UNIVERSITY OF NAIROBI

DETERMINATION OF BISPHENOL A (BPA) IN THERMAL PAPERS, SELECTED SOIL SAMPLES AND THE EFFECT OF TEMPERATURE AND HUMIDITY ON ITS CONCENTRATION

BY
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I56/81182/2015

A thesis submitted in partial fulfillment of the requirements for the award of the Degree of Master of Science in Analytical Chemistry of the University of Nairobi

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DECLARATION

This thesis is my original work except where due references are made. It has not been submitted partially or wholly for the award of degree to this or any other institution of learning.

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DEDICATION

This thesis is dedicated to my dear husband Patrick Odhiambo, my parents Mr. and Mrs. Odera, my sons Giovanni and David, my siblings Florence, Jack, Mark, Stephen, Winnie and Meshack together with my friends and colleagues for their moral and financial support.

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I am fully indebted to the ALMIGHT GOD who gave me the patience, strength and wisdom to accomplish my work. May He forever grant me the desire to serve Him and be an instrument of supporting those in need.

ABSTRACT

Exposure to Bisphenol A (BPA) is associated with various health complications globally. Whereas various research have been conducted in Asia, North America and Europe, limited work has been conducted inAfrica on BPA . The aim of the research was to quantify the amount of BPA in thermal paper and soil samples, and study the effect of temperature and humidity on the concentration of BPA in thermal papers. Soil samples were collected from Dandora Dumpsite where some of the wastes containing BPA get deposited and TUK-garden which was the control site. Thermal paper samples were collected from selected supermarkets and ATM Lobby points within the Central Business District (CBD) of Nairobi City County, in March 2017. Sample analysis was done using GC/MS method after extraction in organic solvent. The method LOD was 0.16 mg/g, while the percentage recoveries were 86% and 83% for thermal paper and soil samples, respectively. The highest concentration of BPA in the bank thermal papers was 3.59±0.24 mg/g, while the lowest concentration was 1.94±0.25 mg/g. The lowest BPA concentration from the supermarket thermal papers was 1.08±0.06 mg/g while the highest BPA concentration was 2.75±0.14 mg/g. The unused thermal papers bought locally had a BPA concentration of 1.74±0.89 mg/g, while both unprinted and printed non-thermal papers did not show any trace of BPA. The soil samples from Dandora Dumpsite site 20 had the highest BPA concentration at 154.82±12.72 mg/g while TUK-garden soil had the lowest BPA concentration at 0.49±0.12 mg/g. The results showed that thermal paper samples collected from the bank's ATM Lobbies had higher concentration of BPA than the thermal papers from the supermarkets. Investigation of the effect of temperature temperature and humidity on BPA extraction showed higher BPA concentrations in the thermal papers at higher temperature and humidity, suggesting that an increased temperature and humidity increased availability of BPA on extraction leading to higher recoveries.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ATM	Automated Teller Machine
BCF	Bio Concentration Factors
BPA	Bisphenol A
BPF	Bisphenol F
BPS	Bisphenol S
CBD	Central Business District
CLP	Classification, Labeling and Packaging standards
CNT	Carbon-nanotube
CV	Coefficient of Variation
°C	Degrees celcious
DNA	Deoxyribonucleic acid
E	East
ECG	Electrocardiogram
EDC	Endocrine Disrupting Chemical
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
ER	Endocrine Receptor
ETR	Electronic Tax Register
EU	European Union
FCMs	Food Contact Materials
FSH	Folicle Stimulating Hormone
GC	Gas Chromatography
GCE	Glassy-carbon electrode
GDP	Gross Domestic Product
g	gram
g/m^2	Gram per squared metre
GIS	Geographic Information System
GLC	Gas-liquid chromatography
GnRH	Gonadotropin-releasing hormone
HPLC	High performance liquid chromatography

IR	Infrared
kg	kilogram
KNBS	Kenya National Bureau of Statistics
LH	Lutenising hormone
LLE	liquid–liquid extraction
LOD	Limit of Detection
LOQ	Limit of quantification
m	metre
MEKC	Micellar electrokinetic chromatography
mg/L	milligram per litre
mg/g	milligram per gram
min^{-1}	Per minute
MIPS	Molecularly-imprinted polymer sensors
ml	millilitre
mm	millimetre
MS	Mass-Spectrometer
NCBI	National centre for Biotechnology information
NCCS	National Center for Charitable Statistics
ng/L	Nanogram per litre
NIR	Near Infrared
NIST	National Institute of Standards and Technology
Nm	Nanometre
NPs	Nanoparticles
PAMAM	Polyamidoamine
PCOS	Polycystic Ovary Syndrome
POS	Point of Sale
PVC	Polyvinyl Chloride
QDs	Quantum-dot-based sensors
R^2	correlation factor
Rt	Retention time
S	South

SAS	Statistical Analysis Software
SCF	Scientific Committee on Food
SD	Standard Deviation
SERS	Surface-enhanced Raman scattering
SIM	Selective ion monitoring
SML	Specific migration limit
SPE	Solid-phase extraction
SPME	Solid-phase micro-extraction
SPSS	Statistical Package for the Social Sciences
T	Temperature
TDI	Tolerable Daily Intake
TUK	Technical University of Kenya
U.S. A	United States of America
USEPA	United Nations Environmental Protection Agency
UTP	Unused thermal paper
UV	Ultra violet
UV-Vis	Ultra violet-visible
VAT	Value Added Tax
XRF	X-ray fluorescence
%	Percent
<	Less than
Δ	Change in
μm	Micrometre
μL	Microlitre

CHAPTER ONE

1. INTRODUCTION

1.1 Background of the study

Rapid increase in global population has put pressure on production systems for food, industrial products and services. This has in turn contributed to rapid development of industrial, agricultural and service providing sectors in order to meet the high demand for goods and services. The global population is projected to upsurge from the current 7.6 to 9.2 billion by the year 2050, with majority of population growth anticipated to take place in the developing countries (Lindh *et al*., 2007). In Kenya, the population is projected to rise from the current approximated value of 52.21 million to 95.5 million by the year 2050 (KNBS, 2010). Concurrently, anticipated growth in industrial, agricultural and service industries is likely to lead to high emission of wastes and by-products into the environment. However, there are no rules currently in Kenya that govern the deposition of the thermal papers and therefore they may find there way into the dumpsites and some other areas which may have an adverse effect to the environment. The Bisphenol A (BPA) compound that is used in thermal printing tend to leach from the products into the soil and some other environmental matrices. Similarly, several materials used to support economic development have potential negative effects to human health and environment, hence the need for extended research and development to protect human health and environment.

1.2 The Banking sector in Kenya

Among the major service industries in Kenya are the banking sector, tourism, wholesale and retail markets. By December 2007, the banking sector in Kenya consisted of 43 financial institutions, of which three were owned by the government of Kenya, while the rest were privately owned. Most accredited foreign exchange agencies, small scale banking institutions, credit reference agencies, money transmittal benefactors, non-operating commercial institution holding firms and demonstrative agencies were owned by private sectors (Nyangosi *et al*., 2009). All the public and private owned banking institutions own ATM Lobby points which generate paper receipts that are made up of thermal papers. The increase in the number of commercial institutions and more ATM lobby points could subsequently lead into the production and usage of more thermal papers where Bisphenol A is used as a critical active ingredient. The number of ATMs in Kenya increased from

29,321 in December 2013 (Ali, A.E.E.S., (2015) to 33,542 in December 2017 (Table 1.1). This could subsequently lead into the production and release of more thermal papers into the environment.

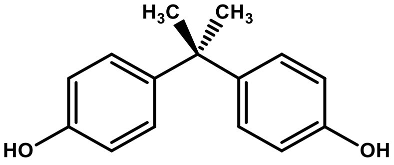
Table 1.1: the growth of ATM Network in Kenya between the year 2013 and 2017

ATM Network in Kenya				
Month	**2013**	**2017**	**Growth**	**%Growth**
January	2,390	2,786	396	16.569
February	2,404	2,795	391	16.265
March	2,397	2,791	394	16.437
April	2,413	2,795	382	15.831
May	2,426	2,779	353	14.551
June	2,439	2,782	343	14.063
July	2,447	2,778	331	13.527
August	2,472	2,805	333	13.471
September	2,478	2,771	293	11.815
October	2,480	2,812	332	13.344
November	2,488	2,823	335	13.465
December	2,487	2,825	338	13.591
Source: ((Nyangosi *et al*., 2009); (Ali, A.E.E.S., (2015)				

1.3 Bisphenol A

Bisphenol A (BPA) is a vital industrial chemical that is required in the manufacture of polycarbonate plastics, epoxy resins and thermal paper which have various applications (Liao *et al*., 2012). The polycarbonate plastics have been used in the production of medical equipment, plastic water bottles, digital media (e.g. CDs and DVDs), electronics such as cell phones and computers, electrical and household appliances, safety shields, glazers that are used for construction, personal protective clothing for sports and automobiles (Loganathan *et al*., 2011). Epoxy resins have also been useful in printed circuit boards, industrial protective coatings, automotive primers, adhesives, powder & can coatings and industrial floorings (Liao *et al*., 2012). Thermal papers are used in supermarket and Automated Teller Machine (ATM) receipt papers.

BPA (Figure 1.1) is one of the highly produced chemical compounds with an annual worldwide production estimated at over 8 billion pounds which is an equivalent of 3.6 billion kg (Liao and Kannan, 2011). The compound has a molecular structure consisting of a chief tetrahedral carbon atom attached to 2 methyl and 2 phenol groups.



Bisphenol A
(2,2'-bis(hydroxyphenyl)propane)

(Source: Krishnan *et al*., 1993)

Figure 1.1: Structure of BPA

BPA slightly dissolves in water at a temperature of 24 °C and breaks down in the matrices that are basic in nature (Mendum *et al*., 2011). U.S. National Institutes of Health Hazardous Substances Data Bank has reported that the compound has a log K_{ow} of 3.64 ± 0.32 with a short half-life in air since it promptly breaks-down and undergoes photo-oxidation (Lu *et al*., 2013). It has been detected in different environmental matrices such as air, soil, wildlife, water and humans despite the fact that it has a short half-life accompanied with the slight ability for bioaccumulation (Corrales *et al*., 2015). Literature reveals that BPA has a low vapor pressure, high melting point and slightly dissolves in water which has contributed to its low volatility (Staples *et al*., 1998). Table 1.1shows some of the physical properties of BPA (NCBI, 2018).

Table 1.1 Physical properties of Bisphenol A

Physicalproperties	**Values**
Melting point	150 -157°C
Boiling point	220 degrees Celsius (°C) at 4 millimetre mercury (mm Hg) ; 398°C at 760mm Hg
Solubility in water	120 -300 (mg/L) at 20-25°C
Henry constant	1.0 x 10^{-10} Atmosphere cubic meter /mol (Atm.m^3/mol)
Henry constant	8.7 x 10^{-10} to 3.96 x 10^{-7} mm Hg at (20-25)°C
Specific gravity	1.060 -1.195 mg/L at (20-25)°C
Logarithm octanol-water partition coefficient (Log K_{ow})	2.20 -3.82

1.4 Statement of the problem

Rapid increase in population has led to expansion of industrial, agricultural and service sectors to support socioeconomic development. However, several products and materials used in these sectors have potential negative effect to human health and environment. The use of thermal papers in the banking sector, and wholesale and retail shops has raised concerns globally because of the negative effects of Bisphenol A (BPA), which is one of the major ingredients in most thermal papers. In addition, the introduction of Electronic Tax Register (ETR) machine by the Kenyan Government, in 2004, to assist in monitoring the collection of Value Added Tax (VAT) (Weru *et al*., 2013) obliged all commercial entities to install ETR machines which use thermal papers for printing.

BPA is an endocrine disrupter which has led to disorders such as; hormone dependent tumors like breast and prostate cancer, early puberty, male and female infertility and polycystic ovary syndrome (PCOS) (Paulose *et al.,* 2015). In one of the previous studies, BPA concentration was reportedly high in urine samples that were analysed; this was linked to a reduction in the number of sperm in the ejaculate and a reduction in the motility and viability of sperms in men which was a possible cause of infertility in men (Laura *et al*., 2007). However, such data is missing in Kenya.

Research has revealed three major ways through which the human beings get exposed to BPA compound; transdermal (through the pores in the skin), oral (through the mouth) and inhalation of the compound if present in the air (Beverly, 2011).

Most of studies on Bisphenol compounds including BPA have been done in the USA, Europe and Asia, with limited studies done in Africa (Corrales *et al*., 2015). The increase access to thermal paper use in Kenya and possibility of use of BPA in them has prompted the need to determine and quantify the presence of BPA in soil, Supermarket and ATM receipts from selected sites within Nairobi County, Kenya.

1.5 Objectives of the study

1.5.1 Overall objective of the study

The overall objective of the study was to determine the extent of contamination of BPA in supermarket, bank receipts and soil samples.

1.5.2 Specific objectives

1. To determine the concentration of Bisphenol A in thermal papers from selected supermarkets and ATM receipt from the banks in the Central Business District (CBD), of Nairobi City.
2. To investigate the effect of storage conditions such as temperature and humidity on the stability of BPA in thermal papers found in Central Business District (CBD), of Nairobi City.
3. To quantify Bisphenol A in the soil samples collected from Dandora Dumpsite which is about 7.5 km from Nairobi CBD.

1.6 Justification

The research conducted previously show that human is at a greater risk of BPA exposure (Vandenberg *et al*., 2013). The public interacts with thermal papers and other consumer products containining BPA and its polymeric forms, from every daily activities in commerce and technology. Due to advance effects of Bisphenol A, there is need to determine its presence in thermal papers and also to monitor and reduce exposure. There is limited data in developing countries on the status of BPA contamination (Corrales *et al*., 2015; Rocha *et al*., 2015;

Staniszewska *et al*., 2015). BPA was found in two hundred and ninety one tap water samples collected in France (Colin *et al*., 2014), at mean concentration of 14 ng/L and the highest concentratins of 1.3 mg/L. Out of about 8 publications on wildlife including reptiles, birds, fish, invertebrates, amphibians and mammals matrices, none was done in Africa (Crain *et al*., 2007). The summary of publications show that most of the publications were done in Europe, Asia, North America and Australia with only about two percent of the publications from South Africa (Corrales *et al*., 2015). The main ingredient in the thermal papers is BPA. The thermal papers and other BPA containing products get disposed off into the dumpsite and other garbage collection sites. There are people currently in Kenya who earn their livelihood from the dumpsite, which also acts as a source of food to some domesticated animals like pigs, goats and cows. There are possibilities of the compound leaching from the BPA products and thermal papers into the soil. This may subsequently contaminate the foodstuff that are disposed off in the site. The compound may also get washed away by rain/ moving water from these products into the nearby water bodies. This may also be a source of contamination if the destined water is used for domestic and agricultural purposes.

Therefore, there was a need to conduct this study in Kenya to determine the extent of contamination of BPA in thermal papers and soil.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Bisphenol A chemicals

This is one of the extensively manufactured compounds in the world (Alonso-Magdalena *et al*., 2006). It is as a raw material that is used in the manufacture of epoxy resins and polycarbonate plastics (Huang *et al., 2011*). It also acts as a stabilizer that is used to get rid of the extra hydrochloric acid in process of making polyvinyl chloride (PVC). It has been extensively applied in the production of contact lenses, healthcare equipment (Vandentorren *et al.*, 2011), toys, , window foils, storage media spectacle lenses and dental composites. The compound is one of the Food Grade Materials used for the packaging of food stuff such as jar cap coatings, kitchenware, plastic packaging and the inner linings of the can that prevents direct contact of the food and metallic surface hence preventing the food stuff from getting corroded (Cwiek-Ludwicka and Ludwicki, 2014).

Its worldwide production was around 5.2 million tons by the year 2008 (Pirard *et al.,* 2012). The United States of America are the top most global producers of BPA with their production amounting to 22.9% of the total global production (Huang *et al*., 2011). The second and the third most global producers are Taiwan and Japan whose percentage productions stand at 13.1% and 13%, respectively (Huang *et al*., 2011). Poland's production of BPA was approximated to be 12,000 tons annually; an equivalent of 0.3% of global production (Huang *et al*., 2011). The largest percentage of BPA produced globally is used in the manufacturing of polycarbonate plastics, an equivalent of 74% while the production of epoxy resins takes about 20% of the total amount of BPA produced. The high production of BPA is a threat to the environment since a bigger portion of the amount produced is deposited into the surroundings which has subsequently led to contamination of various environmental compartments including water, air and soil (Genuis *et al*., 2012).

2.2 Bisphenol A in thermal paper

Thermal paper is a discrete fine paper that is coated with a special substance which changes its colour in the presence of heat (Ted *et al*., 2011). It has diversified applications such as: the receipt papers that are given to customers at the point-of-sale. These include print-outs from recording devices, labels, tickets, cash receipts from the superstores, stalls, retail shops using the ETR machines, ATM Machines also produce transaction receipts which are made of thermal papers (Becerra and Odermatt, 2012). Some labels are also produced on the thermal papers such as the labels on industrial barcodes, prescriptions, packaged food items sold in the supermarket (canned beef, minced meats, peanut butter, ghee, cheese, some plastic bottled water, some plastic bottled drinks). Some transportation tickets are also printed on the thermal papers such as bus tickets, train and airline tickets (Mielke *et al*., 2011). Parking, entertainment and tickets from stalls use thermal papers. Some of the medical receipts are also printed on the thermal papers such as electrocardiogram (ECG), ultrasound and printouts from other laboratory recorders. A study conducted on the thermal papers used for medical records confirmed the presence of BPA in ECG printouts (Benachour and Aris, 2009). The European statistics indicates that half of thermal papers that are currently traded in the market are the Point of Sale receipts (Mendum *et al*., 2011). Virtually, a third of the thermal paper is used in luggage tags, deli trays & shipping labels. On the other hand, lottery tickets use approximate 10 percent of thermal papers while another 10 percent of the thermal papers are applied in fax paper (Geens *et al*., 2012b). Direct thermal printing is the best technology for a diversified applications such as label print outs, faxes, luggage tags and point of sale receipts (Bracewell, 1989).

2.3 Thermal printing technology

It is an instantaneous and an effective printing technology with vital applications such as labels, luggage tags, point-of-sale (POS) receipts and faxes (Liao and Kannan, 2011). It forms a coloured image when particular compounds in the layer of thermal paper are exposed to heat.

2.3.1 Constituents of thermal paper

Thermal paper is an enormously designed substance whereby the paper is concealed with a thermal sensitive coating that produces a coloured appearance upon the exposure of the paper to the source of heat (Mendum *et al*., 2011). The thermal sensitive coating is known as thermal reactive layer. It also consists of a pre-coat/base coat which is a coat smeared to the base-paper to assist in increasing the resolve by barring the transfer of heat to all the coatings of the paper and improves on the paper’s levelness (Geens *et al*., 2012b). A thermal sensitive layer smeared to the pre-coat contains very crucial components that are required for thermal printing. Furthermore, thermal paper may also consist of a top coat and/or back coat which may shield the paper (Figure 2.1). The top coat is crucial in shielding the thermal paper from an automated tension or the chemical responses that may take place during printing. Likewise, back coats may be useful in providing extra guard in the course of lamination, printing, or other mechanical practices (Liao and Kannan, 2011). Thermal papers used for receipts usually do not have the upper and rear coats.

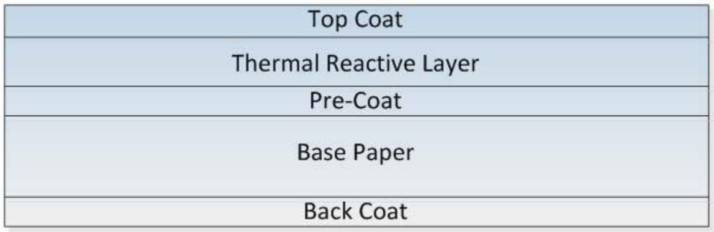


Figure 2.1: Cross-Section of Thermal Paper

Thermal papers are produced in “gigantic rolls,” which are treated as semi-finished products. The rolls are then acted upon by the paper converters which print on them and size them appropriately, reverse them onto a precise core referred to as slit rolls and then package them for trade. They are grouped into three categories based on their weights or density (usually g/m^2 or pounds per ream).

i. Point of Sale Receipt and Fax papers grades; they possess a mean weight of 58 grams.
ii. Ticket and Label grades- possess a mean weight of 80 grams.
iii. Heavy ticket grades- possess a mean weight of 120 grams (Lu *et al*., 2013).

Thermal papers are not produced from the recycled materials, as these materials lack the homogeneity which is a crucial attribute for the thermal papers. The printing of the thermal paper can be done in two different formats. The printing can be done on one side or both sides of the printing paper.

2.3.2 Chemistry of thermal printing

The paper coating that is thermally reactive comprises three major constituents as illustrated in Figure 2.2. These include: dye (color-former), a developer (coreactant) and a sensitizer which is also known as a modifier. The modifier exists only in definite systems. The thermal paper also consists of a binder such as polyvinyl alcohol or latex which ensures that the thermal paper coatings do not come out of the paper (Gehring *et al*., 2004). The image color, scanning characteristics and durability of the paper depend on the mixture of the constituents and their characteristics.

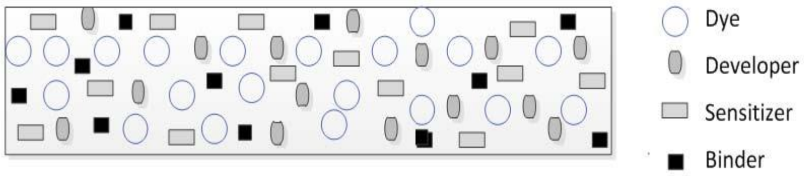


Figure 2.2: elements of the Thermal Reactive layer

2.4.2.1 Dye

The commonly used dye in the thermal paper is the leuco-dye. The leuco-dye is always colorless at the normal temperature (Biedermann *et al.*, 2010) and produces a coloured image when exposed to a temperature that is slightly above its melting point. It alters its configuration as it accepts hydrogen ions in the presence of heat and Bronsted acid (developer). The alteration of its configuration leads to the formation of a coloured image. During thermal printing, the thermal head of the printing unit transfers heat to the paper hence prompting the constituents of the paper to melt. Sensitizer used has a lower melting point. The presence of heat triggers the melting of sensitizer which prompts the developer to donate a proton to the dye. The proton donated prompts the leuco dye particle to alter its configuration hence leading into the production of a coloured image (Geens *et al.*, 2012a).

2.4.2.2 Developer

The developer (coreactant) acts as a Bronsted acid. It is feebly acidic in nature and donates hydrogen ions which lead to the formation of a coloured image (Geens *et al.*, 2012b). Bisphenol A acts as the developer in thermal printing, where it donates a proton (Liao and Kannan, 2011). A good developer must possess the following crucial characteristics:

1) it should be able to react fully with a leuco dye when heated,
2) it should be colourless to avoid the formation of any background imaging during the process of thermal printing,
3) it should be less soluble in water with a good solid morphology to form a uniformly high-quality suspension,
4) its synthesis should be affordable for money-making and viability in large-scale production, it should possess a low bioaccumulation hazard potential to minimise the chances of environmental contamination (Jang *et al.*, 2013).

5) it should be odourless to avoid production of hazardous smell during the printing process.
6) it should have of pKa value ranging between 9.78-10.39 which makes it more acidic enough to be able to donate a proton during the thermal printing process to aid in the formation of a coloured image (Regueiro *et al.,* 2015).
7) It should have a lower melting point to facilitate the transfer of protons upon the heating of the paper which will subsequently aid in the formation of colour and quicken the rate at which printing takes take. This will lead into the formation of a substance that could be used in printers that require low energy.
8) It should have a low vapour pressure to avoid the production of more fugitive emissions during thermal printing process (Liao and Kannan, 2011).

2.4.2.3 Sensitizer

Sensitizers are also known as modifiers and also act as solvents. They have a low melting point which creates a conducive environment for the dye and developer to react leading to the formation of a coloured image (Harlbrook, 2001). Sensitizer is a long-chain aliphatic compound which could be a fatty acid, an alcohol, an amide which has a melting point that ranges between 45 and 65˚C (Mendum *et al*., 2011) such as propyl amine, isopropanol, allyl alcohol, among others.

2.4.2.4 The process of thermal printing

A coloured image is formed in thermal paper when the layer that is thermally reactive is exposed to a temperature higher than the melting point of the sensitizer (Goldinger *et al*., 2015). The developer produces a hydrogen ion upon heating at a temperature higher than the melting point of the sensitizer. In the case of the Crystal Violet dye, the hydrogen ion makes the lactone ring to open and increases the conjugation of the system, resulting in colour formation as shown Figure 2.3. It then hardens to form a steady image.

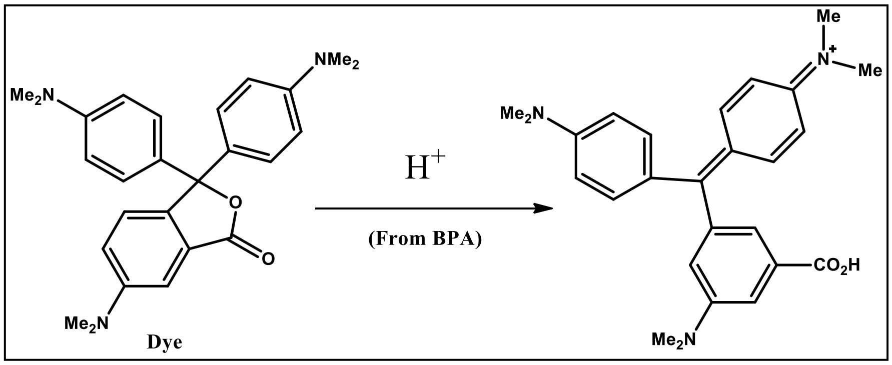


Figure 2.3: Reaction scheme of thermal printing (Mendum et al., 2011)

Mechanistically, the mixture under slight warming (35°C), BPA dissociates into a proton and a phenoxide as shown in Figure 2.4. BPA acts as a Bronsted acid by donating a proton (H^+) forming a phenoxide ion as represented in in Figure 2.4 below.

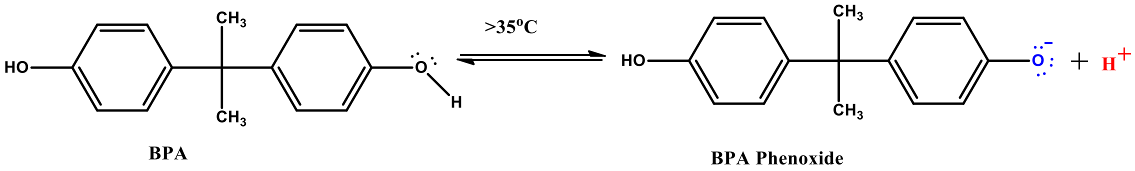


Figure 2.4: Dissociation of BPA

The lactone oxygen in the dye is protonated by the hydrogen ion from the dissociation reaction in Figure 2.4 which triggers electron movement to give a fully conjugated molecule. The resultant conjugated ammonium dye is stabilized by the phenoxide to form a salt that gives a characteristic colour.

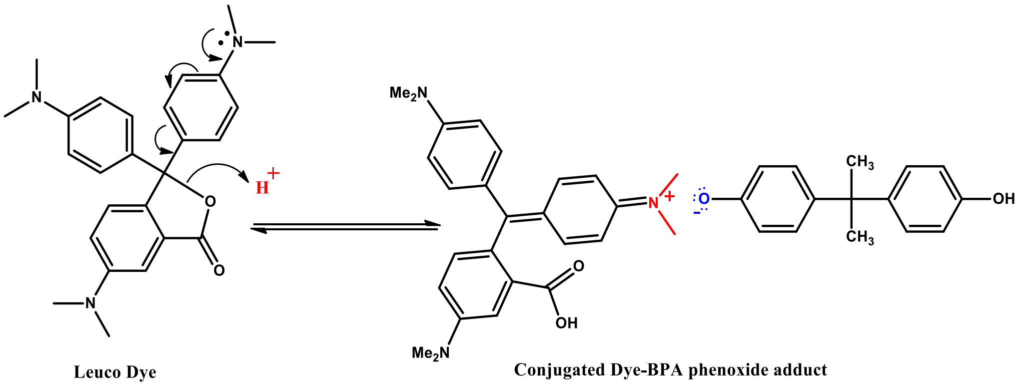


Figure 2.5: Mechanism of colour formation at molecular level

The system of thermal printing entails three main constituents which include: thermal paper, a printer head and a platen (roller of the thermal printer; the flat end that exerts pressure against the paper). The printer head contains small heating units that are found along the length of the printer. These spontaneously transfer the amount of heat required for thermal printing to occur. The platen (the roller of the thermal printer) drives thermal paper making the print head heating entities to transmit heat into the thermal paper prompting the melting of the paper components and triggers a chemical reaction to take place between the dye and the developer. This consequently leads to the formation of a coloured image on the paper (Lu *et al*., 2013).

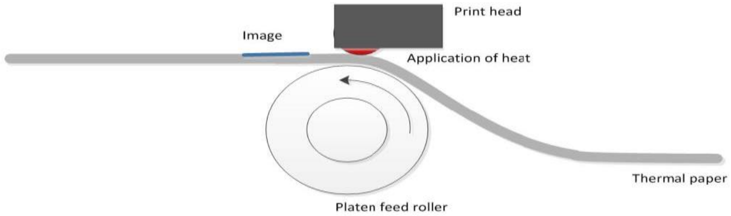


Figure 2.6: Overview of thermal printing process

The features of the thermal paper and the quality of the printer used should be well factored in to obtain ideal printing outcome. Diverse ranks of thermal paper have definite features which make them more relevant to agiven applications. One significant feature is dynamic sensitivity, which is the duration that the thermal paper gets in contact with the heat (Porass *et al*., 2014). The thermal paper has less contact with the heating elements if the printer runs faster. A higher dynamic sensitivity thermal paper is required while undertaking higher-speed or lower-energy printing. Using inadequate amount of heat on the thermal paper leads to less long-term stability of the finished product if a low dynamic sensitive thermal paper was used (Ndaw *et al*., 2016).

Static sensitivity is an additional crucial feature of the thermal paper. It refers to the temperature at which the thermal paper components are prompted to melt (Yalçin *et al*., 2016). Its value is core for the thermally-sensitive applications, namely environments with high temperatures (such as coffee cup labels and pizza boxes) or parking tickets (Rocha *et al*., 2015). The duration that the print job lasts depends on the varying degrees of thickness and sensitivities which are displayed by varied grades of thermal papers. A thermally printed image normally lasts for a period of five months if suitable thermal paper, suitable printer combination and appropriate storage conditions are considered (EFSA, 2013).

2.4.2.5 Benefits and short-comings of thermal printing technology

Thermal Printing Technology has the following benefits:

a. There are no additional inks or chemicals required for printing, paper is the only useable element. This makes the technology quite affordable,
b. Printing takes place fast (up to 406 mm per second),
c. The printers used for thermal printing have a limited number of detachable parts; this makes them reliable and fairly long-lasting,
d. The printers do not produce any sound during printing, they are lighter in weight and some are portable.

Nonetheless, the thermal printing technology has some short-comings which include the following:

a. Bisphenol A, which is the mostly used developer in thermal papers is purported to be an endocrine disrupter; this has increased alarm about exposure to BPA,
b. Substitutes to BPA also have shortcomings like harmful human health effects, ecotoxic, persistent to the environment with a potential to bio-accumulate,
c. The rolls of thermal paper are affected by heat, water, friction, exposure to chemicals and persistent sunlight hence reducing the half-life of the thermal papers.

There are techniques of improving the resilience of a thermal paper like improving the thickness of paper, top and back coating, choice of developer (Brunner *et al.,* 2013). The other alternative way is to replace thermal paper with an absolutely different technology.

2.4 Health risks related to Bisphenol A (BPA) exposure

BPA has a phenolic structure which enable it interrelate with estrogen receptors. It acts as agonist or antagonist via endocrine receptor (ER) reliant on signaling passageways (Ma and Sassoon, 2006).

Statistics from the experiments conducted on various animals demonstrate that exposure to BPA can also result into early puberty. The prenatal rats that were exposed to BPA compounds of 2 mg/kg body weight per day had an enhanced sexual maturity compared to the standard samples (Yasuyoshi *et al.,* 2004). Early puberty results from BPA exposure because of the feeble activity of the estrogen which kindles the GnRH pulse generator activity hence triggering the pituitary gland to secrete Lutenising hormone (LH) and Folicle Stimulating Hormone (FSH) (Paulose *et al.*, 2015). There are studies that have implicated BPA compound in the occurrence of breast cancer. The *in-vitro* investigates that were done have indicated that the introduction of BPA to human breast cell line heightened its spread and triggered an augmented oxidative pressure (Wetherill *et al.,* 2007). The mammographic mass of the breast tissue is also associated with the large amount of BPA serum in women who are past their menopause stage (Sprague *et al.,* 2013). It is also reported that the prevalence of breast cancer is associated with work-related exposure to BPA (Brophy *et al.,* 2012).

Different studies conducted have also linked BPA with the subsequent negative health conditions such as rise in obesity (Vom Saal *et al*., 2012), increased threat of diabetes mellitus type 2 (Mendum *et al.,* 2011), rise in the cases of heart related complications (Lang *et al*., 2008), threat of autoimmune diseases (Yurino *et al*., 2004), asthmatic conditions (Vaidya and Kulkanrni, 2012), adverse effects of BPA on the brain development to the foetus (Castro *et al*., 2013), hostile effects of prenatal exposure for behavior and immune disfunction (Roy *et al.,* 2012). BPA has also been allied to male sexual dysfunction (Li *et al*., 2010).

2.5 BPA acting as an Endocrine Disrupting Chemical (EDC)

EFSA defines an endocrine disrupting chemical as any non-natural or ordinary substance that shows endocrine action, leads to the occurrence of any hostile health effects and act as linkage between its endocrine activity and hostile effects (EFSA, 2013).

Bisphenol A has been proven to have a weak activity of the estrogen which may interfere with the effective functioning of the endocrine system (Cwiek-Ludwicka and Ludwicki, 2014). Majority of the international authorities have shown their distress on BPA exposure, particularly among sets of people with greater vulnerability to EDC.

BPA satisfies all the previously mentioned standards; therefore it is undeniable that it can be classified as an endocrine disrupting chemical (Anderson and Castle, 2003). The human exposure to BPA should be approximated by conducting varied tests on biological samples such as quantifying the BPA concentration in the body fluids such as breast milk, urine or blood (Brophy *et al.,* 2012).

2.6 The exposure of BPA to human beings in everyday life

BPA is extensively applied in day-to-day life. Consequently, there are different ways through which the human gets exposed to it. The various ways of exposure include oral, inhalation and transdermal (Beverly, 2011). The foremost substances that lead to human exposure to BPA include: thermal paper, articles for children and infants, dental materials, food packaging, dust, healthcare equipment and plastic toys (Beverly, 2011). Food packaging and products are the core sources of exposure to BPA; this contributes to the highest percentage as compared to the other sources (Geens *et al.*, 2012a). The chief source of BPA nutritional exposureare the canned foods. There is a high possibility of Bisphenol A being confirmed present in fresh foodstuffs like eggs, meat or milk once the animals feed in the contaminated regions or drink water polluted with BPA (Van Landuyt *et al.*, 2011).

BPA is mostly used to make the plastic containers that are used in preserving food and to prepare the linings of the jar lids. It tends to leach into the content of the can when the cans are being heated during purification or while cooking food hence increasing the possibility of BPA nutritional exposure (Cooper *et al.*, 2011). Studies have also shown that the sanitization of the tinned food causes the leaching of about eighty to a hundred percent of the non-conjugated BPA to the component inside the container. This may be dependent on the conditions under which the process occurs and the composition of the substance (Cabado *et al*., 2008). Studies conducted have also revealed that the foodstuffs which have low pH values and greater quantities of fat have higher concentrations of Bisphenol A. Heating or preparing of food using a microwave also has a possibility of enhancing the leaching of food stuff from the packaging material to its content. BPA could also leach into dust from laminate floorboards, epoxy resin glues, dyes and domestic electrical equipment (Mendum *et al*., 2011). A research was conducted to quantify the amount of Bisphenol A present in the dust samples; the study revealed that 95% of the fifty six samples analysed had a Bisphenol A concentration ranging between 0.0008 g to 0.001 g per gram of dust particle sample. Greater quantities of BPA were tested in dust from offices and laboratories, mostly due to the fact that they were furnished with enormous amount of furniture and electrical equipment. Domestic exposure of children and infants could be greater owing to the existence of products that contain BPA, which most frequently are being taken by the children orally and through inhalation from the contaminated air (Calafat *et al.*, 2007).

2.7 BPA migration from the packaging materials to the food products

It is seeming that there is an increase in the concern given to BPA notably from an escalation of the number of publications arising from BPA and its derivatives. Research has been conducted by many scholars involving the transfer of BPA compound and Bisphenol derivatives from the plastic packaging materials food products (contents) on different conditions such as increased temperatures. BPA compounds tend to transfer from the poorly packaged materials into the food products (Biles *et a*l., 1999). The Scientific Committee on Food (SCF), a European Commission regulatory body on the safety of food analysed thoroughly BPA at all phases that would be harmfull to humankind. Through their research, they have settled on a specific tolerable daily intake (TDI) of BPA as 0.01 mg kg^{-1} body mass/day. The TDI allowable values have been set within a range of 0.48-1.60 µm kg^{-1} body mass per day for adults and children, respectively. The other important aspect of BPA compound that has been regeulated is the specific migration limit. This refers to the maximum amount of BPA that can be allowed to move from the packaging material to the food content. SCF has also settled on BPA specific migration limit (SML) of 3 mg kg^{-1} body mass (EU, 1990).

2.8 Bisphenol derivatives

BPA has been associated with different health concerns as has been revealed by most studies. This has led to the search of BPA alternatives which can probably decrease the predominance of the diseases/ conditions previously mentioned. Some countries such as USA and Japan have stopped BPA usage and its products have been substituted with other BPA alternatives which include Bisphenol S (BPS) (Liao *et al.*, 2012).

2.9 The alternatives in use are alleged to be BPA-free

The BPA derivatives tha are currently in use and are alleged to be BPA- free iscussed below.

2.9.1 Bisphenol S

Bisphenol S (4,4-Sulfonyldiphenol) is a Bisphenol compound which is currently the main substitute of BPA in the thermal papers (Liao and Kannan, 2011). It is a carbon-based composite with the molecular formula $(HOC_6H_4)_2SO_2$. The compound has two phenol functional groups attached to the sulfonyl group as shown in Figure 2.8 below. The compound is normally applied for drying fast-drying epoxy resin bonding agents.

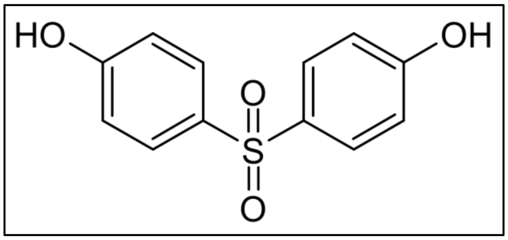


Figure 2.7: Structure of Bisphenol S (4,4-Sulfonyldiphenol)

BPA usage in viable goods is steadily being substituted with other Bisphenol derivatives which serve the same purpose as BPA. Such a derivative include Bisphenol S (BPS) (Fernandez *et al.*, 2007).

There has been substantial substitution of BPA with other Bisphenol derivatives by the manufacturers of BPA to match the statutory standards that have been set by the regulatory bodies (Chen *et al.*, 2002). Most of the producers of thermal papers have been reportedly replacing Bisphenol A with other compounds. For example, Japan which is one of the leading Bisphenol A producers started replacing BPA with BPS back in the year 2001 (Liao *et al.*, 2012). The European Commission reported that about 30% of the thermal papers have been undergoing recycling yearly. The recycling process has led to the following paper products: newspapers, napkins (facial tissue), advertisement brochures (flyers), mailing envelopes, tickets, toilet papers, serviettes and food packaging boxes (Vinggaard *et al.*, 2000). It is anticipated that the recycling of a BPS containing paper may result into the contamination of the new batch of paper that is produced after recycling (Gehring *et al.,* 2004).

There is no synchronized European Union grouping for Bisphenol S; conversely, manufacturing plants have reported the succeeding self-grouping in regards to CLP (Classification, Labeling and Packaging) standards (Liao *et al*., 2012).

Subsequently, there is inadequate research conducted (Chen *et al*., 2002 and Grignard *et al*., 2012) revealing endocrine disrupting properties of BPS. Chen *et al.* (2002) in their study revealed that acute noxiousness and estrogenicity was significantly minimal for Bisphenol S than BPA. Further studies were conduced by Grignard *et al*. (2012) which revealed the same estrogenic activity for BPA and Bisphenol S. It was proven that both of the two compounds (Bisphenol S together with BPA) act as anti-androgens which hinder androgenic hormones from taking up their biological effects on receptive matters) suggesting endocrine disrupting activities.

2.10.1.1 Environmental protection

An environmental transport appraisal was done on Bisphenol S and it was established based on the investigation and assessement of its physical and chemical features (Liao *et al*., 2012). In regard to this, Bisphenol S is predicted to partition in soil, it occurs in two forms: anionic and neutral forms at environmentally-relevant pH. It is more mobile in soil in its ionic form but exhibits less mobility in its neutral form. It doesn’t leach to the groundwater and it is not volatile from superficial water but occurs as a particulate matter in the air which can easily be inhaled. However, it can be eliminated from the air through wet or dry purging of the particulate matter.

2.10.1.2 Persistence of BPS in the environment

Liao et al. (2012) reported on the tenacity of BPS (Liao *et al.*, 2012). This is pinpointed on decrepitude tests that were conducted in anaerobic and aerobic conditions. It is reported that the studies which were conducted for about eight hours revealed that BPS reacts with atmospheric hydroxyl radicals with an anticipated half-life of 30 days in soil matrix (Liao *et al., 2012*).

2.10.1.3 Bio-concentration

Liao et al 2012 reported less BPS bioaccumulation (centered on two experimental bio concentration factors (BCF) which were noted to be lower than benchmarks cut-off points (Liao *et al., 2012*).

2.9.2 Bisphenol F (BPF) [Bis (4-hydroxyphenyl) methane]

The compound is a raw material that is used during the manufacture of epoxy resins and coatings (Rastkari *et al*., 2010). It is a trivial organic compound that bears a cyclic shape. It has a chemical formula $C_{13}H_{12}O_2$ and a chemical structure represented in Figure 2.8 below. It is a bisphenol derivative with two phenol groups connected via a linking group. They are mostly used in the systems that require an improved thickness and suppleness; especially in the high solid/high build schemes. The products that are manufactured using BPF as one of the raw materials include structural coatings, pipe linings, adhesives, industrial floors, tank and grouts and electrical varnishes (Rochester and Bolden, 2015).

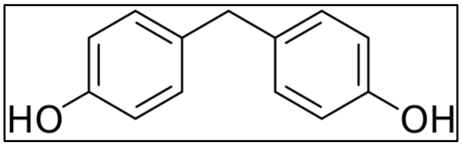
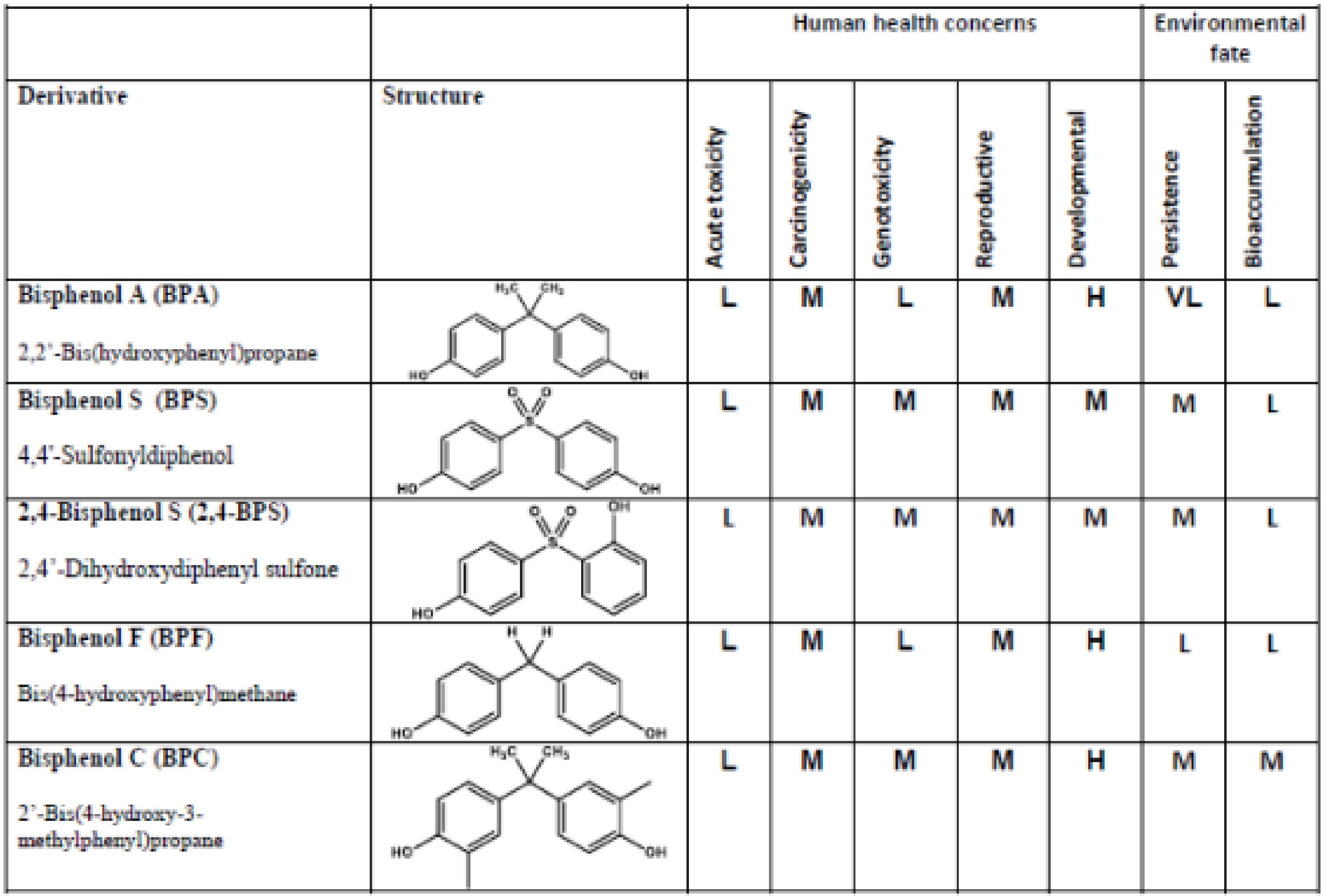


Figure 2.8: Structure of BPF [Bis (4-hydroxyphenyl) methane]

BPF epoxy resins are also applied in varied end user goods such as food packaging, water pipes, varnishes, liners, plastics, dental sealants, lacquers and adhesives (Rochester and Bolden, 2015). The two Bisphenol compounds i.e. BPS and BPF have been confirmed present in large amount in the products that are used in everyday life including; paper products like tickets, flyers, airplane boarding passes, mailing envelopes and currency) (Liao *et al*., 2012), foodstuffs like dairy products, canned foods, vegetables, cereals, meat and meat products (Liao and Kannan, 2013). It has also been detected in the personal care products such as hair care products, toothpaste, body make up, body wash and lotions) (Liao and Kannan, 2014). Research conducted have also confirmed the presence of BPS and BPF compounds in different environmental matrices such as sewage effluent, surface water and sediment at reduced concentrations compared to BPA, nonetheless in the same order of level (Rochester and Bolden, 2015). BPF and BPS compounds have also been confirmed present in human urine at concentrations and levels similar to BPA (Liao *et al*., 2012; Rochester and Bolden, 2015).

Report prepared by EPA on the evaluation of BPA and its derivatives indicated that the substituents of BPA have not exclusively resolved the complications related to BPA as some of the substitutes have allegedly done worse than the BPA (EFSA, 2013).

Table 2.2 Selected Bisphenol derivatives and their hazardous nature on human health and the environment**.**



		Human health concerns					Environmental fate	
Derivative	**Structure**	Acute toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Persistence	Bioaccumulation
Bisphenol A (BPA) 2,2'-Bis(hydroxyphenyl)propane		L	M	L	M	H	VL	L
Bisphenol S (BPS) 4,4'-Sulfonyldiphenol		L	M	M	M	M	M	L
2,4-Bisphenol S (2,4-BPS) 2,4'-Dihydroxydiphenyl sulfone		L	M	M	M	M	M	L
Bisphenol F (BPF) Bis(4-hydroxyphenyl)methane		L	M	L	M	H	L	L
Bisphenol C (BPC) 2'-Bis(4-hydroxy-3-methylphenyl)propane		L	M	M	M	H	M	M

Table showing selected Bisphenol derivatives and their hazardous nature on the human health and to the environment.

KEY: VL=Very Low, L=Low, M=Moderate, H=High, VH=Very High Hazards.

(Source; EFSA, 2013)

2.10 Review on the Analytical Techniques used for BPA determination.

The two major techniques that have intensely been used to analysise Bisphenol A in diverse compartments include High performance liquid chromatography (HPLC), electrochemical methods of analysis and Gas Chromatography (GC). However, the choice of the most appropriate analytical technique is not easy due to the low concentration and polarity of the compounds. The studies that have been conducted to analysise bisphenol A and bisphenol derivatives demonstrates three foremost methods. These include solid-phase micro-extraction (SPME) (Moeder *et al.*, 2000), solid-phase extraction (SPE) (Zafra *et al.*, 2002) and liquid–liquid extraction (LLE) (Del-

Olmo *et al*., 1997). These have commonly been used for the isolation and quantification of the compounds. The most commonly used analytical technique is Liquid–liquid extraction because the method is easy to undertake. However, Solid-phase extraction (SPE), has recently been much considered for use because it involves an easy sample preparation method and the process does not take much period of time. It can be done by the extraction columns which are available in the market. Another technique that has has been mostly used to analyse bisphenol A is the Solid-phase micro-extraction (SPME). Solvents are not needed in this method and small amounts of matrix are needed for determinations as compared to the other techniques like SPE. Once the isolation of the compound is done, high-performance liquid chromatography (HPLC) has been extensively used to analyse the extracts. It has been coupled with varied detecting agents like UV, fluorescence, MS etc. Other techniques that are also applied in the analysis of BPA and its derivatives include GC coupled with Mass spectrometer detector, micellar electrokinetic chromatography (MEKC) (Takeda *et al*., 2002) and electrochemical methods (Lin *et al*., 2006). HPLC has been extensively used for the quantification of BPA in varied matrices like water (drinking, sea, surface and underground water) (Pacakova *et al*., 2009). BPA has also been determined from the food products that are kept in plastic packagings made from the polycarbonates and food products store in infant plastic feeding bottles, foodstuffs or food simulants (García & Losada, 2004), solid samples (Patrolecco *et al*., 2004), human body sample like urine (Lakind and Naiman, 2008), human breast milk (Sun *et al*., 2004), sterilized medical devices (Downs *et al*., 2010), fish tissue (Pedersen and Lindholst, 1999).

2.10.1 High Perfomance Liquid Chromatography (HPLC)

2.10.1.1 Working principle

This analytical technique is fundamentally an enhanced method of column liquid chromatography. In it, the mobile phase is passed through the column under intense pressures of up to 400 atmospheres in place of being endorsed to drip through a column under gravity as applies to some chromatographic techniques. This hastens the separation process. The sample separation into its respective components occur due to the variations in the relative affinities of diverse particles for the mobile and the stationary phase that are used to aid in the separation process (LoBrutto *et al.*, 2008).

2.10.1.2 Advantages

HPLC is more superior as compared to some other chromatographic techniques like Thin Layer Chromatograph. It is very quick and more effective. It is a technique which makes use of a pump instead of gravity aid in forcing a liquid solvent via solid adsorbent material, with diverse chemical constituents separating out as they travel at varied speeds (LoBrutto *et al*., 2008). The procedure takes a shorter period of time to take place i.e. about 10-30 minutes and it provides high resolution. It is precise and produces vastly reproducible results (Kamal-Eldin *et al.*, 2000). Operation of HPLC can be done with insignificant training because it is mainly automated.

2.11.1.3 Disadvantages

HPLC has the following disadvantages: it may show uncommon peak shapes, it lacks high sensitivity as compared to GC (Araki & Sako, 1987), it shows poor sample recovery technique, it exhibits pressure problems, changes in retention times could be caused by late elution of analytes from a previous run (Hughes *et al*., 2007).

2.10.2 Gas Chromatography

2.10.2.1 Working principle

The basis of separation of elements is dependent on the delay of the separable constituents as they are carried along the stationary phase (column) by the carrier gas which in most cases are helium or nitrogen gas. The column comprises of a glass or steel tube packed with an inactive stuffing substance like ceramic beads or glass. The stuffing substances are concealed with an in unsteady liquid to increase the surface area of the liquid that interacting with the gas in gas-liquid chromatography (GLC). Some of the techniques have a solid packing which are not covered by any liquid, these are known as Gas-solid chromatography (Kupiec, 2004). An injection of the sample is done into the carrier gas stream. The particles of respective element that are found within the sample gets distributed between the gas and the liquid as the sample is carried along the column with the carrier gas (Fatemi *et al*., 2014). Specific particles will continuously get distributed between the gas and the liquid in a dynamic equilibrium. The molecules of a more volatile element elute faster through the column, gets separated and finally appear after different periods of time. Retention time (Rt) describes the amount of time taken from sample injection to appearance. It is unique for individual elements operating under different established settings. It is determined by the element volatility, column length, diameter and temperature. Different types of detectors are used based on the nature of substances being separated (AL-Bukhaiti *et al*., 2017).

2.11.2.2 Advantages

GC has the following advantages:

i. It has a good resolution due to its high-pitched and regular peaks.
ii. Produces high repeatable and reproducable retention times
iii. Shows very precise and accurate compound concentrations which are dependable on the peak areas.
iv. GC performs both qualitative and quantitative analyses, hence can be used to determine the presence of an impurity in a given compound.
v. GC has very high sensitivity and can therefore be used to determine and quantify very trace elements.
vi. Results to minimal desruction of the subtle sample constituents (Kupiec, 2004). The use of fused-silica capillary columns with improved surface inertness, thermal stability and resolution highly accomplishes majority of these necessities. The purity of the carrier gas used can also influence the GC resolution (AL-Bukhaiti *et al*., 2017).

2.11.2.3 Disadvantages

On the other hand, GC has the following shortcomings:

i. It is only limited to the separation of volatile samples or the sample which can be volatilized (Shellie *et al*., 2001),
ii. A lot of keenness is key while injecting gaseous samples (Pantsar-Kallio and Korpela, 2000),
iii. The gaseous sample injected has to be thermally stable to avoid its degradation during heating (Carabias-Martınez *et al*., 2003).

2.10.3 Electrochemical methods of analysis

2.10.3.1 Chemical sensors used for BPA detection

These are an important category of sensors which have been applied widely in medical diagnosis, process control, environmental and food analysis (Rodriguez-Mozaz *et al*., 2004). These kinds of sensors provide a way of altering chemical information from the definite sample concentration to total configuration analysis to produce a crucial analytical signal. The section discussed below will encompass the varied chemical-sensing systems that have been invented for the analysis of BPA.

2.10.3.1.1 Electrochemical sensors

These are composed of electrochemical transducers (chemically-modified electrode) glazed with asubstances or chemical films which function as conductors (Rodriguez-Mozaz *et al*., 2004). These sensors are extensively recognized, are simple to use and exhibit high sensitivity. BPA is a molecule that is electrochemically-active because of the phenolic groups. However, its direct determination is not so easy to accomplish due to its weak response in conventional electrochemical sensors (Zhu *et al*., 2014). Varied kinds of electrochemical sensors with radical constituents improve the electrode's surface area improving on the oxidation signals.

2.10.3.1.2 Molecularly-imprinted polymer sensors (MIPS)

These are artificial substances that assist as recognition components to design sensors. They are widely used because of higher thermal stability, reusable and highly selectivity when matched to other organic receptive cells. They tend to fix to the specific elements subject to their functionality, shape and charge resulting into differences in their physical quantities like absorbance, mass or refractive index (Avila *et al*., 2008). Their specific nature against BPA is determined by the synthesis method and the choice of monomers. The BPA binding to MIPs is a chemisorption process which entails the establishment of 2 hydrogen bonds amid 4-vinylpyridine and BPA in the embossed openings. The extent of BPA binding to varied categories of MIPs, which consequently leads to advanced-sensitive detection of BPA (Yang *et al*., 2015). These sensors are used together with nano-particles to assist in enhancing the specificity and sensitivity of the analyte since the nano-particles exhibit large surface area (Ragavan *et al*., 2013). Synthesis of MIPs was done via polymerization of 4-vinylpyridine (functional monomer) by means of ethylene glycol dimethacrylate as a cross-linker and glazed on the gold-glared glassy-carbon electrode surface (GCE) (Zhang *et al*, 2013). The sensor used for synthesis was established to have high selectivity towards bisphenol A and cyclic voltammetry was used to test the electrochemical reaction (Zhang *et al*, 2013). Likewise, a gold-nano particle-modified GCE was used to insert 2-aminothiophenol using bisphenol A as the model (Huang *et al*., 2011). BPA oxidation was evaluated through linking it to the peak current. Studies conducted by Apodaca and coworkers confirmed that electro-polymerized MIPs can be used in the determination of bisphenol A using electrochemical-impedance spectroscopy method (Apodaca *et al*., 2011). A potentiometric sensing device was established by the use of bisphenol A-imprinted polymers acting as the receptive cells glazed on the electrode surface to enhance specificity and sensitivity on BPA determination (Ragavan *et al.*, 2013). Ragavan et al in his study noted that Chitosan produces a better slurry with good mechanical force and proper adhesion. Chitosan is therefore used together with MIPs to manufacture electrochemical sensors (Ragavan *et al.*, 2013). Similarly, Acetylene-black electrodes have better electrical conductivity, large surface area and adsorptive qualities which make them possible to be applied in place of GCEs for BPA determination (Deng *et al.*, 2013). Liu in his study prepared a photo-electrochemical sensing device using tin dioxide nanotubes and polypyrrole MIPs applied on the surface of electrode (Liu *et al.*, 2014b). The designed sensing device had a limit of detection in the nano-molar series with a capability of overcoming the side-effects of the un-original electrodes. Lately, a sensor was established by Dadkhah and coworkers which contains a MIP which is rich in amine with the core-shell covered with gold nanoparticle to be used as a substrate to undertake surface-enhanced Raman scattering (SERS) for bisphenol A determination (Dadkhah *et al.*, 2016). Signals were produced by Bound and unbound MIPs, which had a linear relation to varied BPA concentrations.

2.10.3.1.3 Carbon-nanotube (CNT) sensors

These have been widely studied due to their crucial physical properties like better chemical and thermal stability, higher aspect ratios, larger surface area, better electronic and optical qualities that aid in the fabrication of the electrochemical sensors. CTNs are continuously being used as transducer elements due to the crucial qualities that they possess, more so as nanoscale electrodes being used as amperometric sensors for design of the electrochemical sensors (Beitollahi and Tajiki, 2015). The usage of carbon-nanotubes on a Glassy-carbon electrode considerably increases the oxidation rate of bisphenol A because of their fundamentally high surface area. A carbon nanotube with more than one wall coupled with gold nanoparticle hybrid layer glazed on a glassy carbon electrode has been applied for bisphenol A determination in the micro-molar limit (Shahrokhian *et al.*, 2012). The carbon nanotubes with single-walled were strongly bonded with b-cyclodextrin to increase on the action of the amperometric sensing device. The designed sensing device was more sensitive in nanomolar series (Sun *et al.*, 2012). Fullerene (C60) is a nano-material that is comparable to carbon nanotube with qualities like good electron conduction, large electroactive surface area and bio-compatibility. This was also applied in the designing of an electrochemical sensing device. The sensing device plat-form highly improved the detection with a limit of detection of 3.7nM. This was attributed to the kinematic properties of carbon nano tubes like electrode-surface area, diffusion and charge-transfer coefficient (Wang *et al*., 2013). CNTs have notably increased the action of electrochemical sensors with respect to sensitivity, speed, electrochemical reactivity, lowering anodic over potential and electron-transfer efficiency.

2.10.3.1.4 Graphene-based sensing devices

Graphene is an important nano-material with 2-dimensional films of SP_2-hybridized carbon (Kuila *et al*., 2011). It is used for sensing because of the better qualities that it exhibits such as higher electrical conductivity, possibility of surface functionalization, large surface area and fluorescence quenching (He *et al*., 2012). A graphene-modified glassy carbon electrode was created and established using potassium ferricyanide to have a limit of detection in the sub-micromolar series (Ntsendwana *et al*., 2012). Equally, exfoliated graphene glazed on the surface of an electrode was established and used the for the determination of BPA (Idris , 2016). Nitrogen-doped graphene displays excemplary electron-transfer ability and electro-catalytic qualities better than unmodified graphene (Zaidi, 2017). Nitrogen-added to the graphene sheets coupled together with a chitosan-based electrochemical sensing device was applied for determination of BPA in water samples and a limit of detection of 5 Nm was obtained (Zaidi, 2017). A graphene-carbon nano tube nano-composite that was made using easy, environmental-friendly means was used together with platinum nanoparticles to prepare an electrochemical sensing device which was used to quantify the amount of bisphenol A in the thermal papers (Zhu *et al*., 2015). The glassy carbon electrode effective surface area was improved 1.7 times better than bare electrode upon the glazing of a compound of graphene nanofibers and gold NPs on the surface of electrode. The compound participated in the electro-catalysis, which considerably decreased the oxidation over-potential of bisphenol A and enhanced the oxidation peak current for the quantification of bisphenol A (Zhu *et al*., 2015).

2.10.3.1.5 Quantum-dot-based sensors (QDs)

These are nano-scale semiconductor configurations with luminous qualities. They are one of the best sensors that can be used for nano probes fabrication since they exhibit better fluorescence quantum yields than dyes, more stable against photo-bleaching and their size-control which leads to better fluorescence (Verma *et al*., 2011). An amperometric sensor consisting of a GCE restrained with cobalt-tellurium quantum based sensors and covered with polyamidoamine (PAMAM) dendrimer were used to determine bisphenol A in water samples (Li *et al*., 2012). Likewise, an improved conductivity of the solution was noted and this was linked to PAMAM dendrimers and led to the formation of better signal peaks (Li *et al*., 2012).

2.10.3.1.6 Nanocomposites

These are gradually being applied in formulating electrochemical sensors because they possess shared qualities of polymers and nano-materials. Such qualities like large surface area arise from the divided configuration of the polymers and exhibit better bio-compatibility which improves the oxidation rates of BPA (Yu *et al*., 2011). An amperometric sensor was designed using a polyamidoamine–Fe_3O_4-made electrode. This largely decreased the oxidation over-potential leading to determination of bisphenol A at a level of 5 nM (Yu *et al*., 2011). Likewise, a chitosan–Fe_3O_4 nanocomposite was applied in the designing of an amperometric sensing device for the determination of bisphenol A due to its desired qualities like superior-paramagnetism of Fe_3O_4. Chitosan is a poly-aminosaccharide that offers steady consistent suspension of nanoparticles because of their chemical configuration during sensor designing (Yu *et al*., 2011). An electrochemical-printed sensing device was designed by electrochemical glazing of more than one wall carbon nanotubes and gold-nano particles on the gold electrode surface. Saturated molecularly-imprinted polymer sensing device improved the signals and led to careful sensitivity on the determination of bisphenol A (Hua *et al*., 2014). Similarly, the polyamidoamine dendrimers and a gold nanoparticles-silk fibronin compound were applied in the modification of the electrode. The heightened bisphenol A oxidation peak current was caused by the conductive and catalytic property of the gold nanoparticles together with enhanced conductivity and adsorption capacity of positively-charged polyamidoamine (Yin *et al*., 2010). A microfluidic chip-based sensing device was developed to determine endocrine disrupting compounds such as BPA (Liu *et al*., 2014a). This is an enhanced form of the electrochemical-detecting scheme which connects pre-concentration of a sample with a micellar electro-kinetic separation system. In this form of a sensor, a cellulose-dsDNA/ gold nanoparticle-designed carbon-paste electrodes were applied. This aided the quantification of bisphenol A in water at femto-molar range. The nanoparticles increased the seeming movement of the solutes because of an enhanced collaboration sites on the surface which caused an improved characterization and determination of endocrine disrupting compounds. Lately, an electrochemical sensing device was designed by the use of a reduced graphene oxide linked to magnetic nanoparticles. Graphene nano-composite produced better chemical sensors because of their chemical and physical features like surface modification, geometric symmetry and electrical conductivity; these have been studied further to help in coming up with the ultrasensitive assays.

2.10.3.1.7 Chemiluminescence-based sensors

Chemiluminescence process involves the production of light rays resulting from an occurrence of a chemical reaction. In this method, a chemical species gets excited to a higher energy state and extemporaneously emits light when it gets back to its neutral (ground) state. It is acknowledged as a better and an essential method in molecule analysis due to its simple instrumentation, high sensitivity and a notable rectilinear reaction up to a definite level. A flow-injection chemiluminescence-inhibition technique was used to determine bishenol A in water samples. This was achieved via the use of potassium hexacyanoferrate and luminol. It can be prompted through the passage of electric current in place of oxidation. Determination of BPA was done through an electro-chemiluminescence process. This technique is easier to perform than chemiluminescence since small amounts of reagents are needed for analysis and its reaction can be simply examined closely and managed effectively (Akiyoshi and Suzuki, 2007). It was established that silver NPs can be used to improve chemiluminescence method of luminol and that it can effectively be applied in quantifying the amount of bisphenol A in water samples (Ragavan *et al.*, 2013). The LOD 1 ng/L was calculated and the technique was established to be appropriate for a prompt analysis that is mostly required to be done at the point of sample collection (Ragavan *et al.*, 2013).

2.10.4 Biosensors used for the detection of BPA

These are chemical sensing devices which have been modified and uses biological substances as a detection component. The biosensor refers to as a means that relies on the biochemical responses controlled by specific tissues, organelles, microbes, enzymes, immunosystems or whole body cells to identify a compound commonly by thermal, electrical or optical signals (Thakur and Ragavan, 2013)

2.11 Choice of the analytical technique

The choice of the analytical technique used for the research was mainly determined by the availabilty of the instrument and the fact that GC/MS is very sensitive and can be able to detect very trace elements as compared to other analytical techniques. GC/MS was also used for the study since it can be used to do both qualitative and quantitative analyses.

CHAPTER THREE

3. MATERIAL AND METHODS

3.1 The Study area

The study was conducted in Nairobi County, which is the capital city of Kenya. The commercial banks and supermarkets were located within the CBD of Nairobi County. This was due to the fact that the area comprises of a good number of commercial banks and supermarkets which generate thermal papers as one of their waste products. The thermal papers were the core samples to be used while conducting the resesarch. The same kind of commercial activities could be taking place within the same area and hence concentration of BPA in the thermal papers would not vary greatly. The soil sampling points were determined by the following factors. Dandora dumpsite serves the whole County and therefore there were possibilities of dumping BPA containing products in the site. Since BPA tend to leach from these products to the soil, there was need to quantify BPA in the soil samples collected from Dandora dumpsite. The dumpsite acts as a source of livelihood to some netizens such as collection of metallic substances for sale, collection of cartons for resale, collection of plastic bottles for resale and some netizens get to the extent of using disposed off food products in the dumpsite as their food stuff. It was also noted that there were domestic animals like goats, pigs and cows which feed from the dumpsite wastes and drink the dumpsite water seepages. These observation highlighted the basis of determining the level of BPA contamination on the dumpsite soil. On the other hand, TUK- garden was selected as a soil sampling site because there was need to compare the concentration of BPA in a soil sample found within a locality without BPA containing materials like thermal papers, plastic bottles etc but found within almost the same locality as the thermal papers sampling sites.

The sampling sites were confined within the boundaries of University Way, River Road, Haile Selassie Avenue and Uhuru Highway within CBD area (Figure 3.1). The soil samples were also collected from the Technical University of Kenya (TUK) garden (Figure 3.1) and Dandora dumpsite (Figure 3.2).

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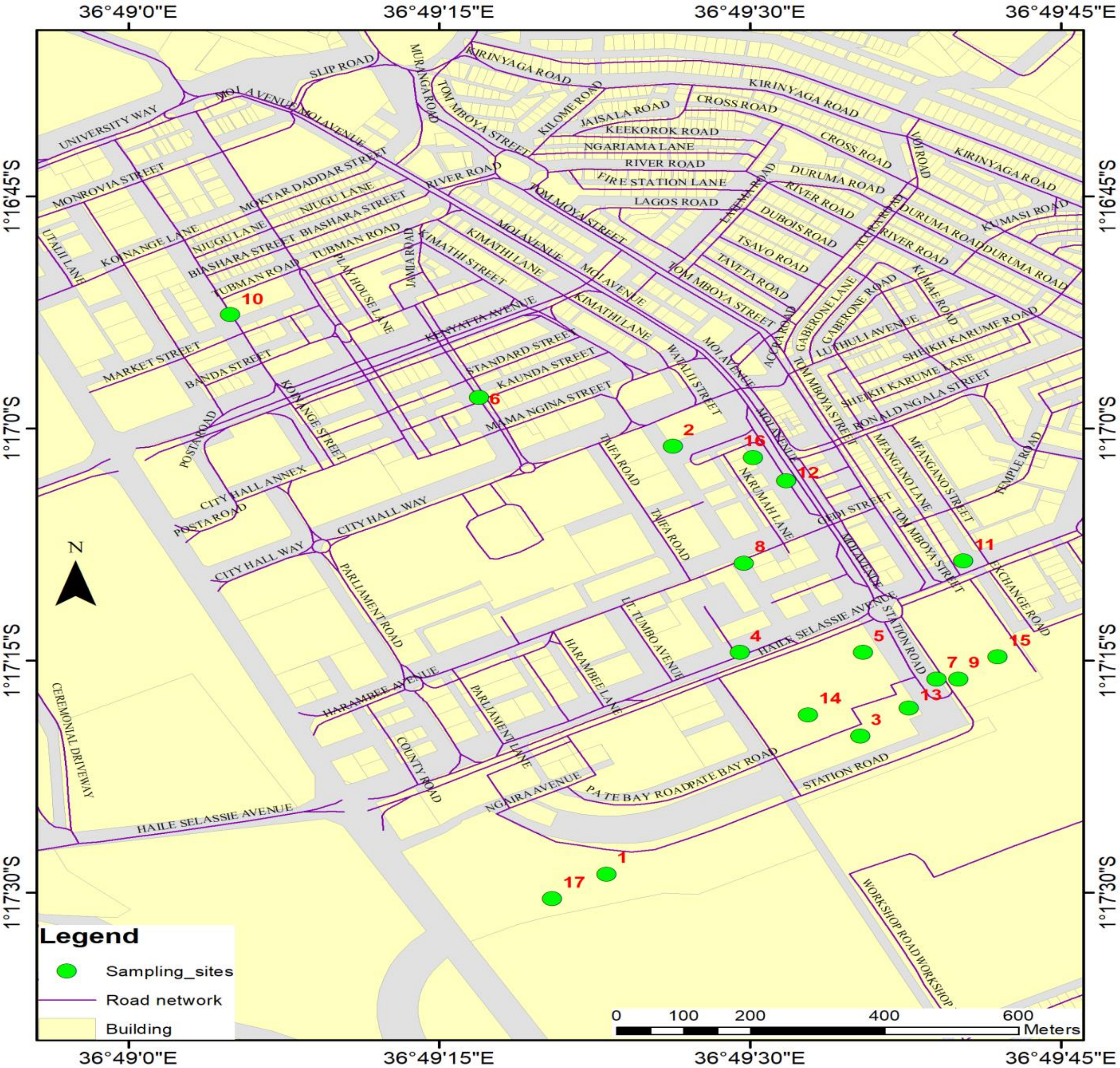

Figure 3.1: sampling site for the thermal papers and soil samples within the CBD area, Nairobi County

The selected sampling sites were four commercial banks and each had more than one branch and Automated Teller Machine (ATM) Lobby points (Figure 3.1). The commercial banks included: Barclays, Kenya Commercial, Cooperative and Equity banks (Table 3.1). The study area also had supermarkets and grocery stores which included Nakumat

Holdings, Tuskys, Ukwala, Naivas, Uchumi Supermarkets and some retail shops (Table 3.1). Each of these stores had more than one outlet in the study area except for the Uchumi supermarket and each had thermal overhead receipt printers. Unused thermal paper sample were also considered for the study, together with non-thermal paper.

Table 3.1: Sampling sites for the thermal papers samples within the CBD of Nairobi City

Site No.	Sampling site	Coordinates	Economic activities taking place at the sampling point
1	Commercial bank 1	1° 17' 28.835" S 36° 49' 23.095" E	Public transportation, banking, wholesaling and retailing services
2	Commercial bank 2	1° 17' 1.169" S 36° 49' 26.289" E	Public transportation, banking, wholesaling and retailing services
3	Commercial bank 3	1° 17' 19.907" S 36° 49' 35.335" E	Public transportation, banking, wholesaling and retailing services
4	Commercial bank 4	1° 17' 14.492" S 36° 49' 29.536" E	Public transportation, banking, wholesaling and retailing services
5	Commercial bank 5	1° 17' 14.492" S 36° 49' 35.465" E	Public transportation, banking, wholesaling and retailing services
6	Commercial bank 6	1° 16' 58.005" S 36° 49' 16.925" E	Public transportation, banking, wholesaling and retailing services
7	Commercial bank 7	1° 17' 16.210" S 36° 49' 39.022" E	Public transportation, banking, wholesaling and retailing services
8	Commercial bank 8	1° 17' 8.718" S 36° 49' 29.726" E	Public transportation, banking, wholesaling and retailing services
9	Commercial bank 9	1° 17' 16.210" S 36° 49' 40.073" E	Public transportation, banking, wholesaling and retailing services
10	Supermarket 1	1° 16' 52.644" S 36° 49' 4.919" E	Public transportation, banking, wholesaling and retailing services
11	Supermarket 2	1° 17' 8.577" S 36° 49' 40.310" E	Public transportation, banking, wholesaling and retailing services
12	Supermarket 3	1° 17' 3.397" S 36° 49' 31.760" E	Public transportation, banking, wholesaling and retailing services
13	Supermarket 4	1° 17' 18.074" S 36° 49' 37.679" E	Public transportation, banking, wholesaling and retailing services
14	Supermarket 5	1° 17' 18.524" S 36° 49' 32.822" E	Public transportation, banking, wholesaling and retailing services
15	Supermarket 6	1° 17' 14.773" S 36° 49' 41.966" E	Public transportation, banking, wholesaling and retailing services
16	Supermarket 7	1° 17' 1.885" S 36° 49' 30.155" E	Public transportation, banking, wholesaling and retailing services
17	TUK-Garden soil sample	1° 17' 30.420" S 36° 49' 20.460" E	Teaching, printing and photocoping activities

(***The real names of commercial banks and supermarkets are not disclosed due to legal implications***)

The soil samples were collected from Dandora Dumpsite that serves the greater part of Nairobi County (Figure 3.2). The dumpsite is located North-East of Nairobi City in a densely populated low income residential area. Nairobi County has one authorised garbage disposal site that is owned and operated by the County government. It is situated in

Dandora, Eastland, about 7.5 km from the city Centre, where about 30 per cent of the wastes collected are dumped.

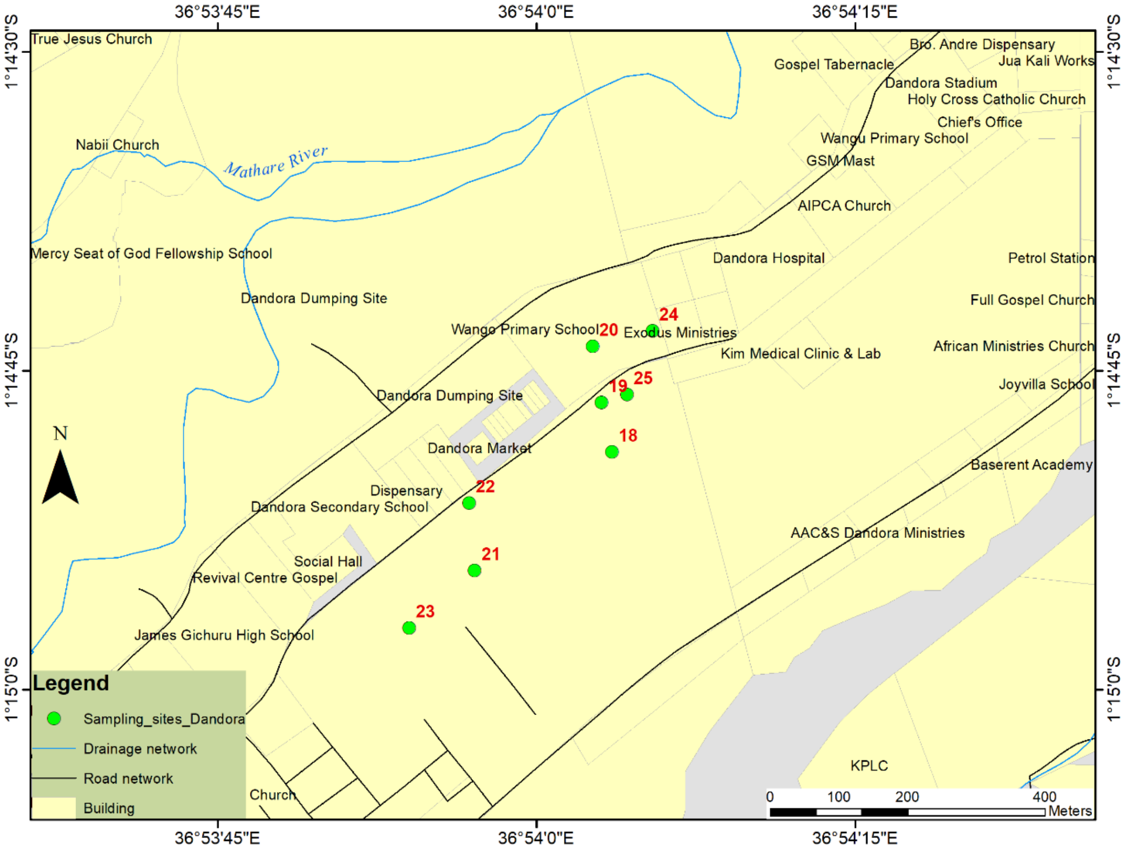

Figure 3.2: The sampling sites for soil samples from Dandora dumpsite, Nairobi County

Dandora dumpsite was selected as a primary receiving point of thermal papers from all commercial activities (Table 3.2). The control soil samples were collected from Technical University of Kenya (TUK) garden (Table 3.1).

Table 3.2: The sampling sites for soil at Dandora dumpsite, Nairobi County

Sampling site	Coordinates	Altitude (m)	Activity at the sampling site	Soil
18	01°14’814" S 036°54’059" E	1605	Grazing area and paper deposits, old dumpsite	Fine red soil with small rock particles
19	01°14’775" S 036°54’051" E	1602	Grazing area and paper deposit, old dumpsite	Slightly dark brown soil, few small rock particles
20	01°14’731" S 036°54’044" E	1601	Grazing area and paper deposits, old dumpsite	Slightly dark fine soil, few stones
21	01°14’916" S 036°54’928" E	1612	Grazing area and paper deposits, current dumpsite	Slightly dark brown soil, more rock particles
22	01°14’854" S 036°53’947" E	1611	Open field, pieces of metal, feeding ground for birds, stagnant water, current dumpsite	Black fine soil with root fibers, no rock particles
23	01°14’952" S 036°53’900" E	1614	Stagnant water, pathways for waste trucks, metal pieces, the feeding ground for birds, current dumpsite	Light brown soil with slightly more rock particles
24	01°14’719" S 036°54’091" E	1599	Plastic and paper, pigs, goats, birds and dogs feeding, sorting of wastes, water for domestic use, most active dumpsite	Fine black soil, no rock particles
25	01°14’769" S 036°54’071" E	1598	Plastic and paper wastes, waste sorting out, pigs, goats, birds and dogs feeding, water for domestic use, most active dumpsite	Black soil with small rock particles, slightly course soil particles

3.2 Samples collection

3.2.1 Thermal paper sampling

Thermal receipt paper samples were collected from four major banks within the CBD. Thermal papers were also collected from four leading supermarkets (Figure 3.1). The thermal paper samples were collected from the bins used by various commercial banks and supermarkets to collect the used receipts from their customers.

Sample collection was done after acquisition of permission from the relevant authorities from each site. Two branches were considered for each bank and store (Table 3.1). Each set of thermal paper sample was packed in its own sterilized polypropylene bag to avoid chances of cross-contamination, labeled based on the name and branch of the bank/supermarket from where they were collected. 10 thermal paper samples were collected from each collection point, packed, labeled, placed in cool box and transported to the laboratory for analysis. The pictorial representation of the thermal papers collected from the selected commercial banks and supermarkets are shown in appendix 3.1a-31d and 3.2a-3.2e.

In the laboratory, the thermal paper samples were stored at room temperature away from ultra violet light until analysis was done. Thermal paper samples collected for analysis were coded depending on the name of the bank/ supermarket and the branch. For comparison, ordinary used and un-used printing papers (i.e., regular photocopying paper) were also obtained and analyzed.

3.2.2 Soil sampling

Soil samples that were used for this study were collected from Dandora Dumpsite (Phase 6), located in the outskirts of Nairobi City (Figure 3.2). 100 g of soil was dug using hoe and scooped using a pre-cleaned stainless steel shovel down to the depth of 15-30 cm from three different spots within the site with same GIS points (Table 3.2). The three different samples were thoroughly mixed to form a composite sample. 200 g of the soil sample was taken and wrapped in a piece of aluminum foil and kept in zip-lock polythene bag, labeled, packed in cool-box and transported to the laboratory and kept at a temperature of 4 °C waiting analysis. For each site a composite sample was analysed in triplicates.

Eight soil samples were collected from different location from the old, most recent and from active dumpsites (Table 3.2). The Dandora sampling site covered a latitude from 01°14’719’’ S to 01°14’592’’ S and longitude 036°54.091E" to 036°53.900E". The soil collection sites were identified as Sites 18, 19 and 20 representing the old dumpsite which had not been active for about 5 years. Sites 21, 22 and 23 represented the current dumpsite which started its operations in 2015, while Sites 24 and 25 represent the most active dumpsite being used for deposition and collection of wastes at the time of the sample collection. The pictorial representation of the old, current and active dumpsites where the soil samples were collected from Dandora are shown in Appendix 3.3a-3.3d.

3.3 Chemicals, reagents and apparatus

3.3.1 Apparatus and instruments

The apparatus used for sample preparation included test tubes, mercury thermometer, water bath, digital weighing balance, aluminum foil, 10 ml pipette, rotary evaporator, Soxhlet extractor, spatula, 100 ml volumetric flasks, retort stands, 50 ml volumetric flask, 15 ml glass vials, wash bottles, timer, oven, labels, mortar & pestle, 2 mm soil sieve, shaker, GC-MS and GC/MS-accessories.

3.3.2 Reagents

The reagents used included acetone- Analar grade, distilled water and anhydrous sodium sulphate. The consumables were supplied by Kobian Kenya Limited, Nairobi Kenya. Pure BPA standard with a purity of 99% used for this study was purchased from Associated Chemical Enterprises (Pty) Ltd (ACE Chemicals), located in Johannesburge, South Africa. This pure standard remained a core reagent in the entire project.

3.3.3 Stock and working standard solutions

1000 mg/L of BPA standard stock solution was prepared by dissolving 0.01g of the BPA standard in 10 ml of acetone solvent-analar grade. The working standard solutions were prepared from the 100 mg/L standard solution that had been initially prepared from 1000 mg/L stock solution using the dilution formula $C_1V_1 = C_2V_2$. (C_1 and V_1 represent the concentration and volume of the stock standard respectively while C_2 and V_2 represent the concentration and volume of the working standard, respectively).

3.3.3.1 Preparation of secondary standard solutions.

Appropriate portions of 100 mg/L standard solution were diluted to 20 ml mark to make, 20.00, 10.00, 5.00, 2.50, 1.25 ppm and 0.63 mg/L standard solutions of the BPA. Calibration blank was 20 ml of acetone solution (solvent used for sample extraction) without any piece of thermal paper dissolved in it.

3.4 Measuring soil pH

An aliquot of 30 ml of the deionized water was added to 20 g of representative soil sample, that had been ground and sieved through 2 mm mesh. The mixture was shaken in a level shaker for 10 minutes at a speed of a hundred revolutions per second and allowed to stand for 1 hour. An aliquot of 10 grams of the paste sample was afterwards taken and mixed in a small beaker with 25 milliliters of 1 M potassium chloride solution (74.56 g/litre). The mixture was allowed to stand for 1 hour before measuring its pH using HANNA pH 211 Microprocessor pH meter.

3.5 Soil analysis using XRF

Soil samples were removed from the refrigerator and allowed to defrost for about 4 hours prior to extraction. The soil samples were dried using an hydrous sodium sulphate, they were then ground finely using mortar and piston and the particle size was homogenized and sieved through a 2 mm mesh. Each composite soil sample was placed in a shaker and homogenised well for a period of one hour. Each of the homogenised soil sample was analysed in triplicates. The soil samples were then analyzed using Hand held XRF by Bruker (MODEL: S1TITAN 600) in order to determine the various metallic components. The soil samples were ground and sieved through 2 mm. The metal content was measured directly using XRF.

3.6 Thermal paper sample extraction for GC-MS analysis

The thermal papers were shredded into small pieces using acetone sterilized scissors in order to facilitate ease of handling and rapid dissolution of BPA in acetone. An aliquot of 50 mg of shredded thermal paper samples were transferred into a clean 20 ml boiling tube and 10 ml of acetone was added to the sample. The sample was immersed in a water bath maintained at a temperature of 35 °C for a period of 1 hour. The sample extract was then decanted into a clean test tube and the paper residues washed twice using 5 ml of acetone. The supernatant used for washing the paper residues were decanted and mixed with the extracts, the aliquots of acetone were concentrated to 10 mL under a gentle stream of nitrogen gas. One milliliter of the aliquot was transferred into a vial and analyzed by Gas chromatography with an Mass Selective detector. Different concentrations of BPA standards were prepared for GC/MS analysis with the highest standard concentration being 10 mg/L; followed by 7.0 mg/L, 2.0 mg/L, 1.0 mg/L and 0.5 mg/L. A calibration curve was prepare and used for quantification of BPA in the samples.

3.6.1 Analysis and Quantification of the thermal paper sample extracts using GC-MS

Analysis and identification of BPA was done using AGILENT 6890N series Gas Chromatography equipped with Agilent 5973 series MS detector, coupled with Agilent Technologies 7683 auto-injector. The column used was DB-5 MS silica fused high performance capillary column, (length of 30 m, internal diameter of 0.25 mm and film thickness of 0.25 μm). The carrier gas was Helium at 99.99% purity (N6) at a flow rate of 1.0 ml min^{-1} with an injection volume of 1 μL, injected in splitless mode at a temperature of 250 °C. The method programme was set as follows: 90 ˚C (1 min), 90 °C to 185 ˚C (at 35˚C min^{-1} and hold time of 0 min), 185 ˚C to 220 ˚C (at 4 ˚Cmin^{-1} and hold time of 0 min) and from 220 °C to 320 ºC (at 25 ºCmin^{-1} and hold time of 0 min). The instrument was run on a SIM (selective ion monitoring) mode with data processing using Chemstation software. Compound identification was by NIST MS Search Program Version 2.0.

3.7 Soil sample extraction for GC-MS analysis

Soil samples were removed from the freezer and allowed to defrost for about 4 hours prior to extraction. The soil samples were dried using an hydrous sodium sulphate, they were then ground finely using mortar and piston and the soil particle size was homogenized and sieved though 2 mm mesh. Each portion of the composite soil sample was placed on a shaker and homogenised for one hour. Each of the homogenised soil sample was analysed in triplicates. After particle size homogenization, 20 g of the soil samples was transferred into a soxhlet extraction thimble and extracted using 200 mL of acetone-analar grade for 6 hours at a temperature of 60°C. The sample extracts were concentrated using the Eyela rotary evaporator, that was connected to eyela digital water bath-SB 1000 to a volume of 5 ml and transferred to a 5 ml glass vials, corked well and wrapped using an aluminum foil. The sample extracts were dried using anhydrous sodium sulphate before being injected into the GC-MS for analysis, quantification and identification following the procedure in section 3.7.1. Since BPA is sensitive to UV-light, no plastic or rubber material was allowed to get into contact with the samples, and all glass containers were wrapped with aluminum foil.

3.8 The quality assurance

The procedure for extraction as defined above for the analysis of thermal paper and soil samples was used for the quality assurance. A blank (acetone solvent) was also used with the other blank of an ordinary plain paper taken through the same extraction procedure. In the case of soil analysis, acetone solvent was used as a blank together with a soil sample that was collected from TUK's garden. The soil sample was taken through the extraction and analysis following the procedures in sections 3.8 and 3.7.1, respectively. The blanks were used for checking any interference and contaminations during the analysis.

3.9 Limit of detection (LOD) and Limit of quantififcation (LOQ)

The LOD of a substance is defined as the lowermost quantity of the analyte that an analytical technique can dependably identify, but not certainly quantified as the actual amount. It is calculated as the concentration of analyte showing a signal that is equal to the blank signal, YB plus twice standard deviations of the blank, SB (Miller and Miller, 1993). This is written as 3SB =Y- YB. Therefore BPA's limit of detection compution was dependent on the least amount (concentration) of the calibration standards that were auto-injected into the equipment and the equivalent noise signals by eploying the equation below below.

$$\mathrm{LOD} = \frac{3 \times \text{ Noise peak area } \times \text{ Concentration of lowest standard injected (ng)}}{\text{Analyte response in the lowest calibration point}}$$

The limit of detection for BPA on the thermal paper was 0.16 mg/g. Any other value detected below the recorded values in the analytical instruments were considered as noise and hence reported as <0.16 mg/g.

The limit of quantification (LOQ) of the machine does not only refer to the least quantity of analyte that an analytical equipment can constantly and reliably detect and measure, but it also adresses the point at which some predefined objectives for imprecision and bias are attained (Armbruster and Pry, 2008). This was calculated by using the formula

LOQ = LOD * 10
= 0.16mg/g * 10
= 1.6 mg/g

3.10 Percentage recoveries from the thermal paper and soil samples

The concentration of BPA in the soil sample was first determined before undertaking the standard addition method that was very crucial in the calculation of BPA percentage recovery in the soil sample. Standard addition method was done by spiking the soil and thermal paper samples with 1 mg/L of pure BPA standard. Extraction of BPA from thermal paper and soil was done following the extraction procedures in sections 3.6 and 3.7 and analysed following the procedure outlined in section 3.6.1. The chromatograms that were used for the calculation of BPA percentage recoveries in soil and thermal paper samples are shown in Appendices 4g and 4h, respectively. The BPA percentage recovery was calculated by using the formula

$$\%\, Recovery = \frac{\text{BPA concentration in the spiked sample}}{\text{concentration of BPA standard spiked in the sample}} \times 100$$

BPA concentration in the spiked sample

= (BPA conc. after spiking with known amount of the standard - BPA conc. before spiking)

$$\%\, Recovery\ for\ soil\ samples = \frac{0.83\ \mathrm{mg/g}}{1\ \mathrm{mg/g}} \times 100$$

<u>= 83%</u>

$$\%\, Recovery\ for\ thermal\ paper\ samples = \frac{0.86\ \mathrm{mg/g}}{1\ \mathrm{mg/g}} \times 100$$

<u>= 86%</u>

The GC-MS percentage recoveries of BPA from thermal paper samples had a mean of 86% while for the soil samples had a mean value of 83%, which are within the acceptable limits of a range of 75-125% (Hautman *et al*., 1997).

3.11 Quantification

The peak areas of the various spectra were determined and their corresponding BPA concentrations determined through interpolation using the calibration curve previously drawn. BPA concentrations in the thermal paper and soil samples were determined in mg/g.

3.12 Determining the effects of temperature and humidity on levels of BPA in thermal papers

3.12.1 Effect of temperature on the levels of BPA in the thermal papers

The thermal paper samples were exposed to different temperature conditions at 25°C (room temperature) and 40°C (highest temperature experienced in some regions in Kenya) for a period of one hour in an oven. BPA was extracted from the samples following the procedures in section 3.6.

3.12.2 Preparation of thermal paper samples

50 mg of the shreaded thermal paper samples were weighed and placed in different dry and sterilized clean test tubes and kept in an oven set at two different temperatures of 25˚C (ambient temperature) and 40˚C (highest temperature experienced in some regions in

Kenya) for one hour. BPA was then extracted from the above pre-heated thermal paper samples using the extraction procedure outlined in section 3.6. The two temperature values used above represent the range of actual climatic conditions within various regions in the country.

3.12.3 Effect of humidity on the persistence of BPA

In this study section, the humidity set was dependent on the ystem's temperature. The set up used is shown in Figure 3.4. The corresponding relative humidity of the varied conditions was calculated using the hygrometer conversion Table 3A in the appendix 3.4a and 3.4b.

Figure 3.3: Set up used to obtain the relative humidity in thermal papers

3.12.3.1: Thermal paper sample preparation for relative humidity values analysis

The water bath temperatures were set at different temperatures of 40, 70 and 90 ^oC. 50 mg of the shreaded thermal paper samples were weighed and placed in sterilized clean boiling tubes kept at different humid conditions using the set up in Figure 3.4 for one hour 5 ml of Acetone Analar grade solvent was added to each boiling tube containing the pre-weighed shreaded thermal paper samples and warmed in a water bath at a temperature of 40^{o}C for one hour. The sample extracts were transferred to clean boiling tubes and the residues washed twice with 5 ml of acetone. The washings were added to the respective sample extracts and concentrated under a gentle stream of nitrogen ready for GC-MS analysis. The samples extractions were repeated using the water bath temperatures at 70 ^{o}C and 90 ^{o}C to obtain the corresponding system temperatures respectively. Appendix 3.4, Table 3B, was used to calculate the relative humidity values for the corresponding system temperature.

3.13 Data analysis

Data analysis was done using SAS Software version 8, IBM SPSS Statistics, NCCS STATISTICAL software version 12 for conducting T-Tests and Microsoft Excel. The obtained results were represented using tables. Mean and standard deviations were calculated on the data obtained. The results of BPA concentartions were represented as mean±standard deviation. The means, standard deviations and %CV (coefficient of variations) were calculated using the SAS software. SPSS software was used to calculate the correlations of the variables.

3.14 Calibration curve for GC-MS analysis

The calibration curve for Bisphenol A standard was a straight line with the best line of fit drawn from the plot of instrument signal (peak area) against standard (analyte) concentration. The drawing gave a correlation factor (R^2) of 0.99 (Figure 4.1) which reflected a good correlation between instrument response ratio and analyte concentration.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1 Calibration curve for GC/MS analysis

Calibration followed the external standard method. A calibration curve for bisphenol A followed linear regression equation: y= mx+c, where; y= normalized peak area (instrument response), x= standard concentration, m=gradient, and c= y-intercept. The equation of the line for BPA was y = 177,249x + 47,628 where y represents the peak area, y-intercept was 47,628 and x represents the concentration of Bisphenol A (Figure 4.1).

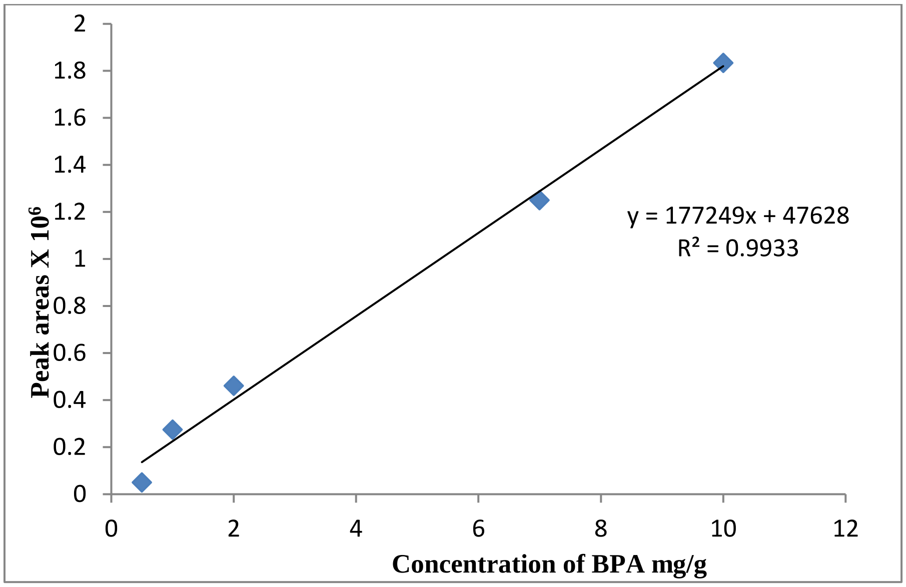

Figure 4.1: the calibration curve for GC/MS analysis

Concentrated samples were diluted to fit in the calibration window.

4.2 Chromatograms

The chromatogram was generated by plotting a graph of the instrument detector response (peak area) against the analyte retention time (minutes). The x-axis indicates the retention time of each analyte which corresponds to that of the reference standard peak for a specific analyte. The retention time for BPA was 11.292 minutes as shown in Appendix 4.1a**.** Appendix 4.1b shows the mass spectrum of BPA in reference standard, whereas Appendix 4.1c shows confirmation by GC/MS library.

4.3 The GC-MS concentration of BPA in thermal papers from the commercial banks

The concentration of BPA in thermal papers from the commercial banks and supermarkets within the CBD of Nairobi varied from site to site (Table 4.1). Thermal papers from bank 4 ATM lobby had the highest concentration of BPA of 3.59±0.24 mg/g while thermal papers collected from Bank 3 had the lowest concentration of BPA of 1.94±0.25 mg/g.

Table 4.1: GC-MS concentrations of BPA in thermal papers from the commercial banks

Site number	Concentration of BPA (mg/g) Mean ± SD	CV%
Commercial bank 1	2.89±0.23	8.03
Commercial bank 2	1.97±0.11	5.80
Commercial bank 3	1.94±0.25	12.99
Commercial bank 4	3.59±0.24	6.68
Commercial bank 5	3.23±0.23	6.99
Commercial bank 6	2.27±0.12	5.46
Commercial bank 7	3.22±0.24	7.51
Commercial bank 8	2.93±0.10	3.29
17(Unprinted Photocopying Paper)	<0.16	-
17(Printed Photocopying Paper)	<0.16	-
Blank	<0.16	-
13 (Unused Thermal Paper)	1.74±0.89	12.89

(***The real names of commercial banks are not disclosed due to legal implications***)

Coefficient of variation (CV) refers to a statistical measure of the dispersion of data points in a data series around the mean. It signifies the ratio of the standard deviation to the mean and used statistically to compare the level of variation from one data series to another. Statistically, standard deviation (SD) represents a measure that is usedful in the quantification of the amount of variation or dispersion of a set of data values. The computations of the mean, standard deviations and the percentage coefficient of variations were done by the use of a SAS software. Each sample was analysed in triplicates and the respective BPA concentrations were used to compute the statistical elements. From Table

4.1, BPA concentration in the thermal papers collected from commercial bank 4 had the highest level (3.59±0.24 mg/g), while that from commercial bank 3 had the lowest value (1.94±0.25 mg/g). Generally, the levels of BPA were lower in the thermal papers from commercial banks 2 and 3, compared to those in the other banks.

The unused thermal paper was also tested of the presence of BPA concentration and it was determined to have a concentration of 1.74±0.89 mg/g of BPA. This showed that BPA is a component of the thermal paper. However, the blank sample, photocopying papers (both printed and unprinted) didn’t show any trace of BPA. The percentage Coefficient of Variation (CV%) of BPA concentration of the thermal papers from the commercial Banks was lower than those of the supermarkets. This could be possibly caused by the fact that the Supermarket waste bins contained some other wastes apart from the receipt papers and hence the rubbing off of the receipt papers against these products could have led to the leaching of BPA from the receipt papers to these products hence leading to a higher variation in the concentration of BPA in the supermarket receipt papers than the banks’ ATM papers.

4.4 Concentrations of BPA in thermal papers sampled from the supermarkets and stores within CBD

The thermal paper from Supermarket 6 had the highest concentration of BPA at 2.75±0.14 mg/g, while those from Supermarket 4 had the lowest level at 1.08±0.06 mg/g (Table 4.2). The unused thermal paper (UTP) had a BPA concentration of 1.74±0.22 mg/g while both printed photocopying paper and unprinted photocopying paper did not show any trace of BPA.

Table 4.2: GC-MS concentrations of BPA in thermal papers from the supermarkets

Site number	**Concentration of BPA (mg/g) Mean± SD**	**CV%**
Supermarket 1	1.98±1.03	52.19
Supermarket 2	1.96±1.47	74.86
Supermarket 3	1.42±0.06	4.13
Supermarket 4	1.08±0.06	6.00
Supermarket 5	1.89±0.14	7.20
Supermarket 6	2.75±0.14	4.97
Supermarket 7	2.08±0.06	2.84
Supermarket 8	2.47±0.32	13.1
Unprinted Photocopying Papers	<0.16	_
Printed Photocopying Papers	<0.16	_
Blank	<0.16	_
Unused thermal paper	1.74±0.22	12.89

(***The real names of supermarkets are not disclosed due to legal implications***)

4.5 Concentration of the BPA in thermal papers at different temperatures

Table 4.3 shows the concentrations of BPA at two different temperatures of 25 ºC and 40 ºC. An increase in temperature from 25 ºC to 40 ºC led to increased recovery of BPA in all the thermal papers, while there was no effect of temperature for both unprinted papers and printed photocopying papers. The results suggest that the increase in temperature enhanced desorption of BPA from the paper making it more available for extraction. The finding is in harmony with a previous study that involved the study of effect of storage time and temperature on levels of phthalate metabolites and Bisphenol A in urine (Guo *et al.*, 2013).

Table 4.3: The GC-MS concentration of the BPA in thermal papers at 25 ºCand 40 ºC

Site	GC-MS concentration of BPA (mg/g) at 25°C Mean± SD	% CV	GC-MS concentration of BPA (mg/g) at 40°C Mean± SD	% CV
Commercial bank 1	0.98±0.08	8.25	2.97±0.79	26.57
Commercial bank 3	0.87±0.10	11.65	3.97±0.37	9.38
Commercial bank 6	0.86±0.04	4.94	2.80±0.10	3.44
Commercial bank 8	1.14±0.10	8.85	4.05±0.15	3.59
Commercial bank 9	0.67±0.25	37.67	3.07±0.20	6.55
Supermarket 1	0.94±0.07	7.62	3.62±0.45	12.39
Supermarket 3	0.43±0.02	4.79	1.58±0.10	6.38
Supermarket 5	0.82±0.01	1.42	3.05±0.11	3.65
Unprinted photocopying paper	<0.16	-	<0.16	-
Printed photocopying paper	<0.16	-	<0.16	-
Blank	<0.16	-	<0.16	-

(***The real names of commercial banks and supermarkets are not disclosed due to legal implications***)

4.6 Concentration of BPA in thermal papers at varied humid conditions

4.6.1 Calculation of the relative humidity values

The calculation of the relative humidity was based on dry bulb temperature measured by using thermometer in Appendix 3.4a. The conversion Table 3B was used to obtain the values of the wet bulb temperature. The relative humidity values were obtained from Appendix 3.4b by calculating the difference between the dry and wet bulb temperature. The data was interpolated against the value of the dry-bulb temperature Appendix 3.4b by at 35˚C and the corresponding wet bulb temperature at 21 ˚C (Appendix 3a). The difference in the two temperatures was calculated as follows:

$$\Delta\ T = (35-21)\ ^{\circ}C$$

$$\Delta T = 14\ ^{\circ}C$$

Relative humidity was obtaine by reading the value on the top column and interpolating against a dry bulb temperature of 35˚C. Similarly the relative humility value for the dry bulb temperature of 45˚C was also obtained following the same procedure.

Table 4.4: The varied humid and relative humidity conditions

	Water bath temperature (˚C)	System's temperature (˚C)	Relative humidity (%)
1.	40	25	22
2.	70	35	27
3.	90	45	30

From Table 4.4, water bath temperature of 70 ˚C and 90 ˚C corresponding to system's temperatures of 35 ˚C and 45 ˚C with the relative humidity of 27% and 30% were found to be the most appropriate for the variation of relative humidity. Table 4.5 shows the concentration of BPA at the relative humidity of 27% and 30%.

Table 4.5: The GC-MS concentration of BPA in thermal papers at 27% and 30% humid conditions

Sites	Concentration of BPA (mg/g) at 27% humid condition Mean± SD	% CV	Concentration of BPA (mg/g) at 30% humid condition Mean± SD	% CV
Commercial bank 9	1.80±0.01	0.75	3.47±0.13	3.63
Supermarket 1	2.85±0.05	1.84	3.08±0.01	0.38
Supermarket 3	2.44±0.11	4.30	3.06±0.19	6.15
Supermarket 5	3.43±0.11	3.06	3.85±0.04	1.09
Unprinted photocopying paper	<0.16	-	<0.16	-
Printed photocopying paper	<0.16	-	<0.16	-
Blank	<0.16	-	<0.16	-

Data from Table 4.5 showed an increase in concentration of BPA with an increase in humidity for the five thermal papers analyzed. The increase in BPA could be due to the presence of the OH-groups in the compound which are polar in nature and could have contributed to the BPA compound dissolving in water i.e the moistened paper and hence facilitating the extraction of more of the compound from the moistened thermal paper as compared to the previous dry thermal paper. The results obtained also agrees with the previous research that was conducted by Biedermann (2010), which assessed the transfer of Bisphenol A from thermal printer paper to the skin at varied humidity levels (Biedermann *et al.*, 2010).

4.7 Properties of the soil samples

4.7.1 The soil sample properties

Table 4.6 below shows the pH of the soil samples that were collected from Dandora dumpsite and the Technical University of Kenya garden. The soil samples at Sites 24 and 17 had pH values of 6.90±0.05 and 6.41±0.07, respectively. The soil samples from Sites 18, 19, 20, 21, and 23 had pH values of slightly above 7, while the soil samples from Sites 22 and 25 had the pH values of 8.14±0.06 and 8.04±0.03, respectively indicating that they were slightly basic in nature.

Table 4.6: Soil pH and metallic composition

Site	Soil pH Mean± SD	Mn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
Dumpsite-18	7.63±0.03	1.06±0.04	0.05±0.001	1.23±0.04	0.10±0.001	0.28±0.02
Dumpsite-19	7.79±0.03	0.85±0.01	0.05±0.002	1.58±0.02	0.07±0.003	0.73±0.03
Dumpsite-20	7.32±0.03	0.86±0.02	0.13±0.004	0.96±0.01	0.15±0.002	0.08±0.01
Dumpsite-21	7.51±0.05	0.97±0.02	0.05±0.001	1.05±0.02	0.14±0.001	0.36±0.02
Dumpsite-22	8.14±0.06	0.41±0.01	0.08±0.002	1.25±0.03	0.18±0.004	0.06±0.001
Dumpsite-23	7.23±0.04	1.18±0.05	0.06±0.004	1.38±0.04	0.07±0.002	0.83±0.02
Dumpsite-24	6.90±0.05	1.23±0.03	0.04±0.001	1.99±0.03	0.17±0.003	0.09±0.001
Dumpsite-25	8.04±0.03	0.32±0.01	0.05±0.002	1.80±0.04	0.10±0.001	0.05±0.001
TUK-Garden soil sample	6.41±0.07	0.46±0.02	0.00±0.001	1.55±0.02	0.05±0.002	0.01±0.001
MEAN		0.82	0.06	8.53	0.11	0.28
CV%		8.73	98.97	7.08	2.76	28.68

The soil samples had different constituents of metals. The variation could be attributed to the fact that the samples were collected from different locations in the Dumpsite, heterogeneous in nature.

4.8 Concentration of BPA in soil samples

Table 4.7 shows the concentration of BPA in the nine different soil samples. Samples 18-25 were from Dandora dumpsite. Site 20 had the highest BPA concentration of 154.82±12.72 mg/g while the sample from TUK-Garden had the lowest concentration of BPA at 0.49±0.12 mg/g. All the samples from Dandora dumpsite had higher concentrations of BPA ranging between 0.86±7.75 to 154.82±12.72 mg/g. This could be attributed to a variety of BPA containing products which are deposited on the dumpsite, such as plastic bottles and thermal papers among others. BPA compound tend to leach from these compounds to the soil. However, the soil sample collected from TUK-garden, which is located about 7.5 km from the dumpsite had the lowest concentration of BPA at 0.49±0.12 mg/g. The garden only consisted of flowers, wild plants and banana plants with limited sources of BPA from the surrounding.

Table 4.7: Concentration of BPA in soil from Dandora dumpsite and TUK

Site	BPA Conc. (mg/g) ± SD	% CV
TUK-Garden	0.49±0.12	24.49
18	6.73±2.04	3.31
19	18.54±8.53	46.01
20	154.82±12.72	8.22
21	0.86±0.19	22.09
22	72.31±10.61	14.67
23	11.53±3.30	28.62
24	56.62±3.79	6.69
25	3.31±0.76	22.96

The high coefficient of variations in the concentration of BPA in the soil samples from the dumpsite showed that the soil samples within the dumpsite were heterogeneous in nature due to different kinds of wastes deposited and age of the specific location.

4.9 Correlation

Correlation study was done using IBM SPSS Statistics. The results showed that the individual means of BPA concentrations in commercial banks and supermarkets had a higher positive Pearson Correlation coefficient of 0.783 (Appendix 4.2). In addition, BPA concentrations in thermal papers at 25°C and 40°C showed a positive Pearson Correlation coefficient of 0.97 (Appendix 4.2). Similary there was a significant correlation between the effect of temperature and humidity on BPA in the thermal paper as illustrated in appendix 4.2. At 25 ^{o}C, the Pearson Correlations coefficient were 0.60 and 0.71 for 27% and 30% humidity, respectively. There was also a positive correlation between the concentration of BPA in soil, temperature and humidity, suggesting that the variation in temperatures and humidity had effect on recoverable BPA concentrations in soil samples. The Pearson Correlations were 0.539, 0.484, 0.338 and 0.264 for correlation of BPA concentrations at 25°C, 40°C, 27% relative humidity and 30% relative humidity, respectively (Appendix 4.2).

4.10 Means separation

The mean separation was done using t-test software. There was no significant difference in the mean concentrations of the BPA concentrations in thermal papers collected from the commercial banks and supermarkets (Apendix 4.3a). This could be attributed to the fact that the two categories of institutions could be sourcing their thermal papers from the same manufacturer. However, there was a signifant difference in the thermal paper samples that were exposed to varied temperature conditions, suggesting that the variations in temperature would make the BPA compound more avaiable for extraction and recovery.

The results obtained in the research conducted were comparable to the results obtained by other scholars such as the study conducted by Mendum *et al*. (2011) on determination of BPA concentration in thermal paper samples that were collected from retail shops in USA, the results for BPA in thermal papers ranged form 1-13 mg/g. The study conducted by Liao and Kanaan, (2011) to determine the concentration of BPA in thermal paper samples that were collected from USA, Vietnam and Korea showed that BPA concentration ranged between <1ng-13.9 mg/g.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The study showed the presence of BPA in supermarket and bank thermal papers collected within the Central Business District of Nairobi. The BPA concentration in Bank thermal papers ranged between 3.59±0.24 mg/g and 1.94±0.25 mg/g. The concentration of BPA in supermarket thermal papers had BPA concentration ranging between 2.75±0.14 mg/g and 1.42±0.06 mg/g.
The presence of BPA in the thermal paper was attributed to the fact that it is a core reagent in the unused thermal papers.

BPA concentration was comparatively higher in Bank thermal papers compared to the supermarket thermal papers attributed to abrasion of the thermal papers against the other products that were deposited in the supermarket waste bins

Increase in temperature increased the concentration of recoverable BPA in the thermal papers. This was attributed to BPA becoming less bound to the thermal paper and readily extracted at an elevated temperature.

Increase in humidity led to increased recovery of BPA from thermal papers, suggesting increased solubility of BPA in water, due to OH-groups. High solubility in water (in the moinstened thermal papers) increased availability of the compound for extraction and hence increasing BPA concentration.

Soil from Dandora Dumpsite had the highest BPA concentration of 154.82±12.72 mg/g, while TUK soil had the lowest concentration of BPA at 0.48±0.12 mg/g. High BPA concentration in the Dump-site soil could have resulted from some other products that are deposited at the site and contains BPA. BPA tends to leach from these products to the soil. The soil samples showed a higher percentage of coefficient of variation because of heterogenous nature of the products deposited in the dumpsite.

5.2 Recommendations

5.2.1 Policy recommendations

The study has shown that both supermarket and bank thermal papers contained BPA at varied concentrations. The public (employees of the bank and supermarkets, bank account holders) should be sensitized on the dangerous component of the supermarket and bank receipt papers. This is because TDI for BPA by USEPA is 0.05 µg/kg/day and since the bank employees get to interact with the thermal papers in their daily activities, there are high chances of getting contaminated with the compound.

5.2.2 Research recommendations

1) The study has shown that BPA concentration tends to increase at elevated temperatures. There is need to extract BPA from thermal papers at slightly higher temperature to increase the percentage recoveries.
2) Prior moistening of the thermal paper should be done before BPA extraction to increase the percentage recovery.
3) The study confirmed the presence of BPA in the thermal papers from the Supermarkets and commercial banks. Further research therefore needs to be done to investigate its persistence in soil.

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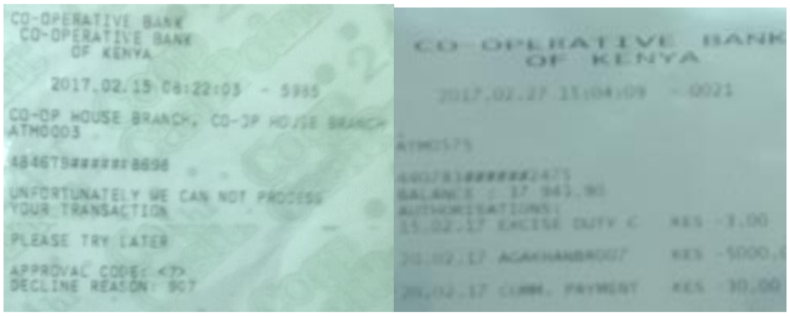
APPENDICES

APPENDIX 3.1

The pictorial representations of the thermal papers samples collected from the Commercial Banks within CDB, Nairobi City

APPENDIX 3.1a



CO-OPERATIVE BANK
CO-OPERATIVE BANK
OF KENYA

2017.02.15 08:22:03 - 5985

CO-OP HOUSE BRANCH, CO-OP HOUSE BRANCH
ATM0003

484679######8698

UNFORTUNATELY WE CAN NOT PROCESS
YOUR TRANSACTION

PLEASE TRY LATER

APPROVAL CODE: <7>
DECLINE REASON: 907

Figure 3 a: thermal papers from Cooperative Bank, Co-op House and Tom Mboya Branches respectively.

APPENDIX 3.1b

Figure 3b: thermal paper samples from KCB Bank; Kencom and Development House branches respectively

APPENDIX 3.1c

Figure 3c: thermal papers from Barclays Bank; Haile Selassie branch

APPENDIX 3.1d

Figure 3d: Thermal paper samples from Equity Bank; Kimathi Street and Moi Avenue branches respectively

APPENDIX 3.2

The pictorial representation of the thermal papers samples collected from Ukwala,Naivas,Tuskys,Uchumi, and Nakumatsupermarkets within CDB, Nairobi City

APPENDIX 3.2 a

Figure 3e: Thermal paper samples from Ukwala Supermarket, Mega and Tom Mboya branches respectively

APPENDIX 3.2 b

Figure 3f: Thermal papers from Naivas Supermarket, Ronald Ngala branches

APPENDIX 3.2 c

Figure 3g: Thermal paper samples from Tuskys Supermarket, Imara and Pioneer branches respectively

APPENDIX 3.2 d

Figure 3h: Thermal paper sample from Uchumi Supermarket, Uchumi House branch

APPENDIX 3.2 e

Figure 3i: Thermal paper samples from Nakumat Holdings, Development House and Life Style branches respectively

APPENDIX 3.3

The pictorial representations of the old, current and active dumpsites in Dandora where the soil samples were collected

APPENDIX 3.3a

Figure 3j: Dandora dumpsite representing a current dumpsite with freshly deposited wastes

APPENDIX 3.3 b

Figure 3k: Dandora dumpsite representing a dumpsite which has not been active for 3 years adjacent to an active one with a lorry offloading the wastes

APPENDIX 3.3c

Figure 3l: Dandora dumpsite representing a current dumpsite ; domesticated pigs and goats feeding on the wastes

APPENDIX 3.3 d

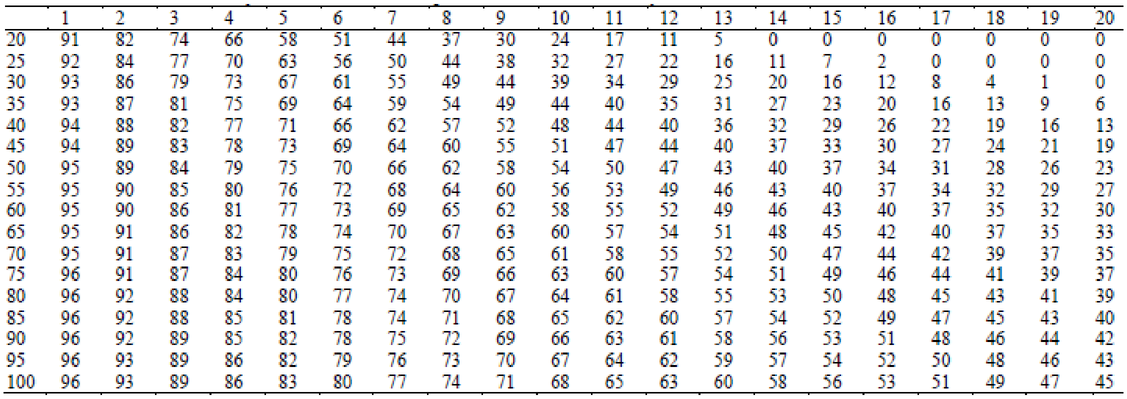
Figure 3m: Dandora old dumpsite with a domesticated dairy cattle drinking stagnant water

APPENDIX 3.4

APPENDIX 3.4 a

Hygrometric and temperature con version tables

Table 3a: Hygrometric conversion table



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
20	91	82	74	66	58	51	44	37	30	24	17	11	5	0	0	0	0	0	0	0
25	92	84	77	70	63	56	50	44	38	32	27	22	16	11	7	2	0	0	0	0
30	93	86	79	73	67	61	55	49	44	39	34	29	25	20	16	12	8	4	1	0
35	93	87	81	75	69	64	59	54	49	44	40	35	31	27	23	20	16	13	9	6
40	94	88	82	77	71	66	62	57	52	48	44	40	36	32	29	26	22	19	16	13
45	94	89	83	78	73	69	64	60	55	51	47	44	40	37	33	30	27	24	21	19
50	95	89	84	79	75	70	66	62	58	54	50	47	43	40	37	34	31	28	26	23
55	95	90	85	80	76	72	68	64	60	56	53	49	46	43	40	37	34	32	29	27
60	95	90	86	81	77	73	69	65	62	58	55	52	49	46	43	40	37	35	32	30
65	95	91	86	82	78	74	70	67	63	60	57	54	51	48	45	42	40	37	35	33
70	95	91	87	83	79	75	72	68	65	61	58	55	52	50	47	44	42	39	37	35
75	96	91	87	84	80	76	73	69	66	63	60	57	54	51	49	46	44	41	39	37
80	96	92	88	84	80	77	74	70	67	64	61	58	55	53	50	48	45	43	41	39
85	96	92	88	85	81	78	74	71	68	65	62	60	57	54	52	49	47	45	43	40
90	96	92	89	85	82	78	75	72	69	66	63	61	58	56	53	51	48	46	44	42
95	96	93	89	86	82	79	76	73	70	67	64	62	59	57	54	52	50	48	46	43
100	96	93	89	86	83	80	77	74	71	68	65	63	60	58	56	53	51	49	47	45

Source; *Res. J. App. Sci. Eng. Technol., 6(16): 2984-2987, 2013*

APPENDIX 3.4b

Table 3b: Dry and wet bulb temperature conversion table

Dry bulb temperature (ºC) (a)	Wet bulb temperature (ºC) (b)	% Relative humidity from (a-b)
20	15	
36	21	
45	29	
58	44	
60	58	
72	62	
85	77	
91	84	
98	87	
100	87	

Source; *Res. J. App. Sci. Eng. Technol., 6(16): 2984-2987, 2013*

APPENDIX 4.1

APPENDIX 4.1a

The GC-MS chromatogram of BPA from the standard and thermal paper samples

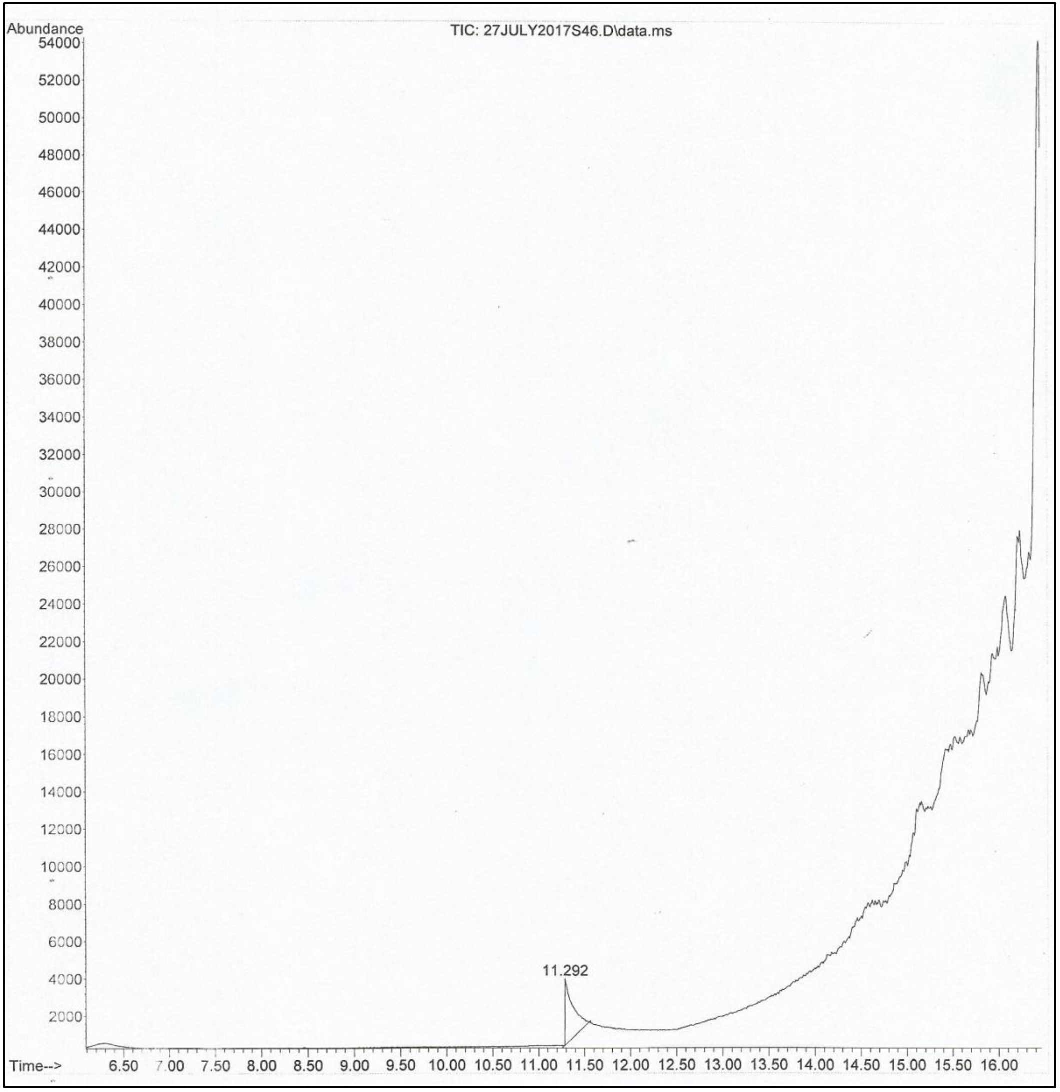


Figure 4a: GC-MS ion chromatogram from the BPA reference standard

APPENDIX 4.1b

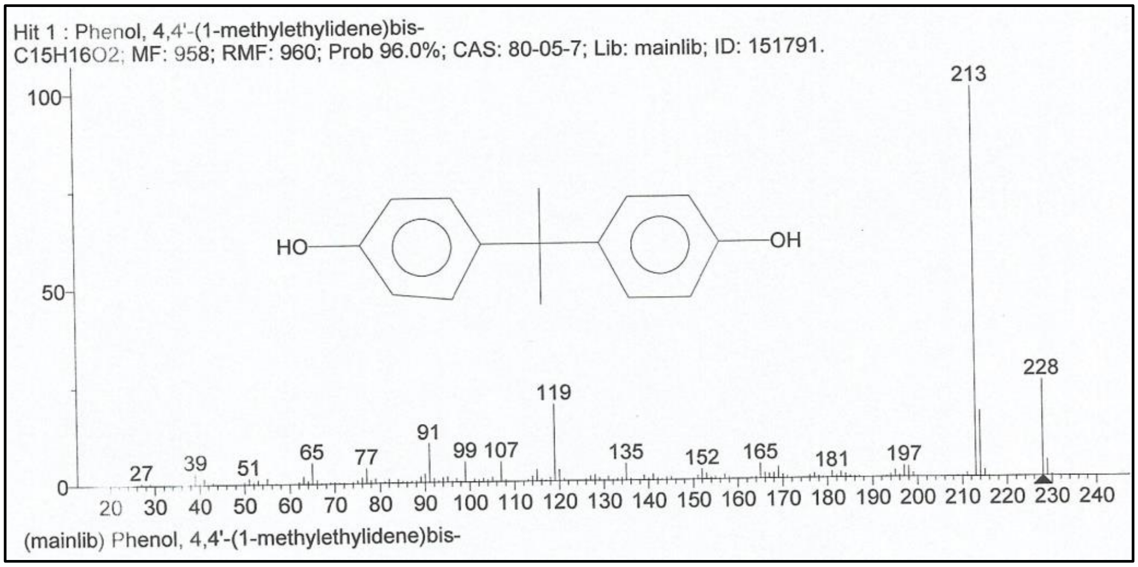
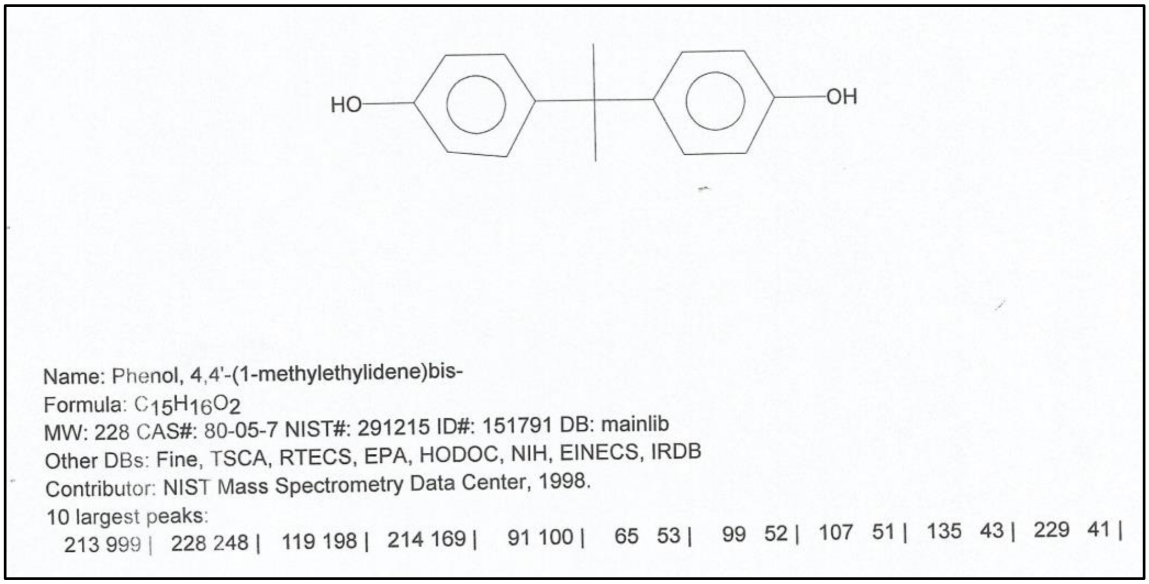


Figure 4b: Mass spectrum of BPA reference standard

APPENDIX 4.1c



Name: Phenol, 4,4'-(1-methylethylidene)bis-
Formula: $C_{15}H_{16}O_2$
MW: 228 CAS#: 80-05-7 NIST#: 291215 ID#: 151791 DB: mainlib
Other DBs: Fine, TSCA, RTECS, EPA, HODOC, NIH, EINECS, IRDB
Contributor: NIST Mass Spectrometry Data Center, 1998.
10 largest peaks:
213 999 | 228 248 | 119 198 | 214 169 | 91 100 | 65 53 | 99 52 | 107 51 | 135 43 | 229 41 |

Figure 4c: Chemical description of BPA from GC-MS main library

APPENDIX 4.1d

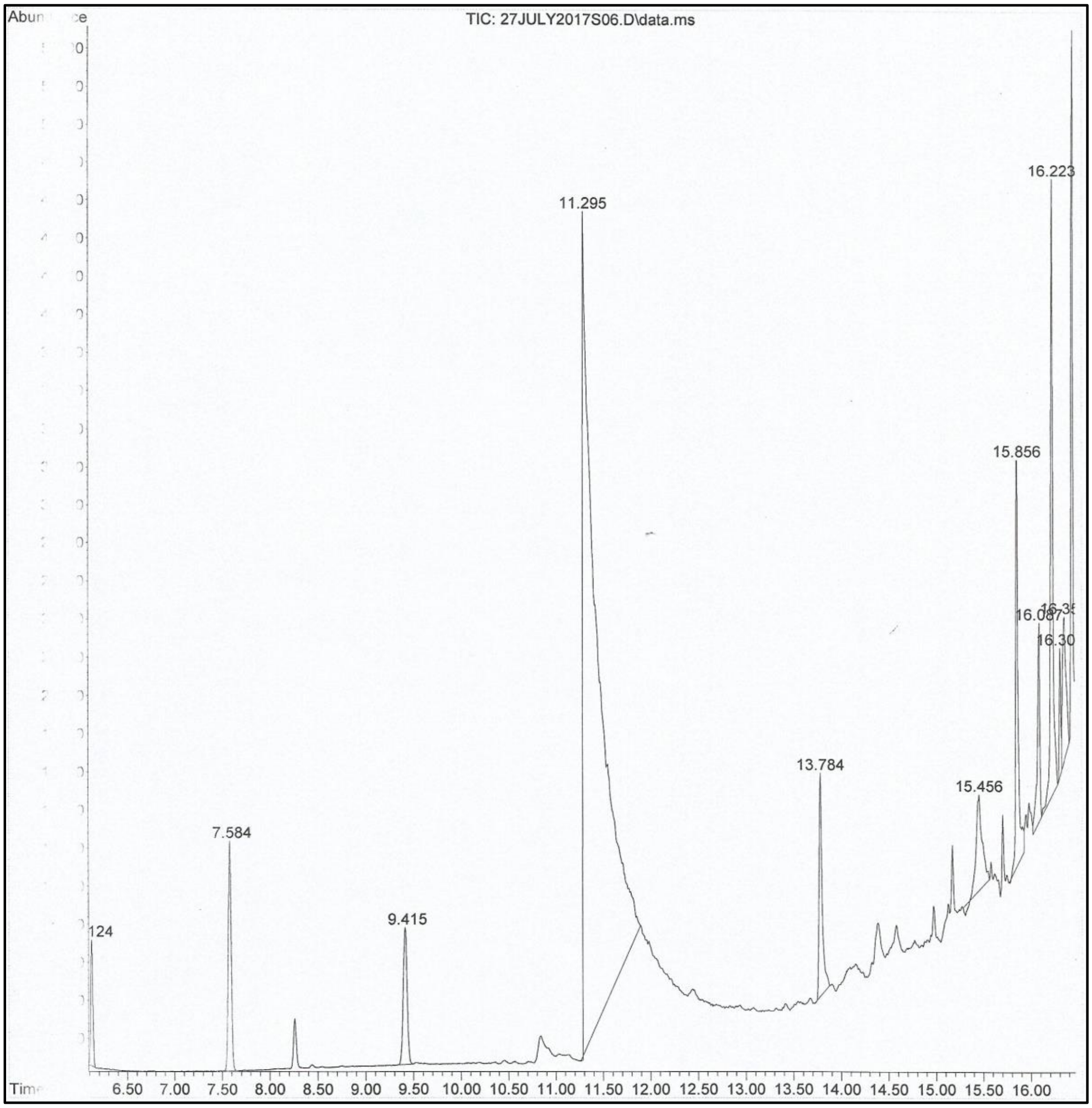


Figure 4d: GC-MS ion chromatogram of the BPA from a bank thermal paper

APPENDIX 4.1 e

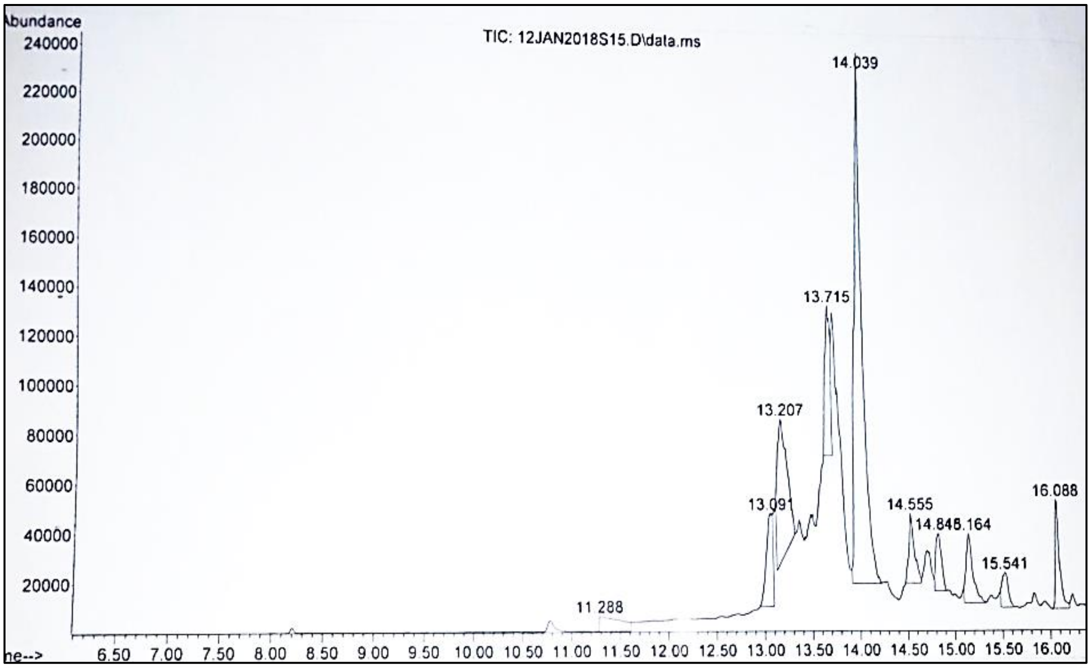


Figure 4e: GC-MS ion chromatogram for soil sample from site number 22 from Dandora dumpsite

APPENDIX 4.1 f

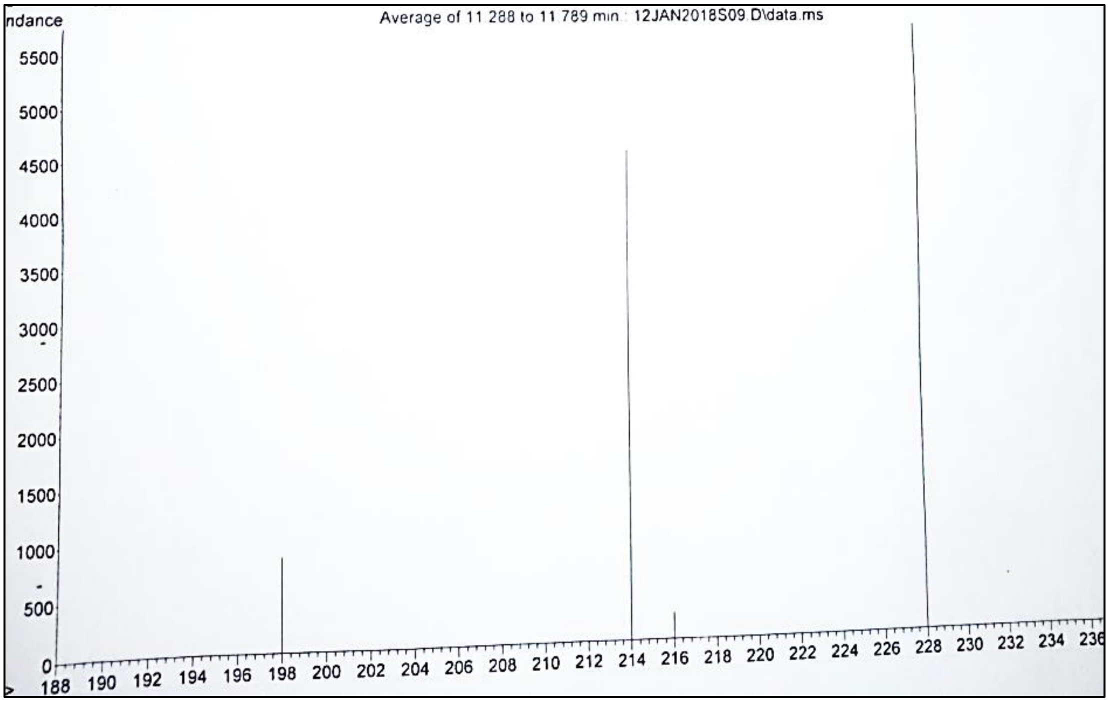


Figure 4f: Chromatogram Fragments for soil sample from site number 22 from Dandora dumpsite

APPENDIX 4.1g

APPENDIX 4.1h

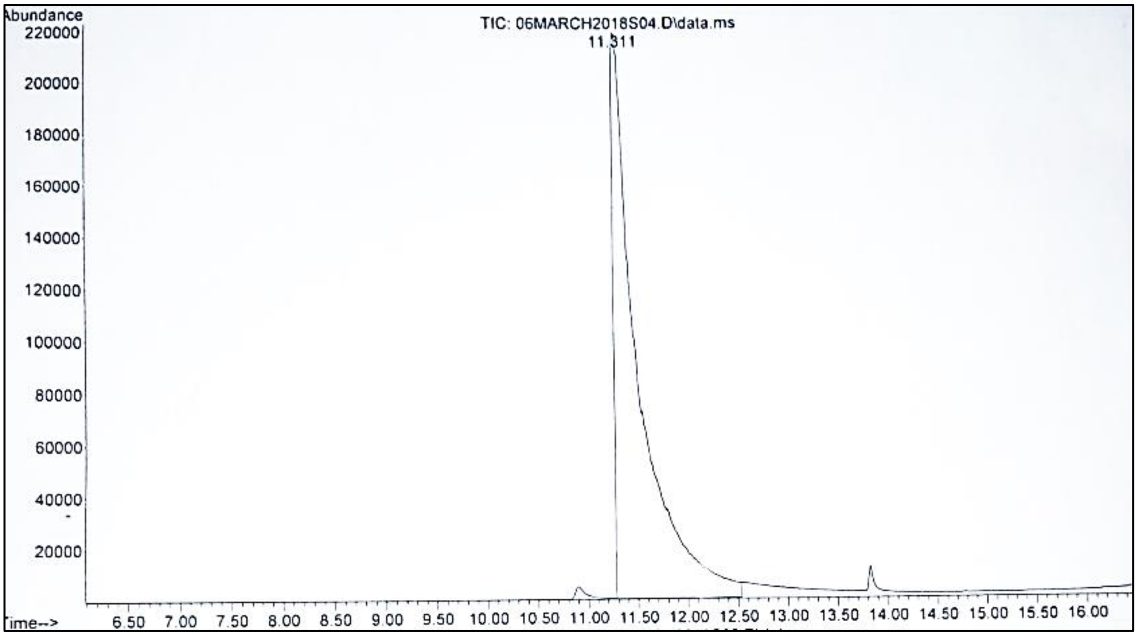


Figure 4h: GC-MS ion chromatogram for thermal paper sample used for the calculation of BPA %tage recoveries from used Bank thermal paper.

APPENDIX 4.2: SPSS Correlations

Appendix 4.2a: Correlations of BPA concentrations in Bank and supermarket thermal papers

		BPA CONCENTRATION IN COMMERCIAL BANK THERMAL PAPERS	BPA CONCENTRATION IN SUPERMARKET THERMAL PAPERS
BPA CONCENTRATION IN COMMERCIAL BANK	Pearson Correlation	1	.783**
	Sig. (2-tailed)		.003
	N	12	12
BPA CONCENTRATION IN SUPERMARKETS	Pearson Correlation	.783**	1
	Sig. (2-tailed)	.003	
	N	12	12

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 4.2b Correlations of BPA concentrations in Bank and supermarket thermal papers at different temperatures

		BPA CONCENTRATION AT 25°C	BPA CONCENTRATION AT 40°C
BPA CONCENTRATIO 0N AT 25°C	Pearson Correlation	1	.970**
	Sig. (2-tailed)		.000
	N	11	11
BPA CONCENTRATIO 0N AT 40°C	Pearson Correlation	.970**	1
	Sig. (2-tailed)	.000	
	N	11	11

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 4.3: Mean separations

Appendix 4.3a: Mean separations for BPA concentration commercial banks and supermarkets

Name	Count	Squares	Least mean Statistic to Test	Reject H0	Error	T- Standard H0: Mean=0
P-Value	at 5%?					
Intercept All smples	17	2.318235	0			
Commercial bank 1	1		2.89	0		
Commercial bank 2	1		1.97	0		
Commercial bank 3	1		1.94	0		
Commercial bank 4	1		3.59	0		
Commercial bank 5	1		3.23	0		
Commercial bank 6	1		2.27	0		
Commercial bank 7	1		3.22	0		
Commercial bank 8	1		2.93	0		
Supermarket 1	1		1.98	0		
Supermarket 2	1		1.96	0		
Supermarket 3	1		1.42	0		
Supermarket 4	1		1.08	0		
Supermarket 5	1		1.89	0		
Supermarket 6	1		2.75	0		
Supermarket 7	1		2.08	0		
Supermarket 8	1		2.47	0		
Unused thermal paper	1		1.74	0		

Appendix 4.3b: Mean separations for BPA concentration in thermal papers at varied temperature conditions

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 BPA (mg/g) at 25°C - BPA (mg/g) at 40°C	-2.30000	.62331	.22037	-2.82110	-1.77890	-10.437	7	.000