (15.50 ± 0.58 %) for FTIR and distillation respectively while the lowest was found in sample 42 (Along Donholm) with a mean value of 8.050 ± 0.186 % (9.00 ± 0.58 %) for FTIR and distillation as shown in table 2 and figure 7. The paired t test for 32 samples with degree of freedom of 31 at 95% confidence level gave a p-value of 0.1209. This value was found to be greater than the α -value 0.05, hence this suggests that the values of FTIR are not statistically different from those obtained by distillation (ASTM D 86). From the wilcoxon sign ranked test with continuity correlation for the 32 samples gave a p-value of 0.0872. This value was found to be greater than the α -value 0.05, hence this suggests that the experimental values obtained by FTIR are not statistically different from those obtained by distillation (ASTM D 86). The correlation between FTIR and distillation for the multinational fuel stations gave a Pearson regression coefficient R value of 0.632 as shown on Figure 8. This shows that there was a correlation between the two methods even though not very good.

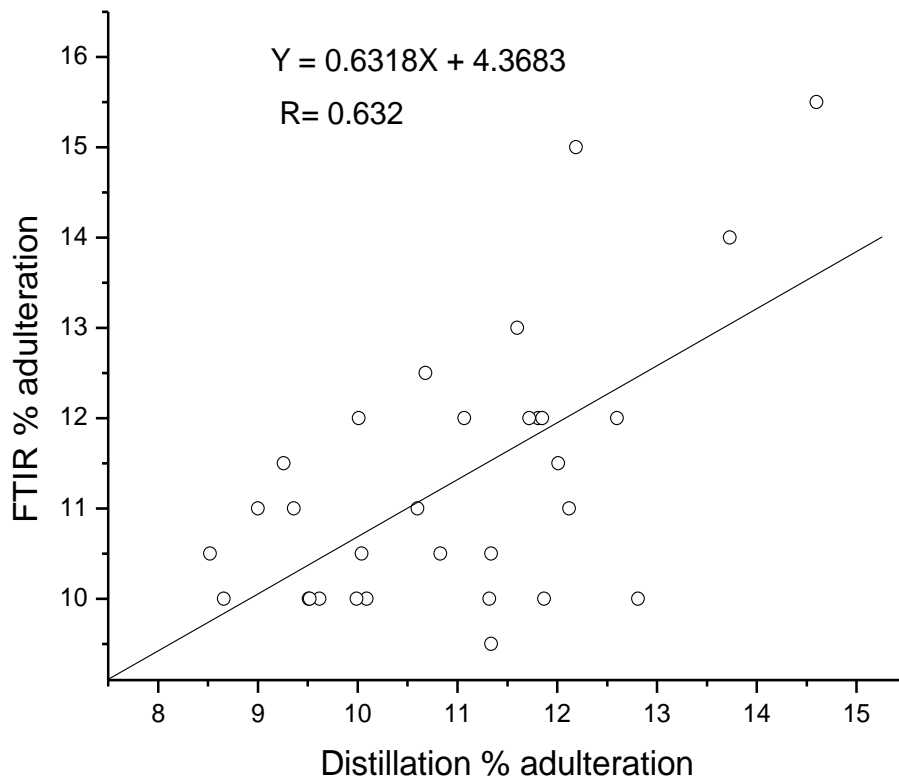


Figure 8: Scatter diagram of FTIR and distillation (ASTM D 86) percentage adulteration of samples collected from multinational fuel stations

3.2.2 National and local fuel stations

The values in table 3 and figure 9 represent a comparison of percentage contamination of gasoline obtained by both FTIR and distillation methods for the national and local fuel stations.

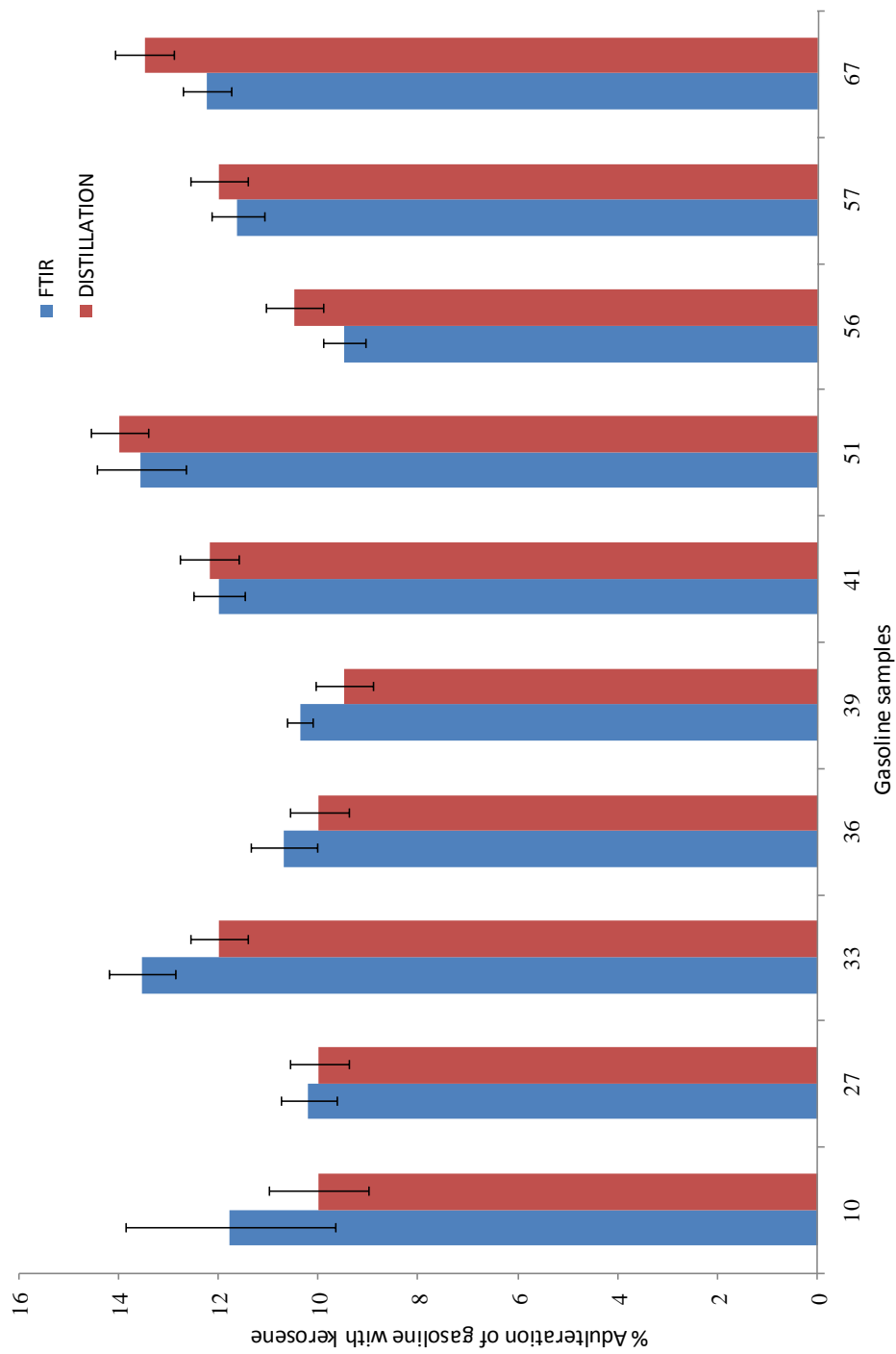


Figure 9: Percentage adulteration of gasoline samples by FTIR and distillation methods collected from national and local fuel stations

The mean percent adulteration for National and local fuel station samples was found to be 11.56 ± 1.37 % (11.37 ± 1.59 %) for FTIR and distillation. The highest adulteration of super among the National and local fuel stations was found in sample 51 (Along Yaya) which had a mean value of 13.567 ± 0.904 % (14.00 ± 0.58 %) by FTIR and distillation respectively while the lowest was found in sample 56 (In South C) with a mean value of 9.489 ± 0.428 % (10.50 ± 0.58 %) for FTIR and Distillation respectively as shown in table 2 and figure 9. The paired t test for 10 samples with degree of freedom of 9 at 95% confidence level gave a p-value of 0.5711. This value was found to be greater than the α -value 0.05, hence this suggests that the values of FTIR are not statistically different from those obtained by distillation (ASTM D86). From the wilcoxon sign ranked test with continuity correlation for the 10 samples gave a p-value of 0.6953. This value was found to be greater than the α -value 0.05, hence this suggests that the experimental values obtained by FTIR are not statistically different from those obtained by distillation (ASTM D86).

The correlation between FTIR and distillation for the national and local fuel stations using Pearson correlation method gave a Pearson regression coefficient R value of 0.771 as shown on Figure 10. This shows that there was a good correlation between the two methods.

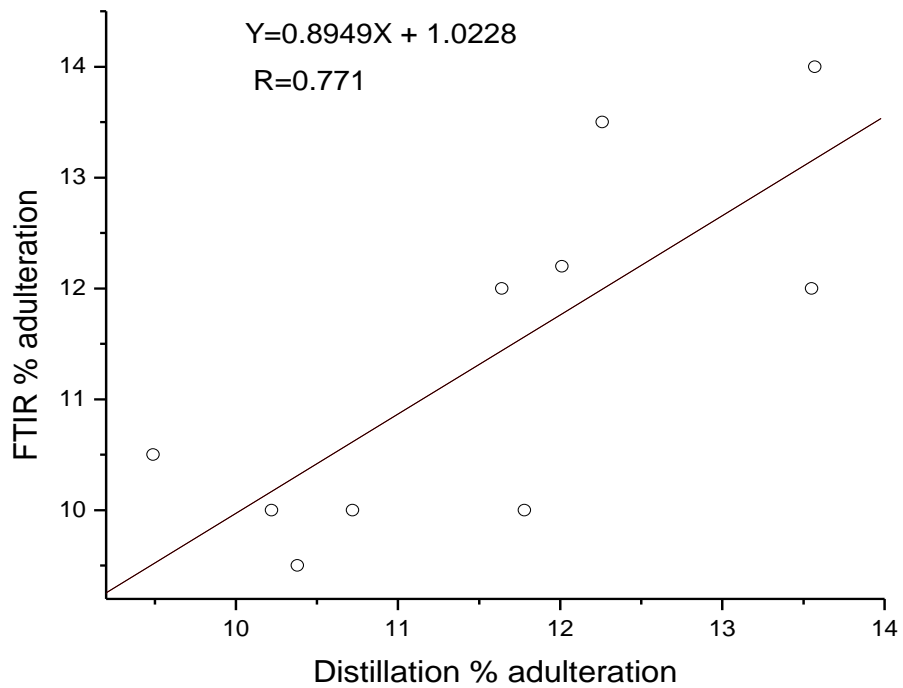


Figure10: Scatter diagram of FTIR and distillation (ASTM D86) percentage adulteration of samples collected from national and local fuel stations

3.2.3 Individually owned fuel stations

The values in table 3 and figure 11 represent a comparison of percentage contamination of gasoline obtained by both FTIR and distillation methods for the individually owned fuel stations.

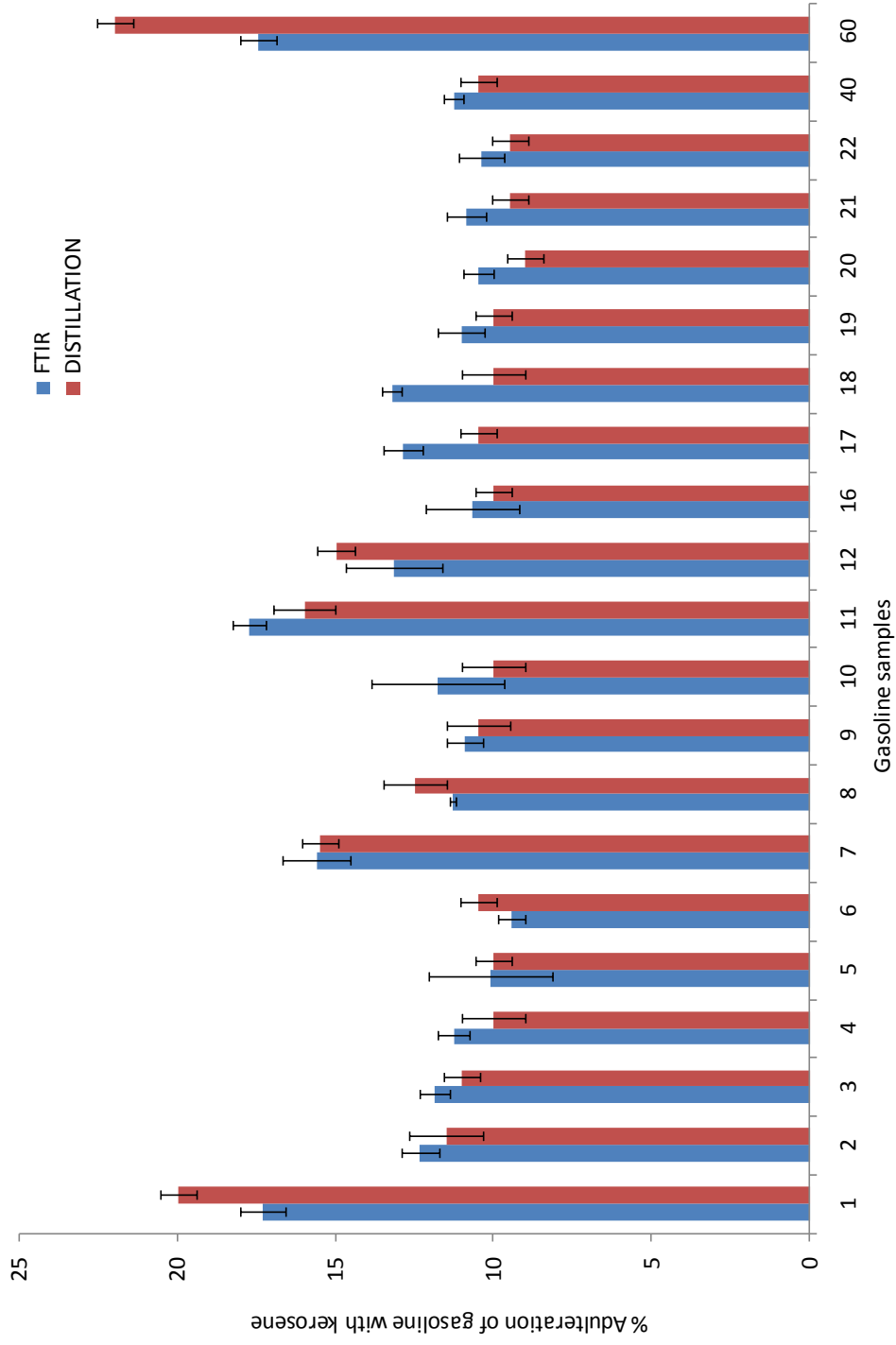


Figure 11: Bar chart representing results obtained by FTIR and distillation methods of samples collected from individually owned fuel stations

The mean percent adulteration for personal owned fuel stations samples was found to be 12.44 ± 2.50 % (11.63 ± 2.91 %) for FTIR and distillation respectively. The means obtained by both FTIR and distillation are not different. The highest adulteration of super among the personally owned fuel was found in sample 60 (along Langata road) which had a mean value of 17.464 ± 0.574 % (22.00 ± 0.58 %) while the lowest was found in sample 6 (at Eastleigh) with a mean value of 9.431 ± 0.446 % (10.50 ± 0.58 %) for FTIR and Distillation as shown in table 2 and figure 11. The paired t test for 21 samples with degree of freedom of 20 at 95% confidence level gave a p-value of 0.3603. This value was found to be greater than the α -value 0.05, hence this suggests that the values of FTIR are not statistically different from those obtained by distillation (ASTM D86). From the wilcoxon sign ranked test with continuity correlation for the 21 samples gave a p-value of 0.6953. This value was found to be greater than the α -value 0.05, hence this suggests that the experimental values obtained by FTIR are not statistically different from those obtained by distillation (ASTM D86). The correlation between FTIR and distillation for the personally owned fuel stations gave an R value of 0.888 as shown on figure 12. This shows that there was a very high correlation between the two methods.

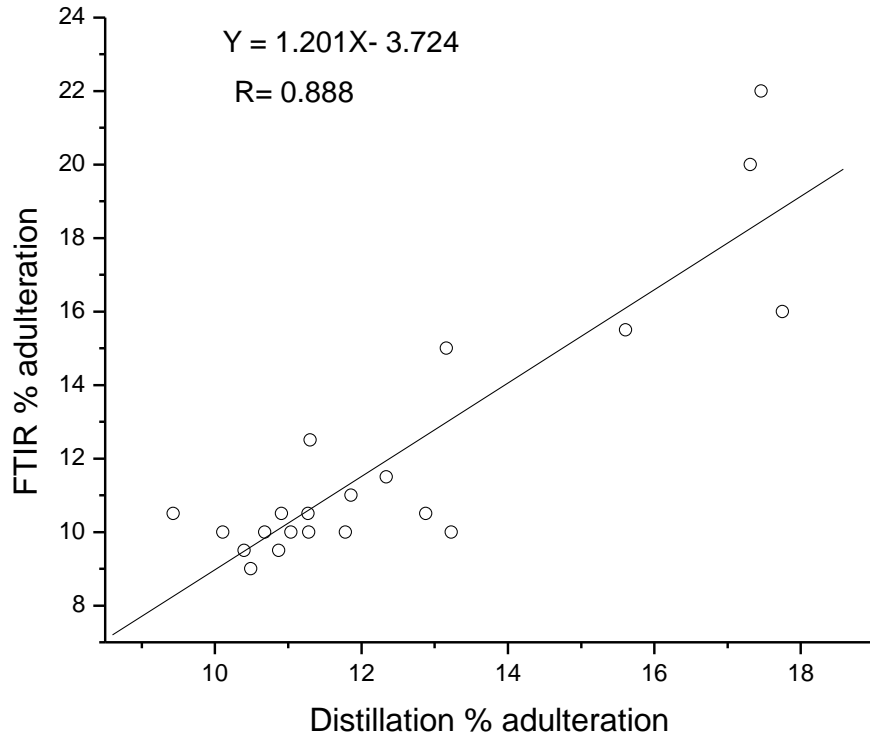


Figure 12: Scatter diagram of FTIR and distillation (D86) percentage adulteration of samples collected from personal owned fuel stations

3.2.4 Mean values for FTIR and distillation (ASTM D 86)

The values in table 3 and figure 13 represents a comparison of mean percentage contamination of gasoline obtained by both FTIR and distillation methods for all the fuel stations.

Table 3: Mean percentage adulteration values for FTIR and distillation (ASTM D86) results obtained from Multinationals, National and locally owned and individually owned fuel stations in Nairobi

Fuel Stations	FTIR (% adulteration)	Distillation (% adulteration)
Multinationals (N = 32)	10.87 ± 1.54	11.23 ± 1.53
National and Local (N = 10)	11.56 ± 1.37	11.37 ± 1.59
Individually owned(N = 21)	12.44 ± 2.50	11.63 ± 2.91

KEY:

N- Number of Samples

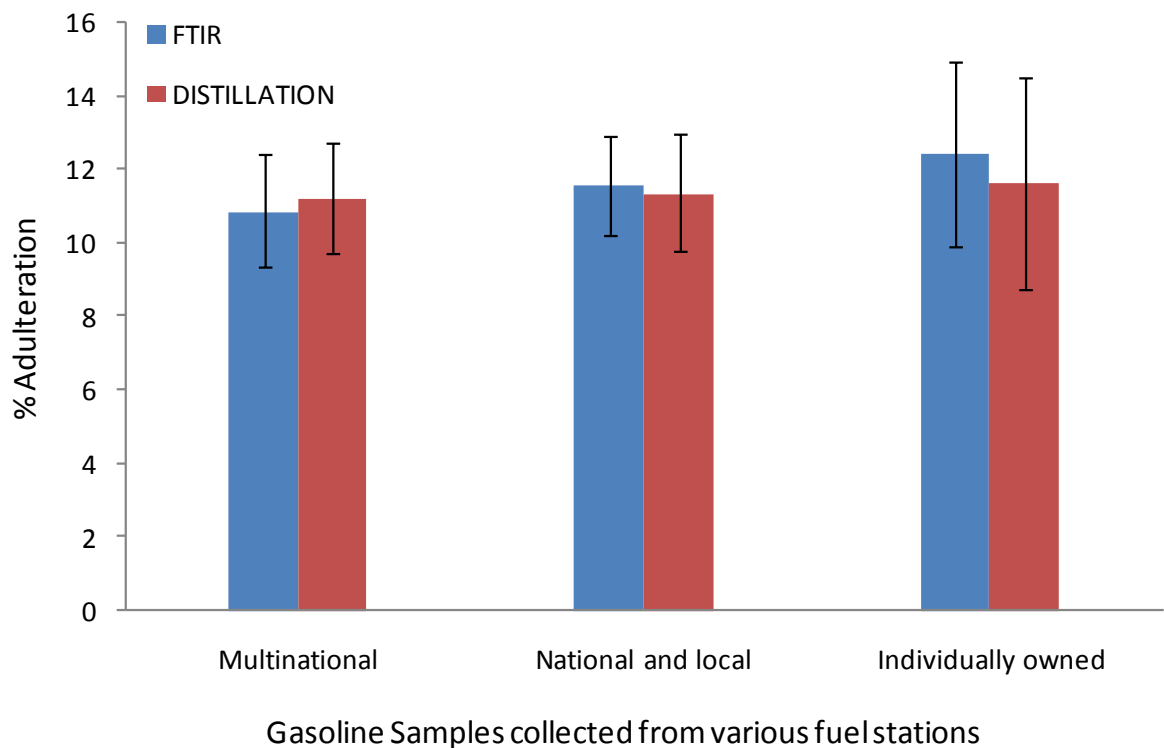


Figure 13: Mean % adulteration of values samples collected from multinationals, national and local owned, and individually owned fuel stations in Nairobi

Table 3 and figure 13 shows that the individually owned fuel station had the highest mean adulteration of 12.44 ± 2.50 % (11.63 ± 2.91 %) using both FTIR and distillation methods, then followed by national and local fuel stations with a mean value of 11.56 ± 1.37 % (11.37 ± 1.59 %) and finally the multinational fuel stations had the least adulteration with a mean value of 10.87 ± 1.54 % (11.23 ± 1.53 %) for FTIR and distillation respectively.

3.2.5 Mean percentage contamination values for FTIR and distillation (ASTM D 86) on various roads in Nairobi.

The values in table 3 and figure 13 represent a comparison of mean values obtained by both FTIR and distillation methods along various roads in Nairobi

Table 4: Mean values for FTIR and distillation (D86) results obtained from various roads in Nairobi

Roads		Mean % adulteration for FTIR & Distillation
Pangani road	(N = 5)	13.837 ± 3.017 (14.17 ± 5.06)
Eastleigh road	(N = 5)	10.273 ± 0.936 (10.17 ± 0.29)
Dagoretti road	(N = 4)	12.390 ± 1.371 (13.17 ± 1.04)
Westlands road	(N = 4)	11.110 ± 0.955 (12.33 ± 0.58)
Nairobi west road	(N = 4)	10.130 ± 1.313 (11.33 ± 0.77)
Langata road	(N = 4)	12.870 ± 3.088 (13.75 ± 5.55)
Guru Nanak road	(N = 4)	13.275 ± 1.832 (11.88 ± 1.89)
Jogoo road	(N = 4)	12.582 ± 1.800 (11.60 ± 2.43)
Outering road	(N = 5)	10.988 ± 0.853 (10.30 ± 0.45)
Pipeline road	(N = 4)	10.020 ± 1.426 (10.24 ± 1.23)
Parklands road	(N = 4)	12.012 ± 0.571 (12.00 ± 0.94)
Ngong Road	(N = 5)	10.790 ± 2.437 (11.70 ± 2.28)
Yaya road	(N = 4)	10.470 ± 1.977 (11.80 ± 1.44)
GSU road	(N = 5)	13.296 ± 2.647 (12.40 ± 2.86)
Barracks road	(N = 4)	11.228 ± 1.041 (9.58 ± 0.38)
Juja road	(N = 5)	9.900 ± 1.410 (10.83 ± 2.04)

KEY:

N- Number of Samples

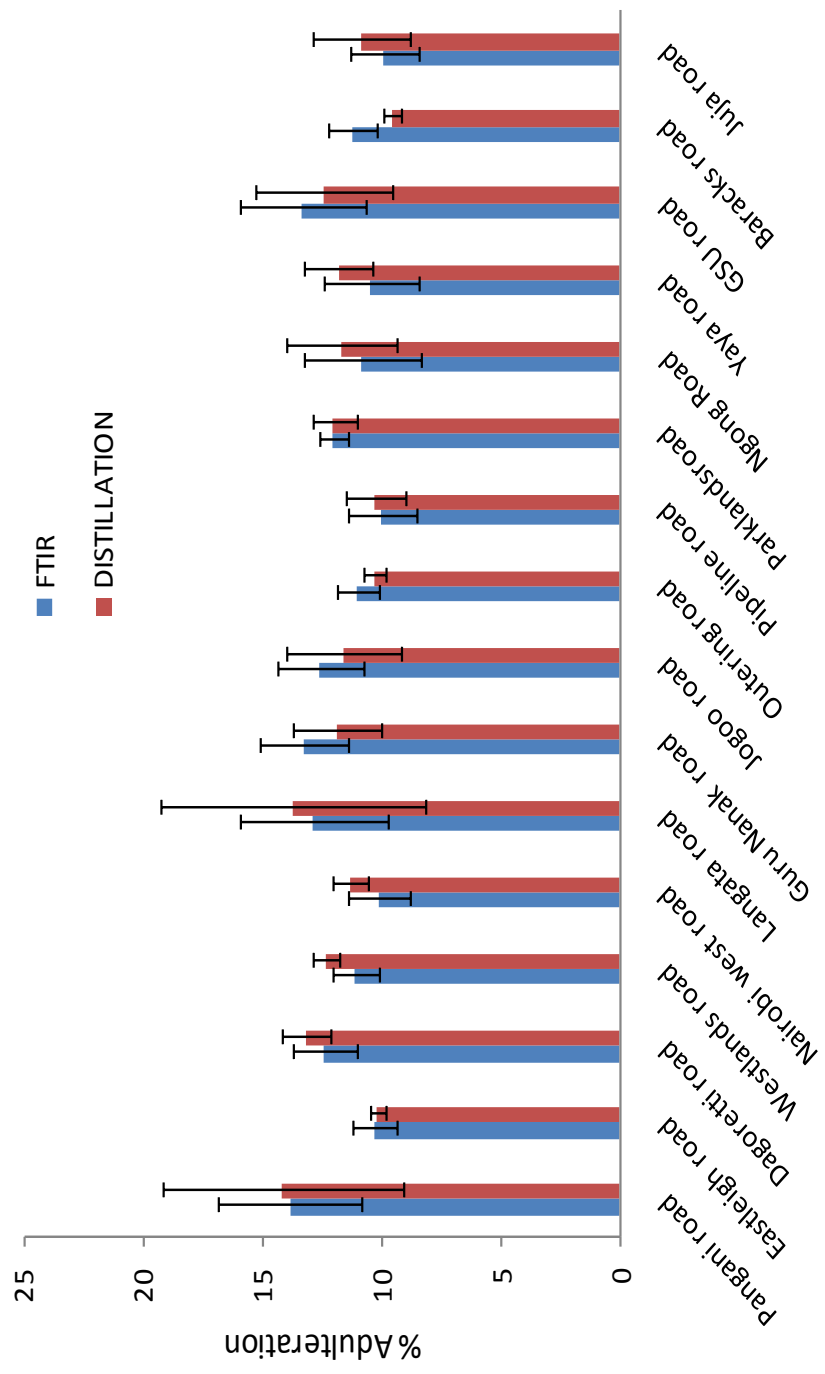


Figure 14: Mean % adulteration of samples collected from various fuel stations along major highways

3.2.6 Pangani, Eastleigh, Dagoretti and Westlands Roads

The highest adulterated sample recorded along Pangani road was sample 1 with a mean value of 17.312 ± 0.729 % (20.00 ± 0.58 %) whereas sample 3 recorded lowest adulteration with a mean value of 11.861 ± 0.469 % (11.00 ± 0.58 %) by FTIR and distillation. Along Eastleigh road, the highest adulterated sample was 4 with a mean value of 11.277 ± 0.515 % (10.00 ± 1.00 %) whereas the lowest adulterated was sample 6 with a mean value of 9.431 ± 0.446 % (10.50 ± 0.58 %) by FTIR and distillation. Dagoretti road had sample 49 with the highest adulteration which gave a mean value of 13.728 ± 0.757 % (14.00 ± 0.58 %) whereas sample 48 had the lowest adulteration with a mean value of 10.985 ± 0.696 % (12.00 ± 0.58 %) by FTIR and distillation. Sample 63 along Westlands road had the highest adulteration with a mean value of 11.716 ± 0.824 % (12.00 ± 0.58 %) whereas sample 65 was the least adulterated with a mean value of 10.014 ± 1.006 % (12.00 ± 0.58 %) by FTIR and distillation respectively.

3.2.7 Nairobi west, Langata, Guru Nanak and Jogoo Roads

Nairobi west road had sample 57 with the highest adulteration with a mean value of 11.635 ± 0.535 % (12.00 ± 0.58 %) percent by FTIR and distillation respectively. The lowest adulterated sample was sample 58 with a mean percent value of 9.259 ± 0.249 % (11.50 ± 0.58 %) by FTIR and distillation. Langata road had sample 60 with the highest adulteration with a mean percent value of 17.464 ± 0.574 % (22.00 ± 0.58 %). The lowest adulterated sample was sample 61 which gave a mean value of 10.831 ± 1.112 % (10.50 ± 0.50 %) by FTIR and distillation. Sample 32 was the highest adulterated sample along Guru Nanak road which gave a mean percent value of 15.680 ± 0.534 % (14.50 ± 0.58 %) whereas

sample 35 with a percent mean value of 11.380 ± 0.549 % (10.50 ± 0.58 %) was the least adulterated by FTIR and distillation. Sample 7 was the highest adulterated sample along Jogoo road which gave a mean value of 15.608 ± 1.063 % (15.50 ± 0.58 %) whereas sample 13 with a mean value of 11.317 ± 0.700 % (10.00 ± 1.00 %) was the least adulterated by FTIR and distillation.

3.2.8 Outerling, Pipeline, Parklands and Ngong Roads

Sample 31 along Outerling road was the highest adulterated with a mean percent adulteration value of 12.280 ± 0.098 % (11.00 ± 0.58 %). The lowest adulterated was sample 30 which had a mean value of 9.990 ± 1.087 % (10.00 ± 0.58 %) by FTIR and distillation. Pipeline road had sample 41 with the highest adulteration which gave a mean value of 12.010 ± 0.514 % (12.20 ± 0.58 %). The lowest adulterated sample was 42 which gave a mean value of 8.050 ± 0.186 % (9.00 ± 0.58 %) by FTIR and distillation. Parklands road had sample 70 with the highest adulteration which had a mean value of 12.596 ± 0.432 % (12.00 ± 0.58 %). The lowest adulterated sample was sample 68 with a mean percent adulteration value of 11.073 ± 1.162 % (12.00 ± 0.58 %) by FTIR and distillation. Sample 47 was the highest adulterated sample along Ngong road with a mean value of 14.602 ± 0.321 % (15.50 ± 0.58 %) whereas sample 46 with a mean value of 8.662 ± 0.484 % (10.00 ± 0.58 %) was the least adulterated by FTIR and distillation.

3.2.9 Yaya, GSU, Barracks, Juja Roads

Along Yaya road, the highest contaminated was sample 51 with a mean value of 13.567 ± 0.904 % (14.00 ± 0.58 %) whereas the lowest contaminated sample was sample 52 with a mean value of 8.520 ± 0.461 % (10.50 ± 0.29 %) by FTIR and distillation. Sample 11 was

the highest adulterated sample along GSU road with a mean value of 17.749 ± 0.513 % (16.00 ± 1.00 %) whereas sample 9 with a mean value of 10.908 ± 0.586 % (10.50 ± 1.00 %) was the least adulterated by FTIR and distillation. Sample 21 was the highest adulterated sample along Barracks road with a mean value of 13.447 ± 0.593 % (9.50 ± 0.58 %) whereas sample 19 with a mean value of 11.037 ± 0.749 % (10.00 ± 0.58 %) was the least adulterated by FTIR and distillation. Juja road had sample 26 with the highest adulteration which had a mean value of 12.187 ± 0.042 % (15.00 ± 0.58 %). The lowest adulterated sample was sample 25 which gave a mean value of 9.505 ± 0.377 % (10.00 ± 0.58 %) by FTIR and distillation respectively.

3.2.10 General observations along the major highways

The highest adulterated sample among all the major roads was sample 60 with a mean value of 17.464 ± 0.574 % (22.00 ± 0.58 %) for FTIR and distillation respectively and was sampled from fuel stations along langata road. The lowest adulterated sample was sample 28 with a mean value of 7.829 ± 1.278 % (10.00 ± 0.58 %) for FTIR and distillation and was sampled along Juja road.

Pangani road had the highest percentage adulteration with a mean value of 13.837 ± 3.017 % (14.17 ± 5.06 %) for FTIR and distillation as shown in table 5 and figure 14. Sample 1 had the highest adulteration with a mean value of 13.837 ± 3.017 % (14.17 ± 5.06 %) for FTIR and distillation. Sample 2 and 3 sampled along the same road had adulteration values of 12.336 ± 0.606 % (11.50 ± 1.16 %), 11.861 ± 0.469 % (11.00 ± 0.58 %) for FTIR and distillation. Comparing sample 1 with the other samples sampled from the same road, it

suggests that a mixture of solvents with high boiling points could probably have been used to adulterate the sample.

Juja road petrol stations had the lowest percentage adulteration with a mean value of 9.900 ± 1.410 % (10.83 ± 2.04 %) for FTIR and distillation as shown in table 5 and figure 14. The highest adulteration among all the 70 samples collected along the major highways was recorded for sample 26 with a mean value of 12.187 ± 0.042 % (15.00 ± 0.58) whereas the lowest adulteration had a mean value of 7.829 ± 1.278 % (10.00 ± 0.58 %) as determined by FTIR and distillation methods.

From Figure 14, the mean percentage adulteration was in the range of 10-12 % adulteration with an exception of Pangani road, Dagoretti road, Langata Road, Guru Nanak road, Jogoo road and GSU road which gave mean values in the range of 12.5-13.84 % adulteration. The mean values in this area could have been affected by some individual samples which had a very high percentage of adulteration. For example the highest adulterated sample 60 with a mean value of 17.464 ± 0.574 % (22.00 ± 0.58 %) was sampled from fuel stations along Langata road. Samples 59, 61, 62 were sampled along the same road and gave adulteration values of 11.339 ± 0.20 % (10.50 ± 0.29 %), 10.831 ± 1.112 % (10.50 ± 0.50 %), 11.849 ± 0.641 % (12.00 ± 0.58 %) for FTIR and distillation an indication that sample 60 could have affected the mean. Samples 1, 7 and 32 sampled along Pangani road, Jogoo road and Guru Nanak road were other examples of samples which had high percentage adulteration and thus could have affected the mean percent adulteration along various roads.

3.3 Density of gasoline Samples

As shown in table 2, the density of the adulterated gasoline varied between 0.735 and 0.769gml⁻¹. When the density is higher it means more emissions are obtained and this would not be sufficient to characterize exact adulteration. The test result of density was compared with corresponding value prescribed by Kenya Bureau of Standards (KEBS). The observations from the experiment suggested that density was within the prescribed range 0.70-0.76gml⁻¹ immaterial of the extent of the gasoline adulteration with kerosene (table 2). The presence of kerosene did not appear to alter density of gasoline appreciably and hence the application of the density test for adulteration with kerosene is not appropriate.

3.4 Boiling Range Characteristics of Gasoline by Distillation

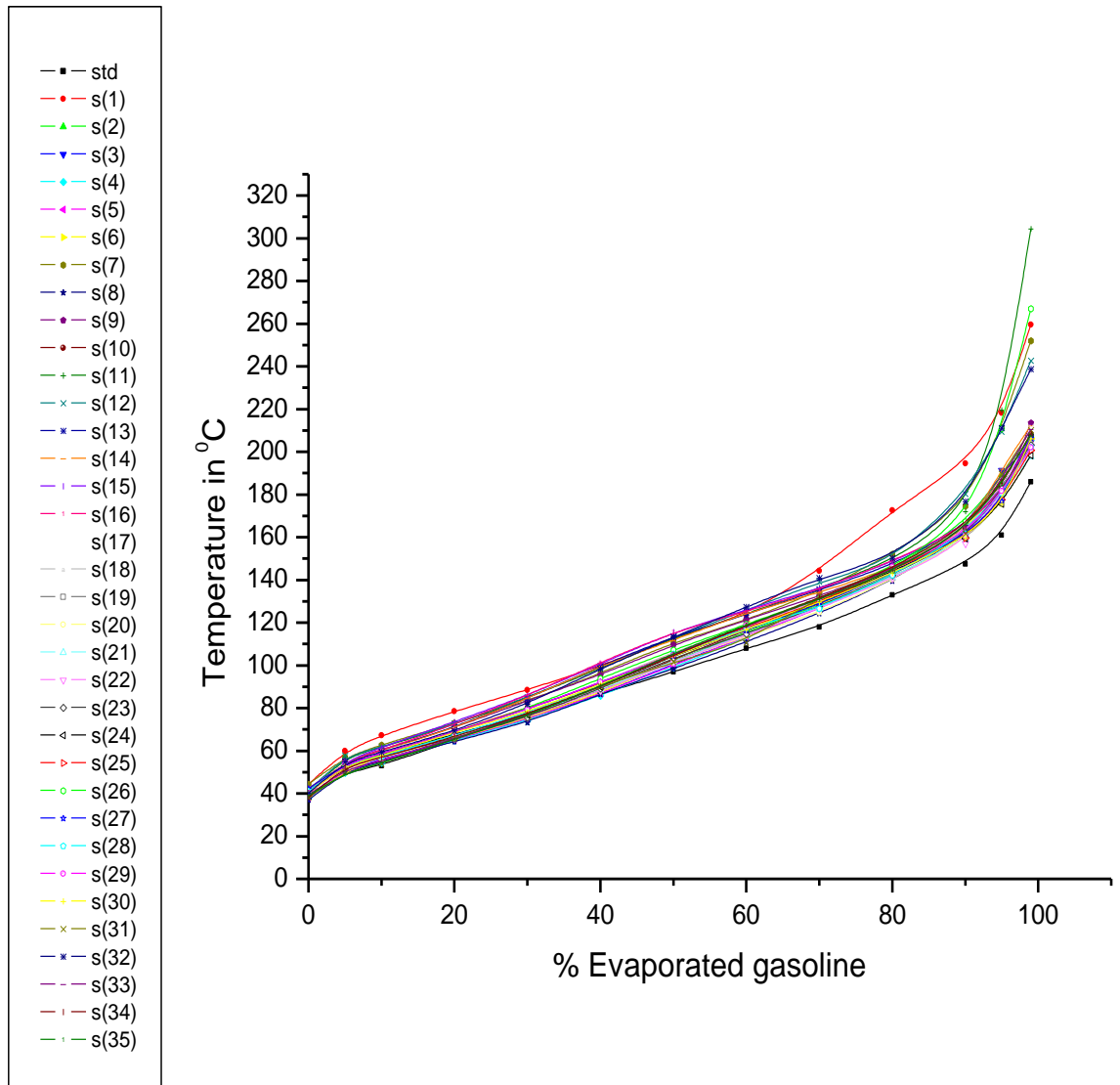


Figure 15a: Distillation profile of samples 1-35 compared with the standard (ASTM D 86)

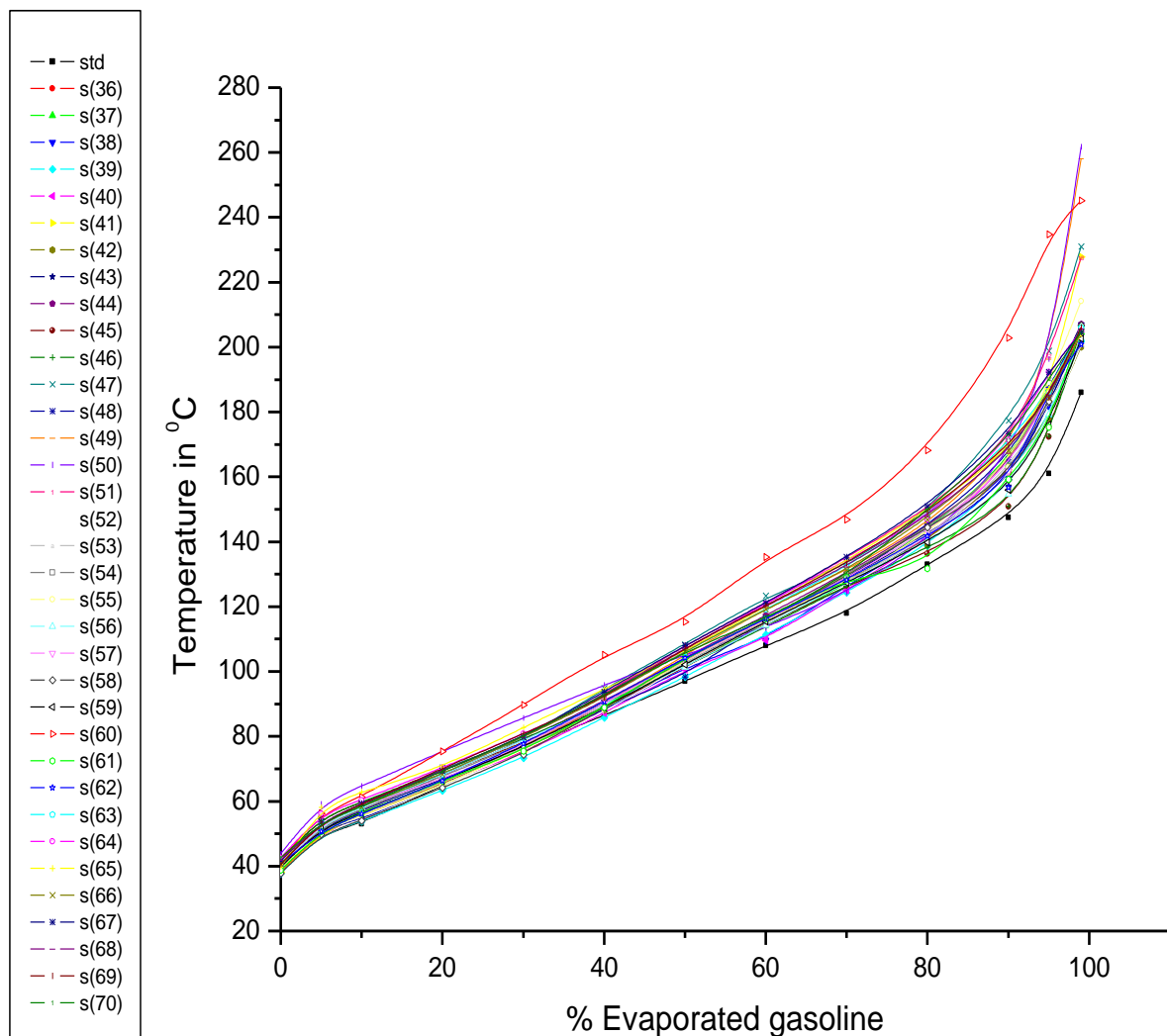


Figure 15b: Distillation profile of samples 36-70 compared with the standard (ASTM D 86)

Figure 15a, 15b and table 6 in appendix I show the results of distillation temperatures of the pure gasoline standard and those of the gasoline samples. From figure 15a and 15b the distillation curves show a continuous and smooth increase in temperature as the distillation

process progresses and a simple visual inspection would not be sufficient to give exact percentage of gasoline adulteration. Generally it can be observed that the standard boils at a lower temperature as compared to the samples an indication that there might be addition of adulterants which increases the distillation temperatures of the gasoline samples. It was also noted that a few of the samples had their boiling points lower at lower temperatures than the standard an indication that lower boiling point solvents could have been used as adulterants. From figure 15a and table 6 in appendix I, it can be observed that sample 1 had the highest initial boiling points as compared to all the samples and the standard at each volume, (up to 85 mls), for all measured temperatures indicating that it had a heavy adulterant which raised the boiling point at each volume collected. This observation can be well corroborated from the results obtained by FTIR and distillation which indicated that the adulterant had a percentage contamination of $17.312 \pm 0.729 \%$ ($20.00 \pm 0.58 \%$) for FTIR and distillation respectively. The other samples that had heavy adulterants added were samples 7, 11, 12, 26, and 32 whose percentage of adulterant added was $15.608 \pm 1.063 \%$ ($15.50 \pm 0.58 \%$), $17.749 \pm 0.513 \%$ ($16.00 \pm 1.00 \%$), $13.155 \pm 1.522 \%$ ($15.00 \pm 0.58 \%$), $12.187 \pm 0.042 \%$ ($15.00 \pm 0.58 \%$), $15.680 \pm 0.534 \%$ ($14.50 \pm 0.58 \%$) for FTIR and distillation respectively. Also from figure 15a and table 6 in appendix I, it can be observed that sample 4 had the lowest initial boiling point as compared to all the samples including the standard at each volume, (up to 40 mls), measured temperatures indicating that it had a light adulterant which lowered the boiling point at each volume collected.

From figure 15b and table 6 in appendix I, it can be observed that sample 60 had the highest initial boiling points as compared to all the samples and the standard at each

volume, (up to 99 mls), for all measured temperatures indicating that it had a heavy adulterant which raised the boiling point at each volume collected. This observation can be well corroborated from the results obtained by FTIR and distillation which indicated that the adulterant had a percentage contamination of $17.464 \pm 0.574 \%$ ($22.00 \pm 0.58 \%$) for FTIR and distillation respectively. The other samples that had heavy adulterants added were samples 41, 47, 49, 50 and 51 whose volume of adulterant added was $12.010 \pm 0.514 \%$ ($12.20 \pm 0.58 \%$), $14.602 \pm 0.321 \%$ ($15.50 \pm 0.58 \%$), $13.728 \pm 0.757 \%$ ($14.00 \pm 0.58 \%$), $12.451 \pm 1.110 \%$ ($13.50 \pm 0.58 \%$) and $13.567 \pm 0.904 \%$ ($14.00 \pm 0.58 \%$) for FTIR and distillation respectively. Also from figure 15b and table 6 in appendix I, it can be observed that sample 39 had the lowest boiling point as compared to all the samples including the standard at each volume, (up to 40 mls), measured temperatures indicating that it had a light adulterant which lowered the boiling point at each volume collected.

The behavior of the distillation curves of 10, 20, 30, 40 and 50% volume for all the adulterated gasoline samples were not similar to the standard as they were either boiling above or below that of the standard. This behavior could be attributed to the properties and composition variations of the adulterants in gasoline samples whereby probably, high intermolecular interactions were formed at lower percentages of adulteration while such interactions kept increasing at higher percentages as can be observed from figures 15a and 15b. This trend was different from that observed by Al-Ghouti *et al.* (2008) where distillation curves of 10, 20, 30, 40 and 50% volume of the adulterant were similar to that of the standard whereby probably, low intermolecular interactions were formed at lower percentages of adulteration.

The distillation curves of all the adulterated gasoline samples did affect, in a significant way, the distillation temperature above 70 percent of the vaporized volume as can be seen on figures 15a and 15b. This trend was different from that observed by Al-Ghouti *et al.* (2008) where distillation curves of the adulterated gasoline with adulterant did not affect, in a significant way, the distillation temperatures above 70 percent of the vaporized volume. The Final end points of all the samples were beyond the maximum limit of $186^{\circ}\text{C} \pm 3^{\circ}\text{C}$. This could have been attributed to the addition of medium to heavy distillates to the pure gasoline samples. Samples 1, 7, 12, 26, 49, 50, 60 with final end points of 259.5°C , 252°C , 242°C , 267°C , 258.17°C , 261.8°C , and 245.17°C had final boiling points very close to that of kerosene whose maximum boiling point is 260°C , an indication that kerosene or medium hydrocarbons could have been used to adulterate the samples.

3.5 Cluster analysis

3.5.1 Use of physical-chemical parameters

Dendogram in figure 16 resulted from hierarchical cluster analysis with physico-chemical data which includes different volume of each gasoline sample analysed and collected at various temperatures as shown in appendix I for all studied gasoline samples.

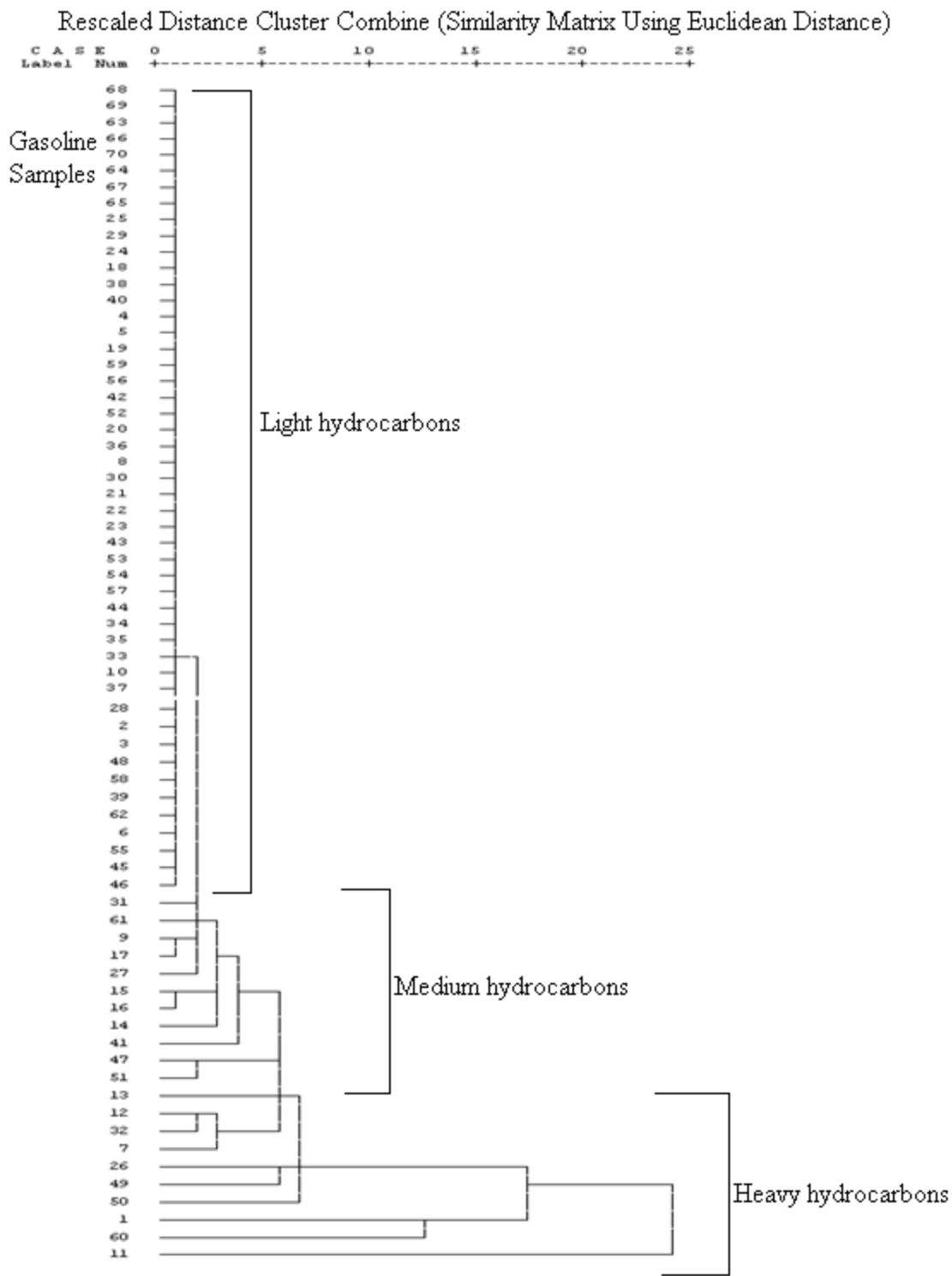


Figure 16: Dendrogram resulting from hierarchical cluster analysis with physico-chemical data from all studied gasoline samples.

Cluster analysis result was obtained from 70 gasoline samples and the standard. The physical and chemical parameters used for the gasoline sample analysis were temperature of distillation at 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95% and 98.5-99% as the final end point and density. On the x-axis of the dendrogram are the gasoline samples indicated by their numbers, while on the y-axis is the similarity matrix using Euclidean distance. From figure 16 the dendrogram was divided into three distinct groups.

The first group consisted of 49 gasoline samples analyzed by the distillation method (ASTM D86). From the cluster analysis the gasoline samples were probably adulterated with solvents, which make gasoline (n-alkanes, branched alkanes, cycloalkanes, alkenes, mono-aromatics, poly-aromatics) and a little kerosene. The final end point temperature ranged between 197.8⁰C to 214.17⁰C as shown in table 2 and appendix I, which was above the gasoline standard end point of 186⁰C. 48 samples meet the KEBS standards of 210⁰C. Only sample 55 was above the KEBS standard. It had a final end point of 214.17⁰C. The density of this group lay between 0.74 to 0.75kg/l and was within the allowable limits set by the KEBS of 0.75kg/l.

The second group consisted of eleven samples analyzed and were probably adulterated with solvents, which make gasoline and a little kerosene. The final end point ranged between 205.8⁰C to 227.7⁰C as shown in table 2 and appendix I. All the eleven samples were above the gasoline standard end point of 186⁰C. Six samples 9, 17,14,41,47 and 51 did not meet the KBS standards of 210⁰C. The density of this group lay between 0.75 to 0.77kg/l an indication that a heavy solvent such as kerosene could have been used to adulterate the fuel. The presence of the heavier solvent altered the density of the gasoline.

The third group consisted of ten samples analyzed and were probably adulterated with a heavy solvent such as diesel and probably kerosene. The final end point ranged between 206.8⁰C to 304.5⁰C as shown in table 2, all the samples did not meet the gasoline standard end point of 186⁰C. The only sample that meet KBS standard of 210⁰C was sample 13. Sample 1, 7, 11, 13, 26, 32, 49, 50 and 60 had extremely high final end points which were higher than KBS standard an indication of a relatively high percentage adulteration which was well reflected in the cluster analysis. The density of this group lay between 0.75 to 0.77kg/l an indication that a heavier solvent such as kerosene and diesel could have been used to adulterate the gasoline samples and hence led to the degradation in the quality of the fuel.

The results obtained from group one, shows that the adulteration varies slightly from one another suggesting that the adulteration may be done at one point and then distributed to various dealers. The difference in concentrations could be attributed to unhomogeneity in tanks during loading to various vehicles. These could mean that adulteration is probably done in storage facilities.

As can be seen from the results of group 2 and group 3, the percentage adulterations vary greatly and unevenly suggesting that individual dealers at various outlets could have adulterated the gasoline.

3.5.2 Use of percentage adulteration measurements obtained by FTIR and distillation (ASTM D 86).

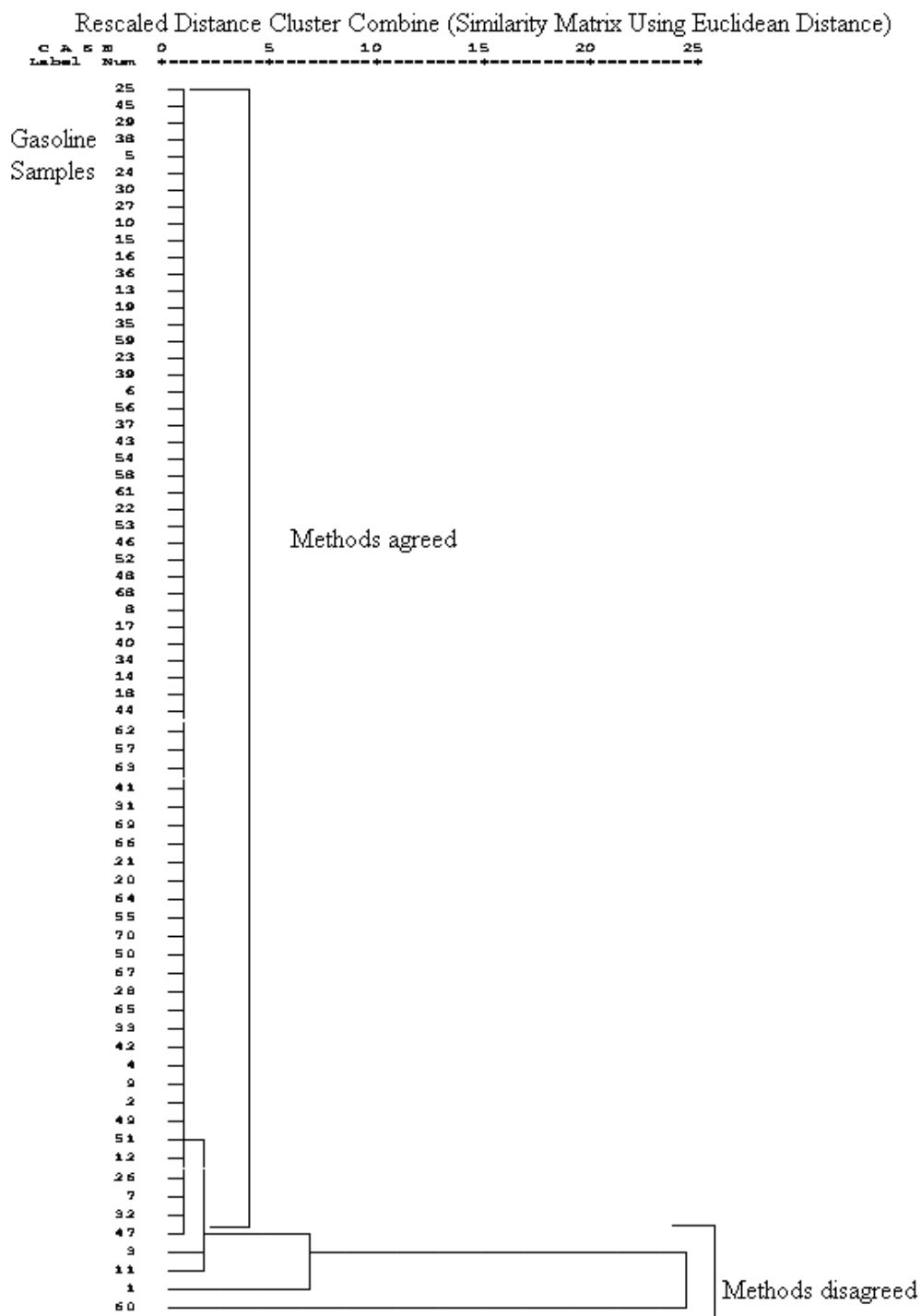


Figure 17: Dendrogram resulting from hierarchical cluster analysis with measurements obtained from FTIR and Distillation (ASTM D 86).

Cluster analysis of the 70 gasoline samples was carried out using two methods of analysis FTIR and distillation (ASTM D 86) as the clustering variables. On the x-axis of the dendrogram is the gasoline samples indicated by their numbers, while on the y-axis is the similarity matrix using Euclidean distance. From figure 17, there were two groups identified, group one showed that most measurements obtained from FTIR agreed well with those measured with distillation method (ASTM D 86). In-group 2, only four measurements out of 70 gasoline sample analysed by the two methods did not agree. This could have been attributed to the different patterns of adulteration employed an indication that may be kerosene was not used for the adulteration of the samples. It can also be noted that sample 1, 60 and 11 were grouped together as samples with a relatively high percentage adulteration in cluster analysis in figure 16 an indication that similar patterns of adulteration could have been employed and a possibility of heavy solvents like diesel could have been used to adulterate the samples.

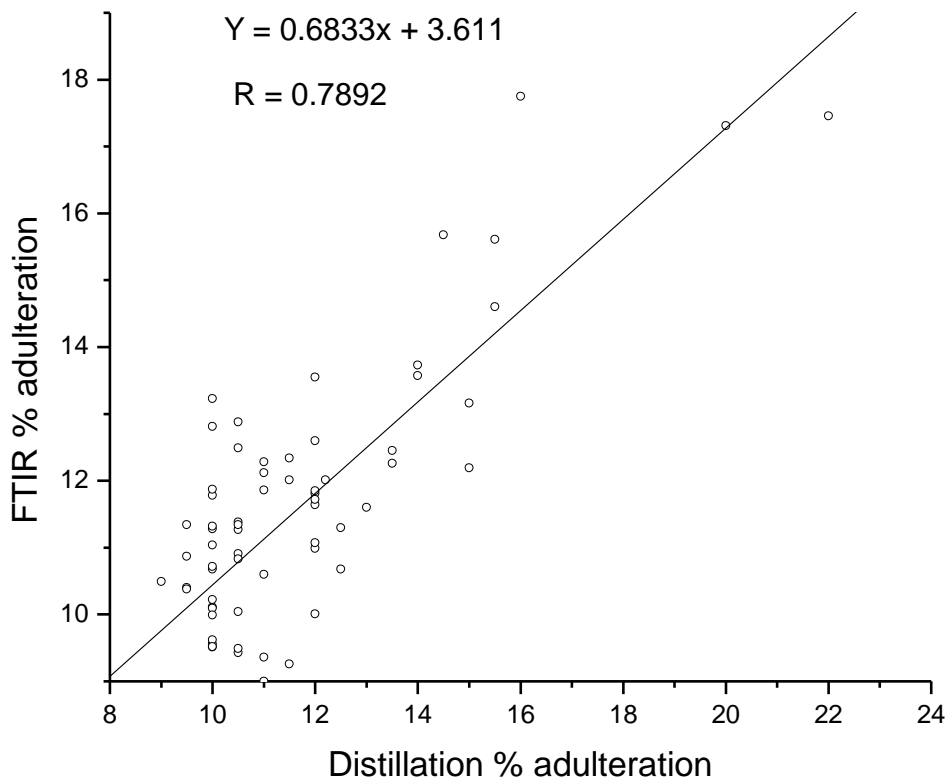


Figure 18: Scatter diagram of FTIR and distillation (ASTM D 86) percentage adulteration of all the 70 samples collected from various fuel stations

Figure 19 shows direct comparison of data obtained by two methods used to measure the adulteration of gasoline. The R value was 0.789 an indication that the two methods have a strong correlation. This type of plot is frequently used as a comparison of two method but (Bland and Altman, 1986), reported that by plotting the difference between the methods against the average was a powerful way of displaying the results of a method comparison study. Figure 19 shows the data from figure 18 replotted in this way.

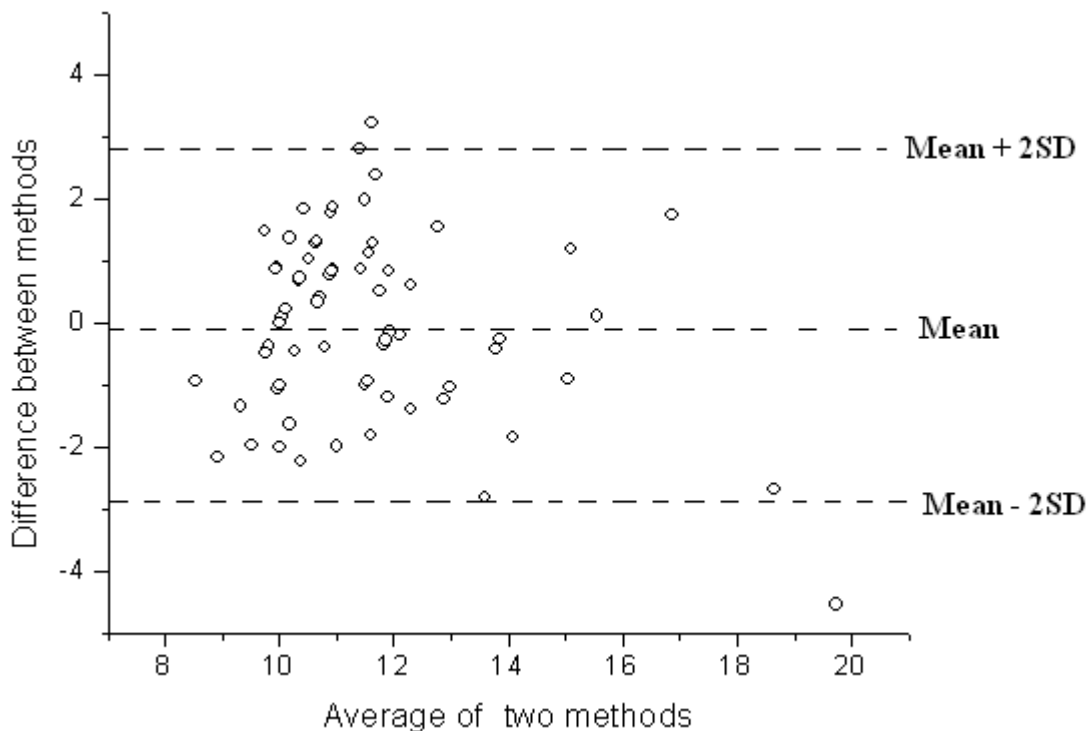


Figure 19: A comparison of adulteration of gasoline measured by FTIR and distillation (D86) using 2σ above or below the mean ($x \pm 2\sigma$)

Figure 19 shows a comparison of adulteration of gasoline measured by distillation and FTIR method. The mean difference was found to be -0.050 percentage point with 95% confidence. Despite this, the limits of agreement (-2.90 % and 2.85 %) are small enough to be confident that the new method can be used instead of distillation method (ASTM D86).

3.6 Box plot of percentage adulteration of gasoline samples with kerosene for FTIR and distillation methods

A box plot summarizes statistical measurements such as median, upper and lower quartiles, minimum and maximum data values.

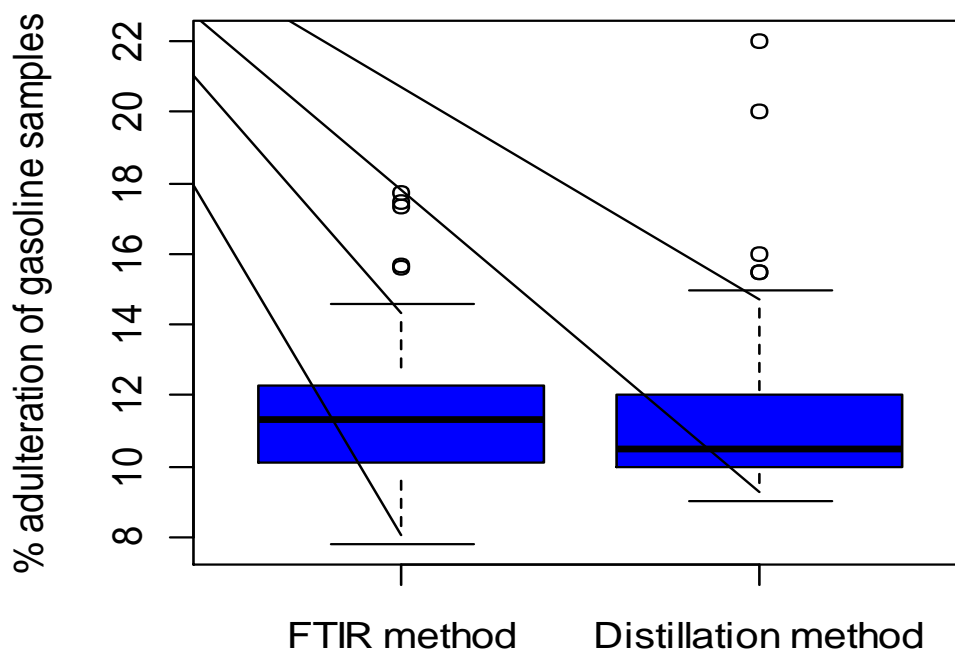


Figure 20: Box plot of percentage adulteration of gasoline samples with kerosene for FTIR and distillation methods

From figure 20, the data symmetry and skewness is graphically displayed as analysed by both FTIR and distillation methods. The median values for all 70 samples was found to be 11.31 (10.50) for FTIR and distillation as shown on figure 20. It can be seen that the median line within the box for the FTIR method is almost equidistant from the hinges an indication that the data is not skewed whereas the median line within the box for the distillation method is not equidistant from the hinges an indication that the data is skewed. The points outside the ends of the whiskers of the box plot for both methods are suspect

outliers. The 25th percentile quartile range gave 10.14 % (10.00 %), whereas the 75th percentile quartile range gave 12.27 % (12.00 %) for FTIR and distillation an indication that the FTIR method measured higher values as opposed to the distillation method.

3.7 Histograms showing the % adulteration of gasoline samples by FTIR and Distillation Method

A histogram is a summary graph showing a count of the data points falling in various ranges. Histograms give data summaries that convey information on symmetry of the distribution and the general shape of the frequency distribution.

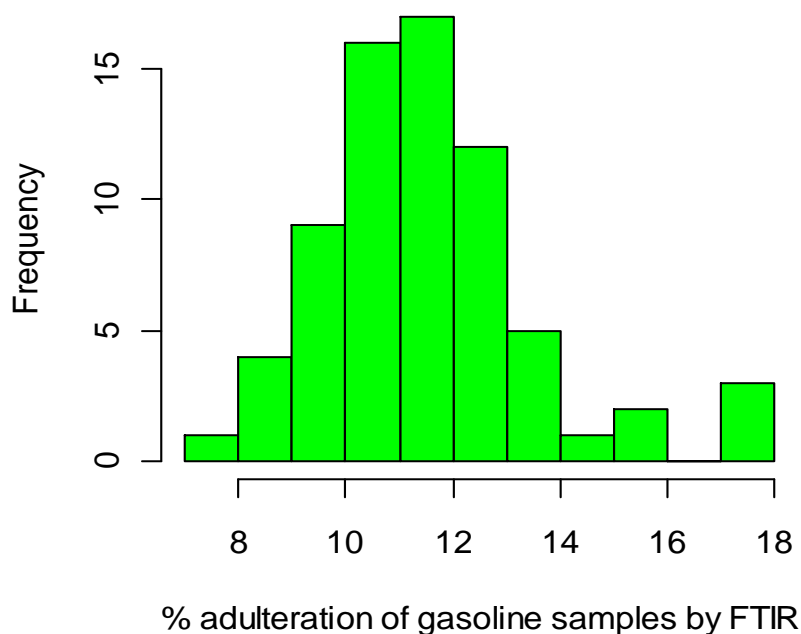


Figure 21 (a): Histograms showing the % adulteration of gasoline samples by FTIR

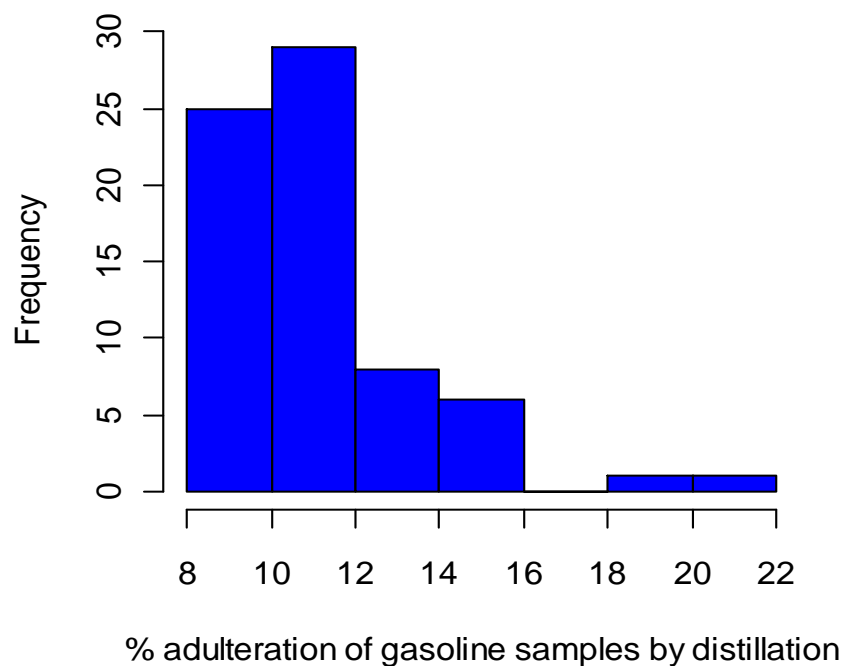


Figure 21 (b): Histograms showing the % adulteration of gasoline samples by Distillation

Figure 21(a) and 21(b) shows the occurrence of the sample contamination determined by FTIR and distillation methods. FTIR method shows almost a normal curve distribution as opposed to the distillation method. High precision could have led to the normal curve distribution of the FTIR data. Lack of a normal curve distribution of data for the distillation method could probably have been attributed to the process of measurement and approximation when using the distillation method hence leading to lack of accuracy. From figure 17, 19, 20 and 21 it has clearly been seen that four measurements out of the 70 samples were outliers.

3.8 Determination of Lead and sulphur for selected samples

Ten gasoline samples were analyzed for lead and sulphur. Three samples namely sample 59, 60 and 70 were obtained from the 70 gasoline samples previously sampled whereas the remaining 7 gasoline samples were sampled afresh.

Table 5: Concentration of lead and sulphur (mg/l) of 10 gasoline samples

Samples	Concentration of Pb (ppm)	Concentration of Sulphur (ppm)
59	6.523 ± 0.025	214.000 ± 4.000
60	5.997 ± 0.035	317.000 ± 3.000
70	6.033 ± 0.015	469.000 ± 4.000
71	3.857 ± 0.032	191.000 ± 4.000
72	3.380 ± 0.010	140.000 ± 5.000
73	4.047 ± 0.035	176.000 ± 3.000
74	3.870 ± 0.020	232.000 ± 5.000
75	3.780 ± 0.010	145.000 ± 4.000
76	3.620 ± 0.020	173.000 ± 6.000
77	3.713 ± 0.021	141.000 ± 4.000

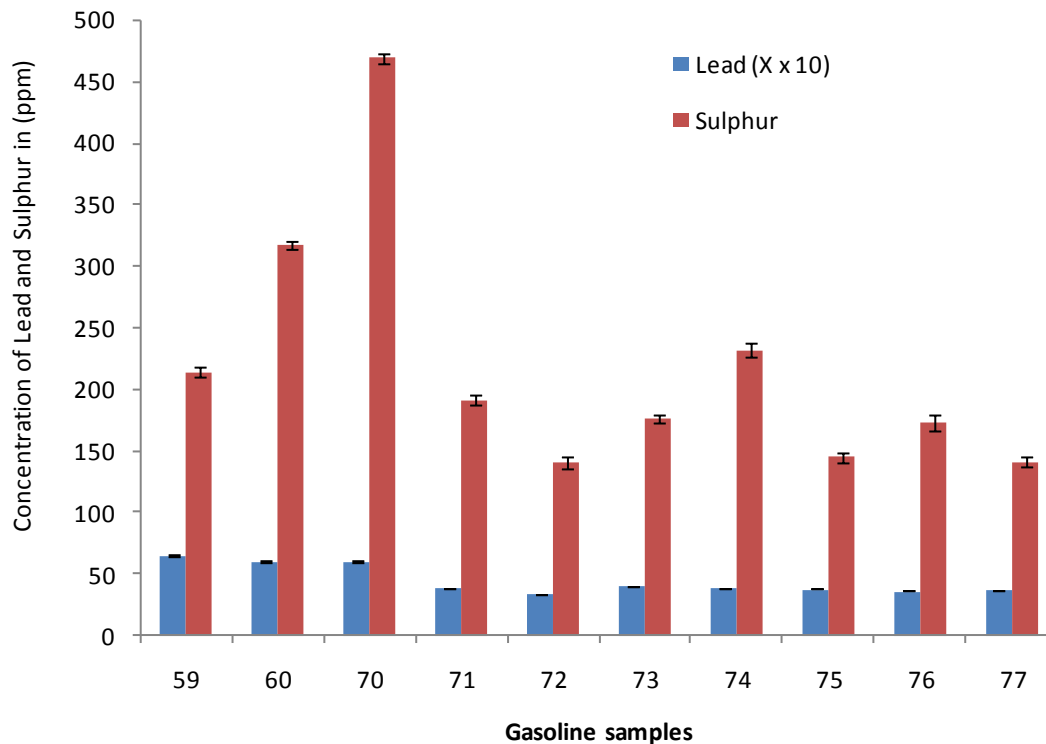


Figure 23: Lead and sulphur concentration (ppm) of gasoline samples

3.8.1 Lead

The mean concentration of lead for the 10 samples was found to be 4.482 ± 1.195 ppm. From table 5 and Figure 23 sample 59 had the highest concentration of lead of 6.523 ± 0.025 ppm while sample 72 had the lowest concentration of lead, with a value of 3.38 ± 0.010 ppm. Sample 59, 60 and 70 were randomly selected from the previously 70 gasoline samples which were analysed for adulteration. Samples 59, 60 and 70 gave higher lead values of 6.523 ± 0.025 ppm, 5.997 ± 0.035 ppm and 6.033 ± 0.015 ppm respectively as compared to sample 71-77 whose values are shown in table 5. The results obtained in this study were higher than those reported by (Akinlua and Torto, 2008) whose concentration ranged from 7.823-941.199 ppb with a mean value of $100.437 \pm 2 34.700$ ppb. However all

the 10 samples were found to contain an appreciable amount of lead even though the fuel dispensed in Kenya is thought to be unleaded. The values were within the allowable limits set by the KEBS of 15 ppm of Lead.

3.8.2 Sulphur

The mean sulphur value for the 10 samples was found to be 219.800 ± 102.655 ppm. From table 5 and Figure 23 sample 70 had the highest percentage value of sulphur of 469.000 ± 4.000 ppm while sample 72 had the lowest percentage value of sulphur of 140.000 ± 5.000 ppm. Sample 59, 60 and 70 were randomly selected from the previously 70 gasoline samples which were analysed for adulteration and gave higher sulphur values of 214.000 ± 4.000 ppm, 317.000 ± 3.000 ppm and 469.000 ± 4.000 ppm respectively an indication that solvents with high sulphur contents like kerosene and diesel could have been used to adulterate the samples. Sulphur content in samples 59, 60 and 70 were found to be high and the percentage adulteration were found to be also high with values of 11.339 ± 0.200 % (10.50 ± 0.29 %), 17.464 ± 0.574 % (22.00 ± 0.58 %) and 12.596 ± 0.432 % (12.00 ± 0.58 %) by FTIR and distillation respectively. These two results further confirm that solvents with high sulphur content like kerosene and diesel could have been used for adulteration. However all the 10 samples were found to be within the allowable limits set by the KEBS of 1500 ppm of sulphur.

CHAPTER FOUR

CONCLUSIONS

From the results obtained from FTIR when compared with those of distillation (ASTM D86) and statistical analysis shows that the developed method FTIR can be used in place of the distillation method (ASTM D86).

Our present study found out that all the 70 gasoline samples analyzed were adulterated with adulterants varying from 7.829 ± 1.278 % to 17.464 ± 0.574 % even though most of them ranged between 10-17%. This could have been due to contamination during transportation from Mombasa to Nairobi through the main pipeline, central contamination like individual companies storage tanks, during transportation from the pipe line depot and at the dispensing points.

It was also noted that some of the adulterations were done by professionals in such way that ordinary methods could not be used to detect the level of adulteration. This could have been done by using solvents which are components of the gasoline or added small amounts of adulterants that could be difficult to detect by the locally available instruments.

The adulteration was found to be highest with individually owned stations with a mean of 12.44 ± 2.50 %, and the lowest was found in multinationals with a mean of 10.87 ± 1.54 %. Sulfur was found to present in all samples analyzed. Sample 60 which was highly adulterated with a mean value of 17.464 ± 0.574 % of the adulterant was also found to contain a high level of sulfur, an indication that the adulterant was sulfur rich. However the concentration of sulphur in the 10 samples analyzed did not exceed the KBS standard limits of 1500 ppm.

There was presence of Pb in all the 10 samples analyzed even though Kenya banned lead in a gasoline. The level of Pb was found to be lower than the allowed limit of 15ppm.

CHAPTER FIVE

RECOMMENDATIONS

In this work, 70 gasoline samples were analysed using FTIR and distillation method (ASTM D86) to check on the level of adulteration. A liquid cell was used for the analysis. It is therefore advisable that the experiment should be repeated using a gas phase cell as it gives better resolution of peaks.

In this research a new method was developed for the analysis of gasoline using FTIR and the major finding was the absorption band at 1380.9cm^{-1} which increased with the amount of kerosene adulterant present. Further research could be carried out by analyzing more samples using the same peak to ascertain its robustness.

The results obtained by FTIR compared well with those obtained by distillation method, therefore further work should be done to compare FTIR results with other methods for example gas chromatography-mass spectrometry and GC-FID.

The experiment involved collecting samples from different fuel stations for analysis. Further research could be done by following the samples from the point of entry to the country or from the refinery to the final dispensing point so as to investigate the patterns of how, where and when the adulteration takes place.

From this research it was found out that unleaded gasoline contained some appreciable amounts of lead and sulphur. It is therefore recommended that more samples should be analyzed to check on the levels of lead and sulphur present.

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7.0 APPENDICES

Table 6: Distillation temperatures of the pure gasoline standard and those of the gasoline samples.

Sample	IBP	10%	30%	40%	50%	60%	80%	90%	FEB
STD	39.50	53.00	76.50	86.50	97.00	108.00	133.00	147.50	186.00±0.29
1	44.33	67.33	88.50	99.67	112.67	123.67	172.67	194.67	259.50±1.00
2	42.67	58.00	76.00	88.17	101.67	116.00	145.50	166.00	207.50±1.00
3	38.33	56.67	76.67	86.50	100.67	113.33	142.16	163.00	202.50±1.00
4	38.17	54.50	74.00	85.83	99.00	113.00	141.83	163.00	205.50±1.00
5	38.17	55.67	74.67	86.83	100.00	113.67	141.83	163.33	205.83±0.58
6	38.67	58.67	75.33	87.17	101.67	120.67	142.17	163.33	206.17±0.58
7	44.33	62.67	83.17	96.17	111.00	121.00	152.17	174.67	252.00±1.00
8	37.00	55.17	73.33	86.5	98.33	111.00	139.50	161.00	207.50±1.00
9	39.67	60.67	83.50	95.50	109.67	121.33	145.17	160.67	213.50±1.00
10	40.33	56.67	76.50	88.50	102.67	116.67	144.83	164.33	208.50±1.00
11	40.33	61.33	84.83	98.33	113.00	124.00	148.5	172.00	304.50±1.00
12	41.33	61.67	85.17	99.00	113.33	125.67	148.5	180.33	242.67±0.58
13	40.67	59.67	84.50	99.67	133.67	123.67	146.5	165.67	206.17±0.58
14	40.67	59.67	84.50	99.67	111.67	124.67	145.50	161.67	212.17±0.58
15	40.17	61.67	85.83	100.67	115.67	126.00	148.17	164.67	207.17±0.58
16	35.17	55.33	85.83	101.33	115.67	125.33	148.83	164.67	205.83±0.58
17	37.67	54.67	80.83	92.83	106.67	119.67	144.83	161.67	211.83±0.29
18	42.50	58.50	79.50	91.83	106.33	118.33	144.83	164.33	200.33±0.29
19	41.333	58.5	76.83	88.83	102.17	114.67	141.17	158.50	205.17±0.58
20	41.00	56.00	76.83	88.83	101.83	113.67	140.17	159.33	198.67±0.29
21	41.33	57.83	76.83	88.83	101.83	114.67	141.17	158.83	197.83±0.29
22	40.33	57.83	75.67	88.17	101.50	114.33	140.83	157.00	200.67±0.29
23	41.00	57.83	75.67	89.17	103.67	114.83	142.17	160.00	203.17±0.58
24	41.00	58.67	77.00	90.00	104.67	116.67	144.17	159.50	198.33±0.29
25	42.17	58.67	80.17	91.17	105.67	117.67	145.17	159.67	200.83±0.29
26	40.83	58.33	79.83	93.83	107.33	119.33	145.83	167.33	267.17±0.57
27	42.167	58.67	79.17	92.17	104.67	116.50	143.17	160.67	206.50±0.50
28	41.00	57.33	77.83	90.83	105.33	117.50	142.17	161.50	202.33±0.29
29	40.17	58.67	79.17	92.17	104.83	118.67	146.17	160.67	202.17±0.58
30	40.17	57.67	78.17	91.17	104.67	116.67	143.17	159.67	206.17±0.58

Sample	IBP	10%	30%	40%	50%	60%	80%	90%	FEB
31	38.17	53.83	77.17	90.17	101.67	110.67	145.17	161.67	210.17±0.58
32	40.17	59.33	81.83	98.33	113.33	127.33	150.17	176.67	238.67±0.58
33	38.83	54.83	76.83	89.83	105.33	118.33	144.83	162.33	210.00±0.50
34	38.17	56.67	77.17	90.17	104.67	118.37	145.17	164.67	208.33±0.29
35	38.83	54.17	76.50	90.17	105.67	119.00	143.83	163.33	207.83±0.29
36	37.83	55.33	75.17	88.00	101.5	115.33	139.83	161.33	205.83±0.58
37	38.17	56.67	76.17	88.17	102.67	114.33	143.67	164.00	204.67±0.29
38	37.83	55.33	76.33	88.00	101.67	109.67	141.17	159.50	206.17±0.58
39	37.83	53.83	73.33	85.83	98.33	111.50	138.38	159.33	201.83±0.58
40	38.17	55.67	74.67	87.17	100.67	109.67	141.17	162.67	204.17±0.58
41	38.17	55.5	75.33	88.83	104.33	116.33	144.83	162.33	227.83±0.58
42	38.17	55.5	75.5	88.17	103.67	116.67	139.17	161.67	200.17±0.58
43	39.17	57.17	76.67	89.17	102.67	115.67	142.67	157.17	204.33±0.29
44	38.83	57.17	78.83	90.83	104.33	117.33	144.83	162.33	207.17±0.29
45	41.63	59.67	78.00	88.83	101.33	117.5	136.33	150.83	205.83±0.58
46	42.17	59.67	79.00	90.17	101.5	113.67	138.83	151.00	203.67±0.29
47	39.67	58.17	78.83	94.83	108.33	123.33	144.83	177.33	231.00±0.50
48	38.67	54.17	76.83	88.67	98.33	116.33	144.83	165.33	206.67±0.29
49	38.17	56.33	76.83	89.83	105.33	119.33	144.83	168.33	258.17±0.29
50	41.67	64.67	85.67	95.83	105.33	113.33	139.83	165.33	261.83±0.29
51	40.83	58.17	79.83	92.83	108.17	121.00	149.83	170.33	227.67±0.29
52	38.83	54.83	75.67	87.50	102.17	115.33	141.33	159.33	200.67±0.29
53	38.83	55.67	76.33	89.50	102.83	115.33	141.33	161.50	200.67±0.29
54	38.83	57.33	77.67	89.67	104.33	116.00	143.83	163.33	204.67±0.29
55	39.17	55.67	76.33	88.33	103.66	115.67	142.50	163.00	214.17±0.58
56	40.33	58.00	78.83	89.83	101.33	114.33	140.33	154.83	202.83±0.58
57	40.50	58.67	77.17	90.17	103.67	116.00	143.5	161.83	204.33±0.29
58	37.83	54.00	74.33	88.83	104.33	116.17	144.5	159.17	206.83±0.58
59	39.83	56.33	76.83	89.00	102.17	115.5	139.83	156.00	202.67±0.29
60	41.83	61.33	89.67	105.17	115.33	135.33	168.17	202.83	245.17±0.29

Sample	IBP	10%	30%	40%	50%	60%	80%	90%	FEB
61	38.83	56.33	75.50	89.00	104.33	116.33	131.83	159.33	206.00±0.50
62	40.67	56.17	77.83	90.67	104.33	116.33	141.83	156.83	200.83±0.58
63	41.67	58.33	79.67	93.00	106.00	119.17	147.83	170.33	206.00±0.50
64	42.67	60.33	80.83	91.67	107.00	120.83	146.83	171.33	205.00±0.50
65	39.67	63.00	82.83	94.67	106.17	120.00	149.83	167.33	204.00±0.50
66	40.67	58.33	79.83	91.83	106.33	119.17	146.83	168.17	204.67±0.29
67	41.67	59.33	79.83	93.67	108.00	121.17	150.83	173.33	204.67±0.29
68	41.83	59.17	79.83	92.67	107.33	120.33	147.83	167.33	205.67±0.29
69	40.5	59.00	80.83	91.83	107.33	120.33	148.33	169.33	206.17±0.29
70	40.67	58.33	79.83	92.83	106.17	116.33	149.83	171.33	204.67±0.29

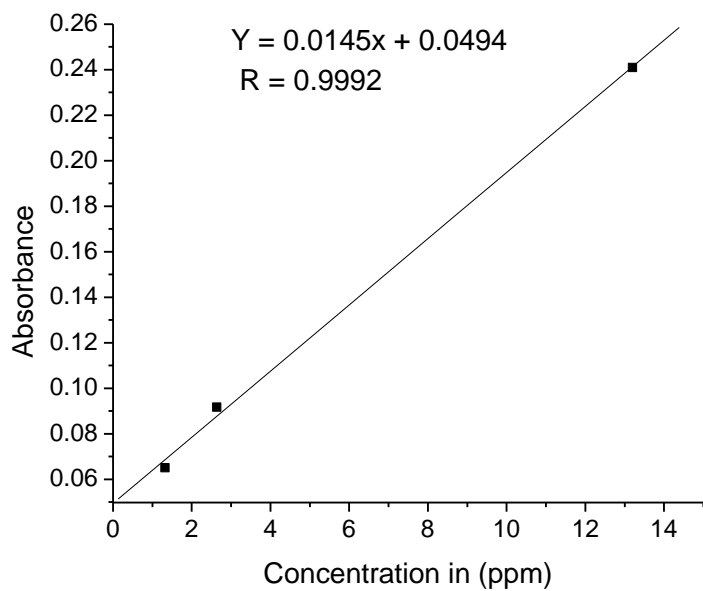


Figure 22: Calibration curve of absorbance versus concentration of Lead standard.

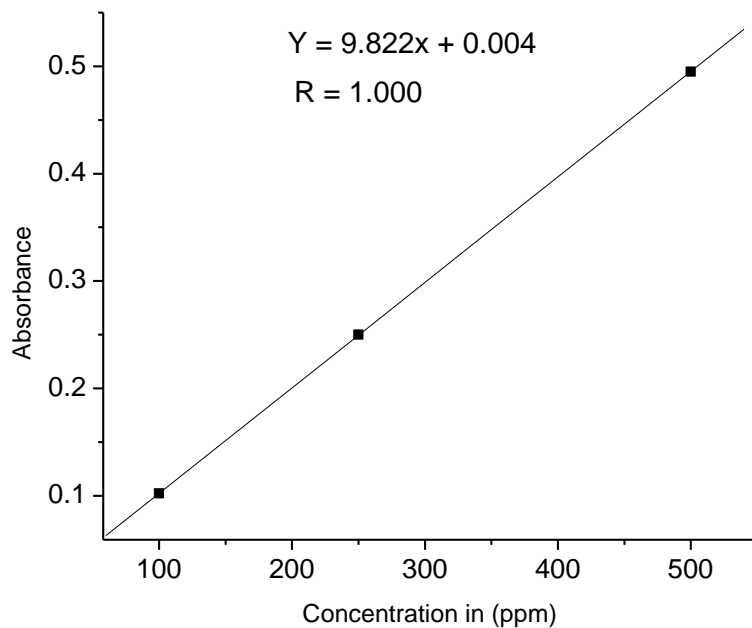


Figure 24: Calibration curve of absorbance versus concentration of Sulphur standard.