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ANTIMONY AND ACETALDEHYDE MIGRATION FROM NIGERIAN AND BRITISH PET BOTTLES INTO WATER AND SOFT DRINKS UNDER TYPICAL USE CONDITIONS

concentration of migrants and some trace elements in polyethylene terephthalate and in bottled contents

Aminu TUKUR

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School of Engineering, Design and Technology
University of Bradford

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Aminu Tukur

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Keywords: antimony, acetaldehyde, trace elements, polyethylene terephthalate, bottled water, leaching, reuse, microwave digestion, ICP-MS, headspace GC-FID

ABSTRACT

Polyethylene terephthalate (PET) is an excellent material for bottling water, beverages, edible oils and other liquids because it is light, tough and transparent. PET bottles are also extensively reused for storage of drinking water, beverages and other liquids and for solar disinfection of microbiologically unsafe drinking water in the tropics. In spite of the usefulness of PET bottles earlier works have reported leaching of antimony and acetaldehyde from the bottle matrix into the liquid contents. Both antimony trioxide and acetaldehyde belongs to Group 2B (possible carcinogens) in the International Agency for Research on Cancer (IARC) carcinogen classification. Additionally acetaldehyde associated with alcoholic beverages (derived from alcoholic beverage and formed endogenously) has recently been upgraded to IARC Group 1 carcinogen (carcinogenic to humans).

The research aims to assess the pattern and extent of antimony and acetaldehyde migration from British and Nigerian polyethylene terephthalate bottles into bottle contents under typical use and reuse conditions. The research compares the assessed extents of migration with the current regulations to determine whether the maximum acceptable levels of antimony and acetaldehyde are being exceeded and whether current regulations might need to be reassessed.

To achieve these goals the pattern and extent of PET bottle use and reuse in Britain and Nigeria were appraised through survey. The survey revealed that new bottles with contents are typically stored prior to use for periods ranging between one and 7 days, with Nigerians storing for longer periods than British respondents. However storage of up to one year was reported. The extent of bottle reuse was high and similar for the two countries. Nevertheless Nigerian respondents reuse bottles for longer periods than British respondents. The survey findings together with relevant literature were used to design laboratory experiments that assessed the extent of antimony and acetaldehyde migration from PET bottles into water/beverages.

A total of 82 brands of bottled water and soft drinks in plastic and glass bottles and in cartons were collected. A few samples from Nigeria in plastic pouches were collected. Materials used in bottling including glass and plastic bottle materials, metal and plastic bottle cap materials and plastic cap lining materials were collected. All samples were collected in supermarkets and shops in Britain and Nigeria except drinking water from taps which was collected in Britain only. Some bottles were aged for the purpose of studying the impact of bottle aging on chemical migration. Other bottles were stored with their contents to study the impact of long term storage of bottle contents on chemical migration.

Energy dispersive X-ray spectrometry (EDX) and Raman spectroscopy were used to characterise PET bottle material and other materials associated with water and soft drink bottling. Antimony and other trace metals in water and soft drinks were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Antimony content of PET and other plastics was determined by microwave digestion and ICP-MS. Acetaldehyde content of water and soft drinks and PET were determined using headspace gas chromatography with flame ionisation detection (GC-FID). Accuracy and precision for determination of antimony and other trace elements in bottle materials and bottle contents were good as recoveries were around 100% and coefficients of variation were less than 15% for all analysis types. Accuracy and precision for determination of acetaldehyde in bottle materials and bottle contents were also good as recoveries were around 100% and coefficients of variation were less than 15% for all analysis types. Impact of long term storage, elevated temperatures, bottle thickness, carbonation, bottle aging and bottle size on migration of antimony and acetaldehyde were also assessed.

All plastic bottle materials analysed were found to be PET. Bottle cap materials were either polyethylene or polypropylene. All plastic cap lining materials from Britain and some from Nigeria were found to be ethylene vinyl acetate/polypropylene copolymer. Plastic cap lining materials from some Nigerian soft drinks were identified as polyvinyl chloride. Glass bottle materials analysed were found to be soda-lime glass. Metal bottle caps were identified as tinplate, tin-free-steel coated with chromium or aluminium coated with chromium.

The antimony concentration in 32 PET bottle materials from Britain and Nigeria were similar and ranged between 177 and 310 mg/kg with an average of 250±30 mg/kg. The concentration agrees well with the industry reported concentration of between 150 and 350 mg/kg. The concentration of residual acetaldehyde in 25 fresh PET bottle materials from Britain and Nigeria ranged between 0.95 and 12.52 μg/g. The average concentration in British and Nigerian soft drinks PET materials are 4.76 and 2.17μg/g respectively. Concentration of residual acetaldehyde was higher in soft drinks and still water PET materials than in sparkling water materials. The concentration of residual acetaldehyde decreases as the bottle wall material becomes older. Also the thinner the bottle walls the lower the concentration of residual acetaldehyde.

Antimony concentration in 47 freshly purchased British bottled water and soft drinks ranged between 0.03 and 6.61μg/L with only one sample going above the EU acceptable limit. Concentrations of other trace elements measured were low except titanium which was detected at part per million levels in soft drinks. Lead content of a Nigerian soft drink in glass bottle stored for 2 months was above the EU acceptable limit for lead. At realistic temperatures of 40 and 60°C antimony concentration in the water remained below the EU acceptable limit even after 48 hours of exposure but the concentration exceeded the limit for most exposures at 80°C. Concentration of antimony in some Nigerian bottled water and soft drinks was above the EU limit after 11 months of storage at room temperature. Aged bottles leach lower amount of antimony than new bottles. Similarly larger bottles leach lower amount of antimony than smaller bottles.

The average acetaldehyde concentrations found in British fruit juices, carbonated soft drinks, sparkling water and still water were 5113, 1458, 22 and 8 µg/L respectively. Acetaldehyde was not detected in water bottled in glass. The concentration of acetaldehyde in five fruit juice samples in PET bottles and carton was beyond the EU specific migration limit (SML) of 6mg/kg. Also the tolerable daily intake of acetaldehyde could be exceeded as a result of intake of some soft drinks and fruit juices. Acetaldehyde content in soft drinks increase with storage but the increase cannot be accounted for by the residual acetaldehyde in PET. Acetaldehyde was found to be outgassing from some bottles. It was also found to be capable of migrating from soft drinks into bottle wall. Without replenishment the concentration of acetaldehyde in solution decreases with time.

The use of PVC cap lining in Nigeria as found in this study is a cause for concern as PVC is associated with health risk issues. The study recommends actions to ensure that antimony in fruit juices and other bottled products remain within the regulatory standard from bottling to consumption for the purpose of safeguarding the health of consumers. Glass used in bottling should be well scrutinized to ensure that it does not contain high levels of lead or other chemical substances that can cause harm to consumers through migration into contents. PET bottles can safely be used for solar water disinfection without the risk of antimony intake at concentrations above safe limits as water temperature achievable as the result of the technique doesn't go beyond 60°C. Also aged bottles are safer to use than new bottles because their chemical leaching was found to be lower than that of new bottles. This study recommends the reassessment of the absence of international guidelines for acetaldehyde in water and foods. The study also recommends that the amount of acetaldehyde that can be added to soft drinks as flavouring agent should be below the specific migration limit (SML) for migration of acetaldehyde from PET bottle into bottle contents. This is essential since the SML was designed to ensure that exposure to acetaldehyde, as a result of intake of bottled water and soft drinks in PET bottles, is below the tolerable daily intake (TDI) for acetaldehyde. As antimony was reported to go beyond the safe limits in some Nigerian bottled water and soft drinks after 11 months of storage this study discourages the use of bottle contents stored for a very long time.

DEDICATION

This work is dedicated to my mother Fatima, my elder brothers Tukur, Uwaisu and Ahmed, my elder sister Halima, my wife Fatima and my son Muhammad.

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ABBREVIATIONS

ACGIH	American Conference of Industrial Hygienists
Al	Aluminium
ANOVA	Analysis of variance
ATSDR	Agency for Toxic Substances and Disease Registry
Be	Beryllium
bis-HET	Bis-hydroxyethyl terephthalate
C	Carbon
CAGR	Cumulative annual growth rate
Cd	Cadmium
CFR	Code of Federal Regulations
Cl	Chlorine
CO	Cobalt
CO_2	Carbon dioxide
Cr	Chromium
CWQG	Canadian Drinking Water Quality Guidelines
DEHA	Bis(2-ethylhexyl) adipate
DEHP	Bis(2-ethylhexyl)phthalate/ dioctyl phthalate
DMT	Dimethyl terephthalate
DNA	Deoxyribonucleic acid
EAWAG	Swiss Federal Institute for Environmental Science and Technology)
EC	European Commission
EDX	Energy Dispersive X-ray
EFSA	European Food Safety Authority
EG	Ethylene glycol
EPA	Environmental Protection Agency
EU	European Union
EVA/PP	Ethylene vinyl acetate/polypropylene copolymer
FAAS	Flame atomic absorption spectrometry
FACS	Food Advisory Consumer Service
FAO	Food and Agriculture Organization
FDA	Food and Drug Administration
Fe	Iron
FSA	Food Standard Agency
GC-FID	Gas chromatography–Flame ionization detector
GC-MS	Gas chromatography–mass spectrometry
GDP	Growth domestic product
Ge	Germanium
HCl	Hydrochloric acid
HDPE	High density polyethylene
HPLC	High Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
ICP-MS	Inductively coupled plasma mass spectrometry
IDLH	Immediately Dangerous to Life and Health
IMF	International Monetary Fund
INAA	Instrumental Neutron Activation Analysis
IPCS	International Programme on Chemical Safety
ISBM	Injection Stretch Blow Moulding

M	Mean
MAC	Maximum Admissible Concentration
max	maximum
MCL	Maximum Contamination Level
Mg	Magnesium
min	minimum
Mn	Manganese
m/z	mass-to-charge ratio
N	Nitrogen
NAFDAC	National Agency for Food and Drug Administration and Control
nd	not detected
NIOSH	National Institute for Occupational Safety and Health
O	Oxygen
OSHA	Occupational Safety and Health Administration
P	Phosphorus
Pb	Lead
PE	Polyethylene
PEL	Permissible Exposure Limit
PET	Polyethylene terephthalate
PETRA	PET Resin Association
PP	Polypropylene
ppb	Part per billion
ppm	Part per million
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
r	Pearson’s correlation
r^2	coefficient of determination
Sb	Antimony
SD	Standard deviation
SEM	Scanning Electron Microscope
Si	Silicon
SML	Specific Migration Limit
Sn	Tin
SODIS	Solar Water Disinfection
t	Student's t-test
TDI	Tolerable Daily Intake
TLV-C	Threshold Limit Value - Ceiling
TPA	Terephthalic acid
Ti	Titanium
UAE	United Arab Emirate
US	United States
USGS	United States Geological Survey
UV	Ultra violet
V	Vanadium
V	Volt
WRAP	Waste & Resources Action Programme’
W	Watt
WHO	World Health Organisation
wt	weight
XRF	X-Ray Fluorescence Spectroscopy

Zn	Zinc
Zr	Zirconium

SYMBOLS

cm^{-1}	per centimetre
gcm^{-3}	gram per centimetre cube
$gmol^{-1}$	gram per mole
L	litre
mg/kg	milligram per kilogram
mg/L	milligram per litre
mg/ml	milligram per millilitre
ml	milliltre
m	metre
mm	millimetre
ng/L	nanogram per litre
Pa.s	pascal-second
µg/g	microgram per gram
µg/L	microgram per litre
$µg/m^3$	microgram per metre cube
µg/kg/day	microgram per kilogram per day
µl	microlitre
µm	micrometre
χ^2	Pearson's chi-square
φ^2	Cramer's phi coefficient

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CHAPTER 1: INTRODUCTION

1.1 Polyethylene terephthalate bottles and chemical migration

Polyethylene terephthalate (PET) bottles are excellent containers for water, beverages, edible oils and other liquids because they are light, tough and clear. PET bottles are also extensively reused for storage of drinking water, beverages and other liquids and for solar disinfection of microbiologically unsafe drinking water in the tropics. In spite of the usefulness of PET bottles earlier works have reported leaching of antimony and acetaldehyde from the bottle into the liquid contents. Antimony leaches from PET because its compounds are used as catalyst in the manufacture of the polymer at the concentration of 150-350 mg/kg (EFSA, 2004; Thiele, 2004; Westerhoff *et al*, 2008). Acetaldehyde is produced in the polymer matrix as a result of thermal degradation of the polymer during the melt processing stage in bottle manufacture (El-Toufaili, 2006, Ewender and Welle, 2008). Both antimony trioxide and acetaldehyde belongs to Group 2B (possible carcinogens) in the International Agency for Research on Cancer (IARC) carcinogen classification. Additionally, acetaldehyde associated with alcoholic beverages (derived from alcoholic beverage and formed endogenously) has recently been upgraded to IARC Group 1 carcinogen (carcinogenic to humans).

1.2 Justification for research

Migration of antimony and acetaldehyde from the wall of PET bottles into the bottle contents is an issue that warrants thorough investigation for the purpose of safeguarding the health of users. The PET bottle lifecycle is shown in Figure 1.1. Potential exposure to leached material might occur at the stage when the bottle is used to contain the beverage in which it was sold. Equally, this might occur during re-use. Antimony and acetaldehyde leaching propensity has been studied for PET bottles from some countries but not for British and Nigerian samples. The study is unusual in selecting laboratory conditions that mirror the way that these bottles are typically used. This was achieved by using some of the survey information on the pattern and extent of bottled water and soft drink use and PET bottle reuse to design the laboratory investigations on the migration dynamics of the migrant chemicals. The laboratory investigations assess likelihood of consumption of the migrant chemicals above the safe limits base on typical usage behaviour. In spite of the importance of information on bottled water and soft drink use and PET bottle reuse, this information remains scanty in the literature. In particular only one American study carried out some work on PET bottle usage patterns for the purpose of investigating the safety of bottle reuse.

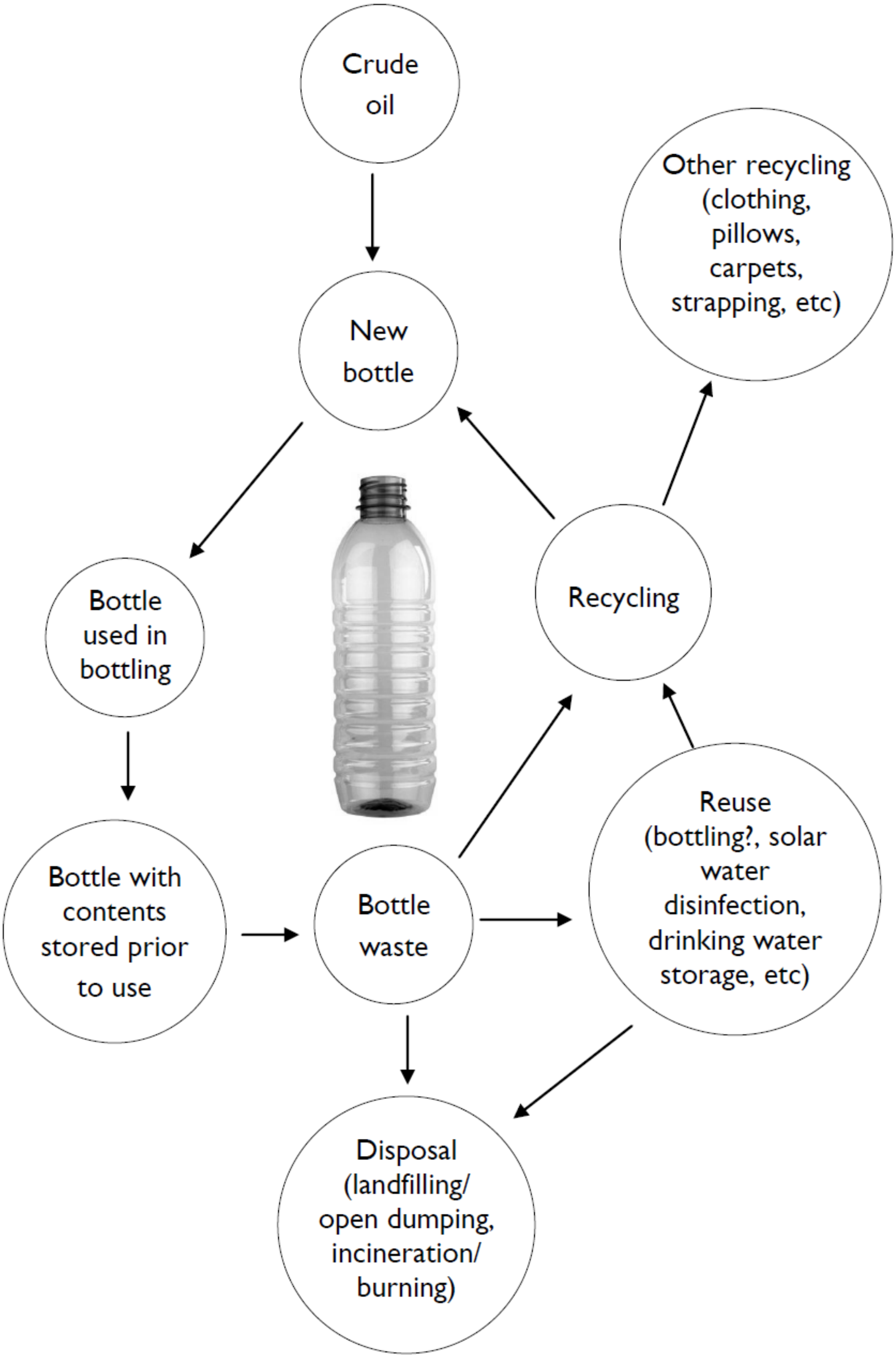

Figure 1.1 Life cycle of PET bottle

1.3 Aims and objectives of research

1.3.1 Aim of the research

The research aims to assess the pattern and extent of antimony and acetaldehyde migration from British and Nigerian polyethylene terephthalate (PET) bottles into bottle contents under typical use and reuse conditions in relation to current regulations and controls.

1.3.2 Objectives of the research

1. To examine the pattern and extent of bottled water and soft drink use and PET bottle reuse in Britain and Nigeria.
2. To assess the extent of antimony and acetaldehyde migration from PET into water and soft drinks under conditions representative of real use and reuse in Britain and Nigeria
3. Drawing on findings from 1 and 2, as well as existing regulations and controls to assess whether acceptable limits of chemicals in foods and water are being exceeded as a result of the chemical migrations
4. To generate recommendations about the extent to which existing regulations and controls might merit re-examination

1.4 Thesis structure

This thesis is partitioned into 10 chapters, bibliography and appendices. Chapters 2-4 provide an introduction to the current knowledge about the nature and usage of PET and glass bottles and about antimony and acetaldehyde migration, their health effect on human body and how they are regulated in drinking water and foods. Chapter 5 (Methodology) gives an account of the approaches employed in identifying the sampling frame for the survey, the different considerations that guided the survey questions content and how the sampling process was carried out. The Chapter also describes the experimental methods used to assess the concentration of antimony and acetaldehyde in fresh bottled water and soft drink samples and samples exposed different conditions and the experiments used to characterise the materials associated with water and soft drinks bottling. Chapter 6 (Survey results) presented the analysis of survey data and also the interpretation of the results obtained. Chapter 7 (Identification of materials used in bottling) describes the chemical nature of the different materials associated with still water and soft drink bottling based on the experiments carried out in Chapter 5. Chapter 8 (Migration of antimony and other elements) analyses and discusses the results obtained in experiments assessing the migration antimony and other elements from PET and glass bottles into bottle contents. Chapter 9 (Migration of acetaldehyde) analyses and discusses the results obtained in experiments assessing the migration acetaldehyde from PET into bottle contents. Chapter 10 (Conclusion) re-examines the objectives of the study and discusses the findings and their implication. The Chapter reflects on the strengths and limitations associated with the research and conclude by exploring potential areas for further research.

CHAPTER 2: MATERIALS ASSOCIATED WITH BOTTLING

2.1 Introduction

This Chapter describes the materials associated with bottling of water and soft drinks. Particular emphasis is given to materials that are in contact with the bottle contents namely bottling materials, cap materials and cap lining materials. The Chapter attempts to explain the processes through which antimony and acetaldehyde become associated with the bottle materials. Bottled water and soft drinks are principally bottled in PET bottles and to lesser extent glass bottles. In Britain, for example, 93% of bottled water is marketed in plastic bottle (Bottled Water Information Office, 2008). Polyethylene bottles, metal cans and paperboard cartons are also widely used for soft drinks. However this research is primarily interested in PET bottles and to lesser extent glass bottles for comparison. Materials associated with the PET and glass bottling process are PET and glass as bottle materials, plastics used as bottle caps, cap liners and label materials, including polyethylene; polypropylene and polyvinyl chloride, paper used in labelling, pigments and dyes for labelling and colouring of bottle parts, adhesives for securing several components of bottles, metals as metal bottle caps, including aluminium and steel usually coated with tin or chromium and lacquers applied to metal caps to provide a durable finish. However the only materials that are in direct contact with bottled contents are the bottle materials, the cap and the cap liner. Additionally the only material documented to be releasing acetaldehyde and antimony into bottle content is PET bottle material. While glass has not been documented to release acetaldehyde Shotyk *et al* (2006) has associated it with leaching of antimony though to lesser extent than PET.

2.2 Polyethylene terephthalate (PET)

2.2.1 Description of PET

PET is a long-chain thermoplastic polymer of the polyester family used in several applications. It is one of the most important raw materials used in man-made fibres. Bottle production accounts for around 30% of global demand of PET (McCarthy, 2007). In 1995, 2.9 million tonnes of PET were consumed worldwide in packaging applications across a wide range of areas including bottles for carbonated drinks, mineral water, edible oil, cosmetics, surfactants, films for thermoforming applications and packaging tape, *etc* (Azapagic *et al*, 2003).

2.2.2 PET synthesis

PET homopolymer is synthesised from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA) (Figure 2.1), all of which are derived from crude oil. Ethylene glycol is generated from ethylene. *P*ara-xylene (*P*-xylene) is either oxidized to terephthalic acid or reacted with methanol to produce dimethyl terephthalate (Azapagic *et al*, 2003). In some cases cyclohexane dimethanol and isophthalic acid substitutes some EG and DMT/TPA molecules respectively to generate a PET copolymer with lesser crystallinity, greater barrier properties, etc.

The first step in the synthesis of PET is the formation of a prepolymer, bis-hydroxyethyl terephthalate (bis-HET). Subsequent polymerization of this material (with the removal of ethylene glycol) forms the polymeric polyethylene terephthalate (Nexant, 2008). Antimony-based catalysts (principally antimony oxide, to lesser extent antimony acetate or antimony glycolate) in the concentration range of 150 – 350mg/kg (0.015 – 0.035%), catalyses the polycondensation of the intermediate prepolymer to PET (Thiele, 2004, EFSA, 2004). The most common catalyst is antimony trioxide, but salts of titanium, germanium, cobalt, manganese, magnesium and zinc are also used (Matthews, 2000). In general catalysts other than antimony trioxide are either less efficient or more expensive than antimony or even both (International Antimony Oxide Industry Association, 2006). Antimony catalyzes the chain prolongation reaction by ligand exchange mechanism within its coordination sphere (El-Toufaili, 2006). Coordination sphere of a metal ion in a coordination complex is the set of ligands immediately attached to the ion. As a rule some of the catalysts remain encapsulated into the polymer matrix or in the polymer chain itself (Matthews, 2000). Blue toners including cobalt compounds are sometimes used to mask undesirable colours in PET (El-Toufaili, 2006)

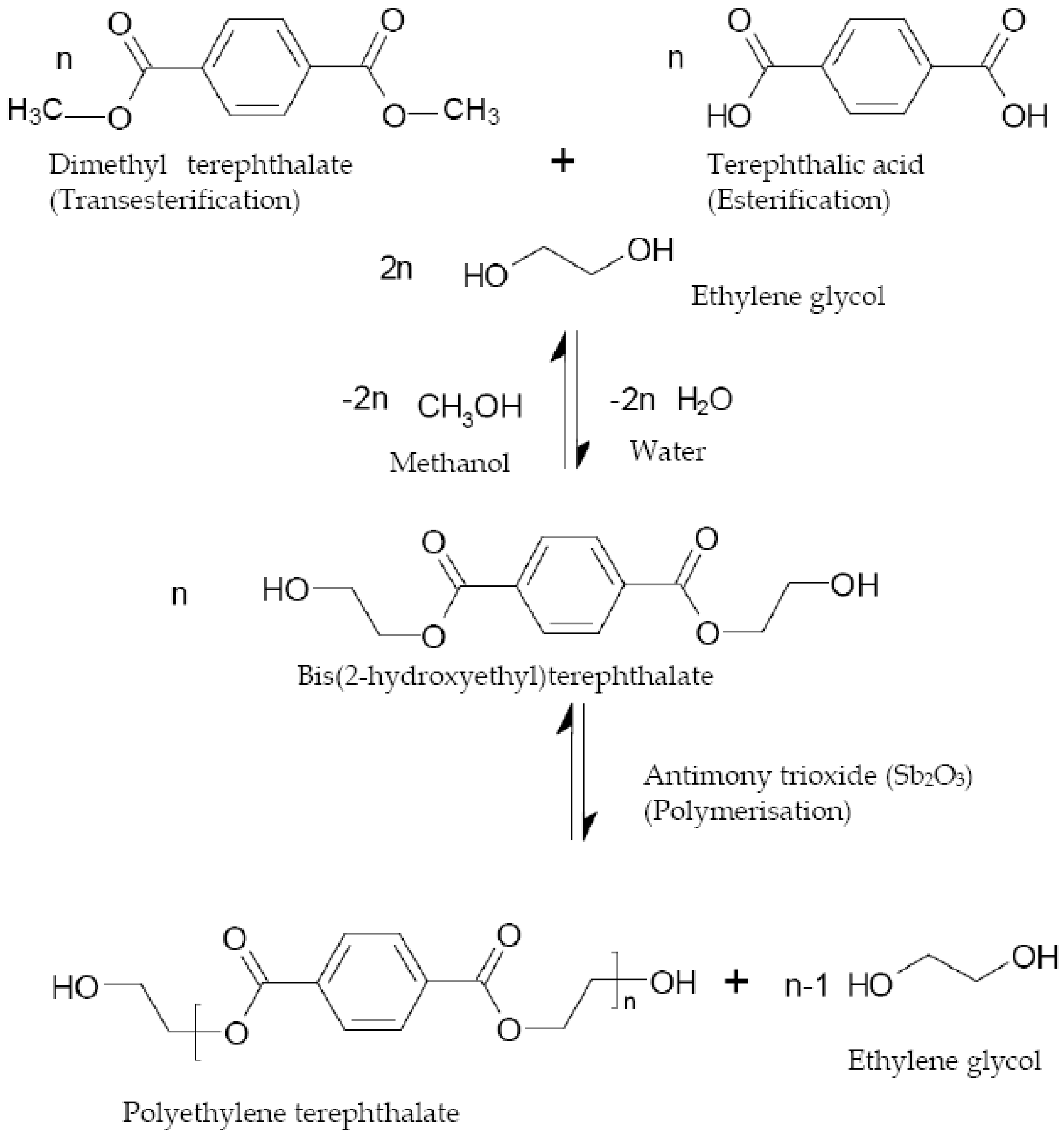

Figure 2.1 PET synthesis (Adapted from El-Toufaili, 2006)

2.2.3 PET bottle manufacture

PET bottles are produced by a two-stage process known as Injection Stretch Blow Moulding (ISBM). The process depicted in Figure 2.2 involves the production of an injection moulded PET bottle “blank” or preform followed by subsequent reheating, stretching and blow-moulding to produce a full-sized bottle. PET naturally absorbs water from its surroundings. Before processing it is usually heated to reduce its moisture content to less than 50 parts per million to avoid hydrolytic reactions which reduces its quality by generation of acetaldehyde.

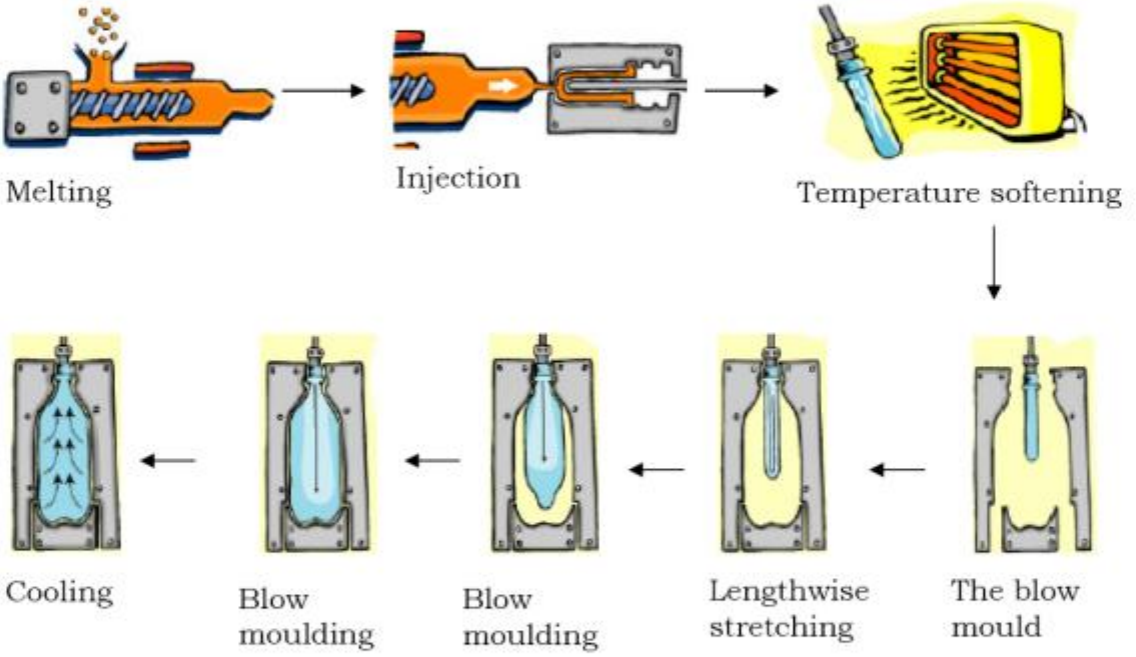

Figure 2.2 PET bottle injection stretch blow moulding process (Adapted from Visy Pty Ltd, 2008)

After about 4 hours of drying at a temperature of not more than 160°C (to avoid thermal degradation), the PET is melted and injected into the preform mould, resulting in the production of the PET bottle preform (Figure2.3). The PET bottle preform is heated to the correct profile for blowing, after which it is introduced into the blow mould. The hot preform is simultaneously stretched and blown in the blow mould to form the bottle (Kenplas, 2008, PET Planet Insider, 2001, VISY, 2008).

Figure 2.3 PET bottle preforms (Source: Aeco-Pack Corp, no date)

2.2.4 Acetaldehyde formation in PET material

Thermo-degradative generation of acetaldehyde in PET material occurs by a number of ways (El-Toufaili, 2006, Ewender and Welle, 2008). At high temperatures the ester bonds cleave via a cyclic transition state to generate acids and vinyl end groups (Figure 2.4). Then the vinyl end groups generate acetaldehyde through transesterification with ethylene glycol (Figure 2.5), through hydrolysis (Figure 2.6) or through chain rebuild by reaction of the vinyl end group with hydroxyl end group (Figure 2.7).

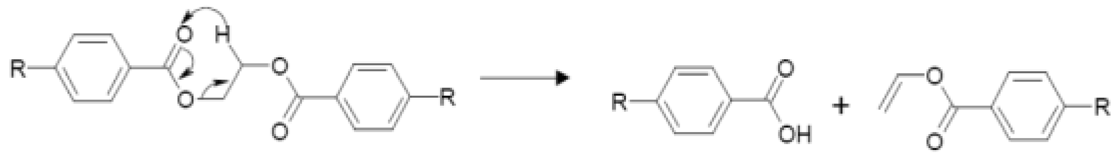

Figure 2.4 Cleavage of ester bonds in PET

Figure 2.5 Acetaldehyde formation by regeneration of the PET hydroxyl end group

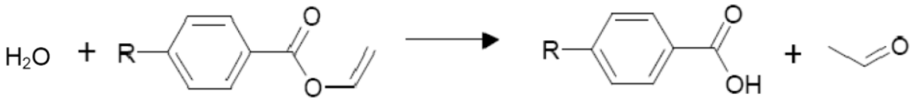

Figure 2.6 Acetaldehyde formation by hydrolysis of vinyl end group

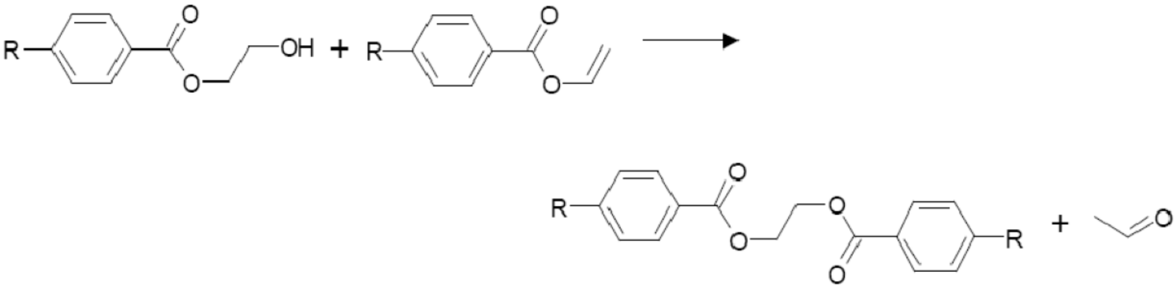

Figure 2.7 Acetaldehyde formation through chain rebuild

Acetaldehyde can also be formed through thermal scission of the PET hydroxyl end group (Figure 2.8).

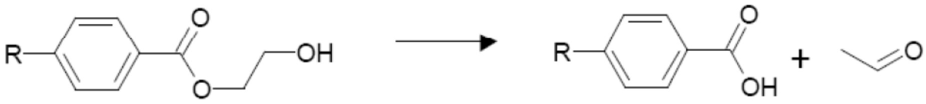

Figure 2.8 Acetaldehyde formation through thermal scission of the PET hydroxyl end group

Acetaldehyde concentrations in PET matrix can be reduced by either use of PET with low intrinsic viscosity or by addition of acetaldehyde scavenger additive to the PET. Low intrinsic viscosity which implies low molecular weight is associated with lower levels of acetaldehyde production during melt-processing stage. On the other hand lower intrinsic viscosity implies less stiff PET material (Kenplas, 2008).

2.3 Glass

Glass is brittle, and often optically transparent non-crystalline solid material primarily made from silica. Several types of glass including silica-free glass are available. The most common glass utilised in bottle making is soda lime glass. Based on Seward and Vascott (2005) the composition of soda-lime glass for containers is 74% silica, 13% sodium oxide, 10.5% quick lime, 1.3% alumina, 0.3% potassium oxide, 0.2% sulphur trioxide, 0.2% magnesia, 0.04 ferric oxide and 0.01% titania. In the course of glass melt processing tiny pockets of air from the atmosphere and from constituent's decomposition tend to get caught in the melt resulting in bubbles that can cause performance and aesthetic issues in the final product. Trapped bubbles are removed by a process referred to as fining, which may be physical or chemical. According to Shelby (2005) arsenic and antimony oxides at 0.1 – 1% by weight (1000 – 10,000mg/kg) are the most efficient chemical fining agents for glass. These oxides are probably not used as fining agents for glass to be used for bottle manufacture because of toxicity issues. If used however, the risk of the elements migrating from the bottle matrix into the bottle content becomes a possibility. In addition to its use as fining agent antimony also serves as opacifier agent in glass. Shotyk *et al* (2006) reported antimony concentrations of 7.6 and 10.1ppm from 2 glass bottles for bottling of water and cola drink respectively.

2.4 Other plastics

Polyethylene (PE) and polypropylene (PP) are olefin polymers of ethylene and propylene, synthesised using Ziegler-Natta catalysts. These catalysts are usually formed by the reactions of transition metal compounds of groups 4-10 (mainly Ti, V, and Zr) with alkyls or hydrides of groups 1, 2, 13, or 14 (Corradini *et al.* 2004). Polyvinyl chloride (PVC) is a polymer of vinyl chloride containing as much as 57% chlorine by mass. A vast array of additives including plasticizers, heat stabilizers, UV stabilizers, etc are usually added to PVC before it is made into finished products. Plasticizers are specifically added to the hard and brittle PVC to make it flexible. Phthalates, which are the most widely used plasticizers in PVC have been reported to be associated with allergies in children and decrease in anogenital distance among male infants exposed before birth, inducement of less male typical play behaviour in boys and other manifestations related to mimicry of human hormones (Bornehag *et al.* 2004, Swan *et al*, 2005, Swan *et al*, 2010). Additionally phthalates have been repeatedly reported to affect various life forms including fish and invertebrates adversely. As a result of the safety debate associated with the use of PVC several major corporations including Microsoft, Wal-Mart, and Kaiser Permanente are said to have announced efforts to eliminate PVC from products and packaging in 2005 (Center for Health, Environment and Justice, 2009). For similar reasons the State of California is currently considering a bill that would ban the use of PVC in consumer packaging (Californians Against Waste, 2010).

2.5 Summary

While many different materials are associated with bottled water and soft drink bottling only the bottle material, which may be PET or glass, the bottle cap and/or the lining of the bottle cap are in contact with the bottled content. PET bottling material has been established to release both antimony and acetaldehyde into bottle contents. Glass bottling material may only release antimony into bottle content and even then in quantities much lesser than in PET. Although the cap and cap lining materials have not been reported to release either of antimony and acetaldehyde these materials may be associated with other safety issues depending on the type of material used.

2.6 Conclusion

This Chapter explained the processes involved in the manufacture of PET and the stages at which antimony and acetaldehyde become associated with the PET material. The Chapter also talked about glass material and the processes through which antimony may become associated with the material. From the information on plastics other than PET it is clear that these plastics are not manufactured using antimony. Consequently these plastics will not be expected to release antimony.

CHAPTER 3: BOTTLED WATER AND SOFT DRINKS USE AND BOTTLE REUSE

3.1 Introduction

The Chapter explores the pattern and known extent to which bottled water and soft drinks PET bottle are used and reused in different countries including Nigeria and Britain. Factors influencing bottled water and soft drinks use and PET bottle reuse are discussed. Bottled water and soft drinks regulations and categorizations and how these regulations and categorizations define the different bottled water and soft drink types are examined. The measures usually taken to ensure that bottles used in packaging are safe are outlined and the impact of bottle quality regulation on bottle reuse is discussed. Bottled water and soft drinks shelf life and "best before" dates and the significance of such dating to migration are stated. The Chapter also look at the discourse on the safety of bottle reuse.

3.2 Bottled water and soft drink use

Water must be consumed by human beings either in its pure form or mixed with other constituents. Regardless of its form it has to be clean otherwise it will not guarantee the wellbeing of human beings. Of the more than 6 billion people in the world, more than one billion have no access to improved drinking water (National Environmental Service Centre, 2006). The WHO Joint Monitoring Programme for Water Supply and Sanitation defined access to improved water-supply services as the availability of at least 20 litres per person per day from a source that is likely to provide "safe" water (household connection, a borehole, *etc*,) within one kilometre of the user's dwelling (Joint Monitoring Programme, 2006). While the water supply coverage was 99% in 2004 in the developed world (Europe, North America, Japan and Australia) it was only 56 and 50% in sub-Saharan Africa and Oceania respectively (Joint Monitoring Programme, 2006). Lesser availability of the most affordable sources of safe drinking water supply in developing countries together with other factors translates into greater need for bottled water as an alternative safe drinking water (Rothschild and Nzeka, 2005). Conversely in most of these countries utilisation of bottled water as a source of safe drinking water may be severely delimited by cost relative to level of prosperity. As a result of this bottled water and soft drink consumption tends to be much higher in the developed world than in developing countries.

3.2.1 Bottled water

The world consumed 154 billion litres of bottled water in 2004, a 57 % increase from the 98 billion litres consumed five years earlier (Arnold and Larson, 2006). US, the highest consumer in terms of total annual consumption consumed 25.8 billion litres. Italy on the other hand was the highest per capita consumer. Even though Britain was not the highest in Europe in 2007, with a cumulative annual growth rate (CAGR) of 8% between 2002 and 2007, the rate increase in consumption was the highest in Europe. With a projected CAGR of around 7% between 2007 and 2012, the per capita consumption is expected to move from 41 litres in 2007 to 57.8 litres in 2012 (Just-Drinks, 2008). Figures 3.1 and 3.2 show the per capita annual consumption of bottled water for Britain, Nigeria and other nations in 1999 and 2004 (for Nigeria bottled water here refers to both water in bottles and water in pouches) and for different regions of the world in 2004. In France, Germany and Italy close to 90% of the population patronises bottled water in comparison to about 50% in Britain (Finewaters, 2009).

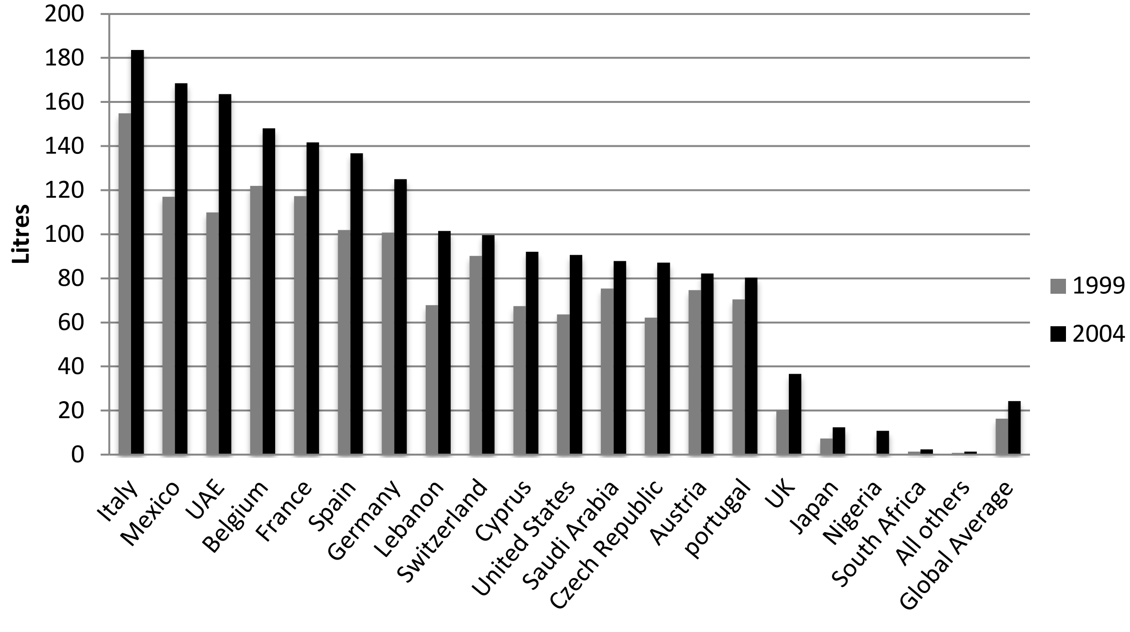

Figure 3.1 Global per capita consumption of bottled water in 1999 and 2004 (Adapted from Arnold and Larson, 2006)

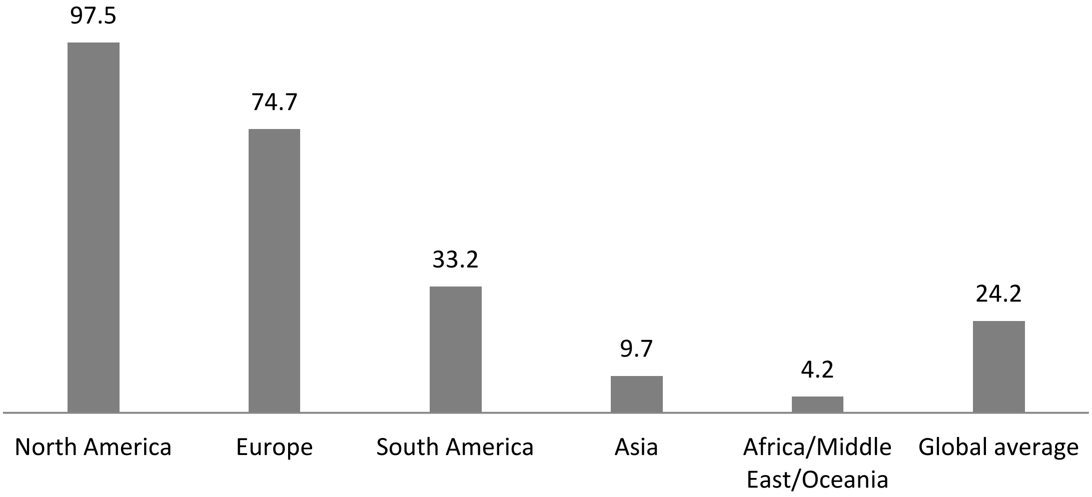

Figure 3.2 Per capita consumption of bottled water in 2004 by regions (Gleick, 2008)

While developing countries' overall bottled water consumption is comparatively lower than that of developed countries, these countries are still important consumers of bottled water. US, the highest consumer in 2004, was followed by emerging and developing countries (Mexico, China and Brazil) and then by Italy. In terms of per capita consumption Italy was followed by Mexico and United Arab Emirates. Of the top 15 per capita consumers of bottled water, Lebanon, the United Arab Emirates, and Mexico have the fastest growth rates, with consumption per person increasing by 44–50 percent between 1999 and 2004 (Arnold and Larson, 2006).

In 2004 the estimated market share of packaged water in Nigeria was 1.4 billion litres valued at approximately $500 million (Rothschild and Nzeka, 2005). According to the authors water packaged in plastic pouch, termed "pure water", accounts for 68 percent of total commercial water and is consumed by the low-income group. The estimated per capita consumption, based on the 2004 Figures and the Nigerian population of 130 million, was 10.77 litres in 2004. Nigeria's low per capita consumption of bottled water in comparison to the world average and most of the countries in Figure 3.1 probably results from the fact that Nigeria's per capita GDP is lower than the world average and is low in comparison to the most countries in the Figure. The water packaged in plastic pouches will not be fully investigated in this study because the packaging for this water is polyethylene rather than polyethylene terephthalate.

3.2.2 Soft drinks

In terms of soft drinks consumption Germany was Europe's largest market with Britain following fast behind (Food navigator, 2004). On average a Briton consumed 156 litres of soft drinks a year. Unlike bottled water some soft drinks are not bottled in glass or plastic bottles. However a Waste & Resources Action Programme's (WRAP) estimate put the number of PET bottles utilised annually in soft drinks in Britain at 6.5 billion (WRAP, 2008) In Nigeria the market share of soft drinks (fruit juice and carbonated drinks) was approximately 1.27 billion litres in 2004 (Rothschild and Nzeka, 2005). If the market share volumes were the same as consumed volumes, the estimated per capita consumption would have been 9.77 litres. According to the authors Nigeria's soft drink sub-sector maintained a 1% growth in five years mainly due to the increasing consumer health concern over products' sugar content and consumers' demand for nutritious beverages. It must be emphasised that in Nigerian carbonated soft drink market refillable glass bottles are more widely used in comparison to disposable PET bottles and aluminium cans. Among other reasons soft drinks are cheaper in refillable glass bottles than in disposable bottles and cans.

3.3 Factors influencing bottled water and soft drinks use

3.3.1 Country economic status

The economic status of a country influences the use of bottled water and beverages. This can evidently be seen from Figure 3.2 where the per capita consumption of North American and European regions by far surpasses the per capita consumption in Asia and Africa/Middle East/Oceania regions. Bottled water is more expensive than pipe-borne municipal water, even though it is perceived to be safer. Consequently in low-income countries there will be lesser tendency for bottled water use to be as widespread as in high income countries. Even though there is no similar data for bottled soft drinks there is no reason to believe that the trend is dissimilar. The extent to which availability of clean drinking water influences bottled water consumption is discussed in subsection 3.3.4.

3.3.2 Climatic conditions

In arid and tropical climates of the world the degree of transpiration in humans is higher than in milder climates, consequently the need to drink water and beverages will be higher. However hotter climatic conditions alone may not necessarily translate into higher consumption of bottled water. Most likely the influence of climate on bottled water usage will be linked to other factors including economic status of countries. For example United Arab Emirate (UAE) and Oman are Middle Eastern and very hot countries that share a common boundary. Whereas the former has a per capita bottled water consumption of 164 litres in 2004, the later has just 12.6 litres (Gleick, 2008). This could be justified to some extent by the fact that the UAE GDP per capita in 2004 almost triples that of Oman according to the IMF (IMF, 2010).

3.3.3 Environmental awareness

Environmental awareness is another factor that has some influence on the extent of use of bottled water and drinks. As mentioned elsewhere, plastic bottles are used in bottling of water and drinks more than glass and aluminium cans due to their superior qualities. Nonetheless the manufacture and utilisation of plastics is associated with release of toxic pollutants and greenhouse gases, littering and accumulation of plastics in world waters which is detrimental to marine life. Consequently increasing numbers of individuals and communities may prefer not to use plastics as a result of growing awareness campaigns by environmental organisations. Notable examples in Britain include Modbury and Hebden Bridge towns where a voluntary agreement between local shop owners and the communities saw to the banning of plastic shopping bags in the towns. This issue is however more prominent in developed countries. Questions are increasingly being asked recently on why so many people should be drinking bottled water rather than tap water. Additional concern is excessive withdrawal of natural mineral water or spring water to produce bottled water (Li, 2008).

3.3.4 Safety and health

In large number of developing countries safe drinking water is scarce. In such countries demand for bottled water and soft drinks will be raised by the scarcity (Rothschild and Nzeka, 2005; Li, 2008), especially if a cheaper versions of packaged water and soft drinks are available. In Nigeria for example 68% of packaged water is packaged in plastic pouches of 500ml capacity (Figure 3.3) rather than plastic bottles (Rothschild and Nzeka, 2005). By implication the scarcity of safe drinking water coupled with the availability of the cheaper water in pouches raises the per capita consumption of packaged water. In low-income countries scarcity of safe drinking water in the absence of cheap packaged water is not likely to increase packaged water consumption.

Conversely, availability of safe drinking water as in high-income countries may have only small effect on reduction of bottled water consumption. The impact of increasing desire for healthier lifestyle is probably more on soft drinks than for bottled water. In both developing and developed countries people are concerned that the sugar content of soft drinks makes them unhealthy to consume on regular basis.

Figure 3.3 Nigerian 500ml packaged water in polyethylene pouch

3.3.5 Taste

In some areas groundwater, which is usually used as drinking water, tastes bad as a result of dissolution of chemicals from underlying rocks, contaminants reaching the water from surface or leakage of briny seawater into aquifers especially in coastal areas. According to Li, (2008) in such areas patronage of packaged water can be expected to be high. In some countries people do not like drinking tap water because of its aftertaste which is associated with use of chlorine as disinfectant. In such cases bottled water, which is mostly treated using ozone, provides an alternative to tap water.

3.3.6 Other factors

Other factors that influences bottled water and drinks patronage include idolization of bottled water as fashion accessory (Royte, 2008), aggressive marketing strategies by the manufacturers, office working environments (Rothschild and Nzeka, 2005; Li, 2008). The fact that bottled water and soft drinks can be carried conveniently in a backpack or in a car may promote their consumption. Rural-urban divide may possibly influence bottled water and soft drinks patronage to greater extent in developing countries than in developed countries. Income inequality is more prevalent in the developing countries than in the developed countries with people in rural areas been poorer. As mentioned earlier better economic status promote bottled water and soft drinks use. Consequently people from rural areas in developing countries will probably be much less likely to be using bottled water and soft drinks than people from rural areas in developed countries

3.4 Bottled water and soft drinks regulations

Packaged water and drinks together with their packaging are usually regulated by government agencies principally in charge of food safety and in some cases together with drugs and related consumables. Such agencies in Britain, US and Nigeria are Food Standard Agency (FSA), Food and Drug Administration (FDA) and National Agency for Food and Drug Administration and Control (NAFDAC) respectively. In Britain bottled water is regulated under "The Natural Mineral Water, Spring Water and Bottled Drinking Water Regulations 2007 together with subsequent amendments (separately for England, Wales, Scotland and Northern Ireland). Additionally Bottled water must also comply with Directive 2009/54/EC of the European Parliament and of the Council of 18 June 2009 on the exploitation and marketing of natural mineral waters. Fruit Juices are covered by European Commission Directive 2009/106/EC of 14 August 2009 and The Fruit Juices and Fruit Nectars Regulations 2003. Unlike fruit juices and bottled waters, there is no formal legal definition or compositional standard for flavoured water and soft drinks other than fruit juices and nectars. However the colours preservatives, sweeteners and other additives used are all covered by separate EU directives and British regulations. In the US bottled water is covered by the bottled water standard of identity and quality regulations (21 CFR § 165.110) and current Good Manufacturing Practice regulations for the processing and bottling of bottled drinking water (21 CFR part 129). Additional regulations are the labelling regulations (21 CFR part 101) and current Good Manufacturing Practice regulations (21 CFR part 110) for all other foods are also applicable bottled water. Canned fruit juices are covered by Title 21 CFR part 146. In Nigeria soft drinks and fruit juices are regulated under Soft Drinks Regulations 2005 and Fruit Juice and Nectar Regulations 2005 together with Pre-Packaged Food (Labelling) Regulations 2005. For packaged water (bottled water and water in pouches) registration with NAFDAC is mandatory as required by the provisions of ACT CAP F33 LFN 2004 (formerly decree 19 of 1993) which also covers other foods. In addition to the mandatory registration, NAFDAC guideline documents “NAFDAC/EID/003/00” and “NAFDAC/RR/005/00” specifies the guidelines for establishment of packaged water plant in Nigeria and the guidelines for registration of food and water manufactured in Nigeria. Generally bottled water and soft drinks regulations are rules and restrictions meant to fully define and differentiate the different types of bottled water and soft drinks, treatments allowed, packaging and labelling, levels of contaminants allowed, good manufacturing practice and also define what constitutes breach of these rules and restriction and sanctions associated with so doing.

3.5 Bottled water and soft drinks categorisation

As earlier mentioned flavoured water and soft drinks other than fruit juices and nectars are not defined by law in Britain. Consequently, legally binding categorisation is non-existent. Nevertheless the British Soft Drinks Association defined flavoured water and soft drinks as "a manufactured drink, optionally sweetened, acidulated, which may contain fruit, fruit juice and other salts; the flavour may derive from vegetable extracts or flavourings" (British Soft Drink Association, no date). In Nigeria however the Soft Drinks Regulation 2005 defined soft drinks as “non- alcoholic carbonated or non-carbonated ready to drink beverages”. In both Britain and US the name of a fruit or fruits followed by juice can only legally be used to describe a product which is 100% pure juice. If diluted (to a degree limited by regulations) with water and/or contain additives besides fruit juice, including natural and artificial sweeteners, and preservatives, it is then referred to as nectar. Fruit juices may be categorised into, freshly squeezed, short life and long life juices if they have a shelf life of no more than 14 days, up to 30 days and between 6 and 12 months respectively (British Soft Drink Association, no date)

The British Bottled Drinking Water Regulations 2007 together with its subsequent amendments categorised bottled water into natural mineral water, spring water and bottled drinking water. While all the water type must meet safety criteria as specified in schedule two of the regulations, they differ in other attributes as described in Table

3.1. Bottled water categorisation in the US is generally similar to that in Britain. However in the US other categories exist in addition to the categories defined in Britain. These include artesian water, ground water, sterilised water and well water. In Canada bottled water is legally either mineral water also called spring water or just bottled water if it is not labelled as the former (Health Canada, 2009).There appears to be no legislation categorising packaged water in Nigeria. From their labels bottled water in Nigeria are either categorised as table water or spring water. Water in plastic pouches is sometimes referred to as sachet water and less formally but popularly "pure water". An additional categorisation for bottled water is whether they are still or sparkling. While this categorisation does exist in Britain, US and other countries, it is non-existent in Nigeria as carbonated water is not available in the bottled water market.

Table 3.1 British bottled water categorisation

Attribute	British bottled water type		
	Natural mineral water	Spring water	Drinking water
Source	single non-polluted ground water source	single non-polluted ground water source	may come from many sources
Recognition process	must undergo a 2-year recognition process	no formal recognition process required	no formal recognition process required
Stable composition	chemical composition must be stable except for an inevitable permissible variation	chemical composition does not have to be stable	chemical composition does not have to be stable
Treatment	altering chemical or microbiological quality not permitted, removal of unstable elements permitted	may undergo permitted treatments to meet the microbiological criteria in the Drinking Water Regulations	permitted
Bottling	must be bottled at source	must be bottled at source	not restricted to source
Labelling	mineral analysis, name of source and place of exploitation must be on the label	name of source and place of exploitation must be on the label	No restriction as for spring and natural mineral water

The above categorisations have some implications on the presence and or migration of chemicals including acetaldehyde and antimony. For example concentrations of antimony and acetaldehyde were reported to be higher in carbonated drinks than in still drinks (Nawrocki *et al* 2002, Keresztes *et al* 2009). Also Mutsuga *et al* (2006) reported higher amount of acetaldehyde in sterilised water than unsterilized water supposedly because the degradative activity of bacteria on acetaldehyde is absent in the former.

3.6 The significance of shelf life

Bottled water produced in accordance with current good manufacturing practice and quality standard regulations is considered to have an indefinite safety shelf life if stored in an unopened, properly sealed container (FDA, 2009). Bottled water is still labelled with 'best before' dates even though this is voluntary and unrelated to interaction between bottle content and bottle material. In fact according to Foods Standard Agency (no date) for most food products 'best before' dates are more about quality than safety. Bottled water and carbonated drinks in PET bottles from Nigeria have a shelf life of one year and six months respectively based on the production and 'best before' dates stamped on the bottles. In the US and Canada bottled water's stamped shelf life is usually two years (Environmental Health & Safety Online, 2006; Health Canada, 2009). Actually Health Canada (2009) suggested storing bottled water for emergency use for as long as one year. While still water does not expire, the 'best before' dates on carbonated water and soft drinks are probably in part related to their vulnerability to loss of carbon dioxide with time. Bottled water and soft drinks are most likely typically consumed before their 'best before' dates. However information on the actual time span between purchase and consumption of bottled water and drinks is unavailable in the literature. Even though shelf lives labelled on bottled water and drinks are not related to migration of chemicals, concentrations of migrants have been reported to rise with storage time as will be discussed later.

3.7 Bottle reuse in Nigeria, Britain and other countries

PET bottle reuse in the context of this work refers to putting the PET bottles in any use other than the original intended use. In developed countries health authorities sometimes discourage the reuse of the single-use PET bottles. For example Health Canada, the department of the government of Canada with responsibility for national public health, does not recommend the reuse for the sole reason of doing away with microbiological risk (Health Canada, 2009). PET bottle reuse may be a wide spread practice and may vary in application depending on where it is practiced. However data on PET bottle reuse is scarce in the literature. Reuse will probably be more widespread in developing countries than in developed countries in large part due to lesser need to reuse bottles in developed countries as a result of greater prosperity. On the other hand greater availability of empty bottles as a result of higher use may elevate extent of reuse in developed countries. Interestingly Lilya (2001) in a preliminary survey of the university of Idaho community in the US found that 88% of the participants reused polyethylene terephthalate (PET) plastic bottles used for bottled water, in some cases, for as long as six months.

PET bottles are not only used in packaging of water and soft drinks but also for packaging of edible oils, cosmetics, detergents, *etc* (Azapagic *et al*, 2003). In terms of reuse PET bottles initially used for products other than water and soft drinks are probably less likely to be reused at all because reusing them will require more vigorous cleaning than for bottles used for water and soft drinks. While reuse may not necessarily be limited to drinking water, reuse for drinking water will almost certainly turn out to be the most common form of reuse. In the temperate developed countries like Britain where the weather is generally cool, there may be only marginal need to store drinking water in the refrigerator. In such countries reuse of PET bottles will probably be limited to drinking water storage by people on the move and in work places than in homes. Nevertheless reuse at home may not be ruled out completely. In Nigeria in almost all households that can afford to own a refrigerator, empty bottles, mostly PET bottles serve as a means of storing water in the refrigerators to make the water cool (Figure 3.4). Additionally local beverages and medicinal herbal concoctions are vended in used PET bottles (Figure 3.5).

Figure 3.4 Storage of drinking water in used PET bottles in a refrigerator in Nigeria

Figure 3.5 Medicinal herbal concoctions vended in used PET bottles in Nigeria

A wide spread use of used PET bottles in developing countries is in the disinfection of drinking water by solar radiation, a process called Solar Water Disinfection (SODIS) (Figure 3.6). SODIS, a low-cost technology with a great potential to improve the health of those without access to safe drinking water, was developed by the Swiss Federal Institute for Environmental Science and Technology (EAWAG) and its Department for Water and Sanitation in Developing Countries (SANDEC). SODIS utilizes solar UV-A radiation and temperature to inactivate pathogens in water. According to EAWAG (2008) SODIS is used for the daily treatment of drinking water by over 2 Million users in more than 20 countries including Ecuador, Bolivia, Peru, Brazil, Congo, Uganda, Tanzania, Mozambique, Cameroon, Ivory coast, Pakistan, India, Vietnam, Cambodia and Sri Lanka (Figure 3.7). Additionally it has been shown that SODIS, combined with improved hygiene behaviour, can reduce diarrhoea incidence by 20 to 70% (Wegelin, 2006). SODIS can be achieved using both glass and PET bottles however as PET bottles are more readily available than glass bottles they are almost certainly more commonly used in SODIS.

Figure 3.6 SODIS in an African setting (Source: The Water School, 2008)

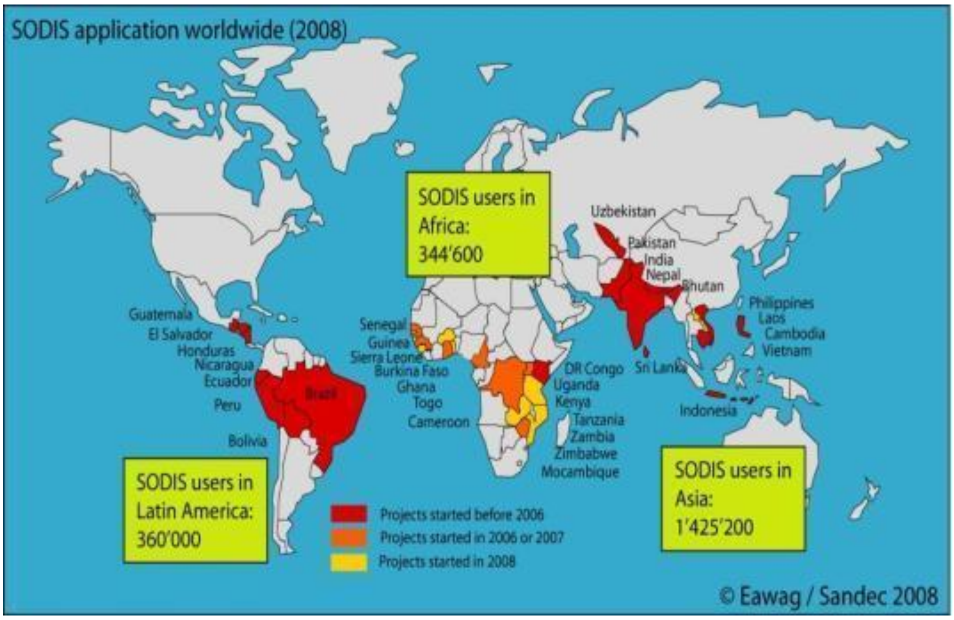

Figure 3.7 SODIS application worldwide (Eawag, 2008)

3.8 Bottle quality regulation

Even though the many plastics used in packaging of foods are generally inert, some may still transfer substances which can present a risk to human health. Directive 2002/72/EC of the European Union came into force for the purpose of ensuring that plastic materials used in packaging of foods are not releasing chemicals at levels that can unacceptably change the quality of packaged foods and/or present a risk to human health. The directive specified the maximum migration of antimony and acetaldehyde from PET bottling material into bottled contents at 40 and 6000 µg/kg respectively. The specific migration limits (SML), as they are called, are derived from tolerable daily intakes for antimony and acetaldehyde and by law they should not be exceeded in any interaction between plastic packaging and the packaged foods. As the provision of this directive deals with safety, the provision can also be extended to PET bottle reuse situation. The provision may not be legally binding in the case of bottle reuse as single use PET bottles are not originally meant to be reused after initial use. Consequently, for the sake of safety, reused bottles should not transfer antimony and acetaldehyde into water or any other content for consumption at concentration greater than the SMLs.

3.9 Factors influencing PET bottle reuse pattern

3.9.1 Country economic status and climate

People from high income countries are probably less likely to reuse PET bottle than those from low income countries simply because they have greater ability to buy bottled water and they have greater access to clean water. PET bottle reuse will probably be more widespread in hot low-income countries than in other countries. Currently SODIS is promoted and practiced only in tropical developing countries (Figure 3.7).

3.9.2 Safety debate

At present there is on-going debate mainly in developed countries about the safety of reusing PET bottle. PET bottles and other plastic containers have been demonstrated to leach chemicals at low concentrations. Improperly cleaned bottles have also been shown to harbour indicator bacteria which point to possible presence of pathogenic microorganisms. In some quarters people went to the extent of alleging that reuse of bottles can cause cancer as will be discussed later. Due to these on-going debates some people may opt not to reuse PET bottles.

3.9.3 Cost

Cost influence reuse of PET bottle because it is cheaper to refill a bottle with tap water than to buy a new bottle of water. Conversely other people especially in developed countries may prefer to buy new bottles seeing them as cheap and safer.

3.9.4 Other factors

Other factors that may influence the reuse of PET bottles include the availability of used bottles, age of bottles, environmental concern, original content of bottles, convenience due to portability of bottles, knowledge of and access to SODIS and the availability and pattern of supply of potable pipe-borne water supply to places of residence.

3.10 PET bottle reuse and bacterial contamination

Oliphant *et al*, (2002) in a study involving the assessment of bacterial water quality of elementary students' PET water bottles found that the Canadian Drinking Water Quality Guidelines (CWQG) criterion was exceeded for total coliform in 13.3% of 75 samples. Faecal coliform and total heterotrophic bacteria criteria were exceeded in 8.9% (of 68 samples) and 64.4% (of 76 samples) respectively. The presence of faecal coliforms in water implies possible contamination of the water with faecal material of human or animal origin and hence elevated possibility of the presence pathogenic organisms in the water. Identification of pathogens in PET bottles should clearly be related to introduction of the contaminants by the human handlers through repeated usage. Usage of a bottle by single person and thorough washing of the bottles with detergent before use can do away with microbial contamination hazard. However studies on the impact of long-term rigorous washing on bottle behaviour are unavailable.

3.11 PET bottle use and reuse and the safety debate

Water quality guidelines and standards provide a benchmark for measuring safety in terms of the amount of chemicals in drinking water including chemicals that may migrate from plastic materials into the water. However according to Lichter (2009) in online material titled "Are chemicals killing us?" different interest groups portray the risk associated with chemical migration possibilities differently. While environmental organisations and media are believed to be overstating the risk associated with release of chemicals from many products, industry sources are seen as understating these risks. Government agencies and professional associations are on the other hand believed as providing mainly accurate portrayals of associated risk. In an online document authored by an architectural firm (PM Architecture) with interest in sustainable portable water consumption and titled “Bottled water – do we need it?” a purported carcinogen named bisphenol A was alleged to be leaching from PET bottles into the water content. In reality this chemical is not in any way associated with PET and has not been established as a carcinogen. Another chemical widely publicised in the media as a carcinogen migrating from PET bottles is Bis(2-ethylhexyl) adipate (DEHA) based on a Masters degree thesis of a university of Idaho student (Lilya 2001). According to South African Food Advisory Consumer Service (FACS 2009) DEHA commonly used as a plasticizer in other plastics, has not been identified either as a raw material in PET or as its decomposition product. Additionally even if DEHA migrates from PET it falls in Group 3 in IARC carcinogen classification rendering it not classifiable as to its carcinogenicity to humans. There is also the same stance for antimony; the chemical established to be leaching from PET bottles. Even though this chemical has only been established as a possible carcinogen (IARC Group 2B), in many web pages it is usually referred to as if it is a confirmed carcinogen. On the other hand many documents released by industry stakeholders including International Antimony Oxide Industry Association, International Bottled water Association and PET Resin Association (PETRA) attempt to completely exclude the potential for harm in terms of chemicals migrating from PET even though some studies have established concentrations beyond the regulatory levels.

3.12 Summary

Unavailability of safe drinking water in the developing countries promotes bottled water use in those countries. In spite of that usage is still higher in developed countries. Regulations and categorisations may have some implications on the presence and migration of chemicals from bottle material into content. Even though shelf lives labelled on bottled water and drinks may be voluntary and unrelated to migration of chemicals, concentrations of migrants have been reported to be influenced by storage time. Reuse is probably, as widespread in developed countries as in developing countries. However, impact of long-term reuse and rigorous washing of bottles on bottle behaviour is not well documented in the literature. As a result of the varied interests on the subject of PET bottle use and reuse safety by different interest groups a lot of debate still remains on the subject.

3.13 Conclusion

Chapter 3 presented background information on the pattern and extent of bottled water and soft drinks use and PET bottle reuse and the factors influencing bottled water and soft drinks use and PET bottle reuse. The Chapter discussed bottled water and soft drinks regulations and categorizations and how the regulations and categorizations define the different bottled water and soft drink types. The Chapter revealed that bottles must meet some quality criteria in term of antimony and acetaldehyde migration before they can be used in bottling. From the information in the Chapter it is clear that the "best before" dates on water are unrelated to safety implying that bottle contents may not be unsafe to use even after the "best before dates". Because PET bottle reuse information is scanty in the literature this study will attempt to establish the bottle reuse pattern in Nigeria and Britain to further enrich the literature. Impact of long-term reuse and rigorous washing of bottles on bottle behaviour, which is not well documented in the literature, will be studied in this work.

CHAPTER 4: CHEMICALS MIGRATING FROM PET BOTTLES

4.1 Introduction

This Chapter presents an overview of antimony and acetaldehyde in terms of their abundance in the environment, their health effects on human beings and how they are regulated for the purpose of safeguarding human health. The Chapter review the literature on the migration of antimony and acetaldehyde from bottle wall into bottle contents. Factors affecting the migration of chemicals from bottle wall into bottle contents are also discussed.

4.2 Antimony

4.2.1 Background information

Antimony is silvery lustrous grey metalloid occurring principally as sulphide ores (stibnite and jamesonite) and to lesser extent as oxide ores (senarmontite and valentinite). Important properties and uses of antimony are summarised in Table 4.1. Identified world resources of antimony are estimated to be in the region of 4 to 6 metric tons and are located mostly in China, Bolivia, Mexico, Russia, and South Africa (Butterman and Carlin, 2004).

Table 4.1 Properties and uses of antimony

Chemical symbol	Sb
Atomic number	51
Electronic configuration	2,8,18,18,5
Group, period, block	15, 5, p
Atomic mass	121.76gmol^{-1}
Density	6.684gcm^{-3}
Natural isotopes	^{121}Sb (57.21%), ^{123}Sb (42.79%)
Melting point	631°C
Boiling point	1587°C
Oxidation numbers	-3, 0, 3, 5
Uses	Lead-acid batteries, bearing metal, solders, flame retardants, ceramics and glass, plastic stabilizers, plastic catalyst and pigments

4.2.2 Abundance in earth crust and world waters

At an estimated concentration of 0.2 to 0.5 parts per million, antimony accounts for between 0.00002 and 0.00005% of the earth crust (USGS, 2010). Filella *et al* (2002) in an extensive review of literature on occurrence of antimony in the environment reported typical concentrations of dissolved antimony in unpolluted waters as being less than 1µg/L. In two Polish studies involving the antimony concentration in 49 groundwater samples from southern and eastern Wielkopolska (Niedzielski *et al*, 2001) and in groundwater samples from Poznań city (Niedzielski and Siepak, 2005) the maximum antimony concentrations reported were 1.25 and 0.71 µg/L respectively. In the earlier study the lowest and average concentrations were 0.2 and 0.53 µg/L correspondingly. Shotyk *et al* (2006) reported antimony concentrations of as low as 0.0022 ± 0.0012µg/L for pristine ground water from Canada. Antimony concentrations have been reported to reach up to 100 times the natural levels in the proximity of anthropogenic sources. A typical example of this elevation due to anthropogenic activities was reported in the work of Fu *et al*, (2010) where the average antimony concentrations in water bodies (including drinking water reservoirs) located between one and 8 kilometres away from an antimony mining area in Hunan, China ranged between 8.7 ± 1.2 and 156 ± 4 µg/L with an average of 53.6 ± 46.7µg/L. An earlier reported case of high elevation of antimony concentration in water as a result of human activity as reported by Grimes *et al.* (1995) was near a gold deposit containing antimony and arsenic minerals in Nevada, USA. In this case the antimony concentration in groundwater was found to rose up to 260µg/L. For antimony in sediments and unpolluted soils the review by Filella *et al* (2002) reported the concentrations as being in the order of a few µg/g. Table 4.2 gives concentration ranges of antimony in fresh water systems, oceans, estuaries, sediments and soils as reported by these authors.

Table 4.2 Antimony concentration in the environment (Filella *et al.* 2002)

Environmental system	range	consulted publications
Freshwater	0.0001 – 96 µg/L	62
Seawater	<0.007 – 17.045 µg/L	52
Estuarine systems	0.0047 – 3.25 µg/L	9
Sediments	0.04 – 12500 µg/g	21
Soils	0.1 – 5000 µg/g	47

Antimony concentration in environmental waters and soils has an important bearing on the quality of bottled water and beverages as it is an important determinant of the ultimate antimony concentration in the finished products.

4.2.3 Health effects of antimony

Antimony trioxide and antimony pentoxide are the most important compounds of antimony with antimony pentasulfide, antimony chloride, antimony potassium tartrate, antimony trichloride, antimony trisulfide and antimony hydride been of lesser importance (Australian Department of the Environment, Water, Heritage and the Arts (2006). Antimony trioxide, which is the catalyst in the production of PET, is the form in which most antimony emission into the environment occurs (WHO, 2003). Antimony compounds are hardly absorbed in the gastrointestinal tract, resulting in less hazard of acute poisoning. Long-term animal studies have reported liver damage and blood changes when animals ingested antimony (ATSDR, 2007). Meglumine antimoniate is a pentavalent antimonial drug, used for the treatment of leishmaniases for over half a century. In a 21-day study to investigate its developmental toxicity as well as the transplacental transfer of antimony in rats by Miranda *et al.* (2006) no adverse effect was noted on the mothers at any dose level and no embryotoxicity was observed at the lowest dose. At the highest dose, Meglumine antimoniate increased embryo lethality, reduced foetal weight and augmented the occurrence of some soft-tissue and skeleton variations. In a 60-day short-tailed field vole antimony trioxide ingestion experiment no harmful effects were evident even though elevated organ concentrations were observed (Ainsworth *et al*, 1991). Similarly Kirkland *et al* (2007) detected no clinical signs of toxicity in rats exposed to antimony trioxide for 21 days except for some reductions in body-weight gain in the top dose group. The fact that antimony is not well absorbed in the gastrointestinal tract (ATSDR, 2007a) and does not bioaccumulate (WHO, 2003) could be an explanation for its low toxicity on short-term exposure in laboratory animals. Ainsworth *et al* (1991) observed rapid establishment of equilibrium between uptake and excretion with no subsequent occurrence of progressive increase in organ concentrations. Additionally the researchers observed rapid clearance of antimony on termination of dietary intake.

Long-term inhalation of high levels of antimony irritates eyes and lungs and causes heart and lung problems, stomach pain, diarrhoea, vomiting, and stomach ulcers. In rats lung cancer and problems with fertility were reported when rats breathed very high levels of antimony (ATSDR, 2007). However, except for corneal irregularities and dose-related increase in cataracts, no adverse clinical observations were attributed to antimony trioxide in a subchronic and chronic inhalation rat study by Newton *et al*

(1994). In spite of lung cancer development in rats as reported by other studies Newton *et al* (1994) did not find antimony trioxide to be carcinogenic in an inhalation study involving rats. These researchers concluded that previously reported studies, which found antimony trioxide to be a carcinogen, were run at higher lung burdens. Even though WHO made a pointer on some existing evidence on the carcinogenicity of certain antimony compounds by inhalation (WHO, 2003), the International Agency for Research on Cancer (IARC), and the Environmental Protection Agency (EPA) did not classify antimony as human carcinogen (ATSDR, 2007). However based on inadequate evidence for the carcinogenicity of antimony trioxide in humans and sufficient evidence for its carcinogenicity in experimental animals the IARC categorised antimony trioxide as being possibly carcinogenic to humans (IARC Group 2B) (IARC, 1989). Additionally arsenic, a chemical element that shares some chemical and toxicological properties with antimony, is a proven carcinogen (Gebel, 1997).

4.2.4 Guideline and regulatory standards for antimony in water and foods

The tolerable daily intake (TDI) for humans and the corresponding WHO guideline value for antimony in drinking water used to be 0.86 µg/kg/day and 5 µg/L before they were changed to 6 µg/kg/day and 20 µg/L respectively in 2003 (WHO, 2003). The elevated values imply increased margins of consumer safety for antimony. While the Japanese maximum admissible concentration changed from 2 to 15µg/L (Wakayama, 2005), the EU maximum admissible concentration and the EPA maximum contamination level remain unchanged at 5 and 6µg/L respectively (European Commission, 2003; EPA, 2010). The EU specific migration limit (SML) for antimony from PET into foods is 40µg/kg of food (EFSA, 2004).

4.3 Acetaldehyde

4.3.1 Background information

Acetaldehyde is a colourless, volatile, flammable, organic liquid with a pleasant, fruity odour at low concentrations and a pungent, suffocating odour at high concentrations. Important properties and uses of acetaldehyde are summarised in Table 4.3.

Table 4.3 Properties and uses of acetaldehyde

Chemical group	Aldehydes
Molecular formula	CH_3CHO
Molecular mass	44.05 gmol^{-1}
Melting point	−123.5 °C
Boiling point	20.2 °C
Solubility in water	Miscible in all proportions
Density	0.788 g cm^{-3}
Viscosity	2.456 X 10-4 Pa.s
odour threshold	0.05 ppm
Flash point	−39 °C
Autoignition temperature	185°C
Uses	intermediate in the manufacture of acetic acid, pyridine and pyridine bases, and esters, manufacture of disinfectants, drugs, perfumes, explosives, lacquers and varnishes, also as flavouring agents in foods including milk products, baked goods, fruit juices, candy, desserts, and soft drinks

4.3.2 Abundance in the environment and use as food additive

According to EPA (2007) Acetaldehyde is ubiquitous in the ambient environment occurring naturally in bread, and ripe fruit, as an intermediate product of higher plant respiration and as a product of incomplete wood combustion in fireplaces and woodstoves, coffee roasting, burning of tobacco, vehicle exhaust fumes, and coal refining and waste processing. In water, wide range of foodstuff and in air, concentrations are generally believed to be less than 0.1 μg/L (ppb), less than 1 μg/g (ppm) and averaging about 5 $\mu g/m^3$ (2.78ppb) respectively (IPCS 1995). In Los Angeles, California, levels of acetaldehyde up to 32 ppb have been measured in the ambient environment (EPA 2007), and in smoky indoor atmospheres its concentrations may reach as much as 100 ppb (Morris 1997). In some foodstuffs particularly some fruit juices and vinegar concentrations up to several 100 ppm were reported (IPCS 1995). While food and beverages, cigarette smoke and, to a lesser extent air are the major source of exposure to human population, the main source of human exposure to acetaldehyde is said to be through the metabolism of alcohol (IPCS 1995).

In addition to its natural presence in fruit juices acetaldehyde is added to some soft drinks as a flavouring agent (Miyake and Shibamoto 1993, Food Safety Commission 2005, National Toxicology Program 2010). Acetaldehyde is one of the chemical substances in the US FDA's Everything Added to Food in the United States (EAFUS) database (FDA 2011). According to FDA the EAFUS list of substances contains ingredients added directly to food that FDA has either approved as food additives or listed or affirmed as Generally Recognized as Safe (GRAS).

4.3.3 Health effects of acetaldehyde

Acetaldehyde vapour at moderate concentrations causes eye irritation in animals and humans (EPA 1994). In humans signs of eye irritation manifest at 50 ppm, and at 200 ppm red eyes and transient conjunctivitis develop (Clayton and Clayton, 1993). Repeated exposure may lead to chronic irritation of the eyes with resultant permanent damage (New Jersey Department of Health and Senior Services, 2010) In liquid form acetaldehyde can cause skin irritation, painful burning sensation and possibly skin allergy (ACGIH, 2001; New Jersey Department of Health and Senior Services, 2010). Vapour inhalation has been reported to cause adverse respiratory tract effects in both animals and humans (USEPA 1994). In a 4-week study involving acetaldehyde inhalation in rats Appleman *et al.* (1982) reported increased lung weights, and severe degenerative, hyperplastic and metaplastic changes of the nasal, laryngeal and tracheal epithelium at concentrations of 5000ppm. While increased blood pressure and decreased heart rate were observed in acetaldehyde inhalation study in rats (Egle, 1971), the author concluded that concentrations of acetaldehyde producing significant changes of blood pressure and heart rate are somewhat higher than those that would be encountered in cigarette smoking. Limited evidence links acetaldehyde with adverse developmental and neurological effects in animals, including central nervous system depression and neural degeneration (EPA 1994). Acetaldehyde was not found to be mutagenic in *Salmonella* or in *E. coli*, however it was reported to be positive for chromosome aberrations and sister chromatid exchange both in vitro and in vivo mammalian assays (EPA 1994). Additionally Singh and Khan (1995) observed an irreversible breakage of both single and double stranded DNA in addition to significant cell loss in a study evaluating its cytotoxicity and genetoxicity in human lymphocytes. In the concentration range of greater than 1 to 100ppm acetaldehyde has been linked to moderate acute toxicity to aquatic organisms (EPA 1994).

Studies have implicated acetaldehyde in causation of tumours in experimental animals (Feron *et al.* 1982, Woutersen *et al.* 1984, Woutersen *et al.* 1986). Acetaldehyde has also been suggested to be an important factor in alcohol-associated carcinogenesis of the upper aero-digestive tract of humans (Seitz and Meier, 2007). Based on inadequate evidence for the carcinogenicity of acetaldehyde in humans and sufficient evidence for its carcinogenicity in experimental animals the International Agency for Research on Cancer (IARC) categorised acetaldehyde as being possibly carcinogenic to humans (IARC Group 2B) (IARC, 1999). However, an IARC working group of 30 scientists from 10 countries reassessing the carcinogenicity of some carcinogens and identifying additional tumour sites and mechanisms of carcinogenesis concluded that acetaldehyde associated with alcoholic beverages (derived from the alcoholic beverages and formed inside human body as a result of alcohol metabolism) is carcinogenic to humans (Group 1)(IARC 2009)

4.3.4 Guideline and regulatory standards for acetaldehyde in water and foods

International guidelines and standards for acetaldehyde in drinking-water have not been established (IARC 1999). The EU specific migration limit (SML) for acetaldehyde in foods is 6mg/kg (6000 ppb) as specified in the Commission Directive 2002/72/EC of 6 August 2002 (European Commission, 2002). The tolerable daily intake (TDI) for acetaldehyde is 0.1mg/kg body weight per day in humans (European Commission, 1998) The Occupational Safety and Health Administration's (OSHA) Permissible Exposure Limit (PEL), the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Value - Ceiling (TLV-C) and the US National Institute for Occupational Safety and Health's (NIOSH) Immediately Dangerous to Life and Health (IDLH) limit are 200, 25 and 2000ppm respectively (National Toxicology Program 2010).

4.4 Basis and implications of water quality standards

Water quality guidelines and standards for drinking water refers to maximum levels or concentrations of chemical, microbiological and physical contaminants that are allowed in drinking water based on evidence that such concentrations do not result in any significant risk to health over a lifetime of consumption. The primary purpose of both guidelines and standards is protection of the public health. While guidelines are non-legally binding recommendations, standards are legally enforceable national regulations and thus infringement can attract prosecution (Radojević and Bashkin, 1999). WHO guidelines for drinking-water quality are international norms on water quality and human health meant to be used as the basis for regulation and setting of standards in all countries. Consequently standards tend to differ between countries as exemplified by drinking water antimony standard for EU, US and Japan as mentioned in 4.2.4. Standards also tend to be more stringent than the WHO guidelines.

4.5 The implication of IARC's possible carcinogen status

The IARC categorised antimony trioxide and acetaldehyde in Group 2B based on inadequate evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals. The basis and implication of this categorisation is explained in IARC (2010). According to IARC inadequate evidence of carcinogenicity in humans may either imply insufficient quality, consistency or statistical power of the available studies to permit a conclusion regarding the presence or absence of a causal association between exposure and cancer, or absence of data on cancer in humans. On the other hand sufficient evidence of carcinogenicity in experimental animals implies a situation where a causal relationship has been established between the agent and an increased incidence of malignant neoplasms or of an appropriate combination of benign and malignant neoplasms in (a) two or more species of animals or (b) two or more independent studies in one species carried out at different times or in different laboratories or under different protocols. Additionally an increased incidence of tumours in both sexes of a single species in a well-conducted study, ideally conducted under Good Laboratory Practices, can also provide sufficient evidence. Furthermore a single study in one species and sex might be considered to provide sufficient evidence of carcinogenicity when malignant neoplasms occur to an unusual degree with regard to incidence, site, type of tumour or age at onset, or when there are strong findings of tumours at multiple sites.

The overall implication of this categorisation is that the 2 chemicals have been confirmed to be carcinogenic in experimental animals but that there is high degree of uncertainty with regard to their carcinogenicity in humans. However, as mentioned earlier acetaldehyde in alcoholic drinks and acetaldehyde formed in the body as a result of their metabolism has recently been upgraded to Group 1 carcinogen.

4.6 Leaching of antimony and acetaldehyde into water and foods

Chemicals documented to leach from PET bottles/containers into water and/or food include antimony (Hansen and Pergantis, 2006; Shotyk *et al*, 2006; Shotyk and Krachler, 2007; Westerhoff *et al*, 2008), carbonyl compounds including acetaldehyde, formaldehyde and acetone (Sugaya *et al,* 2001, Nawrocki *et al,* 2002, Matsuga *et al,* 2006), PET cyclic oligomers (Matsuga *et al,* 2005; Nasser *et al,* 2005) and UV stabiliser Tinuvin (Begley *et al,* 2004). Bis(2-ethylhexyl) adipate (DEHA) and Bis(2-ethylhexyl)phthalate (DEHP), the plasticisers used with PVC but not with PET, have also been reported to migrate from PET bottles (Lilya, 2001, Nathan and Philip, 2009)

4.6.1 Antimony

In PET polymerisation germanium-, titanium-, antimony-, cobalt-, manganese-, magnesium- and zinc-based catalysts are employed but consequent of lower cost of the antimony-based catalysts in relation to their efficiency more than 90 % of the world PET production is made by addition of 150-350 ppm antimony mostly as antimony trioxide and to lesser extent as antimony acetate or antimony glycolate (EFSA, 2004; Thiele, 2004; Westerhoff *et al*, 2008). Concentration of antimony in PET materials reported by different authors using different analytical methods mostly falls within the industry reported concentrations as shown by Table 4.4 below. Antimony leaches into bottle contents because it is not chemically bonded to PET material. The relationship between antimony, PET bottle material and bottle contents is shown in Figure 4.1

Table 4.4 Antimony in PET material

Concentration (ppm)	method	author
397, 351	INAA	Shotyk *et al*, 2006
98 - 190	FAAS	Lopez-Molinero *et al*, 2007
213	ICP-MS	Westerhoff *et al*, 2008
357 ± 8, 326 ± 6	ICP-MS, XRF	Alt *et al*, 2008
210, 290	ICP-MS	Keresztes *et al*, 2009

As earlier said in Subsection 4.2.2 the typical concentration of antimony in unpolluted water is less than 1µg/L. Consequently the antimony content of freshly bottled water will generally not be expected to go beyond this concentration significantly. As antimony has been established to migrate from PET bottles into content the antimony concentration in water bottled in PET cannot confirm the actual antimony content of the source water. Additionally antimony migration cannot be confirmed unless experiments varying parameters of interest are carried. The antimony content of water from Hungarian well used by bottlers was reported to be below the detection limit of 0.7ng/L in the work of Keresztes *et al* (2009). In an earlier study Shotyk *et al*

(2006) reported antimony concentrations of 3.8 ± 0.9 ng/L for bottled water source in Germany. The antimony concentrations of bottled water samples as reported by different authors are given in Table 4.5. From the Table it can be seen that the EU maximum admissible of 5μg/L has not been exceeded in any of the studies, though it has been attained in the Turkish study. Factors reported to influence antimony migration and the degree to which they effect the migration will be discussed in Section 4.7.

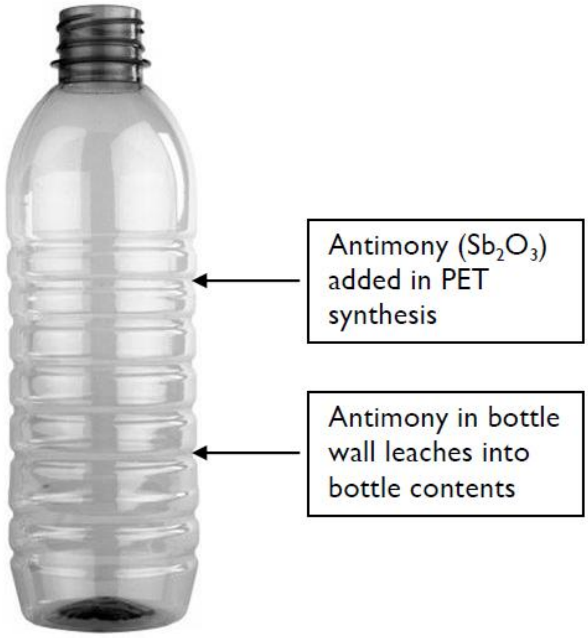

Figure 4.1 Relationship between antimony, PET and bottle contents

Table 4.5 Antimony in bottled water

Concentration (ng/L)	detection limit (ng/L)	Brands	author	country
8.9 – 2570	0.35	69	Shotyk *et al* 2007	16 countries
7 – 249	2	158	Cicchella *et al* 2010	Italy
nd – 931	10	-	Reimann *et al* 2010	many
2.15 – 2350	2	-	Birke *et al* 2010	Germany
95 – 521	4	9	Westerhoff *et al* 2008	US
nd - 5000	-	189	Güler 2007	Turkey

4.6.2 Acetaldehyde

As mentioned earlier in Subsection 2.2.4, acetaldehyde is generated as a result of thermal degradation during the melt-processing stage of PET bottle manufacture. Acetaldehyde formed in the plastic matrix can either diffuse outward into the atmosphere or inward into the contents of the PET bottle (Kenplas, 2008). The relationship between acetaldehyde, PET bottle material and bottle contents is shown in Figure 4.2. The odour and taste threshold of acetaldehyde in water is reported to be 20–40 µg/L (Nijssen *et al*, 1996; Schröder, 2001). In beverages bottled in PET acetaldehyde the taste is masked by the flavour of the beverages. In bottled water however very small amounts of acetaldehyde can be tasted and smelt as the result of the low odour and taste threshold (Kenplas, 2008, Federal Institute for Risk Assessment, 2007). Consequent of such differences PET materials with minimal levels of acetaldehyde are desired for water bottling. The acetaldehyde concentrations in 38 PET bottle materials in the work of Matsuga *et al, (*2005) were 8.4-25.7 µg/g in Japanese bottles, 5.0-13.1 µg/g in French and Italian bottles, and 9.1-18.7 µg/g in US and Canadian bottles, respectively. From the work of the same author the acetaldehyde concentration in 10 different bottle- and sheet-making PET pellets was 3.5 – 12.4 µg/g. Bashir *et al* (2002) reported much lower concentrations (0.3 – 0.8 µg/g) in an earlier study involving nitrogen-cooled ground PET material. While acetaldehyde does migrate from PET bottle materials into bottled water it has also been found in water not in contact with PET. Nawrocki *et al* (2002) reported concentrations ranging of 1.4, 0.1 and 4.5 µg/L for distilled water, deionised water and tap water respectively. Sugaya *et al* (2001) reported a maximum concentration of 1.1µg/L for tap water samples. Concentration found in bottled water and beverages are given in Table 4.6

Table 4.6 Acetaldehyde in bottled water and soft drinks

Type	Concentration (µg/L)	detection limit (µg/L)	Brands	author	sample country
Bottled water	0.9 – 317.8	0.1	14	Nawrocki *et al* 2002	Poland
Bottled water	nd – 260	0.5	32	Sugaya *et al* 2001	Many
Bottled water	nd – 107.8	5	20	Mutsuga *et al* 2006	Many
Beverages	460 - 101900	-	-	Miyake and Shibamoto 1993	US
Carbonated beverages	18.5 – 358.5	10	3	Özlem 2008	Turkey

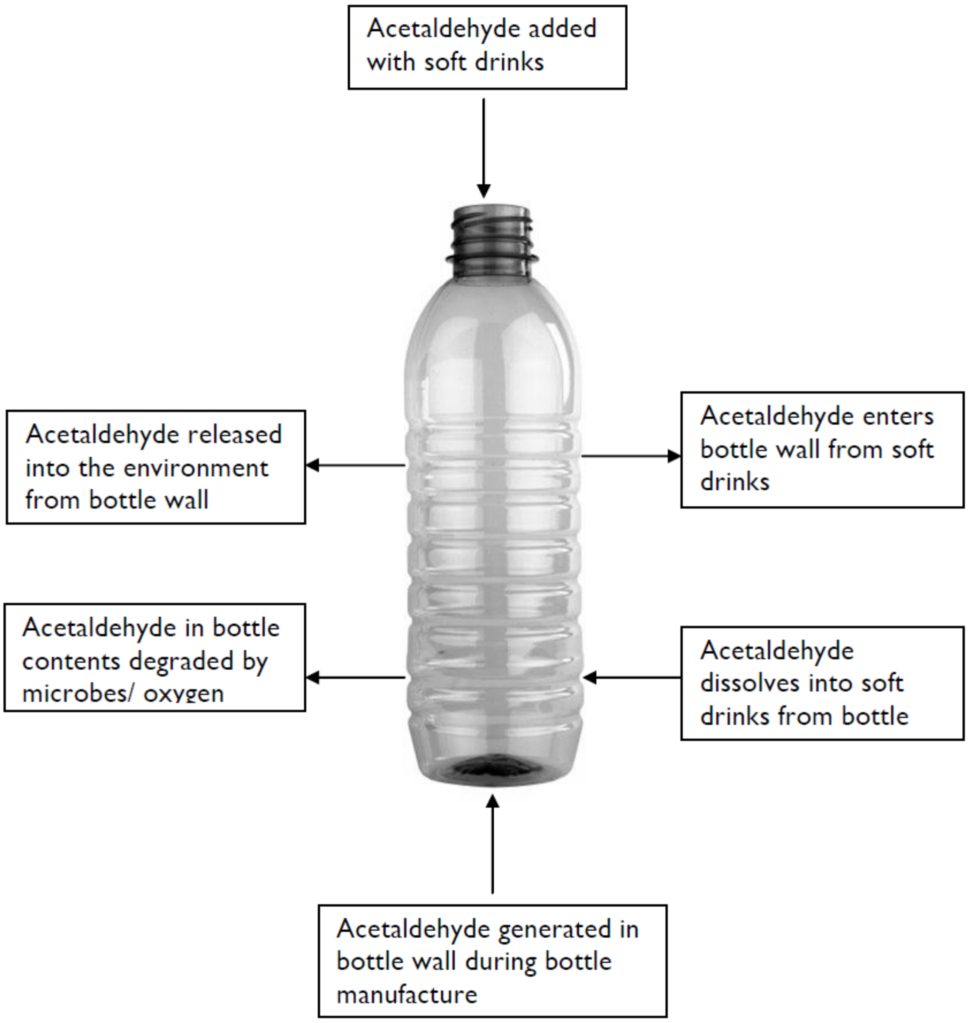

Figure 4.2 Relationship between acetaldehyde, PET and bottle contents

4.7 Factors affecting the leaching of chemicals

4.7.1 Elevated temperatures

Temperature is a measure of kinetic energy of molecules, hence the higher the temperature the faster the molecular movements and chemical reactions. Consequent of higher kinetic energy of molecules at elevated temperatures degradation of PET material and leaching of chemicals from PET bottles into the environment is expected to increase. Westerhoff *et al,* (2008) reported faster rates of antimony leaching from PET bottle into the water with increasing storage temperatures. After 7 days at 80°C, for example, the authors recorded antimony concentration of 14.4 ppb in the water, a concentration more than twice the EPA Maximum Contamination Level (MCL). The authors also extrapolated that for exposure temperatures of less than 58°C, exposure durations of greater than 1 year were required to reach the MCL. For exposure temperatures of 60, 65, 70, 75, 80, and 85 °C, however, the exposure durations required to reach the MCL decrease rapidly to 176, 38, 12, 4.7, 2.3, and 1.3 days, respectively. In the work of Al-Malack (2001) migration of lead and cadmium from PVC pipes into water was not found to be significantly affected by the increase in water temperature. In contrast, tin, barium, and calcium concentrations were found to increase when the water temperature was raised from 35 to 45°C by 42, 85 and 29%, respectively. Nawrocki *et al* (2002), Ahmad and Bajahlan (2007) and Le *et al* (2008) also reported higher migrations of carbonyl compounds from PET bottles into water, styrene monomer from Styrofoam cups and bisphenol A from polycarbonate bottles into drinking water respectively at elevated temperatures. Elevated temperatures not only promote migration of chemicals but also the degradation of the plastic material itself. By implication exposing food, water and beverages in plastic containers to higher temperatures could result in consumption of elevated levels of the different chemicals that leaches from the plastic materials into the foods, water, beverages and the environment. In a SODIS study by Tukur *et al* (2006) a temperature of 58.3 °C was reported to be achievable on exposure of water in glass bottles for 2.5 hours from midday.

4.7.2 Sunlight and UV radiation

Sunlight is made up of infrared, visible and ultraviolet radiations. Light and electromagnetic waves of any frequency can bring about heating effect on surfaces that absorb them. The sun's infrared radiation accounts for 49% of the heating of the Earth (Arizona Solar Center, 2008). Consequently, direct exposure to sunlight can bring about the same effect as heat on the rate of molecular movements and chemical reactions. In SODIS, for example, sunlight treats contaminated water through the synergetic effects of DNA alterations by UV-A radiation, photo-oxidative disinfection and, heat inactivation (Borucke *et al.*, 2001). In addition to the sunlight's ability to accelerate leaching of chemicals as does elevated temperatures the ultraviolet component of solar radiation is known to bring about degradation of plastic materials. It is this UV's degradative ability on plastics that prompts the addition of UV-stabilizing additives to plastics during processing. In the work of Westerhoff *et al,* (2008) UV irradiation increased leaching of antimony significantly even though as the authors reported separating the effects of UV irradiation from those of heating on antimony leaching from the plastic is difficult. Nawrocki *et al* (2002) observed the enhancement of acetaldehyde migration as a result of synergistic effect of sunlight and elevated temperatures. Al-Malack (2001) also reported increased migration of metallic stabilizers from PVC pipes into water as time of exposure to UV radiation increased.

4.7.3 Carbonation

Carbonation is the addition of carbon dioxide into water or aqueous solutions. Carbonation lowers the pH of sparkling water or soft drinks by raising the hydrogen ion concentration through formation of carbonic acid. In the reports of Nijssen *et al* (1996), Schröder (2001) and Nawrocki *et al* (2002) carbonation of water was reported to enhance formation and/or migration of acetaldehyde from PET bottles into water. No report is available on the mechanism by which carbonation enhance formation and/or migration of acetaldehyde. However the acidification of water or aqueous solution brought about by the carbonation process may play some role. Carbonation was not reported to affect migration of other plastic-associated chemicals into water.

4.7.4 Storage

Prolonged storage of bottled water and soft drinks may occur at the supply chain stage (production, wholesale and retail stages) or at consumer stage. In theory the longer the duration of contact between water, soft drinks or foods and the packaging material (PET, glass, etc), the higher the amount of migrant chemicals to be found in the water or soft drinks. In PET bottled water stored for 9 months the content of aldehydes gradually increases over the period of 8–9 months and then begins to decrease (Nawrocki *et al,* 2002). The gradual decrease of aldehydes concentration was associated with the gradual loss of dissolved CO_2, a gas whose presence in bottled water enhances the formation and/or desorption of acetaldehyde. Both CO_2 and aldehydes are believed to diffuse through the bottle wall into the environment. Le *et al* (2008) described noticing the release of bisphenol A from polycarbonate bottles increasing with time at room temperature. Hansen and Pergantis (2006) and Shotyk and Krachler (2007) also reported increased leaching of antimony from PET bottles into citrus juices and water respectively with greater duration of storage. Al-Malack (2001) in an investigation on metal stabilizers leaching from PVC pipes into water reported observing increase in metal stabilizer concentrations with respect to time of exposure. After 10 h of exposure, lead concentration reached a value of 0.43 mg/l, and by the end of the experiment (48 h), it increased to 0.78 mg/l. Tin was found to increase to 0.27 and 0.31 mg/l after 24 and 48 h of exposure, respectively. Barium and cadmium were found to increase to 0.42 and 0.1 mg/l, respectively, after 48 h of exposure to double distilled water. Moreover, calcium concentration increased to 46 and 49 mg/l after 24 and 48 h of exposure, respectively.

4.7.5 Bottling material

Acetaldehyde migration is expected to take place only in PET bottle as it cannot be generated in glass. In the work of Sugaya *et al* (2001) acetaldehyde concentrations in mineral water bottled in both glass and paper containers were below detectable levels. Because antimony is used in glass industry as fining agent and as pacifying agent as stated earlier in Section 2.3, its migration from glass bottles will not be unexpected depending on the nature of the glass material. Water bottled in glass was reported to show antimony concentration higher than the source water but lower than for water bottled in PET in the work of Shotyk *et al* (2006). For the source water concentration of 3.8±0.9 ng/L the concentration in glass and PET bottled water were 11.5±4.4 and 359±54ng/L respectively. In the work of Hansen *et al* (2010) the highest concentration of antimony (13.6µg/L) was found in a fruit juice bottled in glass.

4.7.6 Plastic aging

Plastic aging in the context of this study refers to noticeable changes that occur in plastic materials over time due to degradation. Degradation of polymeric materials denotes changes in physical, mechanical, optical, thermal and other characteristics brought about by chemicals, heat, microbial attack and mechanical handling and light. PET bottle ageing brings about yellowing of bottle surfaces, loss of elasticity and some degree of opacity in bottles. Information on the effect of PET bottle aging on leaching of chemicals from the bottles into the water is scanty. However in the work of Nawrocki *et al* (2002) the concentrations of acetaldehyde in 1-month old bottle extract were evidently lower than those from the fresh bottle extract. Such was probably because acetaldehyde content of the bottles diminishes with time and that the older bottle was not exposed to conditions that enhance the formation of acetaldehyde. While Howdeshell *et al* (2003) reported an increased rate of bisphenol A leaching from polycarbonate plastic with age, Le *et al* (2008) did not observe significant leaching difference between new polycarbonate bottles and bottles used under normal conditions for 1 to 9 years. The expectation is that concentration of additives and other plastic chemicals that are not replenished and their ability to leach will diminish with time. On the other hand new chemicals could be generated as a result of the degradative action of the environment on the plastic material.

4.7.7 pH

Low pH and high total dissolved solids were associated with increased migration of metallic stabilizers from PVC pipes into water (Al-Malack, 2001). However in the work of Westerhoff *et al* (2008) pH had no effect on antimony leaching into bottled water within the range of 6.3 to 8.3. In the report of Dental Abstracts (2007) pH values of 20 soft drinks ranged from 2.39 to 4.04. In that report the pH values of non-cola drinks were found to be significantly higher than those of cola drinks and the sugared cola and non-cola drinks had lower pH values than the non-sugared versions.

4.7.8 Bottle colour

In an experiment to evaluate the leaching potential of two PET bottles of different colours (clear and blue-coloured) Westerhoff *et al,* (2008) found that the clear plastic PET released four times more antimony than the blue-coloured PET plastic. This experiment was conducted with only one brand each of the clear and the blue-coloured bottles and was not extended to plastic bottles of other colours.

4.7.9 Other factors

Other factors that are thought to possibly influence leaching of chemicals from PET bottles and other plastic containers are washing with alkaline detergents in the case of polycarbonates (Biedermann-Brem *et al,* 2008), bottle size (Keresztes *et al*, 2009), and aggressive washing to eliminate potential bacterial contamination.

4.8 Summary

Antimony and acetaldehyde are the most important chemicals reported to be migrating from PET bottle material into bottle contents. Antimony leaches out of PET because it is used as a catalyst in the manufacture of PET at concentrations of 150 – 350mg/kg. Acetaldehyde is generated in PET as a product of PET degradation at elevated temperatures. The European Union maximum admissible concentration of antimony in drinking water is 5µg/L. The tolerable daily intake (TDI) is 6µg/kg body weight per day in humans. Typical concentrations of dissolved antimony in unpolluted waters are less than 1µg/L. Nonetheless concentrations can reach up to 100 times the natural levels in the proximity of anthropogenic sources. Concentrations of antimony reported in bottled water ranged from low levels that cannot be detected by analytical instruments to 5 µg/L. Acetaldehyde, a volatile organic compound occurring naturally in ripe fruits, is used as a flavouring agent in soft drinks and other foods. International guidelines and standards for acetaldehyde in drinking-water have not been established. The tolerable daily intake (TDI) is 0.1mg/kg body weight per day in humans. The odour and taste threshold of acetaldehyde in water is reported to be 20-40 µg/L. Concentrations of acetaldehyde are generally less than 0.1 µg/L, less than 1 µg/g and averaging 5µg/m^3 in water, wide range of foodstuff and in air respectively. Maximum concentrations of acetaldehyde reported in bottled water and soft drinks are 317.8 µg/L and 101.9 mg/L respectively. Factors reported to influence the migration of antimony and acetaldehyde from PET bottle materials into bottle contents include, temperature, sunlight and UV radiation, carbon dioxide content, storage, bottling material, age of plastic material, pH and bottle size.

4.9 Conclusion

Typical concentrations of antimony and acetaldehyde in unpolluted water in the environment and in bottled water and soft drinks have been revealed in this Chapter. The Chapter also revealed the maximum concentrations of antimony and acetaldehyde allowed in bottled water and soft drinks for the purpose of safeguarding human health. The typical concentrations together with the maximum allowable concentrations will be used as the basis for assessment of the concentrations of antimony and acetaldehyde in bottled water and soft drinks in this study.

CHAPTER 5: METHODOLOGY

5.1 Research strategy

5.1.1 The role of literature in streamlining the research objectives

The literature reviewed has helped in streamlining the different objectives this study focuses on. The first objective sought to *examine the pattern and extent of bottled water and soft drink use and reuse in Britain and Nigeria*. The objective was to be achieved by quantifying bottled water and soft drinks use and PET bottle reuse, assessing storage periods and PET bottle reuse periods and establishing the number and sizes of bottles being used and reused in the two countries. The Objective also sought to assess how PET bottle reuse is been perceived and also the factors influencing reuse in the two countries. From the literature bottled water and soft drinks use have been shown to be higher in developed countries than in developing countries. However the literature gave little information in terms of bottle reuse pattern and extent in developing and developed countries. This observation points to a need to investigate the pattern of reuse in both developing and developed countries and also to see whether the factors influencing this behaviour are similar in the two countries. Because bottled water does not technically expire, Health Canada recommended a period of up to one year for storage of emergency bottled water. Considering the fact that some freshly purchased Turkish bottled water was reported to contain antimony at a the EU MAC (5µg/L) (Güler, 2007), it will be worthwhile to know how long people store purchased bottled water and soft drinks before consumption and what happens during extended storage periods in terms of chemical migration. From the literature review some internet pages associate PET bottle reuse with consumption of carcinogenic chemicals. A question arise here as to whether carcinogenic chemicals actually migrate from reused bottles. It is also worth knowing the extent to which this information in the internet does influence PET bottle reuse.

The second objective sought to *assess the extent of antimony and acetaldehyde migration from PET into water and soft drinks under conditions representative of real use and reuse in Britain and Nigeria*. The literature review outline the stages involved in the manufacture of PET including how antimony is added in the manufacture of PET and how acetaldehyde is generated. Based on the information in the literature acetaldehyde is only formed in PET at temperatures above 160°C. Consequently acetaldehyde will not be expected to be formed in the PET in any other stage apart from the bottle manufacturing process. This information also revealed that a temperature of up to 150°C can be used in determination of acetaldehyde in PET material using headspace GC-FID. Information on the concentration of acetaldehyde and antimony in the environment, in PET and in bottled contents from previous works has been revealed in the literature. This presents an opportunity for comparison of what has been found in the study and what the literature revealed. For example the review revealed that antimony concentration in unpolluted water is below 1μg/L. The literature review has also revealed that acetaldehyde is naturally present in fruit juices at concentration up to several 100mg/L and that it is added to processed foods including soft drinks as flavouring agent. Consequently this study will attempt to quantify the acetaldehyde contents of bottled fruit juices and other soft drinks. Bottle caps and caps linings, are the other bottling materials in contact with bottled contents in addition to the bottle material. These bottle components are not expected to release antimony and acetaldehyde as they are made from constituents different from those used in making PET. Additionally unlike in PET, chemicals other than antimony are the catalysts used in the manufacture of these plastics. Notwithstanding, these expectations, this study will analyse these material for the purpose of confirming their identity (i.e. whether they are made up of PP, PE, etc) and also to rule out the presence of antimony in the materials. It has been established from the review that antimony may be used in the course of glass manufacture for the purpose of removing bubbles trapped in the glass. A single study has also found antimony in glass bottles at much lower concentrations than in PET (Shotyk *et al*, 2006). Another study also revealed migration of antimony from glass bottles at lower rate in comparison to PET (Cicchella *et al*, 2010). The current study did not quantify the antimony concentration in glass bottle materials. However the study looked at antimony concentration in bottled water and soft drinks bottled in glass. The study also assesses the migration of antimony from some glass bottles at elevated temperatures. The review discussed factors that are reported to have some influence on the migration of chemicals from bottles into their contents. Some of these factors and other factors not reported in the literature were assessed in this study for the purpose of monitoring how these factors may influence migration.

The third objective *draw on findings from 1 and 2, as well as existing regulations and controls to assess whether acceptable limits of chemicals in foods and water are being exceeded as a result of the chemical migrations*. The review clearly stated the different regulations currently in force regarding the presence of antimony and acetaldehyde in foods and water, the degree of chemical migration permitted and quantities of antimony and acetaldehyde that can be taken on daily basis without the risk of suffering from harm over the lifetime. This information from the review form the basis for the assessment of what is happening in terms of migration of antimony and acetaldehyde into foods and water against the existing regulations.

The fourth objective sought to *generate recommendations about the extent to which existing regulations and controls might merit re-examination*. Useful information obtained from the review that may have some significance on the achievement of this objective is the recent decision by IARC to upgrade acetaldehyde in alcoholic drinks to the status of group one carcinogen (Human carcinogen).

5.1.2 Issues informing the adoption of the strategies used in the research

5.1.2.1 Sampling locations

Bottled water and soft drinks are consumed worldwide and PET bottles are possibly reused in large number of countries. Any study relating bottled water and soft drinks use and PET bottle reuse with presence and migration of chemicals, will be better if it involves many countries. Behaviour may differ with countries and regions. Also regulations guiding the use of chemical ingredients in the manufacture of bottles and the ambient quality of ground water utilized in bottling may differ. However feasibility is the main issue that should guide a study of this nature. Consequently this study resolved to use Nigeria and Britain for the purpose of the survey and collection of samples for laboratory analysis. Nigeria and Britain were chosen based on the evidence of differences in terms of weather and prosperity. Apart from these two factors there could also be other socio-cultural differences between the 2 countries. The two countries can be seen as representation of developing sub-Saharan countries and developed western countries. An additional advantage associated with the selection is the fact that the researcher is familiar with the two countries, and consequently the relative ease of basing the research on the countries. Thus, the selection of the two case study countries provides a route towards exploring how the differences between the countries may influence the answers to the research questions. It is believed that the results of the survey could be generalized to a large extent to cover other developing sub-Saharan countries and developed western countries. Laboratory findings may or may not differ for the two countries. In general laboratory findings may not be easily generalizable to other countries. However generalization is by and large more likely to be possible between Britain and other developed western countries than between Nigeria and other developing sub-Saharan countries. This is in large part due to the existence of European Union, a platform through which a standardised system of laws and regulations are generated and applied in all member states.

5.1.2.2 Use of survey

The decision to embark on the survey was as a result of the quest to understand how the behaviour of respondents regarding bottled water and soft drink use and PET bottle reuse may affect the migration of antimony and acetaldehyde. The survey also has the potential to enrich some of the user behaviour information that is currently scanty in the literature. For example only a single study was found revealing the pattern and extent of PET bottle reuse (Lilya 2001). A survey was selected as a good means of collecting this information because the data needed was not complex, it included relatively few issues of interpretation, and data could be collected from a larger number of people than would have been possible through interviews or other more in-depth social science investigation techniques.

5.1.2.3 Bottle samples

The samples primarily targeted by this study are bottled water and soft drinks in PET bottles. These samples are targeted because antimony and acetaldehyde are expected to migrate only from PET plastic. However a resolve was made to also have a look at some samples bottled in glass, cartons and plastic pouches for comparison. The laboratory analytical equipment utilized in this study includes ICP-MS, GC-FID, EDX and Raman spectrometer. These instruments were selected because of the strength they have in analyzing the analytes of interests. EDX and Raman spectrometer were not as essential as ICP-MS and GC-FID. However their use helped in confirming the identity of plastic samples analyzed in this study in addition to providing an interesting secondary information as will be discussed in Section 7.7. Use of household microwave oven to digest PET for the purpose of quantifying antimony has not been described in the literature. The study explores this method based on earlier report involving the digestion of polyethylene for quantification of metals. (Sakurai *et al*, 2006)

5.2 Survey strategy and sampling

As earlier stated the first objective of this research is to examine the pattern and extent of bottled water and soft drink use and PET bottle reuse in Britain and Nigeria. This objective will be addressed through survey. The objective is further divided into sub-objectives listed below:

i. To establish the pattern and extent of typical bottled water and soft drink use and PET bottle reuse including, the approximate proportion of individuals/ households using and reusing plastic bottles, bottled water and soft drinks storage periods prior to use, bottle sizes most often used and reused, bottle reuse periods, the number of bottles being used and reused by an individual or a household at any one time, etc.
ii. To determine public perceptions of the safety of reusing plastic containers to store drinking water, beverages, etc
iii. To find out factors influencing people's preferences with respect to reuse of plastic water containers

This Section describes the approach employed in identifying the sampling frame for the survey, the different considerations that guided the survey questions content, how the sampling process was carried out and how the data was analysed.

5.2.1 Sampling strategy

Ideally, this survey would have sampled a representative proportion of the population in Nigeria and Britain. However, for a study such as this, identifying such a representative sample poses significant issues, namely:

- Not enough is known about plastic bottle use and reuse to identify what factors (age, household size, gender, social class) should be used to achieve a 'representative' sample;

- The resources devoted to this part of the study are not sufficient to sample across multiple locations, in particular, it is not viable to visit many households individually;

- Attention needs to be given to the likelihood of invited participants choosing to fill in the survey.

In response to these issues, the study was conducted in university environments. Specific advantages associated with this sampling strategy are as follows:

- While University populations cannot be said to be completely representative of the wider population, there is no reason to think their plastic bottle use and/or re-use is atypical of the societies concerned.
- The data will yield indicative results, enabling identification of general patterns of bottle use and re-use, and perhaps identifying significant factors that contribute to its variation. As such, the study could guide the dimensions of future better resourced studies of plastic bottle use and re-use.
- The sample population is easily accessible, and because based in a University environment, are more likely to be sympathetic to the objectives of carrying out research;
- Multiple households can be accessed within a small number of locations (i.e. the semi-'public' spaces within University campuses).

5.2.2 Questionnaire development

This Subsection discusses the different considerations that have guided the development of the questionnaire used in the survey. Initially the survey was intended to be in the form of an interview containing open ended questions. Interviews were agreed to be more efficient in extracting information from respondents than questionnaires. Among other issues questions not understood by respondents could easily be rephrased and potential compromise to response could be avoided.

Interview questions were developed in collaboration with supervisors. Ten copies of the interview questions were piloted among fellow research students between 24th and 27th of November 2008. One of the supervisors was interviewed on Thursday 27th of November, 2008 and feedback on the suitability of the survey was obtained. The supervisor suggested more detailed introduction of the survey to prospective respondents. The supervisor also advised on the need to avoid reading direct from document when interviewing respondents and also the need for greater confidence and composure in the course of future interviews. However, the other supervisor advised that the introduction needs to explain the survey without telling so much as to influence responses. The Interview was found to last for an average of 20 minutes.

To reduce the amount of time required to collect survey information from one respondent a suggestion was made to explore the possibility of using questionnaires rather than interviews. Questionnaires were seen as been more effective in gathering large quantity of data within smaller time duration in comparison to interviews. Additionally questionnaires were perceived as a better means of minimizing prestige bias, which could be compounded in person-to-person interviews. Prestige bias is the tendency for respondents to answer in a way that make them feel superior. The survey questions were modified for use in questionnaires. Questions were reduced from 31 in 3 pages to 24 in 2 pages. In the course of the questionnaire development both closed ended and open ended systems were considered. Open ended questions were finally adopted because in such situation response is not restricted to options. With open ended questions situations where no category fits the position of a respondent is avoidable. Even though the questionnaire was meant to be the open format type in some instances options, including *none* and *don't know*, were typed immediately after a question. This was meant to remind the respondents that if applicable *none* and *don't know* are also valid answers. The ultimate aim was to reduce the occurrence wrong or ambiguous answers. Additionally a decision was made to restrict questionnaire collection to only 2 universities rather than the 6 universities earlier proposed. The 2 agreed universities were the University of Bradford in England and Ahmadu Bello University in Nigeria. Ten questionnaires were piloted in the Hub (a central student oriented area of the University of Bradford) on 2nd of December 2008. Out of the 13 people approached only three declined because they did not have time. Nine out the ten respondents filled the 2-page questionnaire fully. One respondent stopped halfway. A quick look at the filled questionnaires revealed that they are as good as interview in collecting the required information.

Appendix I shows the survey questions asked. The preamble aimed to set participants at ease, and to explain the purpose of the survey to encourage them to participate. Against this objective, the preamble was designed not to tell the participants so much about the survey as to influence their answers. A picture of some bottled water brands was pasted on the top right-hand corner of the questionnaire to further help the respondents to differentiate between PET bottles and other plastic bottles. The first question in the survey is to give an idea of the proportions of the respondents that uses different bottled liquids. The survey categorised bottles into unopened bottles, opened bottles with original liquid content and reused bottles. Those questions under unopened bottle aim to reveal the proportion of respondents that usually have unopened bottle in their places of residence, and the average time the bottles remain unopened. As mentioned in Subsection 4.7.4 quantities of chemicals found in liquids bottled in PET bottles increase with duration of storage. The questions on proportions of the different sizes of bottles used and reused will reveal what bottle sizes are most commonly used and reused. The study will look at the relationship between bottle size and migration of chemicals. The answer to the question on bottle storage places is also important because migration of chemicals is generally accelerated by light and elevated temperatures. Questions under bottle reuse are intended to reveal the proportion of respondents that are in the habit of reusing PET bottles at home, at work and when on the move, the number of bottles being reused and the average and longest times of bottle reuse. Questions at the end of the questionnaires relate to respondents' awareness of the safety debate on use and reuse of PET bottles and to reveal what factors influence respondents' choices to reuse PET bottles. Factors that are thought to influence reuse are discussed in Section 3.9. The demographic data at the end of the questionnaire were meant to provide a means for understanding the demographic characteristics of the samples. For example behaviour of British respondents can be compared to the behaviour of non-British respondents; the behaviour of males can be compared to the behaviour of females, *etc.*

5.2.3 Sampling procedure

The survey aimed to achieve 1000 responses. However, a total of 995 questionnaires were collected from the University of Bradford (464 questionnaires) and Ahmadu Bello University (531) in Nigeria. In the University of Bradford the questionnaires were collected between 2nd of December 2008 and 7th of April 2009. At the beginning a questionnaire consisted of 2 sheets of paper printed on one side. After collection of 168 questionnaires from the University of Bradford the questionnaire was converted into back to back print to make it look less lengthy in response to complaints from some respondents. In Ahmadu Bello University the questionnaires were collected between 21st of April 2009 and 5th of May 2009. The respondents included students (undergraduate and postgraduate) and members of staff (academic and non-academic). Data from students was collected by approaching the student in public spaces and issuing them with the questionnaires. In some instances data was collected from lecture halls. Data from members of staff was collected from offices. Of the 464 respondents from the University of Bradford 399 disclosed their country of origin (54% British, 46% non-British) and 412 disclosed their gender (59% males, 41% females). Of the 531 respondents from Ahmadu Bello University 495 disclosed their country of origin (98.8% Nigerians, 1.2% non-Nigerians) and 494 their gender (68% males, 32% females).

5.2.4 Data analysis

Survey data collected was analysed using SPSS and EXCEL. Results are presented using descriptive statistics (measures of central tendency, tables, charts, *etc*) and inferential statistics (statistical significance testing). Pearson's chi-square test was used to test whether 2 or more qualitative variables are homogeneous. The ability of Chi square to establish the status of similarity or dependency between variables depends on the strength of the relationship between these variables and the sample size. So with large samples it is possible to find significance even when the differences or associations are very small (Morgan *et al*, 2004). This potential problem is taken care of by a statistic called squared Cramer's phi coefficient (φ^2), a measure similar to correlation coefficient in its interpretation. Phi statistics eliminate the effect of sample size by dividing chi-square by the sample size. According to Cohen (1998) the relationship between 2 variables is small if φ^2 approximates 0.01, medium if φ^2 approximates 0.09 and large if φ^2 approximates 0.25. None of the quantitative data encountered in this study were normally distributed as shown by Kolmogorov-Smirnov and Shapiro-Wilk tests of normality. Most of the data were skewed to the right (positively skewed). Consequently nonparametric (Mann-Whitney U test) rather than parametric test (*t* test) was used to test whether 2 or more of these quantitative data are similar. Unlike their parametric counterparts nonparametric tests make no assumptions about the probability distributions of the variables being assessed and can thus be used for data that is not normally distributed.

5.3 Survey influence on laboratory analysis

The survey carried out in this study was in most part meant to provide information on bottled water and soft drink use and PET bottle reuse patterns. The information from the survey was expected to be used in designing some of the laboratory experiments carried out in this study. Table 5.1 gives some insight on the role played by the different questions in the survey towards designing some of the laboratory experiments carried out in the study. The laboratory experiments influenced by the survey questions are explained in Sections 5.8 and 5.9. These Sections primarily deal with quantification of antimony and acetaldehyde in PET materials and bottled water and soft drink samples.

Table 5.1 The role of the survey in defining laboratory experiments

Group	Question number(s)	Topic of question	Influence on laboratory component	Location of laboratory experiment	laboratory result / discussion
1	1, 2, 7, 11, 15 and 16	status of use and reuse			
2	4, 5, 9 and 10	storage of bottles with contents	influence of storage on antimony and acetaldehyde migration	5.8.12, 5.9.8	8.7, 8.13, 9.12
3	6 and 9	storage places of bottles with contents	storage at room temperature		
4	3, 8 & 14	sizes of bottle being used/reused	influence of bottle size on antimony migration	5.8.16	8.14
5	12, 13 and 17	Bottle aging	influence of bottle aging on antimony and acetaldehyde migration	5.8.14, 5.9.10	8.12, 9.7
6	18 and 19	reuse safety perception			
7	20	Factors influencing bottle reuse			
8	21, 22, 23 and 24	Demographic information			

Answers to other questions provided background information forming the basis for going ahead with laboratory experiments. Other questions provided information which is useful without influencing the laboratory experiments. For example misinformation on the danger of PET bottle reuse is common on the internet. So the question on reuse safety perception provided information on respondent's opinion regarding the safety of bottle reuse.

5.4 Materials and experimental methods

In this Section samples, chemicals, instruments and laboratory methods employed in the research and where applicable the basis for employing them will be described. The origin and purity of chemicals and condition of instruments will also be described. This component of the research was achieved principally using ICP-MS and GC-FID. Raman spectroscopy and Energy Dispersive X-ray spectrometry were utilised in authenticating the identity of plastic and glass bottle materials, plastic bottle cap material, plastic cap lining materials and metal crown and screw cap materials. Raman Spectroscopy and Energy Dispersive X-ray spectroscopy are either not sensitive enough to detect the low levels of antimony and acetaldehyde or they are entirely not meant for detection of these analytes. Access to ICP-MS was initially delayed and infrequent essentially because there was not much demand for the instrument to warrant the purchase of argon gas. The research also wanted to compare the microwave digestion-ICP-MS, used in this study to quantify antimony in PET, with laser ablation-ICP-MS. However that was not achieved due to unavailability of the laser ablation system. At the early stages of the laboratory work GC-MS was explored for quantitation of acetaldehyde. Difficulties were encountered in separating acetaldehyde peak from a peak due to nitrogen. In the long run the research resorted to GC-FID because of the greater sensitivity of flame ionization detector (FID) to volatile organic compounds in comparison to GC-MS and its insensitivity to nitrogen and other non-combustible gases.

5.5 Samples and reagents

5.5.1 Samples

A total of 82 brands of bottled water and soft drinks in plastic and glass bottles and in cartons were collected. A few samples from Nigeria in plastic pouches were collected. Materials used in bottling including glass and plastic bottle materials, metal and plastic bottle cap materials and plastic cap lining materials were collected. Plastic bottle material identified as polyvinyl chloride based on plastic identification code was collected for use as a reference in identification of materials made using PVC. The summary of samples collected is given in Table 5.2. Drinking water from taps in the university was collected four times. All samples were collected in supermarkets and shops in Britain and Nigeria except drinking water from taps which was collected in Britain only. Samples from Nigeria were collected on 14th of August 2009 and 1st of August 2010. British samples were usually collected few days to the dates of analysis. The decision to collect bottled water and soft drinks and their bottling materials was based on the aim of this research to quantify antimony and acetaldehyde in bottled water and soft drink samples and also to study the migration of these chemicals from bottle wall into bottle content under different conditions.

5.5.2 Certified reference materials

Certified reference materials used in this research include

- Trace element fortified water TW-DWS.2 (Environment Canada)
- Polyethylene reference material ERM®-EC681k (IRMM, Belgium).

5.5.3 Chemicals and reagents

The following chemicals and reagents were used in the experiments:

Nitric acid TraceSELECT® (69.5%) for trace analysis (Sigma-Aldrich, Britain), nitric acid (70%) analytical reagent grade, 10006ppm antimony ICP/DCP standard solution in 7.7 wt% hydrochloric acid (Sigma-Aldrich, USA), 1000ppm cadmium in ca. 1M nitric acid (Fisher Scientific), 1000ppm germanium in water (BDH Laboratory Supplies, England), 1000ppm zinc in 2% nitric acid (CPI International), 1000ppm aluminium in 0.5M hydrochloric acid (ROMIL, England), 1000ppm beryllium in 2% nitric acid (CPI International), 1000ppm titanium in ca. 2M hydrochloric acid (Fisher Scientific), 1000ppm cobalt in 0.5M nitric acid (ROMIL, England), 1000ppm lead in 0.5M nitric acid (ROMIL, England), Hydrochloric acid TraceSELECT® (37%) for trace analysis (Sigma-Aldrich, Britain), indium ICP standard solution for ICP (Sigma-Aldrich, Britain), deionised water from Direct-Q 3 water purification system (Millipore, USA), sodium chloride extra pure (Acros Organics, USA), acetaldehyde - puriss. p.a., anhydrous, ≥99.5% (Sigma-Aldrich, Britain), sodium hydroxide solution, 1M (Fisher Scientific, Britain), terephthalic acid (Sigma Aldrich, Germany, 98%).

Table 5.2 Summary of samples collected and analysis carried out

Contents/ country	Container		bottling material analysed						Bottled water and soft drink Brands analysed	Analysis type
		Brands collected	Container (bottle or pouch)	Analysis type	Cap (plastic or metal)	Analysis type	Cap lining	Analysis type		
still water/GB	PET	17	10	Raman, ICP-MS, GC-FID	6	ICP-MS, Raman	NA	NA	17	ICP-MS, GC-FID
sparkling water/GB	PET	9	9	Raman, ICP-MS, GC-FID	5	Raman	NA	NA	9	ICP-MS, GC-FID
Soft drinks/GB	PET	13	10	Raman, ICP-MS, GC-FID	4	ICP-MS, Raman	5	Raman	13	ICP-MS, GC-FID
still water/GB	Glass	2	2	EDX	2	Raman	2	Raman	2	ICP-MS, GC-FID
sparkling water/GB	Glass	5	2	EDX	5	Raman	2	Raman	5	ICP-MS, GC-FID
Soft drinks/GB	Glass	7	5	EDX	3	Raman	5	Raman	7	ICP-MS, GC-FID
Soft drinks/GB	PE	1	1	ICP-MS, Raman	4	Raman	1	Raman	1	ICP-MS, GC-FID
Soft drinks/GB	Carton	2	NA	NA	NA	NA	NA	NA	2	ICP-MS, GC-FID
Tap water/GB	NA	4	NA	NA	NA	NA	NA	NA	4	ICP-MS, GC-FID
still water/N	PET	11	11	ICP-MS, Raman	5	Raman	NA	NA	11	ICP-MS, GC-FID
Soft drinks/N	PET	5	5	ICP-MS, GC-FID, Raman	4	Raman	5	Raman, EDX	5	ICP-MS, GC-FID
Soft drinks/N	Glass	5	1	EDX	2	Raman	5	ICP-MS, Raman	3	ICP-MS, GC-FID
still water/N	PE pouch	5	1	ICP-MS, Raman	NA	NA	NA	NA	lost in storage	NA

NA = sample not analysed or not applicable

5.6 Identification of plastic materials by Raman spectroscopy

5.6.1 Introduction

Raman spectroscopy is a non-destructive analytical method that can be used for quantitative and qualitative analysis of organic, inorganic and biological materials. Raman spectroscopy results in sharp spectral bands whose pattern and intensity is dependent on the type of atoms or molecules present in a sample and the concentration of the chemical. In this work Micro-Raman spectroscopy, a procedure integrating microscopy and Raman spectroscopy, was used to characterize plastic materials associated with bottling of water and soft drinks. Samples analysed include bottle material, bottle cap material and cap lining material.

5.6.2 Principle of Raman spectroscopy

As monochromatic light impinges upon molecules of a sample the photons which make up the light may be absorbed, transmitted without interacting with the molecules or may interact with the molecules and consequently get scattered. If interaction occurs, molecules absorb photon energy and begin to vibrate. The vibration results in the movement of the molecules from ground state or a vibrational level of ground state to an unquantized virtual level between the ground state and the first electronic excited state (Figure 5.1). Usually most of the molecules will return to their original level without overall gain or loss of energy. In such circumstance the incident photons will be scattered elastically without any change in energy through a process referred to as Rayleigh scattering. Notwithstanding, a small fraction of the molecules will return to levels lower or higher than their original levels as a result of exchange of energy with the incident photons. Accordingly the photons that exchange energy with the molecules - approximately 1 in 10 million - are shifted to higher or lower frequencies relative to the incident photons. This kind of scattering is called Raman scattering and the spectrum of the wavelength-shifted electromagnetic radiation is called the Raman spectrum. Vibrations that occur as a result of interaction of photons and molecules can be stretching vibrations (symmetrical or asymmetrical) or bending vibrations (scissoring, rocking, wagging or twisting).

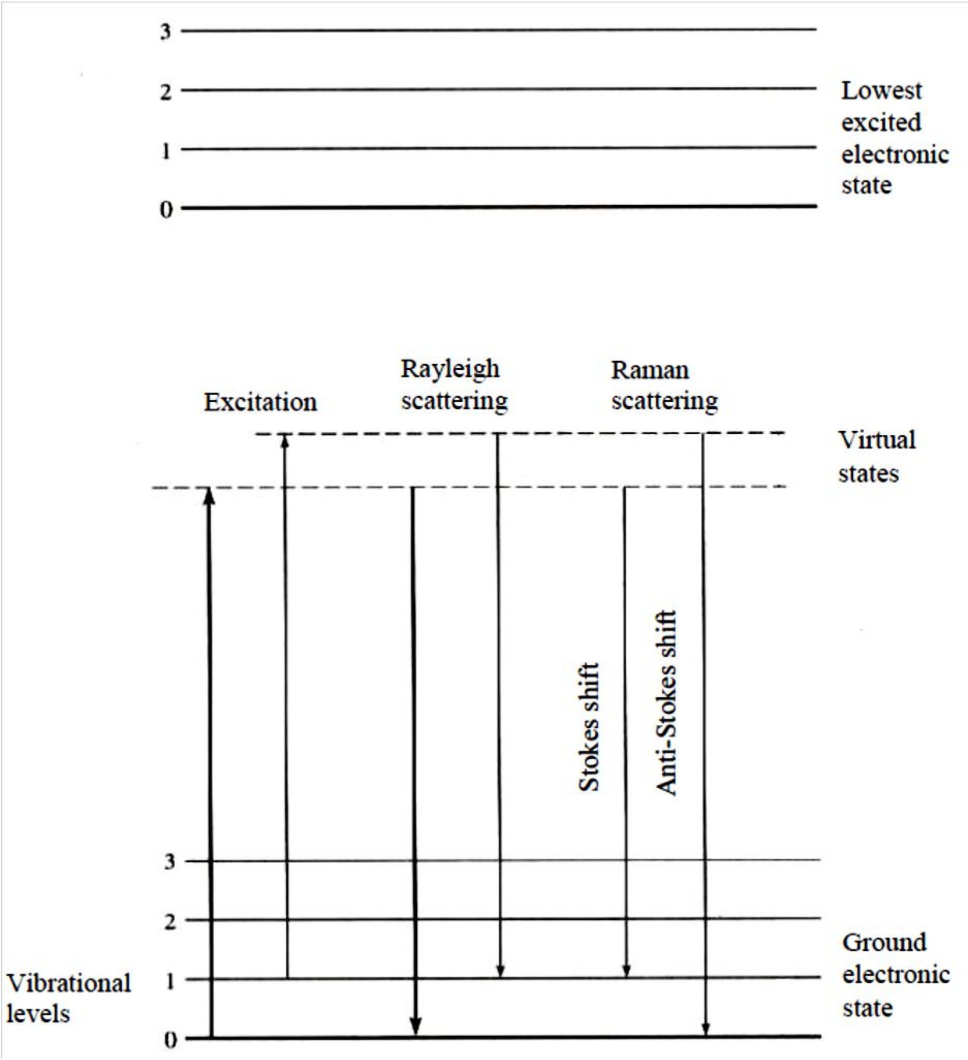

Figure 5.1 Vibrational energy level diagram showing the transitions involved in Raman signal generation (adapted from Skoog *et al*, 1998)

Because energy is transferred either from the molecules to the photons or vice versa after electronic relaxation, two kind of Raman shifts centred around Rayleigh scattering usually occur. Energy shift of the photon to blue region of the spectrum is observed when virtual state molecules originally from excited vibrational levels transfer energy to the photons and thus returning to lower energy ground state. This process is called anti-Stokes shift. Conversely, the energy of the photon will shift to the red region when virtual state molecules originally from ground level gain energy from the photons. These more energetic molecules return to an excited vibrational level rather than their original ground level in a process referred to as Stokes shift. Under normal conditions most molecules are in the ground vibrational level thus stokes shift is more likely to happen than anti-Stokes shift. Consequently in a Raman spectrum the less energetic stokes lines are usually more intense than the more energetic anti-Stokes lines (Figure 5.2). Stokes Raman shift is more commonly utilised in Raman spectroscopy and is generally simply called Raman shift.

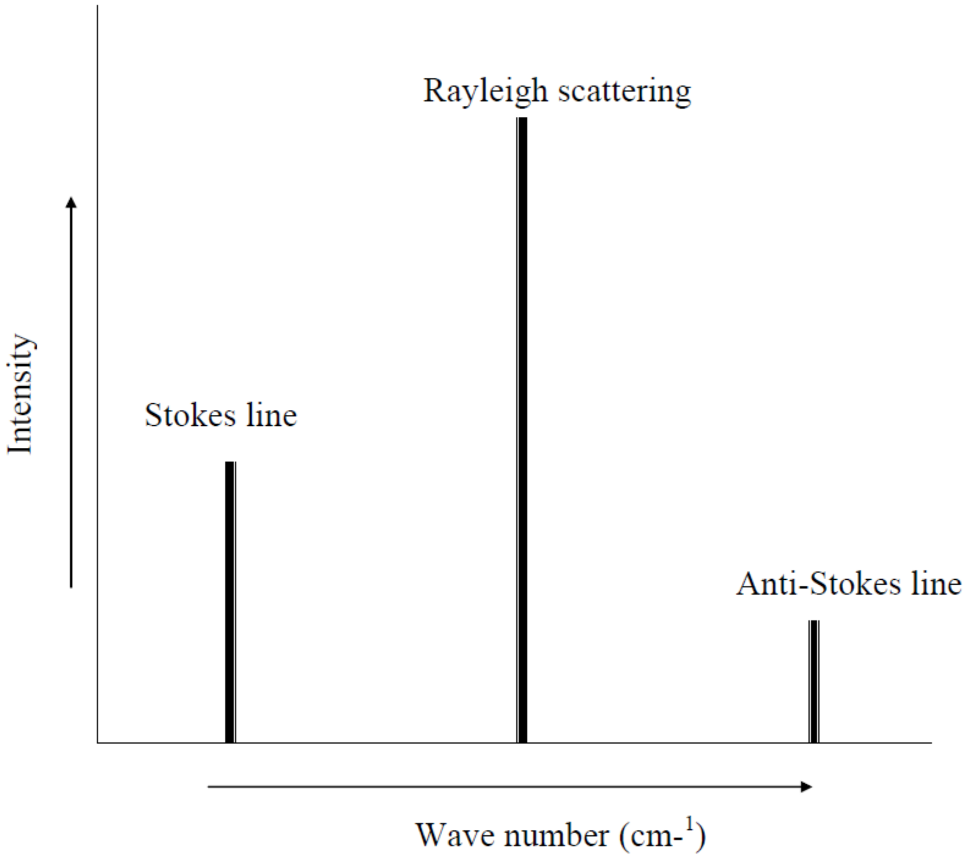

Figure 5.2 Relationship between Raman spectra (stokes and anti-stokes) and Rayleigh scattering (source: author)

Fluorescence, which at times constitutes a nuisance to Raman spectroscopy, occurs when the energy of the excitation photon approaches the transition energy between the two electronic states. It differs from a type of Raman spectroscopy termed resonance Raman spectroscopy in that relaxation to the ground state is preceded by prior relaxation to the lowest vibrational level of the excited electronic state. It is usually avoided by careful selection of appropriate laser excitation wavelength to ensure that either the excitation photon does not provide enough energy to the molecule as to elicit fluorescence or the fluorescence so generated differs remarkably in energy from the Raman signal in such a way that it cannot interfere with the Raman spectrum. Another way of eliminating fluorescence is to expose a sample to the laser beam until the fluorescence decays.

A typical Raman system consist of a powerful laser in the visible region of electromagnetic spectrum, a sample illuminating chamber, a narrow-band rejection filter to minimise the intensity of Rayleigh scattered light, a spectrometer to disperse the inelastically scattered light and a detector (Figure 5.3)

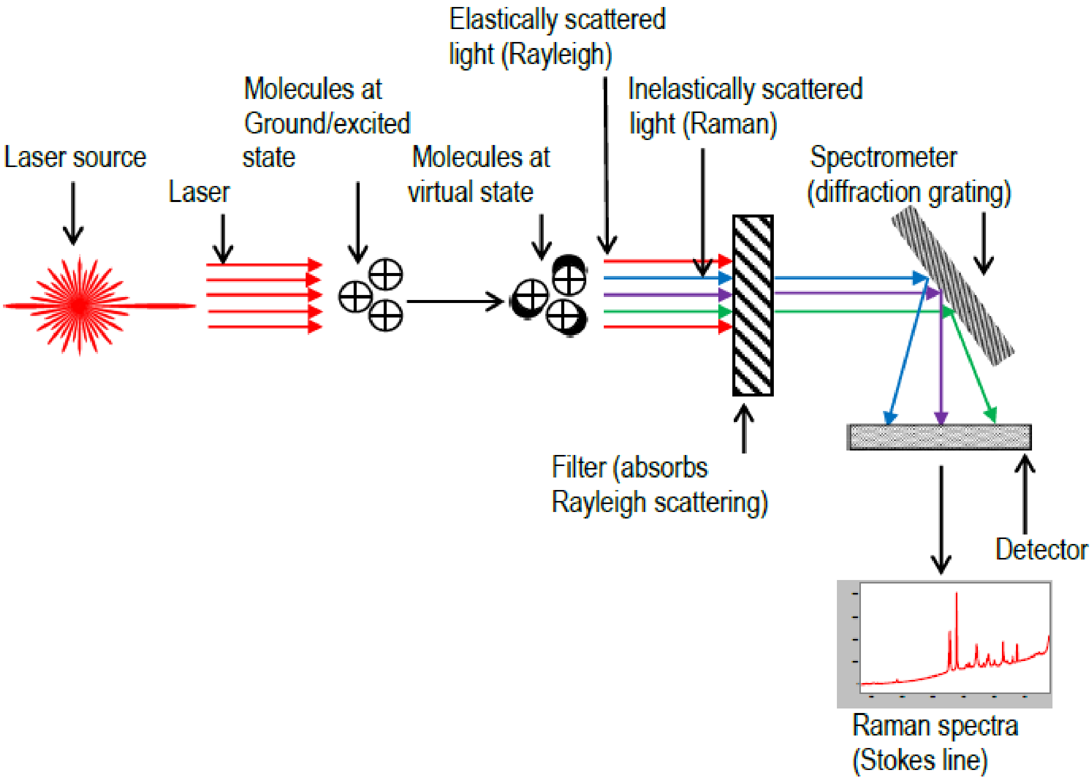

Figure 5.3 Schematic of Raman spectroscopy (source: author)

5.6.3 Instruments

inVia Reflex Raman microscope equipped with Renishaw 785nm near infrared Diode laser (Renishaw plc, Gloucestershire, Britain), glass slides.

5.6.4 Method

Raman spectra were collected using the Renishaw InVia Reflex dispersive Raman microscope (Figure 5.4). The Raman scattering was excited with a 785 nm near-infrared diode laser (Renishaw HPNIR laser) and a 50X objective lens giving a laser spot diameter of 5μm. Spectra were obtained for a 10s exposure of the CCD detector in the wavenumber region 100–3200 cm^{-1} using the extended scanning mode of the instrument. Up to 60s exposure time was used where fluorescence is encountered and this longer exposure time was found useful in eliminating the fluorescence. With 100%

laser power, one, nine or twenty accumulations were collected for samples. Spectral acquisition, presentation, and analysis were performed with the Renishaw WIRE (service pack 9) and GRAMS AI version 8 (Thermo Electron Corp, Waltham, MA, USA) softwares.

Figure 5.4 InVia Reflex dispersive Raman microscope

5.7 Identification of metal caps and glass bottle by EDX

5.7.1 Introduction

Energy Dispersive X-ray (EDX) spectroscopy was used to characterise glass bottles material and metal crown caps. The analytical technique was also used together with Raman spectroscopy to verify the identity of PVC bottle cap lining material. EDX, a variant of X-ray fluorescence spectrometry (XRF), is a non-destructive analysis based on the spectral analysis of the characteristic X-ray radiation emitted from the sample atoms upon irradiation by the focussed electron beam of a Scanning Electron Microscope (SEM). EDX analyzes the top two microns of the sample with spatial resolution of one micron. The minimum detection limits is about 0.1 weight percent equivalents to about 1000 ppm (Kuisma-Kursula, 2000). The schematic of SEM showing the position of the X-ray detector is in Figure 5.5. EDX could be employed for quantitative analysis if appropriate external standards are available. In the absence of appropriate external standards EDX can be used in qualitative and semi-quantitative elemental analysis. In this research EDX was used as qualitative analysis tool.

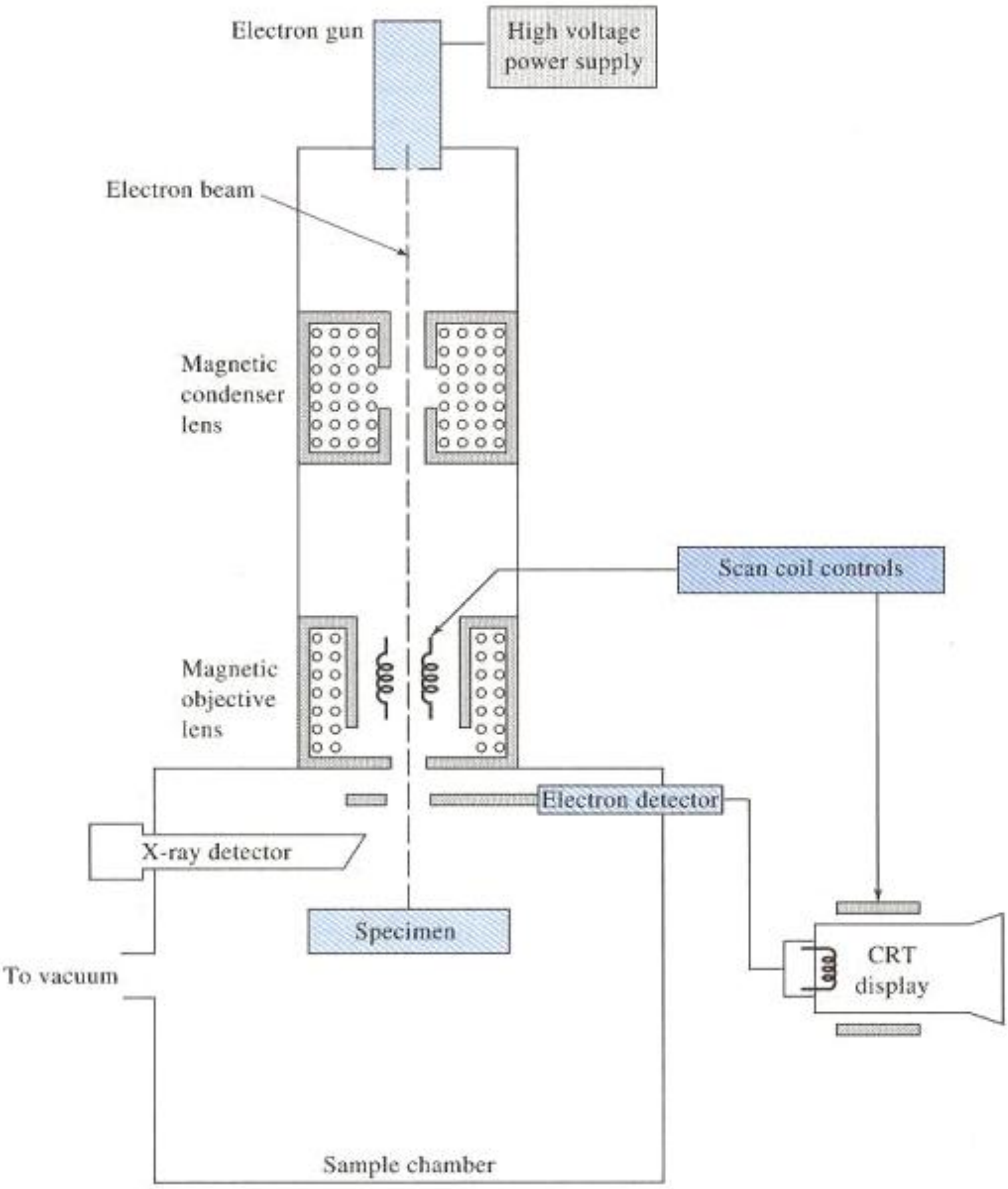

Figure 5.5 Schematic of SEM showing the position of the X-ray detector (adapted from Skoog *et al*, 1998)

5.7.2 Principle of EDX

In EDX the incident beam electrons from the SEM excite electrons in a lower energy states, prompting their ejection and resulting in the formation of electron holes within the atom's electronic structure. Electrons from an outer, higher-energy shell then fill the holes, and the excess energy of those electrons is released in the form of X-ray photons. The release of these X-rays creates spectral lines that are highly specific to individual elements. In this way the X-ray emission data can be analyzed to characterize the sample in question (Walther-Meißner-Institute for Low Temperature Research, 2007). The interaction of the electron beam and the atoms of the sample is shown in

Figure 5.6. The EDX data is presented as atomic and weight percent of the elements contained in the specimen. The data is at most semi-quantitative as the approximate concentrations of the elements in the sample are presented as ratios to each other rather than directly as percentages.

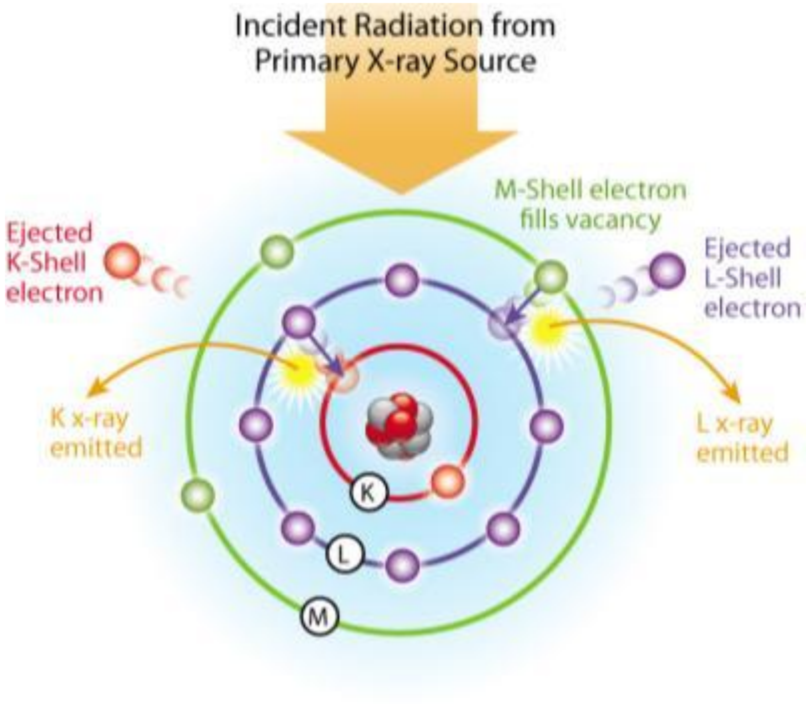

Figure 5.6 Interaction of electron beam and sample (source: Sanama 2008)

5.7.3 Instruments

SEM-EDX Model Quanta 400 (FEI) with INCAx-sight detector and INCAEnergy EDS software (Oxford Instruments), EMITECH K 450 high vacuum carbon-coating unit (Quorum Technologies, East Grinstead, Britain), 12mm extra smooth self-adhesive carbon discs (Aldermaston, Britain).

5.7.4 Method

Glass, metal and plastic samples were mounted on 12mm self-adhesive carbon discs attached to metal stubs. In order to minimize charging effects and improve electrical conductivity before examination all glass and plastic samples were carbon coated using EMITECH K 450 high vacuum carbon-coating unit. Printed metal caps are usually chiselled to reveal the metal. The chemical composition of the samples were then determined using the energy dispersive X-ray of the SEM-EDX unit (Figure 5.7).

Figure 5.7 SEM-EDX Model Quanta 400

5.8 Quantitation of antimony in water, soft drinks and PET

5.8.1 Introduction

ICP-MS couples two components namely an inductively coupled plasma ion source (ICP) and a mass spectrometer (MS). The ICP is radio-frequency generated argon plasma (partially ionised electrically conductive argon) which can reach the temperature of up to 10,000 K. A mass spectrometer is an instrument that separates ions according to their mass-to-charge ratios (*m*/*z*). ICP-MS which is the instrument of choice for the determination of a range of metals and several non-metals in water or solid samples is so sensitive that it can measure elements at concentrations below one part per trillion as reported by Shotyk *et al* (2006). The schematic of ICP-MS is shown in Figure 5.8. In this study ICP-MS is used to measure antimony concentration in water and soft drinks and in digested PET samples. As the instrument has the capability to measure several elements simultaneously, concentrations of cadmium, germanium, zinc, aluminium, beryllium, titanium, cobalt and lead were also determined. Indium was used as internal standard.

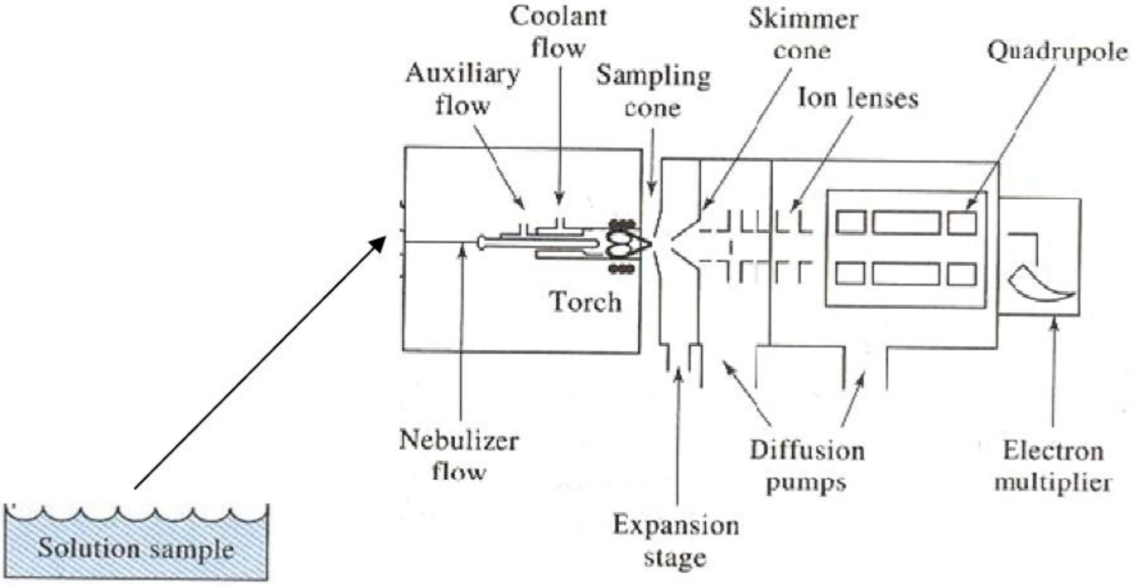

Figure 5.8 Schematic of ICP-MS (Skoog *et al*, 1998)

5.8.2 Principles of ICP-MS

The sample is introduced into the ICP by flow injection or other means depending on the state of sample. In the ICP the introduced sample is nebulised, atomised and ionised after which it is passed into the mass spectrometer. In the mass spectrometer the electric and magnetic fields in the analyser (in this case a quadrupole shown in Figure 5.9) deflects the ions depending on their *m*/*z* ratios with lighter ions getting more deflected by the electromagnetic force than heavier ions. As the voltage is varied ions of different *m*/*z* are brought into focus on the detector which builds up a mass spectrum by recording the relative abundance of each ion type.

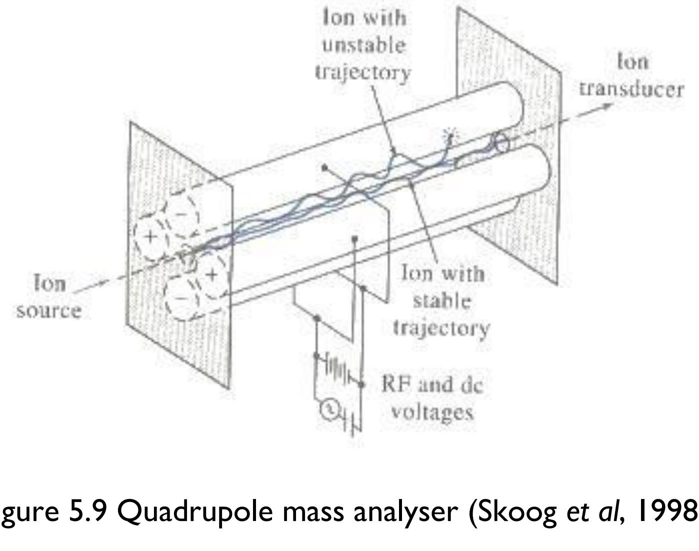

Figure 5.9 Quadrupole mass analyser (Skoog *et al*, 1998)

5.8.3 Glassware preparation

To do away with problem of contamination all glassware used in antimony analysis using ICP-MS were initially soaked in 10% nitric acid for 30days after which they were washed with detergent and rinsed with deionised water. In subsequent works the glassware were soaked overnight in 10% nitric acid after which they were washed with detergent and rinsed with deionised water.

5.8.4 Preparation of standards and blanks

5.8.4.1 Multielement stock standard

To make 250ml of 10µg/ml multielement stock standard, 2.5ml of each of the stock standards of the elements at 1000ppm (including indium used as internal standard) and 0.25ml of antimony stock standard at 10006ppm were added into a 250ml volumetric flask containing 50ml of reagent water (1% nitric acid for trace analysis) and the mixture was made up to 250ml using the reagent water.

5.8.4.2 Multielement working standard

To make 100ml of 1µg/ml multielement working standard 10ml of the multielement stock standard was diluted to 100ml using reagent water.

5.8.4.3 Calibration standards, calibration blanks and method blank

Calibration standards ranging from 0 to 5µg/L (0, 1, 2, 3, 4 and 5 µg/L) of the trace metals analysed were used in this study. Calibration standards ranging from 0 to 20µg/L were initially used. However due to high level of concentration disparity between samples and highest calibration standard a memory effect was encountered which resulted in elevated results. The calibration standards 1, 2, 3, 4 and 5 µg/L were prepared by making 0.1, 0.2, 0.3, 0.4 and 0.5mL of the 1 µg/ml multielement working standard to 100ml using reagent water. Reagent water was used as calibration blank.

5.8.4.4 Rinse blank

To reduce possible memory interference between samples runs to minimal 2% nitric acid was used as serves as a rinse blank for flushing the system between successive samples.

5.8.4.5 Internal standard

Indium at 3µg/L was used as internal standard in samples. 1µg/ml of indium internal standard solution was formed by making 0.1ml of the indium stock solution (1g/L) to 100ml.

5.8.4.6 Method blank

To monitor contamination during sample preparation and analysis a method blank was run at intervals. Reagent water containing the indium internal standard at 3µg/L was used as method blank. Detection limit was determined by multiplying the standard deviation of 10 method blank results by 3.

5.8.5 Instruments

PlasmaQuad 3 quadrupole ICP-MS instrument (Thermo Fisher Scientific, USA), Cookworks MM717CFA microwave oven (Argos, Britain), Gallenkamp thermostat water bath, 60ml PFA digestion vessels and caps with wrench sets (Savillex Corporation, USA), KX+syringe filters PTFE 25mm, 0.45 µm (Kinesis, Britain), 12ml Norm-ject Luer lock syringes(Sigma Aldrich, USA), 125ml PLASTIBRAND® narrow-mouth polypropylene bottles, with screw cap (Sigma Aldrich), Powder free latex gloves (Microflex, Austria), Hand-held pH/mV/temperature/RS232 meter pH 11 series (Oakton/Eutech Instruments (Nijkerk, The Netherlands), HI-9033 conductivity meter (Hanna instruments, Leighton Buzzard, Britain), Mettler AE 200 pan electronic balance (Mettler-Toledo Ltd., Leicester, Britain), Pocket digital thermometer model 314 (Comark Instruments, Britain).

5.8.6 Conductivity and pH of samples

In order to assess the possibility of a relationship between water conductivity and pH in one hand and antimony concentration in water on the other hand the conductivity and pH of samples were measured using the hand-held pH meter and the HI-9033 conductivity meter prior to any analysis.

5.8.7 PET bottle thickness

To assess whether the thickness of PET bottle has any influence on antimony migration bottles thickness were measured using a digital calliper. For each sample three measurements were taken and averaged.

5.8.8 Antimony and other trace elements in water and soft drinks

Bottled water brands (still and sparkling) and soft drinks in PET bottles from Britain and Nigeria and tap water were analysed for antimony as in Shotyk and Krachler (2007). One aliquot of sample was diluted with four aliquots of reagent water to reduce the concentrations of alkaline and earth alkaline elements, to avoid clogging of the cones, to add the internal standard, and to reduce the amount of dissolved CO_2 in the samples. All dilutions were carried out using reagent water. Certified water reference material and reagent water spiked with the elements of interest at 1µg/L were also analysed to monitor accuracy of analysis. The certified water reference material contains the elements of interest at concentrations given in Table 5.3.

Table 5.3 Concentration of the elements of interest in certified water reference material

Element	Concentration (µg/L)
Antimony	3.2
Cadmium	4.2
Zinc	379
Aluminium	58.3
Beryllium	13.4
Titanium	15.1
Cobalt	64.2
Lead	7.82

5.8.9 Sample digestion using domestic microwave oven

Ideally a purpose-built laboratory microwave digestion system should have been used for digestion of plastic samples. However as a result of the unavailability of a microwave digestion system domestic microwave oven placed in a fume chamber was used based on the modification of a method explained by Sakurai *et al.* (2006). With domestic microwave oven digestion vessels containing samples have to be opened and degassed at short interval of times to avoid build-up of pressure.

5.8.9.1 Optimization of digestion parameters

To digest plastic materials and the polyethylene reference material the use of nitric acid alone and a mixture of nitric and hydrochloric acids (5:1) were investigated. Use of heating powers of 120, 230 and 385W was also assessed. About 150mg of samples were usually added to digestion vessels containing 3ml of either nitric acid alone or a mixture of the 2 acids. Addition of 0.5ml HCl to 2.5ml nitric acid resulted in the formation of brown colour possibly due to formation of oxides of nitrogen. Digestion with nitric acid resulted in formation of brownish gas for some samples. Digestion was found to be faster with nitric acid alone. Consequently use of HCl was discontinued. Digestion for 5 minutes at 230W was found to be efficient for PET, PP, EVA/PP and PE. For the PVC and unidentified plastic cap lining materials digestion was achieved after about 8 minutes.

5.8.9.2 Digestion of PET samples

Digestion of PET samples resulted in yellowish or colourless liquid with white precipitate (Figure 5.10). The liquid remained clear even after dilution with deionised water. The white precipitate persisted with addition of excess nitric acid and additional heating in the oven. The precipitate was allowed to settle after which the liquid was decanted into an acid cleaned beaker. The precipitate was washed twice with deionised water and the water decanted into the beaker. The liquid in the beaker were filtered into acid cleaned 100ml volumetric flask using PTFE syringe filters attached to 12ml Norm-ject Luer lock syringes. The contents of the flask were then made to 100ml with deionised water. The precipitate was dried and analysed using Raman spectroscopy and EDX as explained in Sections 5.6.4 and 5.7.4.

Figure 5.10 Digested PET materials

5.8.9.3 Digestion of other plastics

Digestion of polyethylene, EVA/PP copolymer polypropylene and unidentified cap lining material resulted in a clear yellowish solution which became milky with addition deionised water. The milky liquid was filtered into acid cleaned 100ml volumetric flask using PTFE syringe filters attached to 12ml Norm-ject Luer lock syringes. The contents of the flask were then made to 100ml with deionised water.

5.8.9.4 Digestion method blank

To monitor contamination during sample digestion, handling and analysis, 3ml of the nitric acid for trace analysis was digested. After digestion a slightly yellowish liquid containing no precipitate was obtained. This liquid remained clear on addition of deionised water. The liquid was then treated exactly as for samples.

5.8.10 Antimony in digested samples

The filtrate from digested samples, digestion reference and digestion blank were analysed in the same way as water samples using indium at 3µg/L as internal standard.

5.8.11 Bottled water temperature elevation on exposure to sunlight

As earlier stated in the literature a temperature of up to 58.3 °C was reported to be achievable on exposure of water in glass bottles for 2.5 hours from midday in Nigeria (Tukur *et al*, 2006). In this study experiments were carried out to find water temperatures achievable after exposure of water in PET and glass bottles of different colour and size to the sun on a British summer day. In the experiment PET and glass bottles filled with water at initial temperature of 19.1°C were exposed to the sun on a clear summer day with brilliant sunlight. Change in water temperature was monitored on hourly basis from 11am to 6pm using a handheld digital thermometer. Bottles used in the study are given in Table 5.4.

Table 5.4 Bottles used in sunlight exposure experiments

Bottle material	Bottle size (ml)	Bottle colour
PET	500	bluish tint
PET	500	colourless
PET	500	green
PET	500	blue
PET	250	colourless
PET	750	bluish tint
Glass	1000	colourless
Glass	750	green
Glass	750	crimson

5.8.12 Bottled water storage and antimony migration

In the literature storage has been reported as one of the factors that elevates the concentration of migrants from PET and other plastic into water. In this study a survey was conducted for the purpose of establishing the average and maximum storage periods prior to use for bottled water and soft drinks. The concentration of antimony in bottled water and soft drinks samples stored for periods chosen based on the survey results were measured.

5.8.13 Antimony migration at different temperatures and times

To monitor the behaviour of PET and glass bottles of different colours from different brands of water and soft drinks in terms of migration of antimony at different temperatures and exposure times, 300ml of deionised water were added to ten 500ml PET bottles of different colour and from different brands. The bottles were then heated at 40, 60, and 80°C using a thermostat water bath for 6, 24 and 48 hours. Additional 8 PET bottle brands were heated at 60°C for 6 hours. Green and colourless 750ml glass bottles containing 500ml of deionised water were also heated at 60°C for 6, 24 and 48 hours. Temperatures of 40, 60 and 80°C were chosen based on the results of the experiments in subsection 5.8.11 and the information in the literature. Tukur *et al* (2006) reported a water temperature of 58.3 °C in Nigeria on exposure of water in glass bottles for 2.5 hours from midday.

5.8.14 Bottle aging and antimony migration

From the literature PET bottles were found to be reused for storing drinking water by 88% of respondents in the US for as long as 6 months. Additionally, a survey carried out in this study attempted to establish the proportion of respondents reusing PET bottles in Nigeria and Britain and the average and maximum periods of bottle reuse. To assess the effect of PET bottle aging on migration of antimony six 500ml clear bluish PET bottles were aged for a period chosen based on the result of the survey. For simple aging experiment three bottles were filled with water stored at room temperature, emptied on weekly basis, rinsed with water and refilled. For aging experiments involving washing with detergent and hot water the same procedure was followed except that bottles were scrubbed using brush with dilute solution of detergent in hot water. After the aging period an aged bottled, detergent/hot water aged bottle together with fresh bottle were filled with deionised water and sparkling water. The filled bottles were stored at room temperature for 283 days after which the contents were analysed for antimony. To monitor the antimony migration tendency of the aged bottles at elevated temperatures 300ml deionised water were added to an aged bottled, detergent/hot water aged bottle and a fresh bottle. The bottles were then heated at 60°C for 6 hours using a thermostat water bath.

5.8.15 pH and antimony migration

To observe the effect of pH on antimony migration pH values of deionised water were adjusted to 2, 5 and 8 using sodium hydroxide and hydrochloric acid. Three 500ml green PET bottles were then filled with the deionised water (range chosen to reflect the pH range 2.43 – 8.01 obtainable from bottled water and soft drinks). The pH values of the water were adjusted using sodium hydroxide and hydrochloric acid. The water contents were analysed after 266 days. For comparison with the original antimony concentration each of the pH-adjusted water samples was stored in acid-cleaned polypropylene bottles.

5.8.16 Bottle size and antimony migration

Bottled water and soft drinks are bottled in bottles of different sizes. The survey carried out in this study attempted to establish the extent to which bottles of different sizes are used. Westerhoff *et al* (2008) suggested the possibility of an inverse relationship between bottle size and achievable antimony concentration in water due to migration. This suggested phenomenon was related to the relationship between available contact area of PET bottle and the volume of the liquid in the bottle. Also Keresztes *et al* (2009) reported observing higher antimony concentration in water bottled in smaller packages. To assess this at elevated temperatures 5 clear colourless bottles of different sizes from a brand of bottled water were used. The sizes of the bottles used were 2000, 1500, 750, 500 and 330ml. The bottles were filled to half their nominal volumes with deionised water and then heated at 70°C for 9 hours after which the contents were analysed for antimony.

5.9 Quantitation of acetaldehyde in water, soft drinks and PET

5.9.1 Introduction

Headspace GC-MS was initially employed in this study for the quantitation of acetaldehyde in aqueous samples and in PET material. However GC-FID was later adopted because of the greater sensitivity of flame ionization detector (FID) to volatile organic compounds in comparison to GC-MS and its insensitivity to nitrogen and other non-combustible gases. Additionally FID has a large dynamic range and low noise. According to Skoog *et al* (1998) flame ionization detector (FID) is the most useful general detector for the analysis of most organic samples. In headspace GC the headspace vial allows for concentration of organics even from dilute solutions.

5.9.2 Principle of headspace GC-FID

In headspace gas chromatography polar organic volatiles dissolved in aqueous medium are concentrated into the headspace of vials by addition of inorganic salts and by heating. The "salting out effect", together with elevated temperatures, lowers the partition coefficients of organic volatiles in the sample matrix and promotes their transfer into the headspace. The concentrated volatile analytes from the headspace are injected into the GC column where they partition between a solid or liquid stationary phase and a gaseous mobile phase in the column. The differential partitioning into the stationary phase allows the compounds in the sample to be separated in space and time. The schematic of Gas chromatography is shown in Figure 5.11

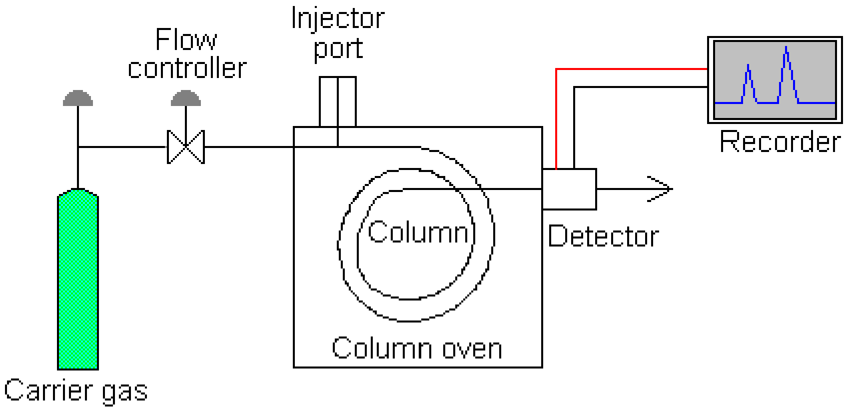

Figure 5.11 Schematic of Gas chromatography (adapted from Sheffield Hallam University, no date)

In FID the partitioned compounds from the column are mixed with air and then ignited by a hydrogen flame. A large electrical potential typically 100 – 300V is applied at the burner tip, and a collector electrode is placed above the flame. The increased current due to electrons emitted by burning carbon particles is then measured. The schematic of FID is shown in Figure 5.12.

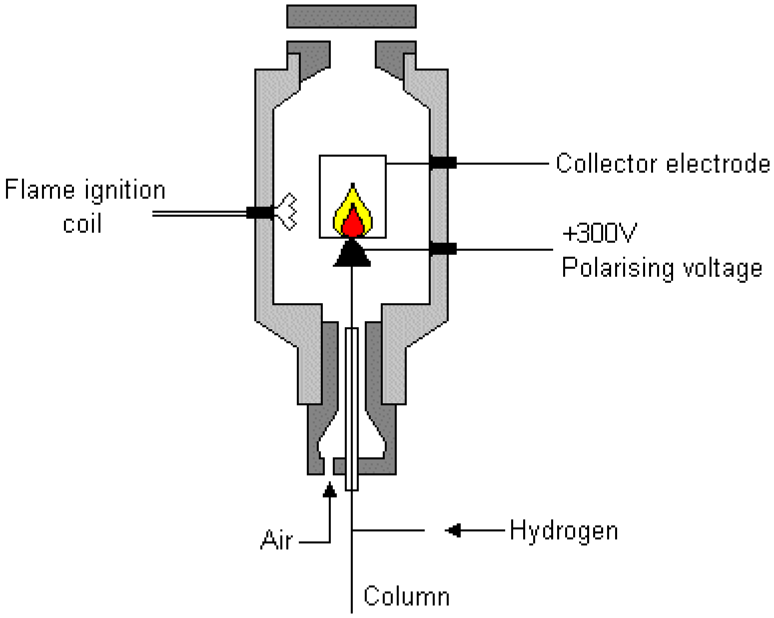

Figure 5.12 Schematic of Flame Ionisation Detector (adapted from Sheffield Hallam University, no date)

5.9.3 Instruments

GC-FID HP 6890 (Hewlett Packard, USA), Headspace screw top 20ml clear glass vials and ultra-clean 18mm screw caps with septa (Agilent Technologies, Germany), 2.5ml gastight syringe (SGE, Australia).

5.9.4 Preparation of standards and blanks

5.9.4.1 Oxygen-free deionised water

Acetaldehyde solutions and all dilutions were made using boiled oxygen-free deionised water. Deionised water were boiled to expel air and to kill microorganisms that may contribute to degradation of acetaldehyde in solution. Nitrogen flushing was carried out to expel oxygen which also contributes in degradation of acetaldehyde. To prepare oxygen-free deionised water deionised water was boiled using electric kettle, transferred into clean one litre capped glass bottles, allowed to cool, and then flushed with nitrogen.

5.9.4.2 Stock and calibration standards

A 10 mg/ml acetaldehyde stock standard was made by dissolving 5grams of acetaldehyde in 500ml of cold oxygen-free deionised water. The stock standard was stored in a refrigerator to keep it cool to minimise evaporation and degradation of acetaldehyde. Calibration standards of different concentrations were formed using the cold oxygen-free deionised water depending on the predicted acetaldehyde concentration in samples.

5.9.4.3 GC-FID conditions

Column used was a Zebron ZB-1 30m x0.32mm id x 0.25µm film thickness 100% methyl polysiloxane. The injector and detector temperatures were maintained at 150 and 200°C respectively. Oven temperature was programmed at 40°C for 1 minute increasing by 10°C to 70°C. While the retention time of acetaldehyde differed with the split/splitless mode, it generally eluted in less than 1 minute. Nitrogen was used as carrier gas.

5.9.5 Acetaldehyde in water and soft drinks

Acetaldehyde determination in bottled water and soft drinks was made based on a variation of the method described by Özlem (2006). In this method the relative volume of the headspace compared to volume of the sample in the sample vial (phase ratio) was one. For the "salting out effect" a salt concentration of 39.1g/100ml was targeted which is the maximum solubility of NaCl at 100°C. Bottled water or soft drink sample of 10 ml was pipetted in to a clean nitrogen-flushed headspace 20ml vial containing 4 g of sodium chloride. The vials were then closed with the ultra-clean 18mm screw caps with septa. The vials were heated in a hotplate for 25minutes at 95°C. To further ensure efficient partitioning vials were agitated slightly at 5minutes interval. Headspace samples of 2.5ml were withdrawn and injected into the GC instrument manually using a gastight headspace syringe heated at 95°C. While bottled water samples were analysed at a splitless mode, all soft drinks samples were analysed using 1:50 split ratio. Calibrations for quantitation of acetaldehyde in soft drinks were from 0 to 10mg/L. Calibrations for determination of acetaldehyde in bottled water were 0 to 500µg/L.

Detection limit at 3 x the standard deviation of 10 samples was determined by analysis of 10 samples containing acetaldehyde at concentration of 10µg/L. To determine recovery acetaldehyde spikes of 50 and 100µg/L were analysed 10 and 4 times respectively.

5.9.6 Residual acetaldehyde in PET materials

Acetaldehyde determination in PET material was made based on a variation of the industry standard French National Acetaldehyde generation test as explained in Howell and Ponasik (2006). The acetaldehyde desorption conditions of 150°C for 60 minutes are chosen because at this conditions no measurable acetaldehyde is regenerated by the sample during the desorption process. In the bottle making, heating of the hygroscopic PET granulate at 160°C for 4 hours reduces its moisture content to less than 50ppm without eliciting acetaldehyde-generating hydrolytic reactions.

Approximately 1 gram of the PET bottle material cut into very small pieces was placed into 20ml clear glass headspace vial. The vial was immediately flushed with nitrogen and capped with the ultra-clean 18mm screw cap with septa. Sample vials were heated to 150°C for sixty minutes to desorb the acetaldehyde from samples into the vial. Vial samples of 2.5ml were withdrawn using a heated gastight syringe and injected into the GC-FID operating at a split ratio of 1:50. Calibration was achieved by use of clean; nitrogen-flushed 520.5ml glass bottles sealed using several layers of PVC cling film. To make calibration standards of between 96.06 to 960.65µg/L, 5, 10 , 20, 30, 40 and 50µl of 10mg/ml solution of acetaldehyde were added to first, second, third fourth, fifth and sixth bottles. The amounts of acetaldehyde added to the bottles being 50, 100, 200, 300, 400 and 500µg respectively. A nitrogen-flushed sample containing no acetaldehyde was used as calibration blank. The bottles were warmed on a hotplate and shaken vigorously to disperse the solution and vaporise the acetaldehyde. A sample of 2.5ml of the content of each of the bottles were analysed by GC-FID at a split ratio of 1:50.

Detection limit at 3 times the standard deviation of 10 samples was determined by analysis of 10 samples in 1.157L bottles containing acetaldehyde vapour at 8.64µg/L. The concentration of 8.64µg/L was achieved by addition of 10µl of 1mg/ml acetaldehyde solution into the bottles. To determine recovery at a concentration within the range found in bottle material analysis, acetaldehyde vapour spike at 385.80µg/L was analysed 5 times. The concentration was achieved by addition of 20µl of 10µg/µl (10mg/ml) solution into bottles having capacity of 0.5184L.

5.9.7 Effect of carbonation on quantitation

Sparkling water and carbonated drinks differ from still water in having dissolved carbon dioxide. To determine the effect of carbon dioxide dissolve in sparkling water on acetaldehyde determination by headspace still and sparkling water samples of similar brand were spiked with acetaldehyde solution at about 500µg/µl. The samples were then analysed in triplicate for acetaldehyde.

5.9.8 Storage and acetaldehyde in PET materials and bottle contents

As mentioned in Subsection 4.7.4 storage elevates the concentration of migrants from PET bottles into their contents. To determine the effect of storage on acetaldehyde content of PET bottle material and bottled water/soft drinks, bottle materials and contents of freshly purchased bottles were analysed together with bottle materials and contents of bottles stored for extended period.

5.9.9 Bottle thickness and acetaldehyde concentration in PET

Bottle thickness may affect acetaldehyde concentration in bottles because thicker bottle walls theoretically trap more acetaldehyde than thinner ones. To determine whether bottle thickness has any influence on bottle material residual acetaldehyde content bottle thickness earlier measured with a digital calliper were correlated with the acetaldehyde content of bottle materials.

5.9.10 Bottle aging and acetaldehyde concentration in PET

To assess the effect of PET bottle aging on acetaldehyde concentration in the bottle material clear green and clear bluish 500ml PET bottles were aged for periods chosen based on the results of the survey. For simple aging experiment three bottles were filled with water stored at room temperature, emptied on weekly basis, rinsed with water and refilled. For aging experiments involving washing with detergent and hot water the same procedure was followed except that bottles were scrubbed using brush with dilute solution of detergent in hot water. After aging the acetaldehyde content of the PET materials were determined as in Subsection 5.9.6.

5.9.11 Acetaldehyde outgassing from PET bottles

Fruity smell resembling that of acetaldehyde at low concentration was perceived when some empty bottled water bottles left to stand for several months were sniffed. Analysis of the gaseous content of the bottles revealed acetaldehyde. To observe the behaviour of different bottles allowed to stand for different period of times, bottles from 3 different brands were used. Two of the brands used were clear bluish still water bottles the other brand was green sparkling water bottle. Two green bottles aged for 266 days were also assessed.

5.9.12 Acetaldehyde migration from water medium into PET

To assess whether acetaldehyde in aqueous solution can migrate into PET materials, three different experiments were carried out using clear bluish and clear green PET bottle materials. Three portions of each of the PET materials weighing about half gram were soaked into 0.1 and 10mg/ml acetaldehyde solutions and into neat acetaldehyde for 24 hours. After 24 hours the PET materials were thoroughly washed with tap water and dried by blotting with paper tissue. The acetaldehyde content of the PET materials was then determined as in Subsection 5.9.6.

5.9.13 Stability of acetaldehyde solutions with storage

To assess the stability of acetaldehyde with storage, three acetaldehyde solutions in propylene bottles with concentrations of 50, 500 and 5000µg/L were stored at room temperature and inside a refrigerator at temperatures slightly above zero. The acetaldehyde concentrations were measured 5 times over 30 days.

5.10 Research timeline

This research work spanned a period of about 3 year and 9 months. The timeline for the activities carried out in the research is given in Table 5.5. The timeline designed at the beginning of this research spanned a period of three years. However the timeline could not be adhered to in large part due to unforeseen delay in accessing some instruments used in this research.

Table 5.5 Research timeline

Period	**2008**												**2009**												**2010**												**2011**					
Activity	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**	**J**
Start date	■																																									
Literature review/	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■						
Research plan	■	■	■	■	■	■	■	■	■	■	■	■	■	■																												
Survey						■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■																				
Survey development						■	■	■	■	■	■																															
Survey in Britain												■	■	■	■	■																										
Survey in Nigeria																■	■																									
Survey report																						■																				
MPhil to PhD transfer															■																											
Change of supervision																					■																					
Laboratory work																		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■						
Sample collection Nigeria																■												■														
SEM-EDX																												■	■	■	■	■	■	■								
ICP-MS																		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■								
GC-MS/FID																							■	■	■	■	■	■	■	■	■	■	■	■	■							
Raman																										■	■	■	■													
PWG conference																										■													■			
SLS poster presentation																													■													
Writing up																																					■	■	■	■	■	■
First draft																																									■	

CHAPTER 6: SURVEY RESULTS AND DISCUSSION

6.1 Introduction

Chapter 5 explained that a survey had been developed with the aim of obtaining an understanding of typical use and re-use patterns for plastic bottles in the UK and Nigeria. This Chapter presents and discusses the results obtained as the result of the analysis of the data obtained from that survey. The Chapter also discusses the implication of the survey results on the laboratory work.

6.2 Reported use of bottled water and soft drinks

Almost all respondents reported using water and/or soft drinks bottled in PET bottles (Nigeria 96%, Britain 98%), additionally 95% of Nigerian respondents reported using water in plastic pouches. It was initially thought that using water in pouches would reduce the likelihood of using bottled water. However use of water in pouches and use of bottled water have been shown to be independent of each other (χ^2 (1, n = 514) = 2.054; p = 0.152). Consequently use of water in pouches, which is about ten times cheaper than bottled water, does not reduce the usage status of bottled water. One possible explanation for this is that even though water in pouches is cheaper than bottled water it is less portable than bottled water because the packaging is flaccid and has no cap. Although usage status of water in pouches does not reduce the usage status of bottled water, it may reduce the quantity of bottled water used especially among the low-income group. As mentioned earlier (Rothschild and Nzeka, 2005) water in pouches accounts for 68 percent of total packaged water consumed in Nigeria.

6.3 Storage and use of bottled water and soft drinks

As mentioned in Section 3.3, prosperity and climatic conditions of a country have an effect on the degree of usage of bottled water and soft drinks in the country, and consequently the degree to which the bottled water and soft drinks would be found in places of residence. In this work the degree to which unopened and opened bottled water and soft drinks in PET bottles were found in places of residence of British and Nigerian respondents differed significantly [χ^2 (1, n = 918) = 104.538; p < .001, φ^2 = 0.11]. The results (Figure 6.1) implied that respondents' country of residence to moderate extent predicts the availability bottled water and soft drinks in places of residence. Bottled water and soft drinks are accordingly more commonly found in the homes of British respondents than those of Nigerian respondents. Greater consumption of bottled water/drinks in Britain results from the fact that Britain is economically more prosperous than Nigeria. According to Finewaters (2009) in France, Germany and Italy close to 90% of the population patronises bottled water in comparison to about 50% in Britain. In this work the availability of bottled water in places of residence of British respondents is 58%. As mentioned in Subsection 5.2.3 54% of British respondents were native Britons with the remaining 46% been visitors. However the two groups were found to be similar in terms of possession of unopened and opened bottles at the time of the survey (unopened bottles – native Britons-74%, visitors-72%; opened bottles – native Britons-70%, visitors-72%; all types of bottles – native Britons-86%, visitors-87%).

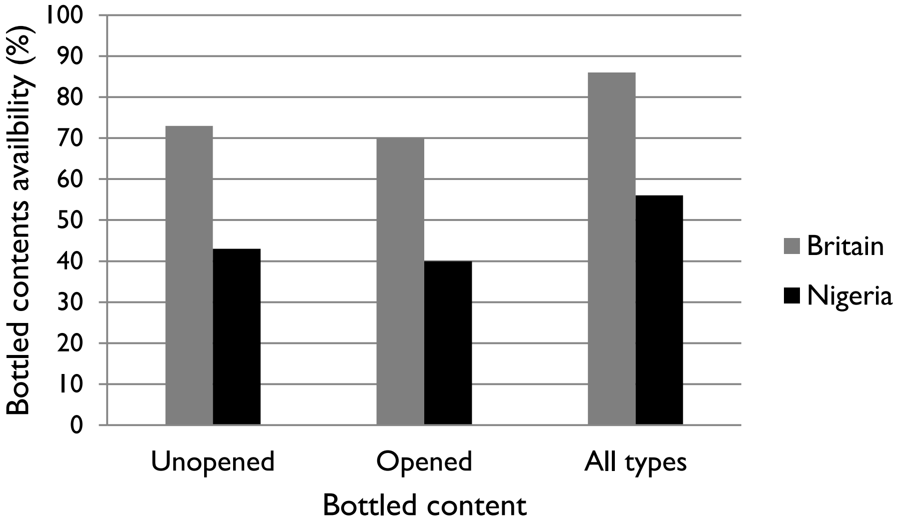

Figure 6.1 Bottled water and soft drinks availability in British and Nigerian places of residence

Many factors including country economic status, climatic conditions, safety and health, environmental awareness, taste, idolization of bottled water as fashion accessory , etc were hypothesised to have some influence on consumption of bottled water and soft drinks. The identification of bottled water and soft drinks in more households in Britain than in Nigeria in this study is consistent with literature about developing and developed countries. Economic status is clearly a factor playing a significant role in the observed pattern. However manner and extent to which all other factors may be influencing the observed pattern is not clear. For example the harsher climatic conditions in Nigeria will be expected to translate into higher consumption, even though this was not observed.

6.4 Bottle size

Bottle size has been mentioned as one of the factors that may be influencing migration of chemicals from bottle wall into bottle content (Subsection 4.7.9). Smaller bottles were reported to release more antimony than bigger ones (Keresztes *et al* (2009)). In places of residence of British respondents 2L bottles were found to be the most commonly available bottles followed by 0.5L bottles and then 1L (Figure 6.2). In places of residence of Nigerian respondents 0.5L bottles were the most common bottles followed by 1L bottles and then 0.33L (Figure 6.2). It is worth mentioning that the bottle size data for Nigerian respondents showed some degree of discrepancy in the sense that bottle sizes (330ml) that are almost unobtainable in Nigeria were reported in the questionnaire. This finding raises a question about the accuracy of all the bottle size data for Nigeria. The misreporting of bottle sizes in Nigeria may have happened either because Britsh respondents are more conversant with bottle sizes than Nigerian respondents or because in Nigeria unlike in Britain centiliter (cl) is more commonly used on bottle labels than milliliter (ml). All the questionnaires used in the survey used milliliter and liter as units of bottle liquid volumes. Further evidence to support the supposition that Nigerian bottle size data is inaccurate is that unlike British respondents, the Nigerian respondents did not specify the size of about 16% of the bottles they reported.

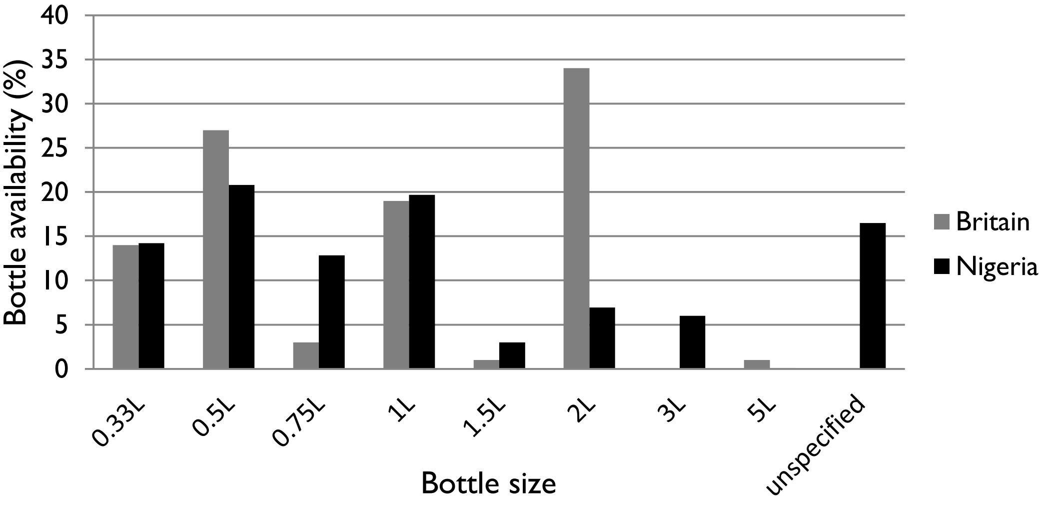

Figure 6.2 Sizes of bottles in places of residences

6.5 Bottle content types

Sparkling water is not marketed in Nigeria. Consequently still water accounted for 82% of bottled liquids stored and used in places of residences in Nigeria, with the remaining 18% accounted for by soft drink. In Britain where sparkling water is consumed it accounted for 5% of bottled liquids reported in places of residence. Bottled drinks and still water accounted for 50 and 45% respectively. Most bottled water from Nigeria is sterilized table water in contrast to Britain where most bottled water is either spring water or natural mineral.

6.6 Storage durations for purchased bottled water and soft drinks

Storage duration for purchased bottled water and soft drinks is an important parameter in terms of chemical migration because as mentioned in Subsection 4.7.4, duration of contact between bottle material and bottle content is one of the factors that influence concentration of migrants in bottle content. In this work the durations of storage of unopened PET bottled water and soft drinks at the time of the survey differed significantly between British and Nigerian respondents (Mann-Whitney U = 11115.5, $n_1 = 235$, $n_2 = 131$, $p < 0.01$). The median period of storage in Britain and Nigeria were 7 and 10 days respectively. Median is given as a measure of central tendency because the data are positively skewed (many low values and few high values). While 79% of British respondents stored for between 1 and 7 days only 50% of Nigerian respondents stored for the same period (Figure 6.3). Nevertheless, for both countries the storage period ranged between 1 day and 1 year. For British respondents the durations are similar between native Britons and visitors. The median period was 7 days for both and the proportion of respondents storing between 1 and 7 days are 84% for native Britons and 76% for visitors. In this case the storage behaviour of the British visitors is more like that of native British respondents than that of Nigerian respondents.

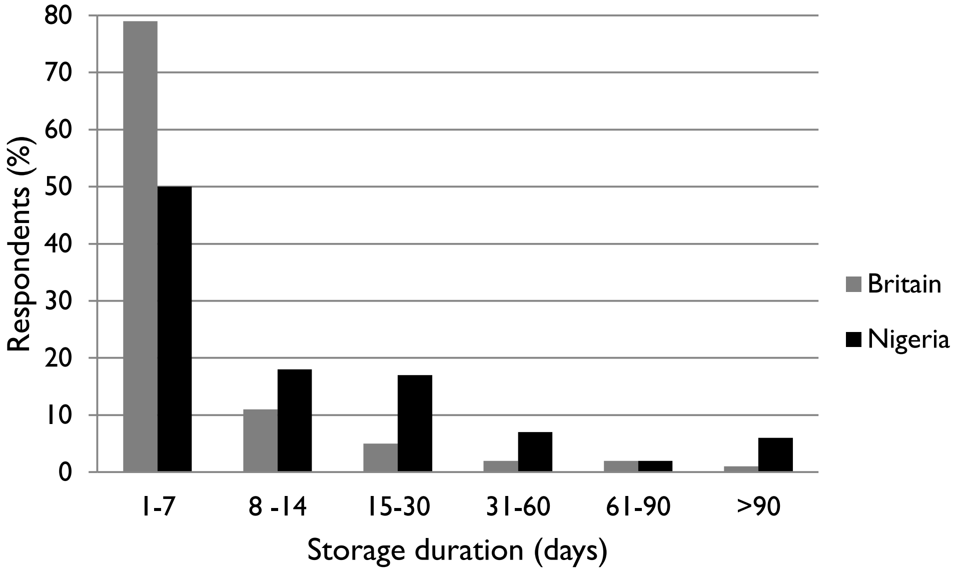

Figure 6.3 Durations of storage for unopened bottles in places of residence

Respondents were also asked a question on the longest time both unopened and open bottles ever remained in their possession as a worst-case scenario. In the case of unopened bottles the storage durations were found to be similar for both British and Nigerian respondents (Mann-Whitney U = 12816, $n_1 = 231$, $n_2 = 121$, $p = 0.197$). The median period in both Britain and Nigeria was 14 days. The longest storage period for about 41% of all respondents was between 1 and 7 days (Figure 6.4). For respondents from both countries the longest unopened bottles storage periods ranged between 1 day and more than a year. It is not known whether unopened bottle contents are still consumed after long storage. For British respondents the median was 14 days for both native Britons and visitors and the durations were similar (Mann-Whitney U = 4642, $n_1 = 126$, $n_2 = 87$, $p = 0.055$). The proportion of respondents that stored for between 1 and 7 days were 42% for native Britons and 47% for visitors. The longest periods contents of opened bottles last before been used up are similar for British and Nigerian respondents (Figure 6.5). Respondents from both countries reported having opened bottles that lasted for periods ranging between 1 day and 1 year. Even so for both countries more than three-quarter of respondents reported consuming bottle contents within 7 days (Figure 6.5).

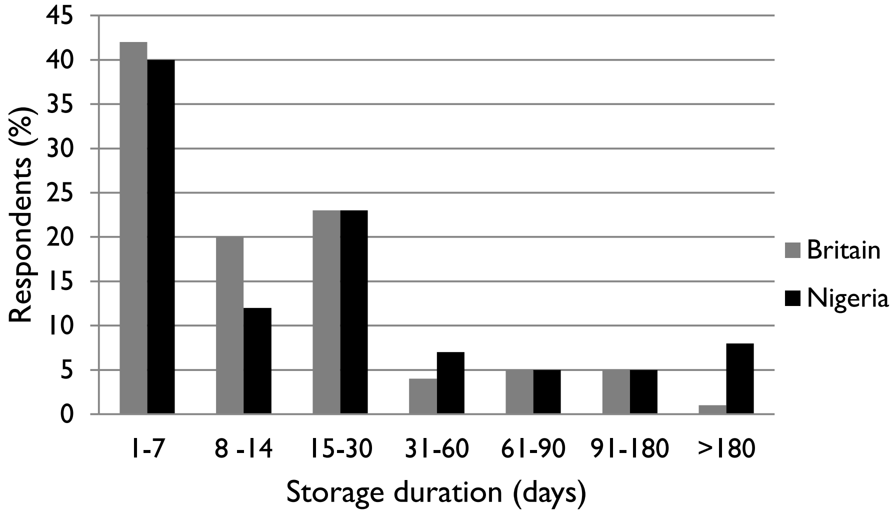

Figure 6.4 Longest reported storage durations for unopened bottles in places of residence

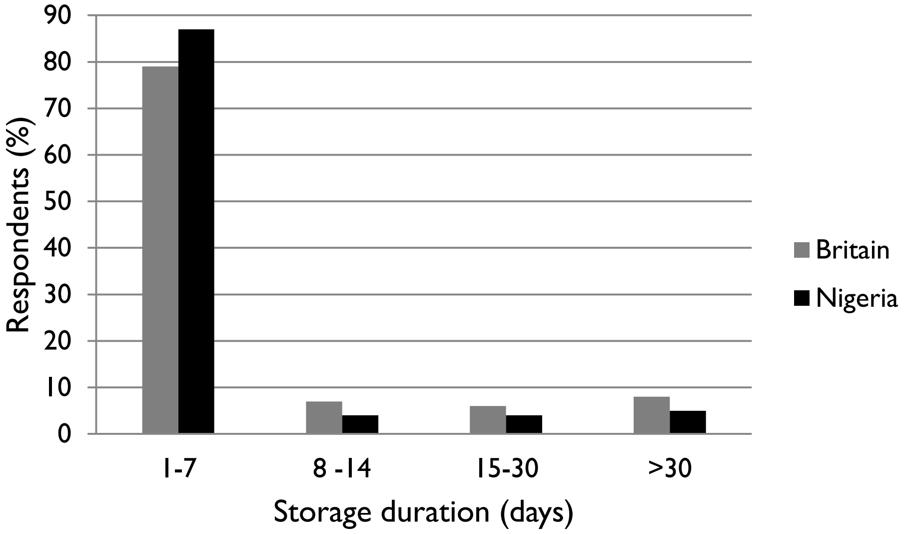

Figure 6.5 Longest reported storage durations for opened bottles in places of residence of residence

A time interval ranging from few hours to several months exists between purchase of bottled water and soft drinks and their consumption. Additionally “best before” dates which, as earlier mentioned, are unrelated to chemical migration, exists for all bottled contents. Bottled water and carbonated drinks in PET bottles from Nigeria have a shelf life of one year and six months respectively based on the production and 'best before' dates stamped on the bottles. In the US and Canada bottled water's stamped shelf life is usually two years (Environmental Health & Safety Online, 2006; Health Canada, 2009). From the results in this work between 1 and 6% of British and Nigerian households were found storing bottled water and/or soft drinks for a period greater than 3 months prior to use. Similarly small percentages (between1 and 8%) of British and Nigerian households reported ever storing bottled water and soft drinks for a period greater than 6 months prior to use. Consequently even if the "best before" dates have any relevance to risk of consumption of liquids with leached bottle contents, the proportion of households to be affected by this will be very low. The risk associated with storage of bottled water and soft drinks will be discussed later in relation to actual antimony and acetaldehyde migration patterns.

6.7 Storage places

As discussed in Subsections 4.7.1 and 4.7.2, both heat and light can speed up the rate at which migration of chemicals from the plastic materials into the contents ensues. In this study no statistically significant difference was found between British and Nigerian respondents in terms of places of storage of unopened bottles [χ^2 (1, n = 453) = 2.639; p = 0.104]. Unopened bottles are stored inside and outside the refrigerator at approximately equal frequencies for both countries. Storage outside the refrigerator was reported by 56 and 48% of British and Nigerian respondents respectively. While it is very cool and mostly dark inside refrigerators, conditions outside the refrigerator could range from dark and cool, dark and warm, to bright and cool and bright and warm depending on the section of place of residence, season, and heating and lighting in a residence. In Leeds the most populous city in West Yorkshire in the UK the mean ambient temperature ranges between 0.2°C (February) and 19.9°C (July/August). In Abuja the capital city of Nigeria the range is between 15.5°C (December) and 36.9°C (March). In Niamey the capital city of neighbouring Niger Republic the mean maximum temperature is as high as 40.9°C (April) (World Weather Information Service, no date). It is not unusual for ambient temperatures in northern Nigerian cities bordering Niger republic to reach 40°C in hot season.

Reported storage places other than refrigerator include cupboard, carton, kitchen, living room, locker, storeroom, wardrobe, window sill, pantry, garage, bedroom, basement and attic. Storage places for opened bottles depend on season. During the coldest seasons of the year more Nigerians stores opened bottles outside refrigerator than British respondents [χ^2 (1, n = 363) = 3.652; p = 0.056 –marginal significance, φ^2 =

0.01]. During these seasons, 55 and 66% of British and Nigerian respondents stores outside refrigerator. During the hottest seasons of the year opened bottles are stored inside and outside refrigerator at approximately equal frequencies for both countries [χ^2 (1, n = 360) = 2.599; p = .110]. Storage outside refrigerator was 29 and 21% for British and Nigerian respondents respectively.

6.8 PET bottle reuse

PET bottles are reused in places of residence, on the move and at work. For both British and Nigerian respondents the extent of reuse in places of residence and the overall reuse were high and were not significantly different (Table 6.1). Proportions of British and Nigerian respondents reusing PET bottles are 80% and 83% respectively. No statistically significant difference could be observed between native British respondents and visitors for all reuse situations. An important observation made was that the reuse information revealed by the first 144 questionnaires collected before the PhD upgrade report was similar to the information revealed by the 320 samples collected after the report. The proportion of respondents reusing PET bottles was similar for all reuse situations. What this implies is that 144 questionnaires are as effective as the 464 questionnaires in terms of revealing the information on PET bottle reuse. Interestingly, the extent of reuse revealed by the study for the 2 countries is similar to what was observed by Lilya (2001) in a preliminary survey of the university of Idaho community in the US. In that study the author found that 88% of the participants reused polyethylene terephthalate (PET) plastic bottles used for bottled water.

Nigeria is a low-income tropical country, on the other hand Britain is a high-income temperate country and Idaho is a temperate region in a high-income country. Higher reuse was initially thought to be more associated with low-income tropical countries than high-income temperate countries in large part due to higher need to drink fluids and presumed lesser need to reuse bottles as a result of greater prosperity. However it is also appreciated that greater availability of empty bottles in high-income countries as a result of higher use may elevate reuse. From the figures obtained PET bottle reuse in places of residence and overall PET bottle reuse are independent of country, and by implication, independent of economic status and climate.

Table 6.1 Comparison between British and Nigerian respondents in terms of PET bottle reuse status

Reuse location	Country	% reusing PET bottles	Chi square test of homogeneity
Places of residence	Britain	67	χ^2 (1, n = 813) = 3.536; p = 0.06, no statistically significant difference
	Nigeria	73	
On the move	Britain	68	χ^2 (1, n = 926) = 32.144; $p < 0.01$, $\varphi^2 = 0.04$, statistically significant difference
	Nigeria	50	
At work	Britain	53	χ^2 (1, n = 902) = 18.029; $p < .01$, $\varphi^2 = 0.02$, statistically significant difference
	Nigeria	39	
Overall reuse	Britain	80	χ^2 (1, n = 961) = 1.620; p =0 .203, no statistically significant difference
	Nigeria	83	

Conversely statistically significant difference was found between the 2 countries in terms of reuse on the move and at work (Table 6.1). For both reuse on the move and at work, more British respondents reuse PET bottle than Nigerian respondents. This observation refuted the assumption that low-income tropical countries reuse PET bottles more than high-income temperate countries. However for both reuse situations the strength of the associations (φ^2) lies between small and medium implying that country of respondent only weakly predicts the degree of reuse. In these situations the observed association between degree of reuse and country can be explained more by lifestyle than by economic status and climate.

While bottle reuse is an environment-friendly activity there is concern that it may not be safe as a result of chemical migration and bacterial contamination. In fact in some developed countries health authorities sometimes discourage the reuse of the single-use PET bottles due to risk of bacterial contamination. Health Canada, the department of the government of Canada with responsibility for national public health, does not recommend the reuse for this reason (Health Canada, 2009). As mentioned in Chapter 3, information is scanty in the literature on bottle reuse pattern in developed and developing countries. However this study provides a useful insight into the pattern of reuse in both developing and developed countries. As mentioned in Section 3.9, some of the factors thought to be influencing bottle reuse include economic status and climate of a country, safety debate, cost, bottle availability, age of bottles, environmental concern, original content of bottles and convenience. The results obtained in this study clearly indicate that economic status and climate of a country may not be factors that influence bottle reuse. This is because the extent of reuse for both Nigeria and Britain were found to be similar at 83 and 80% respectively. While these results are similar for the 2 countries, it is possible that the factors that brought about this behaviour synergistically impacted differently to give the similar results. This will be discussed further in relation to the actual factors found from the survey to be influencing reuse. The results in this study together with the earlier results from the US (88% reuse reported by Lilya, 2001) suggest that PET bottle reuse is similar in both developing and developed countries.

6.9 PET bottle reuse durations

Tables 6.2 and 6.3 together with Figures 6.6 and 6.7 shows the reuse duration attributes for Nigerian and British respondents for different reuse situations. Even though both mean and median are given as measures of central tendency, the median is much more useful in revealing the centres of the distributions than the mean because the distributions are positively skewed (many low values and few high values). The Mann-Whitney U test was used to ascertain whether the British and Nigerian samples are drawn from similar populations in terms of reuse period. The test was also used to see whether reuse durations of the native Britons and those of visitors are similar. The results in Table 6.2 showed that the durations of reuse in places of residence and at work differ significantly for British and Nigerian samples. On the other hand the reuse durations on the move are similar. For British natives and visitors reuse durations were similar in all situations save for reuse at work. The average reuse duration at work was 37 and 16 days for native Britons and visitors respectively. However the median duration was 7 days for both respondents. In places of residence and at work, Nigerian respondents reuse PET bottles longer than British respondents. Nigerian respondents are also at the forefront in terms of longest reported bottle reuse periods for all reuse locations. For Nigerian respondents the longest reported bottle reuse durations are between 4 and 6 years for all reuse situations. For British respondents these periods are between 1 and 2 years. Lilya (2001) in the University of Idaho reported 6 months (approximately 180 days) as longest reuse period.

Table 6.2 Comparison between British and Nigerian respondents in terms of PET bottle reuse durations

Reuse location	Country	Reuse duration attributes			
		Mean (days)	Median (days)	Range (days)	Mann-Whitney U test
Place of residence	Britain	39	14	1 – 360	Mann-Whitney U = 12797.5, $n_1 = 179$, $n_2 = 229$, $p < 0.01$ (two-tailed), distributions in the two groups differed significantly
	Nigeria	150	35	1 – 2160	
On the move	Britain	27	7	1 – 720	Mann-Whitney U = 7894.5, $n_1 = 183$, $n_2 = 87$, $p = 0.912$ (two-tailed), distributions in the two groups similar
	Nigeria	72	7	1 – 1440	
At work	Britain	38	7	1 – 720	Mann-Whitney U = 5024, $n_1 = 141$, $n_2 = 87$, $p < 0.05$ (two-tailed) distributions in the two groups differed significantly
	Nigeria	98	28	1 – 1440	

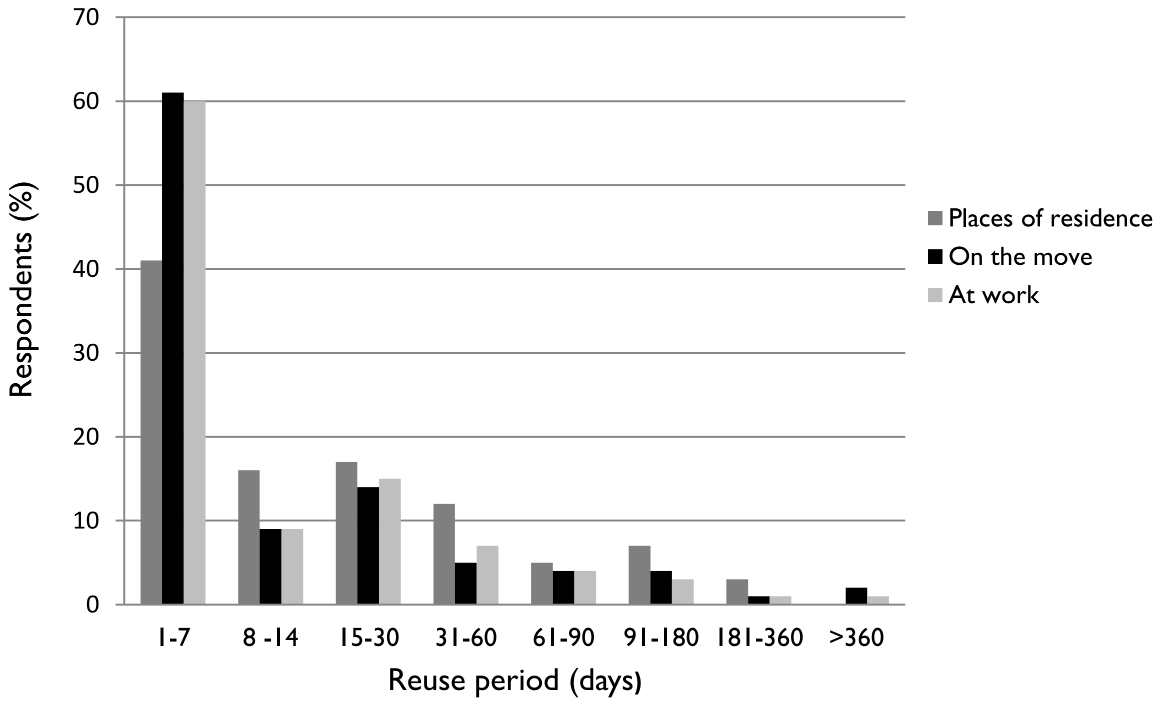

Figure 6.6 PET bottles reuse durations for British respondents

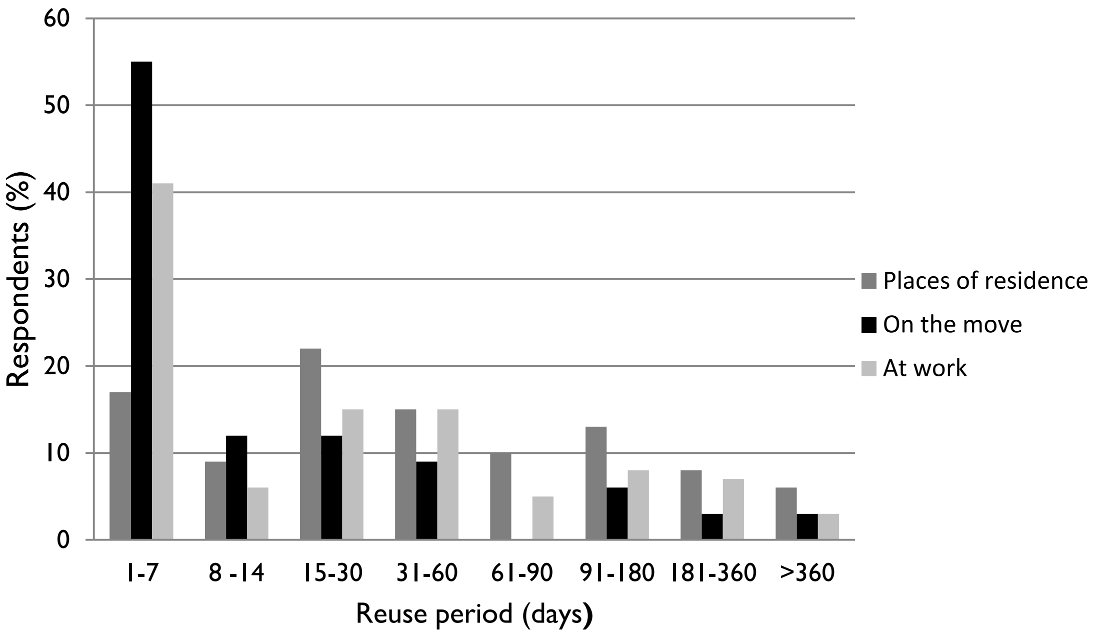

Figure 6.7 PET bottles reuse durations for Nigerian respondents

Table 6.3 Reuse duration cumulative frequency table

Country	Reuse location	Proportion of respondents found reusing within						
		1-7 days	1-14 days	1-30 days	1-60 days	1-90 days	1-180 days	1-360 days
Britain	Places of residence	41%	57%	74%	86%	91%	98%	100%
	On the move	61%	70%	84%	89%	93%	97%	98%
	At work	60%	69%	84%	91%	95%	98%	99%
Nigeria	Places of residence	17%	26%	48%	63%	73%	86%	94%
	On the move	55%	67%	79%	88%	88%	94%	97%
	At work	41%	47%	62%	77%	82%	90%	97%

The longer bottle reuse periods in Nigeria are probably partly attributable to lower availability of used bottles as a result of lower use of bottled water and soft drinks in comparison to Britain. Lesser availability of bottles translates into longer bottle reuse duration. Availability in this context may refer to availability of funds to purchase used bottles in addition to physical availability of the bottles. In developing countries like Nigeria used bottles are in many instances not available for free. These bottles are generally available from collectors who collect them for the purpose of selling them to recyclers and to people wanting to reuse them. The longest reuse durations reported in this work (6 years) may look unrealistic. However, a look at the data will reveal that these long durations were reported by only very small proportions of respondents. Additionally a bottle has been collected from an office in the University of Bradford that had been reused for a period longer than 1 year. Because of their clarity and rigidity it is possible to use PET bottles for an extended period of time without noticing a change that may elicit the need for replacement.

6.10 Number of bottles being reused in places of residence

Figure 6.8 gives details on the number of bottles that were being reused in places of residence at the time of the survey. More bottles were being reused in places of residence of Nigerian respondents than in places of residence of British respondents (Mann-Whitney U = 12957.5, $n_1=218$, $n_2=256$, $p < 0.01$). For instance, 38% of British respondents were reusing one bottle in comparison to only 14% of Nigerian respondents. The median number of bottles being reused was 2 and 6 for British and Nigerian places of residence respectively. Nigerian respondents also recorded the highest number of PET bottles being reused in places of residence. The number of bottles being reuse by native Britons and visitors differed. While only 25% of visitors were found reusing one bottle, the proportion of native Britons reusing one bottle was 45%. However the median number of bottles being reused by both groups is two. It follows that native Britons reuses less bottles in their places of residents than visitors in Britain or Nigerians. One of the factors believed to influence the number of bottles being reused at any given time is the state of potable pipe-borne water supply in places of residence. Supply of potable water is continuous in places of residence of British respondents in contrast to the places of residence of Nigerian respondent where the supply is intermittent. The intermittent supply logically calls for storage of potable water in larger quantities for use when supply ceases.

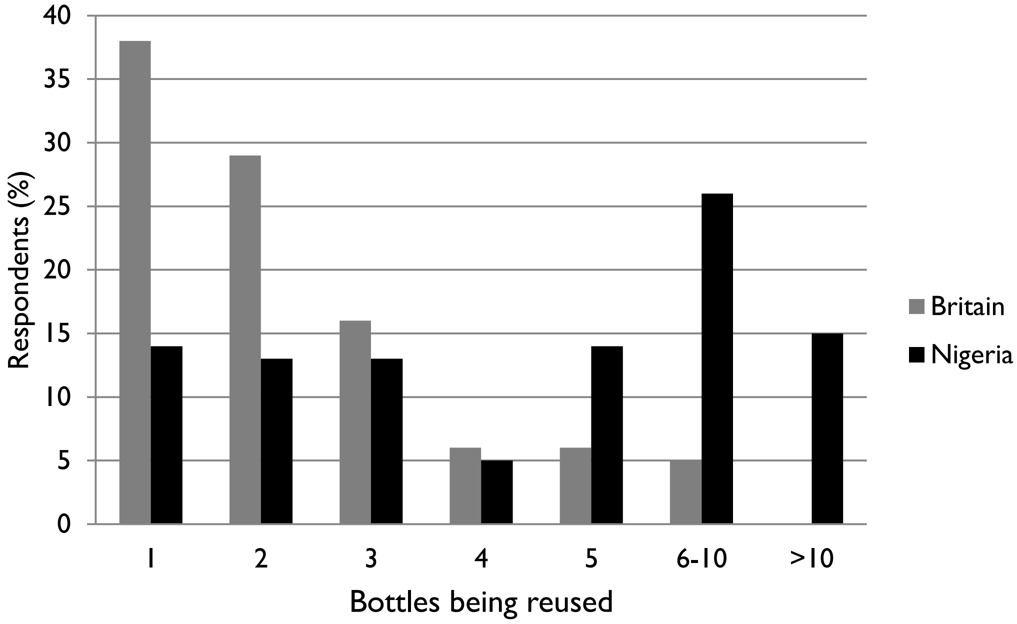

Figure 6.8 Number of bottles being reused in places of residence

6.11 Size of reused bottles

The most commonly reused bottles in places of residence of British respondents were 500ml bottles followed by 250/330ml bottles and then 1L and 2L bottle (Figure 6.9). It is not known whether reused bottles will behave in the same way as new bottles considering the effect of age on them. From Figure 6 the commonly reused bottle in places of residence of Nigerian respondents is 1L bottle. As for unopened and opened bottles (section 6.4) the accuracy of bottle size data for all Nigerian reused bottles is in question as the 250/330ml bottles reported by respondents are unavailable in Nigerian bottled water and soft drink market. Again some evidence to this observation comes in the form of the proportion of users whom reported not knowing the sizes of the bottles they reuse. For reuse in places of residence, which is high for both British and Nigerian respondents, as much 17% of Nigerian respondents reported not knowing the sizes of the bottles they were reusing while only 1% of British respondents reported not knowing the sizes of the bottles they were reusing in places of residence.

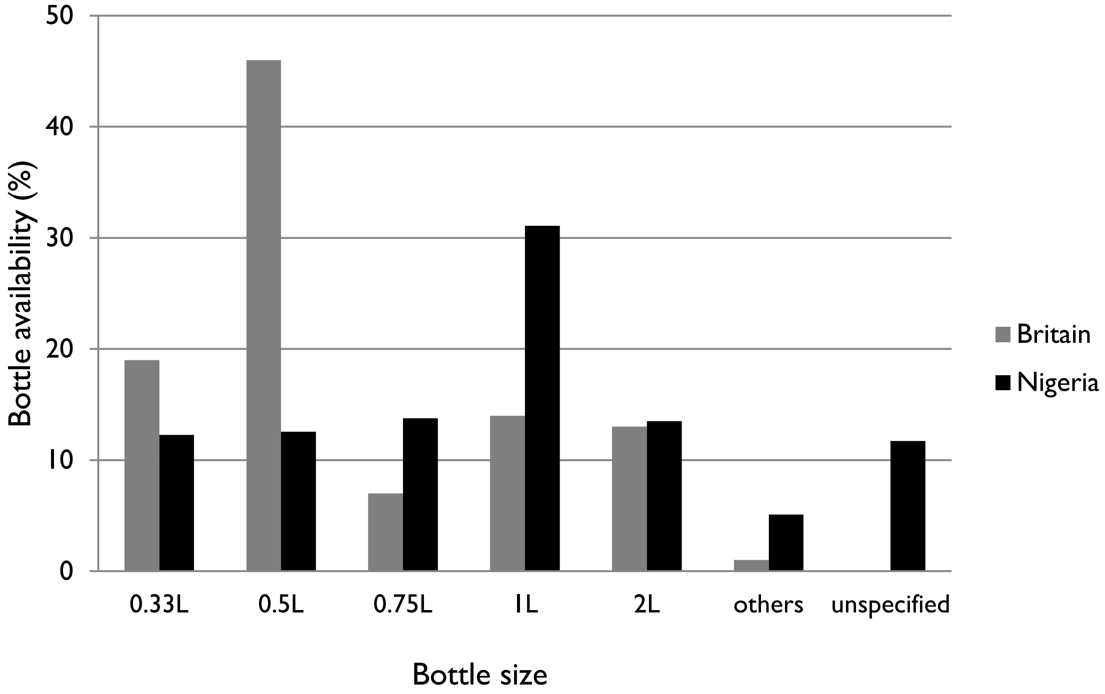

Figure 6.9 Sizes of reused bottles

6.12 Reuse safety perception and safety debate

Safety concerns about PET bottle reuse exist in both developing and developed countries. However the degree and type of concern may vary with country. In this survey the extent to which respondents reported safety concern on PET bottle reuse differ between Nigerian and British respondents (χ^2 (1, n = 926) = 25.076; $p < 0.01$, $\varphi^2 = 0.03$). At 28 and 43% for British and Nigerian respondents respectively, more Nigerians than British respondents are concerned that reusing PET bottle is unsafe. Reusing and non-reusing respondents in both countries were found to have similar levels of safety concern. Also native Britons and visitors have similar levels of safety concern. While some of the concerns reported are similar for the 2 countries others are unique to individual country (Figure 6.10). Eighty and 71% of the concerns reported by British and Nigerian respondents were contamination-related. These concerns include unspecified contamination, chemicals, germs, hygiene and cancer causation. Concerns not related contamination includes water remaining for too long in bottle, age of bottle and water source.

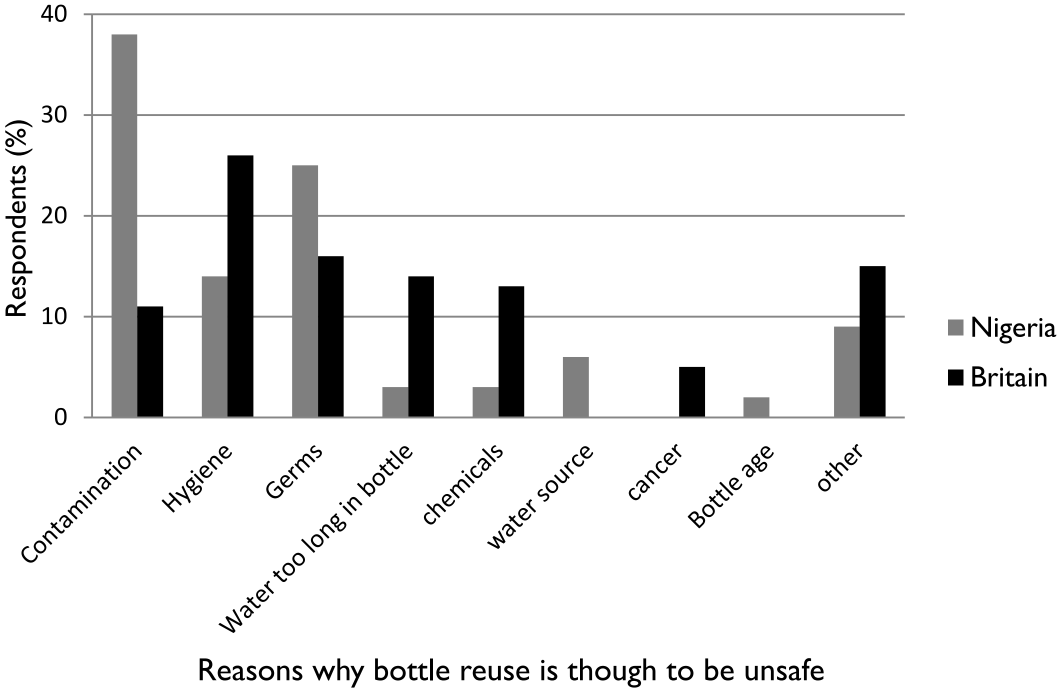

Figure 6.10 PET bottle reuse safety perception

Perceiving bottle reuse as unsafe is one thing and the reuse being unsafe is another. As will be discussed later aged bottles were found to release lesser quantities of migrants than new bottles in this study. In spite of this the results of the survey carried out in this study have confirmed that some respondents are actually concerned that bottle reuse can be unsafe. However the fact that both reusing and non-reusing respondents in both countries have similar levels of safety concern implied that safety concern is not an important determinant of bottle reuse. Even though Nigerian respondents reuse bottles for a longer period of time, they are still concerned that reusing old bottles is health risk. This can be seen as evidence that unavailability of new bottles is part of the reason behind longer reuse of PET bottles in Nigeria. Also as a reflection of insufficiency of clean drinking water in Nigeria only Nigerian respondents reported water source as a concern in bottle reuse. Both British and Nigerian respondents are concerned about presence of harmful chemicals in water contained in reused PET bottles. However British respondents are over four times more concerned about the presence of harmful chemical contaminants in water contained in bottles than Nigerian respondents (Figure 6.10). Chemicals in water contained in reused PET may originate from the water source. In this study most British respondents that mentioned chemical contamination as a concern mentioned something about plastic releasing chemical into water. In contrast none of the Nigerian respondents specifically mentioned the issue chemicals being released from plastic material. This clearly shows that only British respondents nurture the concern about plastics releasing chemicals into the bottle contents. Further evidence to support this interpretation is that 5% of the British respondents believe that there is some risk of getting cancer as a result of drinking water from a reused PET bottle. In other words these respondents believe that reused PET bottles are releasing carcinogenic chemicals at concentrations that can result in the user developing cancer. Risk of bacterial contamination and infection has been mentioned as a safety hazard by both Nigerian and British respondent (Figure 6.10). As stated in Subsection 3.8 bacterial contamination is a hazard associated with reuse of PET bottles, especially if a bottle is being reused by more than 1 person and thorough washing of bottle is not carried out. Usage of a bottle by single person and thorough washing of the bottles with detergent were suggested as a solution. However the impact of long-term rigorous washing on bottle behaviour is unknown.

The extent to which chemical migration risk is overstated by environmental organisations, media and other interest group is believed to have some influence on the bottle reuse safety perception observed in this study. As mentioned in Section 3.11 chemicals that are not associated with PET bottle and are not carcinogenic are in many cases termed as carcinogens leaching from PET bottles. The greater concern about chemical migration and risk of cancer from bottle reuse in Britain than in Nigeria could be connected to greater access to internet in Britain than in Nigeria.

6.13 Other issues affecting reuse

As mentioned earlier factors thought to be influencing bottle reuse include economic status and climate of a country, safety debate, cost, bottle availability, age of bottles, environmental concern, original content of bottles and convenience. Economic status and climate of a country has already been ruled out as a factor influencing bottle reuse. Other issues influencing the respondents' tendency to reuse plastic bottles apart from safety concern are shown in Figure 6.11. The degree to which the British and Nigerian respondents' bottle reuse is influenced by issues other than safety concern was found to statistically significantly differ (χ^2 (1, n = 806) = 4.407; $p < 0.05$, $\varphi^2 = 0.005$). However as can be seen the actual strength of this difference is very small and is deemed negligible. Consequently in spite of the statistical significance of the difference

British and Nigerian respondents are practically not very different in terms of the degree to which their tendency to reuse bottle is affected by issues other than safety concern. Additionally issues other than safety concern influence the bottle reuse status of native Britons and visitors equally.

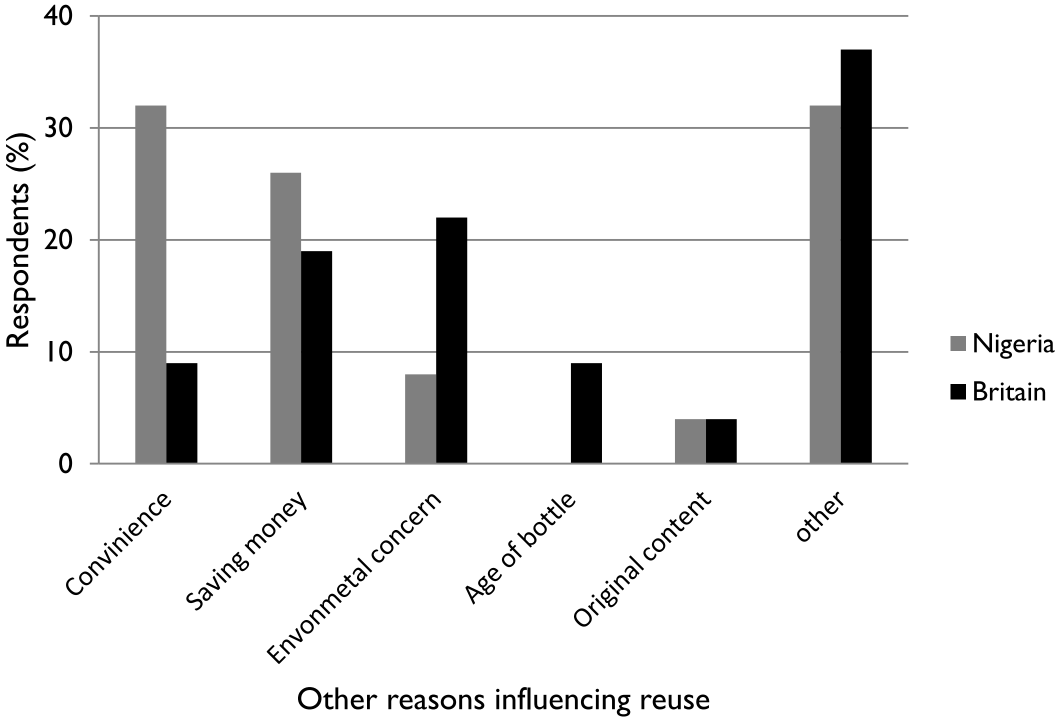

Figure 6.11 Other issues influencing reuse

For respondents from both countries the tendency to reuse bottle is affected by environmental concern, the desire to save money, convenience of reusing bottle and original content of bottles as shown in Figure 6.11. For the British respondents the single most important motivation for reusing bottle is the desire to preserve the integrity of the environment followed by the need to save money. For the Nigerian respondents convenience associated with reuse of PET bottle is the most important motivating factor followed by the need to save money. Cost was initially thought to influence reuse both positively (need to save money) and negatively (preference to buy new bottles because they are cheap). Contrary to this assumption only 1 British respondent reported preferring to buy new bottles because according to this respondent new bottle is cheap and it is easier to dispose the used bottles than to reuse them. Original content of bottle influences bottle reuse to the same degree for both Nigerian and British respondents. The reuse status of both the British and Nigerian respondents is influenced by the age of bottle being reused. However while Nigerian respondents reported the issue of old bottles as a safety concern the British respondents reported the issue under concern not related to safety (Tables 6.10 and 6.11).

6.14 Summary

While British respondents use more bottled water and soft drinks than Nigerian respondents which agree with the fact that Britain is more prosperous than Nigeria, the later stores unopened bottles for longer durations before use. The pattern of storage in terms of storage places is similar for the two countries. However, possibility of migration of chemicals from plastic material into the content is likely to be higher in Nigeria's bottled water/drinks as a result longer storage duration and harsher climate. For both countries the possibility of accumulation of chemicals beyond international guidelines and standards is likely in only few cases where storage periods are long. The extent of reuse was similar for both countries, nevertheless Nigerian respondents reuse bottles for longer duration than British respondents. In case of reuse, the risk of accumulation of chemicals beyond regulatory levels will depend on the influence of age on the consistency of bottle material and migration activity of the chemicals in bottle material. While bottle reuse has not been established as a risk factor in chemical poisoning, perception that this is so has been observed from among a small proportion of British respondents. However, the perception that reuse is risky behaviour does not appear to reduce reuse. For the British respondents the most important motivation to reuse bottle is the desire to preserve the integrity of the environment followed by the need to save money. For the Nigerian respondents convenience associated with reuse of PET bottle is the most important motivating factor followed by the need to save money.

6.15 Implication of the survey results on laboratory work

The survey carried out in this study provided information which was utilised in three ways. Consequently, questions asked in the questionnaire can be grouped into three categories. The first category provided information on issues that were inadequately addressed in the literature. In some cases questions in the first category helped in identifying the eligibility of respondents to answer subsequent questions in the questionnaire. The second category provided information used in designing some aspect of the laboratory work in this study. The third category provided demographic information on respondents including country of origin, gender, age and university status. Questions in the first category include questions 1, 2, 7, 11, 15 and 16. Answers to these questions revealed the extent to which bottled water and soft drinks are consumed in the 2 countries studied and also the extent to which PET bottles are reused. This information acted as an additional justification for this study in that the higher the use of bottled water and soft drinks and the higher the reuse of PET bottle the greater the need to study migration of chemicals from bottles into contents. The remaining questions in the first category are questions 18, 19 and 20. These questions provided information on the issues influencing respondent's choice to reuse PET bottle.

Table 6.4 Influence of survey results on laboratory experiments

Group	Question number(s)	Topic of question	Relevance	Influence on laboratory component
1	1, 2, 7, 11, 15 and 16	status of use and reuse	literature	
2	4, 5, 9 and 10	storage of bottles with contents	laboratory work, literature	influenced the choice of unopened bottle storage period
3	6 and 9	storage places of bottles with contents	laboratory work, literature	influenced the choice of storage temperature (room temperature)
4	3, 8 and 14	sizes of bottle being used/reused	laboratory work, literature	influenced the choice of bottle sizes for experiment
5	12, 13 and 17	Bottle aging	laboratory work, literature	influenced the choice of bottle aging periods
6	18 and 19	reuse safety perception	literature	
7	20	Factors influencing bottle reuse	literature	
8	21, 22, 23 and 24	Demographic information		

Questions in the second category include questions 3, 4, 5, 6, 8, 9, 10, 12, 13, 14 and 17. Answers to these questions influenced the selection of parameters used in the design of the laboratory work as shown in table 6.4. It is worth mentioning that inadequate and irregular access to the laboratory equipment meant that the answers to questions in the second category influenced the laboratory work only partially. For example 41, 57, 74, 86, 91, 98 and 100% of British respondents reported reusing bottles in places of residence at maximum periods of 7, 14, 30, 60, 90, 180 and 360 days respectively. Ideally bottles should have been aged for these periods or a selection of these periods for the purpose of assessing the influence of bottle aging on chemical migration. However rather than aging the bottles based on these periods the bottles were aged based on the availability of the instruments.

6.15.1 Storage and chemical migration

Storage is one of the factors that elevate the concentration of migrants from PET bottles into bottle contents. In the survey conducted in this study both British and Nigerian respondents reported storing bottled water/soft drink at room temperature or in the refrigerator for as long as 1 year after purchase. The typical storage duration for unopened bottles prior to use ranges between one and 7 days. Also the typical period contents of opened bottles last before been used up is between one and 7 days. These periods were chosen as typical storage periods because for all cases (unopened and opened bottles) 50% or more of all observations fell within these period. Based on this information laboratory experiments were designed to store Nigerian and British bottled water and soft drinks in PET and glass bottle at room temperature for 7 days, 3 months, 6 months and one year to assess the migration of antimony and acetaldehyde from bottle wall into the contents. However as a result of instrument availability and sample storage problems Nigerian samples for assessment of antimony migration were stored for two and 11 months and British samples were stored for 19 months. For assessment of acetaldehyde migration Nigerian samples were stored for 12 and 25 months and British samples were stored for 20 months. Even though some British and Nigerian respondents reported storing bottles in refrigerator, chemical migration at low temperatures associated with refrigerator was not assessed.

6.15.2 Bottle age and chemical migration

Concentration of migrant chemicals in PET bottle wall are expected to decrease if the chemicals are not been regenerated in the bottle wall. From the literature 88% of respondents in a University of Idaho study reported reusing PET bottle for up to 6 months. In the results of the survey carried out in this study PET bottles were found to be reused for storing drinking water by 80% of respondents in Britain and Nigerian. In few cases bottles were reported to be used for over a year. The typical bottle reuse durations in Britain are between one and 7 days for reuse on the move and at work and between one and 14 days for reuse in places of residence. In Nigeria the typical bottle reuse durations are between one and 60 days, one and 7 days and one and 30 days for reuse in places of residence, on the move and at work respectively. Typical reuse durations are durations covering 50% or more of all observations for a particular reuse situation. Based on this information laboratory experiments were designed to age Nigerian and British PET bottles for 7 days, 14 days, 2 months, 3 months, 6 months and one year for the purpose of assessing the influence of bottle aging on the concentration of antimony and acetaldehyde in PET bottle wall and on the extent of migration of these chemicals into bottled water and soft drinks. However as a result of instrument availability and sample storage problems clear bluish 500ml PET bottles for assessment of antimony and acetaldehyde concentration in bottle walls and their migration into contents were aged for 368 days only. Clear green 500ml PET bottles also used to assess the influence of aging on the concentration of acetaldehyde in bottle wall, were aged for 266 days.

6.15.3 Bottle size and chemical migration

The ratio between contact area of PET bottle and the volume of the liquid in the bottle increases as the bottle size decreases. Consequently greater build up of chemical migrants was proposed in smaller bottles than in bigger bottles. In the survey carried out in this study the bottle sizes reported are 330, 500, 1000, 1500, 2000, 3000 and 5000ml. According to the survey 61% of bottles in places of residence were 2 litre bottles or 500ml bottles. To assess the influence of bottle size on antimony migration 5 clear colourless bottles within the range of sizes reported in the survey (2000, 1500, 750, 500 and 330ml) were used.

6.16 Conclusion

One of the objectives of the survey was to assess whether the durations of bottled water and soft drinks storage and use and PET bottle reuse could result in migration of chemicals into the content to levels beyond international guidelines and standards. The survey has revealed the typical storage durations and bottle reuse durations in the two countries. The durations played a vital role in the subsequent chapters in assessing whether antimony and acetaldehyde are migrating above acceptable limits as a result of bottled water and soft drinks storage and use and PET bottle reuse.

CHAPTER 7: IDENTIFICATION OF MATERIALS USED IN BOTTLING

7.1 Introduction

Plastic bottles and in some cases plastic bottle caps are coded with the Society of Plastic Industry's three-chasing arrow recycling symbol (plastic identification code) for the purpose of recycling. However bottle cap linings, glass bottles and metal crown and screw caps are not usually coded with these symbols. For the purpose of knowing the identity of the samples used in this research with absolute certainty all samples used were characterised by use of Raman Spectroscopy, Energy Dispersive X-ray spectroscopy or a combination of both techniques. It is worth mentioning that these techniques were only used for characterisation of samples as they are either not sensitive enough to detect the low levels of antimony and acetaldehyde being assessed in this study or they are entirely not meant for detection of these analytes. The results obtained from the characterisation exercise are presented in this Chapter.

7.2 Plastic bottle materials

Forty transparent Nigerian and British bottled water and soft drink bottle materials and one whitish British apple juice bottle material were analysed as explained in Subsection 5.6.4. Thirty one clear bottled water and soft drink materials were colourless, eight were green and one sample was blue in colour. All bottled water and soft drink materials were coded as PET. The apple juice material was coded as HDPE.

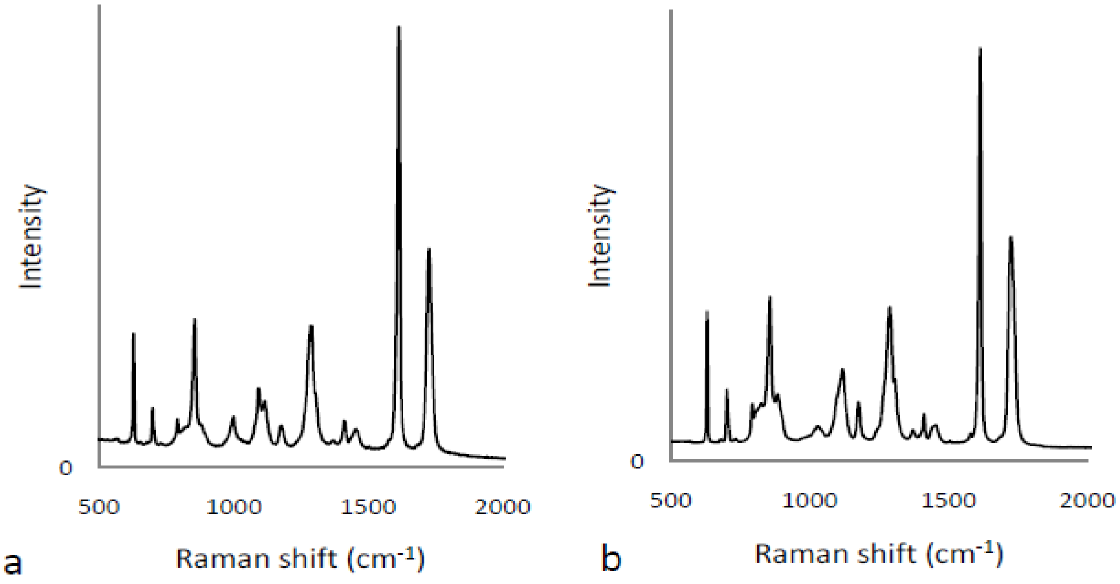

Figure 7.1 Raman spectra for (a) colourless still water bottle material and (b) PET reference spectra at 500 - 2000 cm^{-1}

Spectra were compared against PET and PE spectra from Thermo Fisher Scientific's Spectraonline database and Hendra and Agbenyega (1993). Based on the comparison bottled water and soft drink materials were confirmed to be PET and the apple juice material PE. Figure 7.1 and 7.2 show the Raman spectra of the materials analysed together with the reference spectra from Fisher Scientific's Spectraonline database. In few cases samples suffered from high level of fluorescence.

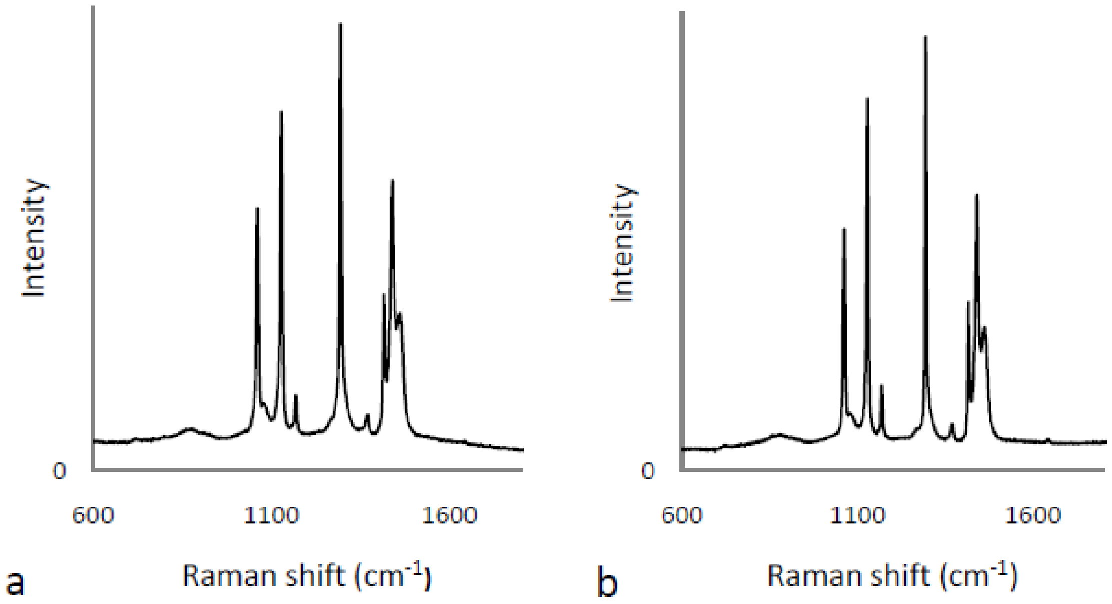

Figure 7.2 Raman spectra for (a) apple juice bottle material and (b) PE reference spectra at 600 – 1800 cm^{-1}

PET bottles are the main bottle types used for commercial bottling of water in large part because they are light, tough and clear. Use of other plastics including polyvinyl chloride and polypropylene is not common but has been reported in the works of Benfenati *et al* (1991) and Shotyk and Krachler (2007). Soft drinks are bottled in PET, PE and other non-plastic materials.

7.3 Powdery substance from PET material digestion

As mentioned in Subsection 5.8.9 white precipitate was obtained in the microwave digestion of PET material. The identity of the white substance could not be ascertained immediately as digestion of PET material using domestic microwave oven has not been reported in the literature. The white substance was initially analysed using EDX. As only oxygen and carbon were detected in significant amounts the substance was presumed to be organic and was thus reanalysed using Raman spectroscopy. A Raman spectra similar to that of terephthalic acid was obtained. Figure 7.3 show the Raman spectra obtained for the white substance and from pure terephthalic acid powder used as reference.

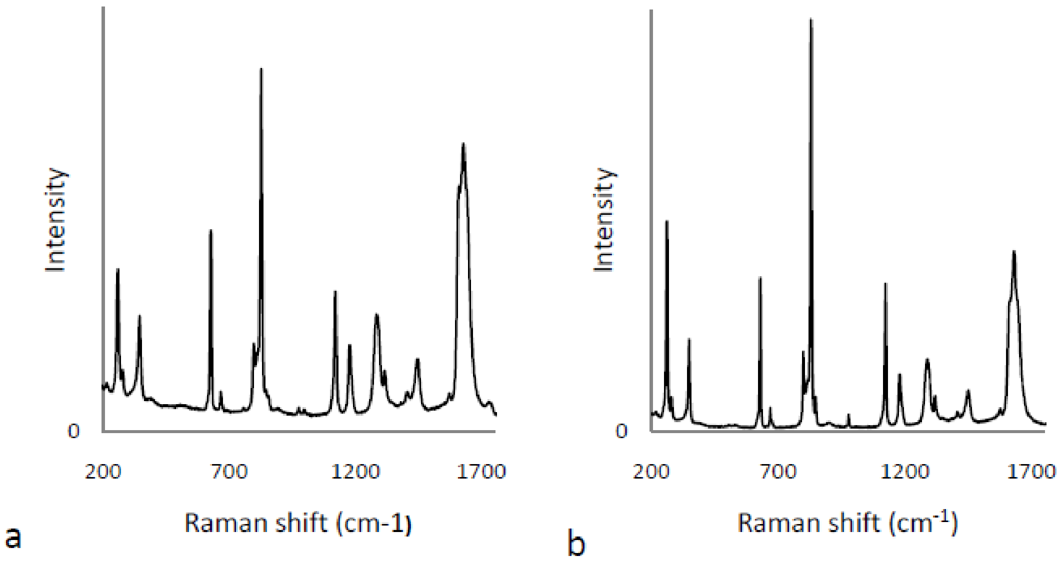

Figure 7.3 Raman spectra for (a) white precipitate from still water bottle digestion and (b) terephthalic acid powder reference spectra at 200 - 1750 cm^{-1}

The white substance was confirmed to be terephthalic acid. It was thus verified that the microwave-assisted nitric acid digestion designed in this study hydrolysed the PET into terephthalic acid (TPA) and possibly ethylene glycol, (the other constituent in the synthesis of PET), oxalic acid (by product of ethylene glycol oxidation by nitric acid), other organic compound(s) or carbon dioxide and water. Yoshioka *et al* (2003) reported a process for the depolymerisation of PET powder from waste bottles by using nitric acid. In that process the ethylene glycol generated was simultaneously oxidized to oxalic acid.

7.4 Glass bottle materials

Glass bottle materials were analysed as explained in Subsection 5.7.4. Figure 7.4 shows a typical EDX spectra obtained for soft drinks glass bottle materials from both Britain and Nigeria. Table 7.1 shows comparison of the relative abundance of the elements in the samples with the weight proportions reported for soda lime glass by Seward and Vascott (2005). This revealed good agreement confirming the glass materials as soda lime glass.

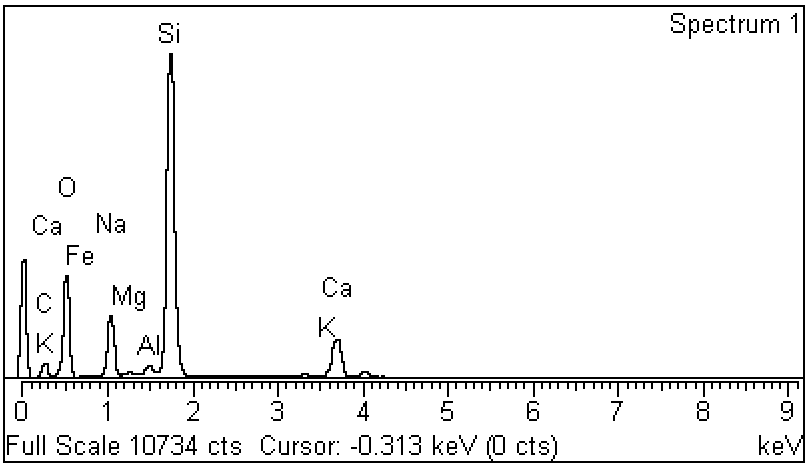

Figure 7.4 Typical EDX spectra for soft drinks glass bottle materials

No arsenic and antimony were detected. Although as mentioned in Section 2.3 arsenic and antimony oxides at 0.1 – 1% by weight may be used as fining agents for glass. Conclusion cannot be made on their presence or otherwise because the actual weight percentage range for elemental arsenic and antimony in glass containing 0.1 – 1% by weight of arsenic and antimony oxides may not be detected by EDX. According to Kuisma-Kursula (2000) the minimum detection limits of EDX is about 0.1 weight percent. In addition, due to the well-known toxicity of arsenic oxide, they are not likely to be used as fining agents in glass for beverage bottles.

Table 7.1 Relative abundance of the different constituent elements in glass bottle materials

Element	British soft drink bottle (% wt)	Nigerian soft drink bottle (% wt)	Soda lime glass for containers (Seward and Vascott, 2005) (% wt)
O	47.73	47.03	49.25
Na	9.70	9.63	7.67
Mg	0.49	0.30	0.12
Al	0.79	0.68	0.69
Si	32.76	34.91	34.00
K	0.32	0.34	0.25
Ca	6.4	6.9	7.46
Fe	0.25	0.23	0.028
Ti	-	-	0.006
S	-	-	0.08

7.5 Plastic bottle cap materials

Plastic bottle cap materials of different colours (light blue, dark blue, green, white, black, light grey, red and orange) were analysed. Raman spectra were compared against Thermo Fisher Scientific's Spectraonline database spectra and Hendra and Agbenyega (1993). Based on the comparison bottle cap materials were found to be either polypropylene-based or polyethylene-based plastics. Most caps for carbonated soft drinks from Nigeria and Britain were made up of polypropylene or a polypropylene based copolymer. Caps for bottled water were found to be made up of polyethylene or a polyethylene based copolymer.

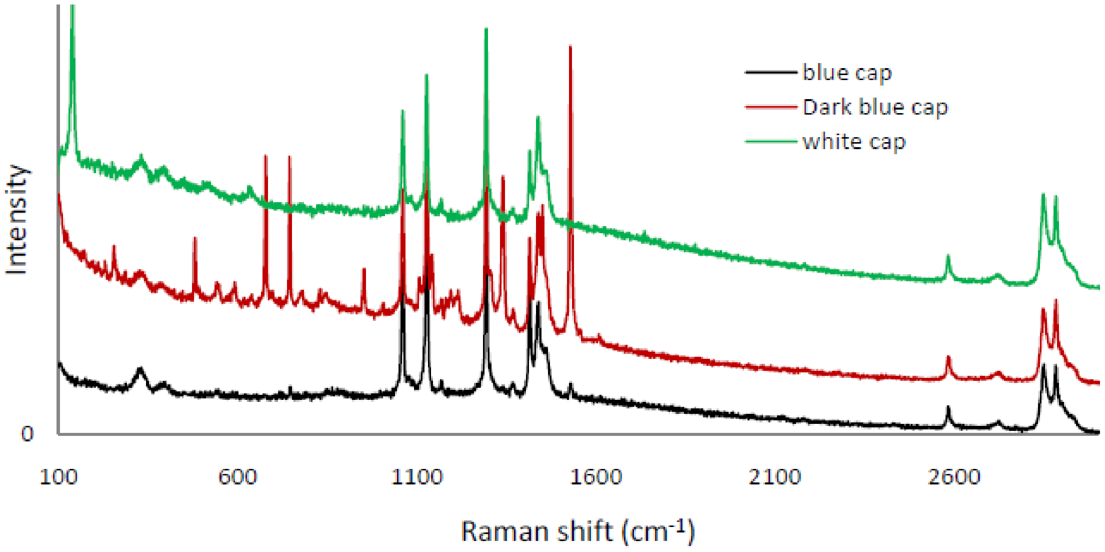

Figure 7.5 Raman spectra for 3 bottled water bottle cap materials at 100 and 3000 cm^{-1}

Figure 7.5 shows the Raman spectra of 3 bottled water bottle cap materials between 100 and 3000 cm^{-1}. The bands at 1061, 1128, 1294, 1401-1547 and 2827-3028 cm^{-1} are common to all samples whilst other bands were found to be sample-specific. The white cap spectra matched exactly with the reference spectra of polyethylene (Figure 7.2b). The blue cap spectra has an additional strong band at 139 cm^{-1}. The spectra for the dark blue cap have 7 additional bands at 254, 477, 678, 739, 951, 1340 and 1526 cm^{-1}. The presence of the additional bands especially for the middle spectra may indicate a polyethylene-based copolymer rather than pure polyethylene. Moreover as the caps are of different colours the additional bands may simply be due to the colorants used.

Figure 7.6 shows the Raman spectra of 3 carbonated drinks bottle cap materials together with the polypropylene reference spectra. While all bands from the reference are present in all samples some bands not present in the reference spectra were found to be sample-specific. These bands appear between 660 and 794cm^{-1} and between 1509 and 1626 cm^{-1}. These bands are probably attributable to colorants or other additives in the samples.

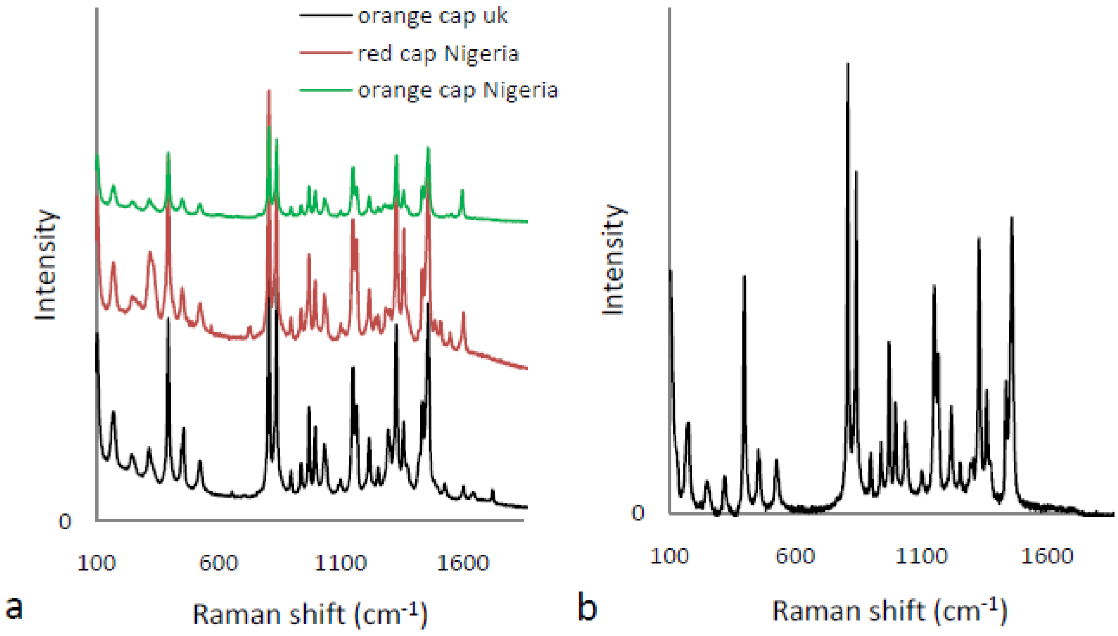

Figure 7.6 Raman spectra for (a) 3 carbonated drinks bottle cap materials and (b) polypropylene reference spectra

7.6 Metal crown and screw cap materials

Metal crown and screw caps from bottled water and soft drinks glass bottles were analysed using EDX (Section 5.7). The results obtained are shown in Table 7.2. Figures 7.7, 7.8 and 7.9 show typical EDX spectra obtained for British glass bottle screw cap, Nigerian glass bottle crown cap and British glass bottle crown cap respectively. According to industry sources crown caps are usually manufactured using printed tinplate or tin-free steel. While the former is tin-coated steel, the letter is steel coated with chromium. As an additional measure to prevent corrosion crown caps are as a rule varnished with lacquer, which is a varnish that dries by solvent evaporation. Aluminium screw caps are manufactured in a similar manner.

Table 7.2 chemical constituents of metal crown and screw caps for glass bottles

Cap	Part	major elements detected	minor elements detected	Remark
British bottle screw cap	outer chiselled surface	Al	C, O, Mg, Mn, Fe	Aluminium
	Inner smooth surface	C	Al, O, Si, P, Cr, Mn	
British crown cap	outer chiselled surface	Fe	C, Sn, N	Tinplate (TP)
	Inner smooth surface	C	O, Sn, Fe, P, Cl	
Nigerian crown caps	outer chiselled surface	Fe	C, Cr	Tin-free steel (TFS) coated with Chromium
	Inner smooth surface	C	O, Fe, Cr, Cl, P	

The EDX spectroscopy findings revealed that Nigerian crown caps are made from tin-free steel while the British crown caps are made from tinplate. Glass bottle metal screw caps from Britain were found to be aluminium.

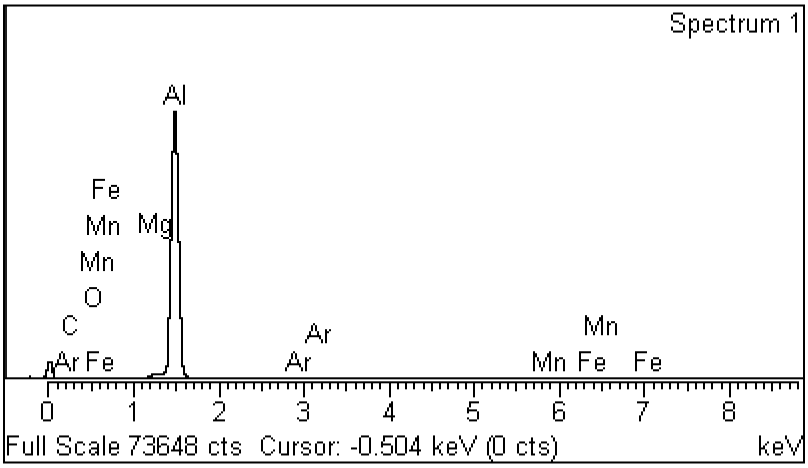

Figure 7.7 EDX spectra for British glass bottle screw cap

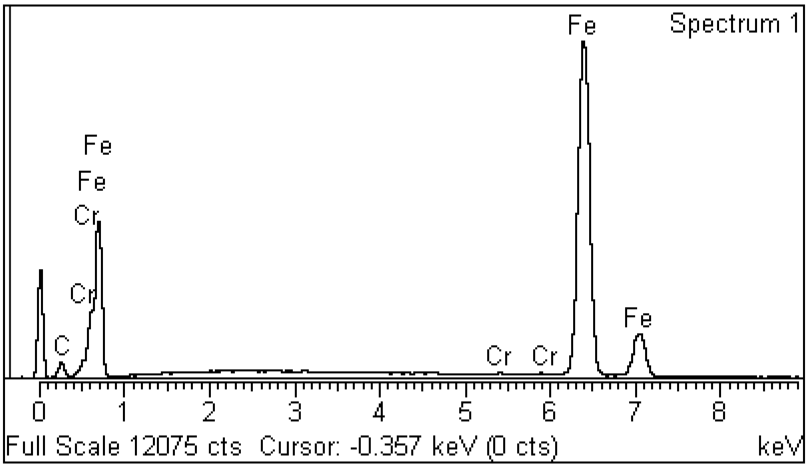

Figure 7.8 Typical EDX spectra for Nigerian glass bottle crown cap

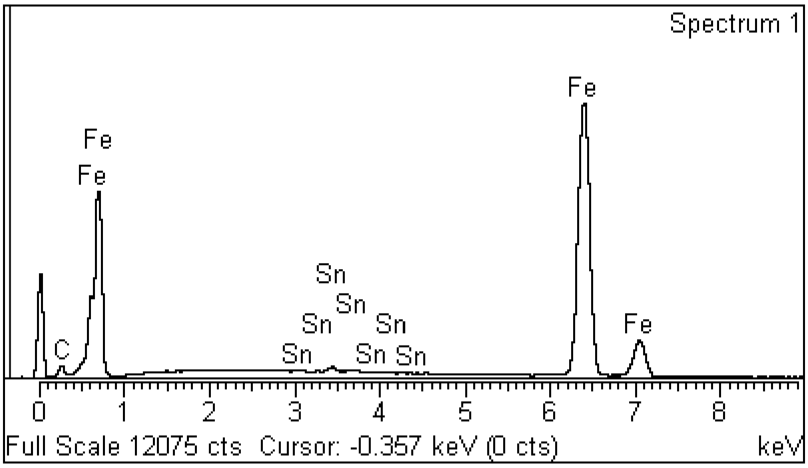

Figure 7.9 Typical EDX spectra for British glass bottle crown cap

7.7 Bottle cap linings

The metal and plastic caps of most PET and glass bottles for soft drinks from both Nigeria and Britain have a plastic material lining the inner part of the cap to help preserve the carbon dioxide and the aroma in the drinks. Cap lining material is as important as the bottle material in chemical migration studies because it comes in direct contact with the bottled liquid even though it does not present larger surface area as for the bottle material. While the linings for all the British bottles and some Nigerian bottles were slightly rigid, those found in some Nigerian bottles were flexible resembling plasticized polyvinyl chloride. The spectra obtained for all the British cap linings and some Nigerian cap linings match that of ethylene vinyl acetate (EVA) copolymer. The plastic materials lining the cap of carbonated drinks in PET bottles from a multinational bottling company in Nigeria were found to be made up of PVC plasticised with a chemical that strongly matches the identity of di(2-ethylhexyl) phthalate also called dioctyl phthalate (DEHP/DOP). The lining for Nigerian glass bottles' crown caps from the same company revealed a plastic material of unknown identity.

Typical Raman spectra for British and some Nigerian cap lining and the EVA reference spectra are shown in Figure 7.10. EVA spectra are virtually similar to that of polyethylene. According to Shimoyama *et al* (1997) PE and EVA differ in that EVA has extra bands at approximately 1740 and 629 cm^{-1} (C=O stretching and O-C=O deformation modes) arising solely from vinyl acetate. In Figure 7.10 these two bands are visible at the extreme ends of the spectra. The size of these bands relative to the bands of PE indicates the proportion of the vinyl acetate polymer relative to PE. The Raman bands at about 806 and 839 cm^{-1} in the cap liner spectra also indicates the presence of some polypropylene in the material. The two bands are usually the most intense bands in polypropylene Raman spectra. EVA-based copolymers are used as cap lining materials in place of pure PE probably because of their superior softness and flexibility both of which are good attributes in terms of sealing ability.

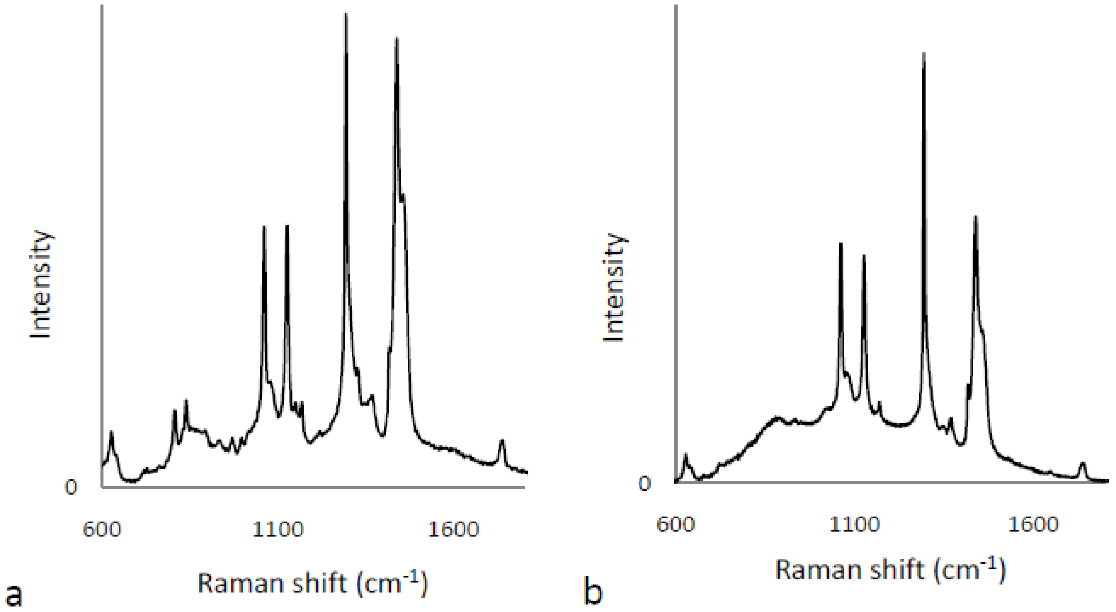

Figure 7.10 Raman spectra for (a) British and some Nigerian cap lining materials and (b) Ethylene vinyl acetate reference spectra

Figure 7.11 shows the spectra of a flexible Nigerian PET bottle cap lining material together with the spectra of a rigid hand wash bottle material coded as PVC. The typical EDX spectra for these samples (Figure 7.12) confirm the presence of chlorine which makes up as much as 57% of the weight of pure PVC. The relative abundance of chlorine in the EDX spectra of the cap lining and that of the bottle material were about 25 and 48% respectively an indication that both materials contains other chemicals in addition to the PVC with the former containing higher proportion of the extra chemicals. The 2 C-Cl stretching bands (about 635 and 698 cm^{-1}) typical of PVC are common to both spectra.

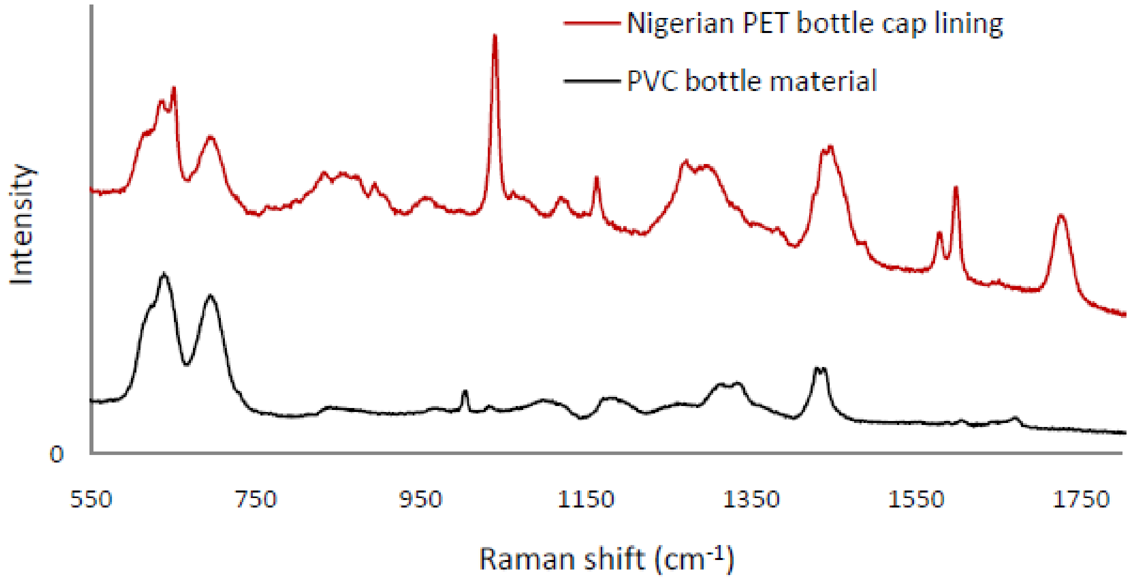

Figure 7.11 Raman spectra of a flexible Nigerian PET bottle cap lining material and a rigid hand wash PVC bottle material

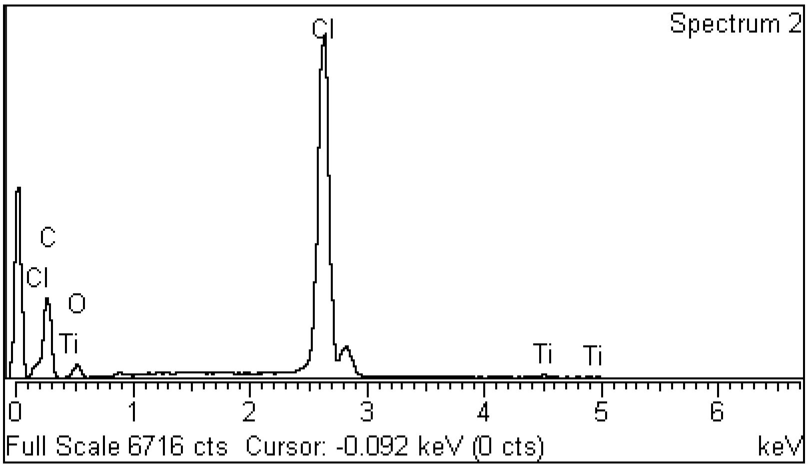

Figure 7.12 Typical EDX spectra for flexible Nigerian PET bottle cap lining material and a rigid hand wash PVC bottle material

Polyvinyl chloride is usually a rigid plastic. To make it flexible for use in applications including cap lining, plasticizers are added to it. Plasticized PVC may contain 30 – 40% of plasticizers in the form of the phthalate plasticiser, DEHP (Tickner *et al*, 1999). PVC may also be plasticised with other types of phthalate plasticisers, adipates, trimellitates, benzoates, citrate esters, etc. Consequently the plasticizer content of a PVC material will have some influence on the Raman spectra of the PVC material. The band at about 1728 cm^{-1} due to C=O stretching, the 2 bands at about 1038 and 1601cm^{-1} and the very weak band at 3075 cm^{-1} (not shown) due to aromatic ring vibrations, occurs in the cap linings spectra but not in the rigid PVC spectra. This confirms the presence of aromatic ester plasticizer in the cap lining material. In fact a closer look at the cap lining spectra reveals it to look very much like a superimposition of the bottle material spectra over the spectra in Figure 7.13 labelled as dioctyl (DEHP). In other words the strong resemblance of the cap lining spectra to the DEHP spectra strongly suggests the presence of DEHP as the used plasticiser in the cap lining material. However because phthalates esters as a group may show similar Raman bands as can be seen in Figure 7.13, it cannot be said with absolute certainty that the aromatic ester in the cap lining is DEHP.

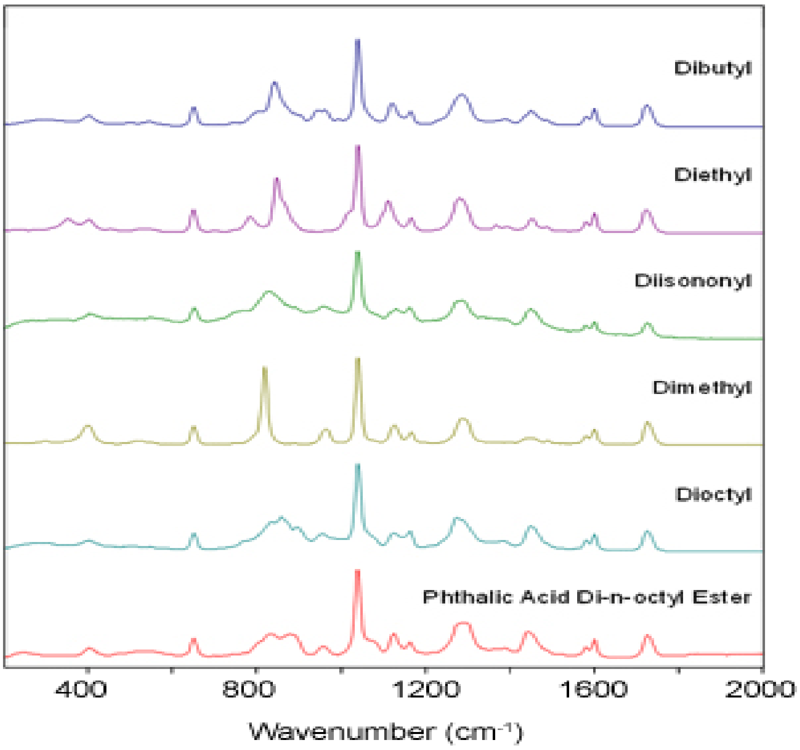

Figure 7.13 Raman spectra of phthalate plasticisers (adapted from IDES 2011)

The Raman spectra in Figure 7.14 was obtained from the analysis of the cap lining for Nigerian glass bottles' crown caps from the multinational bottling company mentioned earlier. The spectra has bands at 1083, 1301, 1439 and 2848 cm^{-1}. While this material looks like plasticised PVC physically, it was not possible to identify the material as comparable spectra could not be obtained from the literature.

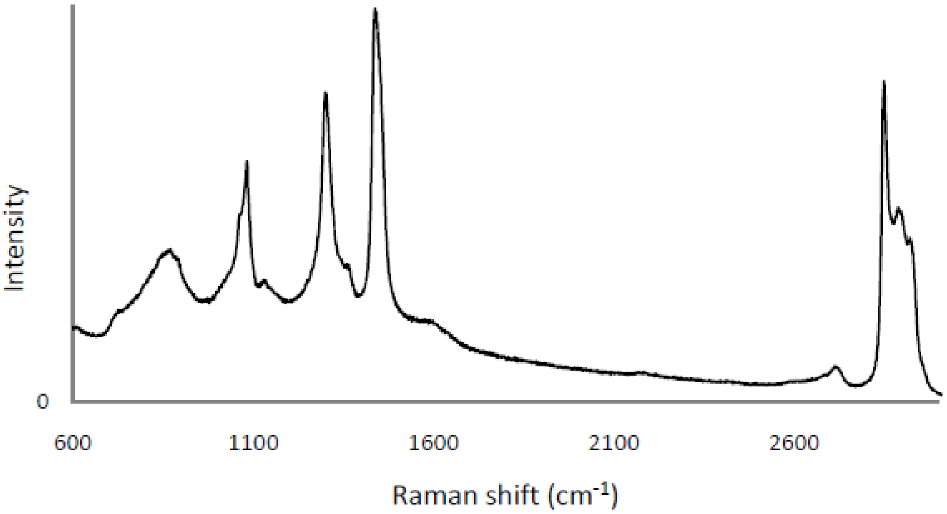

Figure 7.14 Raman spectra for Nigerian glass bottle crown caps cap lining

7.8 Summary

The principal purpose of the characterisation of the bottle materials was to confirm the identity of samples being used in this research. These characterisation experiments carried out were not expected detect or quantify antimony and acetaldehyde, the principal chemicals being investigated in this study. In addition to confirming the identities of the bulk materials studied here an important finding was made. It was found that a bottling company uses ethylene vinyl acetate/polypropylene copolymer, a plastic not associated with any health risk, as bottle cap lining material in Britain. However in Nigeria the company uses plasticised polyvinyl chloride, a plastic material which is associated with health risk issues.

PVC is a polymer of vinyl chloride which is an established carcinogen. In the work of Al-Malack (2001) concentration of vinyl chloride polymer was found to be higher than the U.S. Environmental Protection Agency permissible level in drinking water (2µg/L) after 30 days exposure of water to rigid PVC pipe in sunlight. As mentioned in Section 2.4 major corporations including Microsoft, Wal-Mart, and Kaiser Permanente have announced efforts to eliminate PVC from products and packaging. Also a bill is being considered in the State of California for banning the use of PVC in consumer packaging. Plasticised PVC like the one identified in this study may contain phthalate plasticisers which are associated with health risks as reported by Bornehag *et al.* (2004) and Swan *et al*, (2005). Due to the potentiality of phthalate plasticisers to cause harm in children an EU directive (Directive 2005/84/EC of The European Parliament and of the Council of 14 December 2005) has banned the marketing of plastic toys and childcare article containing more than 0.1% by mass of some 6 phthalates including DEHP, the phthalate plasticiser most likely associated with the Nigerian PVC cap lining material.

It is not clear why the bottling company uses plasticised PVC as cap liner in Nigeria but not in Britain. However legislation and greater consumer awareness in developed countries than in developing countries on the PVC health risk issues could be the reason. The need for a cap sealing material with superior sealing ability to counteract the effect of the warmer Nigerian climate could also be a reason.

7.9 Conclusion

This Chapter characterised the different materials related to bottling and in the process narrow down the bottle components expected to contain and release antimony and acetaldehyde.

CHAPTER 8: MIGRATION OF ANTIMONY AND OTHER ELEMENTS: RESULTS, DISCUSSION AND SUMMARY

8.1 Introduction

This Chapter presents the results obtained from the experiments in Section 5.8. The experiments quantified antimony in PET and other plastic materials and in drinking water from tap, freshly purchased bottled water and soft drink samples in PET bottles, glass bottles and other plastic bottles. The experiments also assessed migration of antimony under different conditions. The Chapter interprets and discusses the results in conjunction with the reviewed literature and the results in preceding chapters.

8.2 Calibration curves

The analysis of antimony, lead, titanium, cadmium, cobalt, germanium, beryllium, aluminium and zinc in water and soft drinks and the analysis of antimony in PET materials were based on calibration curves as explained in Section 5.8. The curves for antimony and the other trace elements are presented in Figures 8.1 and 8.2 respectively. The regression coefficients for all the curves were greater than 0.99, an indication of linearity and hence accuracy of response within the concentration ranges used.

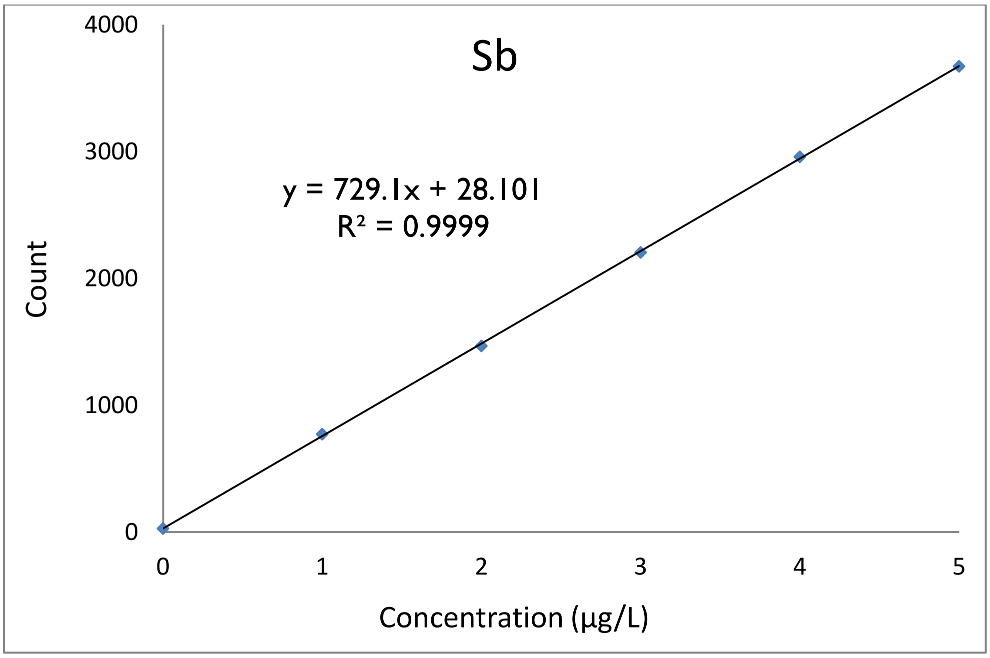

Figure 8.1 Typical calibration curve for antimony

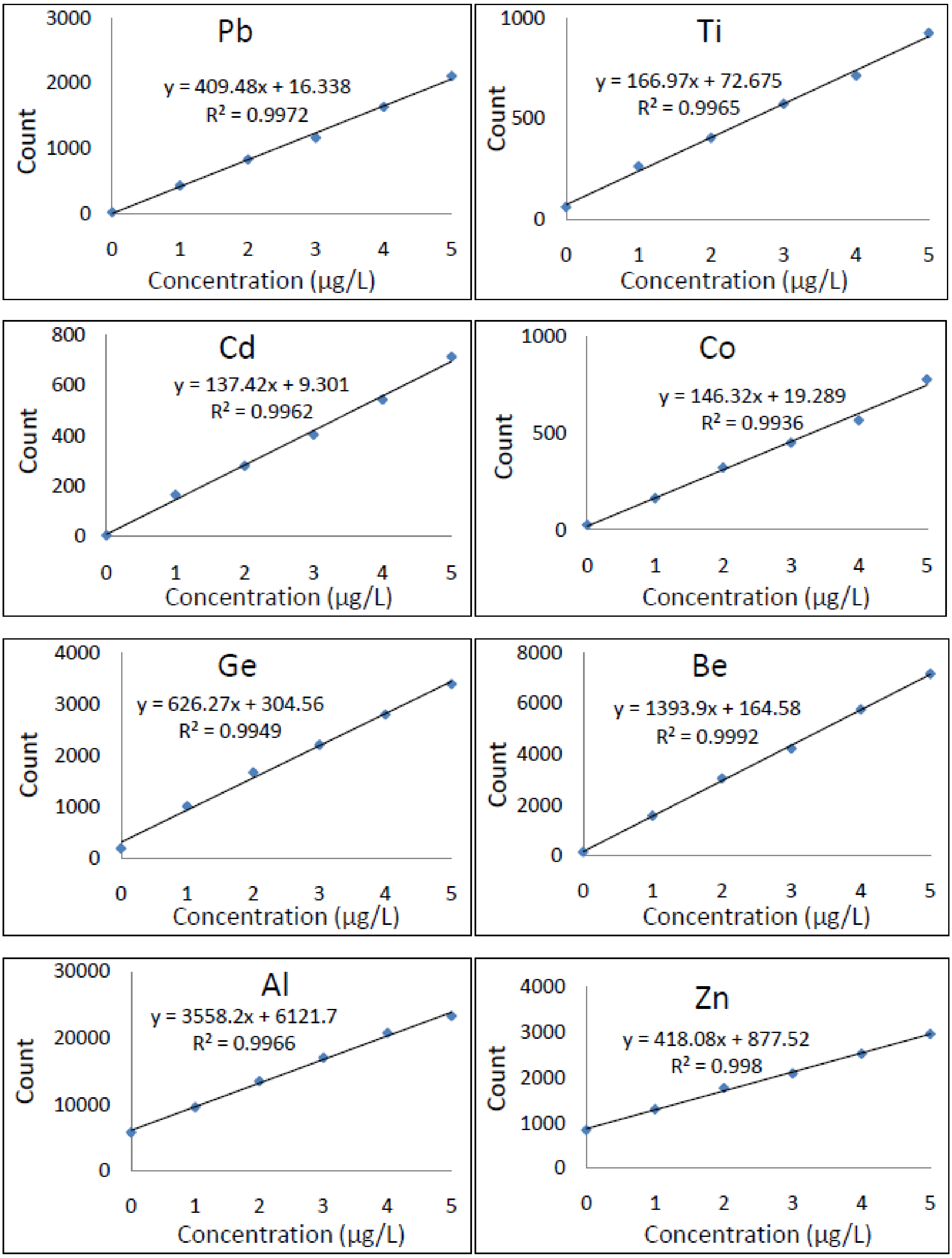

Figure 8.2 Typical calibration curves for other trace elements

8.3 Limits of detection

The limits of detections for antimony and the other trace metals determined in this study are presented in Table 8.1. The limits of detection are based on three times the standard deviations of analyte concentrations in 10 analyses of method blanks.

Table 8.1 Limits of detection

Element	limit of detection (µg/L)
Sb	0.02
Pb	0.03
Cd	0.02
Co	0.01
Ti	0.16
Ge	0.02
Be	0.003
Zn	0.13
Al	0.08

8.4 Sample coding

To conceal the identity of samples all samples were coded using a 4-point coding system consisting of 3 letters and a number as typified by UPA1. The code is similar for bottle material and the content of the bottle. The first letter represents the country of origin of sample with U standing for Britain and N for Nigeria. The second letter represents bottling or packaging material with P standing for PET, G for glass, C for carton and O for other plastic materials. The third letter stands for bottle/carton content (i.e. bottled water or soft drink) with A standing for still water, B sparkling water and C soft drinks. The number is a brand number. It is thus similar for similar brands bottled in different type of packaging or presented as still and sparkling water.

8.5 Antimony in digested PET and other plastics

An important step toward achieving the aims of this study is to quantify the antimony contents of the bottles themselves. Antimony will not be expected to migrate if it is absent in bottle material. Moreover, antimony in bottled water and soft drinks can only be attributed to migration if it can be identified in bottle material.

8.5.1 Digestion method

The most commonly reported method of antimony determination in PET involves complete acid mineralisation of PET followed by analysis by ICP-MS. One of the drawbacks associated with this method is that a purpose-built laboratory microwave digestion system has to be available. A new method for PET digestion using domestic microwave oven has been developed and validated in this study. The method, which is a modification of the method described by Sakurai *et al* (2006) for digestion of polyethylene, is based on total hydrolysis of PET into terephthalic acid (TPA) and ethylene glycol, ethylene glycol degradation products, carbon dioxide and water. The digestion procedure described in Subsection 5.8.9 involved putting about 150mg of PET into a digestion vial containing 3ml of concentrated trace metal grade nitric acid. The PET material is then digested in the microwave oven for 5 minutes at 230W.

8.5.2 Digestion accuracy and precision

Accuracy of the method was assessed by digestion of polyethylene reference material ERM®-EC681k. Ideally a certified PET reference material should have been used. However because there is currently no certified PET reference material containing antimony the polyethylene reference material was used instead. Dobney *et al* (2002) has reported using similar reference material in a study involving the forensic analysis of pressure sensitive adhesive (PSA) tape. An additional indication on the effectiveness of this method is the resultant total hydrolysis of the PET matrix as evidenced by the Raman spectra obtained Section 7.3, which completely matched the description of TPA and also the TPA yield which is in good agreement with the expected yield as will be discussed in the next subsection. Since antimony is a catalyst, it is not expected to be bonded to PET molecules. Thus total hydrolysis of the PET material is expected to completely release the antimony content of the material.

According to the certificate of analysis of the reference material a result is unbiased if the absolute difference between the mean measured value and the certified value is less than or equal to the expanded uncertainty of the difference between the measured and certified value. The measurement is unbiased for antimony and zinc but not for lead and cadmium as shown in Table 8.2. One sample t-test also revealed a statistically significant difference between certified values for lead and cadmium and the measured values. However if the FDA (2001) criteria as stated in the "Guidance for

Industry/Bioanalytical Method Validation" is to be followed, then the difference between the certified values and measured values for lead and cadmium is not significant because mean measured values are within 15% of the certified values. Precision of measurement was determined by measurement of antimony in 14 replicates of PET sample UPA3 as shown in Table 8.3. Precision of measurements is good as the coefficient of variation is not up to 15%. According to FDA (2001) the coefficient of variation for the determination of precision should not exceed 15%.

Table 8.2 Accuracy determination using polyethylene reference material ERM®-EC681k

Element	Sb (ppb)	Pb(ppb)	Cd(ppb)	Zn(ppb)
Measurement 1	104.43	106.58	122.03	1237.97
Measurement 2	94.76	105.32	130.70	1257.59
Measurement 3	104.26	104.56	131.27	1232.28
Measurement 4	103.87	104.88	129.13	1277.50
Measurement 5	87.42	106.25	133.63	1248.75
Measurement 6	91.17	104.69	119.81	1253.75
Mean ± single standard deviation	98±8	105.4±0.9	128±6	1251±16
certified value	99±6	98±6	137±4	1250±70*
Absolute difference between mean measured and certified value	1.35	7.38	9.24	1.31
Expanded uncertainty	8.59	6.04	6.04	71.21
Recovery (%)	99	108	93	100
Coefficient of variation (%)	8.1	0.9	4.7	1.3

*Indicative value

Table 8.3 Precision determination using 14 replicates of PET sample UPA3

Mean (ppb)	247.81
standard deviation (ppb)	15.27
Standard error (ppb)	4.08
Coefficient of variation (%)	6.16

8.5.3 Terephthalic acid yield in PET digestion

Terephthalic acid yield was determined in PET digestion in part to see if the hydrolysis of PET was complete. Based on the molecular weights of ethylene glycol (62) and terephthalic acid (166) and their ratio in PET (1:1), about 27% of PET by weight is composed of ethylene glycol and about 73% terephthalic acid. Getting a TPA proportion of about 73% will thus be an indication of complete hydrolysis of PET. The results obtained for 5 Nigerian and 5 British samples are presented in Table 8.4. One-sample t-test revealed no statistically significant difference between the mean TPA value observed (76%) and the expected value [t(10) = 1.743; p = 0.115] giving an indication of complete hydrolysis of PET.

Table 8.4 Terephthalic acid yield

S/no	PET material	Weight of digested PET(g)	Weight of TPA (g)	%of TPA by weight
1	NPA8	0.249	0.218	88
2	NPA9	0.267	0.203	76
3	NPA10	0.253	0.208	82
4	NPA11	0.255	0.201	79
5	NPC12	0.265	0.184	69
6	UPA1	0.267	0.192	72
7	UPB5	0.233	0.182	78
8	UPB8	0.249	0.186	75
9	UPC24	0.234	0.182	78
10	UPC28	0.212	0.142	67
	Mean			76

8.5.4 Antimony in digestion blanks

The measured antimony in digestion blanks gave a good indication of the absence of contamination in the determination of antimony in PET as shown in Table 8.5. The amount of antimony in 5 digestion blanks is less than 0.2% of the amount of antimony in a digested reference sample.

Table 8.5 Antimony in digestion blanks

Sample	mass (g)	dilution factor	antimony concentration (μg/L)	proportion of Sb in digestion blanks relative to reference
PE reference	0.171	50	357.2	-
digestion blank	0	50	0.45	0.13%
digestion blank	0	50	0.27	0.08%
digestion blank	0	50	0.40	0.11%
digestion blank	0	50	0.28	0.08%

8.5.5 Antimony in PET

PET and glass as bottle materials, other plastics (polyethylene, polypropylene and polyvinyl chloride) used as bottle caps, cap liners and label materials, paper used in labelling, pigments and dyes for labelling and colouring of bottle parts, adhesives for securing several components of bottles, metals (aluminium and steel usually coated with tin or chromium) as metal bottle caps, and lacquers applied to metal caps to provide a durable finish are all associated with bottled water and soft drink bottling.

However, only the bottle material (PET or glass) and to lesser extent the bottle cap and the lining of the bottle cap, are in constant contact with the bottled content. Only PET materials were expected to contain antimony as it is used as catalyst in the synthesis of most PET materials. Even though antimony may be used as fining agent in glass, glass bottles were not expected to contain antimony at concentrations obtainable in PET material.

Antimony concentration in Nigerian and British PET materials are presented in Figures 8.3 and 8.4. Table 8.6 shows the colour of the analysed samples. All PET bottles are transparent. Two-third of still water PET materials analysed have a bluish tint while the remaining one-third are colourless. Most sparkling water PET materials are green in colour. The antimony concentration in the 32 PET bottle materials ranged between 177.89 and 310.86 mg/kg with an average of 250±30 mg/kg. The concentration agrees well with the industry reported concentration of between 150 and 350 mg/kg.

Table 8.6 PET samples colours

Nigerian samples			British samples		
S/no	Code	Sample colour	S/no	Code	Sample colour
1	NPA1	colourless	1	2	colourless
2	NPA2	bluish tint	2	UPA3	bluish tint
3	NPA3	bluish tint	3	UPB3	green
4	NPA4	colourless	4	UPA4	colourless
5	NPA5	bluish tint	5	UPB5	green
6	NPA6	bluish tint	6	UPA6	colourless
7	NPA7	bluish tint	7	UPB8	colourless
8	NPA8	bluish tint	8	UPB10	green
9	NPA9	bluish tint	9	UPA11	colourless
10	NPA10	bluish tint	10	UPA12	bluish tint
11	NPA11	bluish tint	11	UPA13	bluish tint
12	NPC12	colourless	12	UPA15	bluish tint
13	NPC13	colourless	13	UPA17	bluish tint
14	NPC14	green	14	UPC22	colourless
			15	UPC24	colourless
			16	UPC25	green
			17	UPC28	green
			18	UPC44	blue

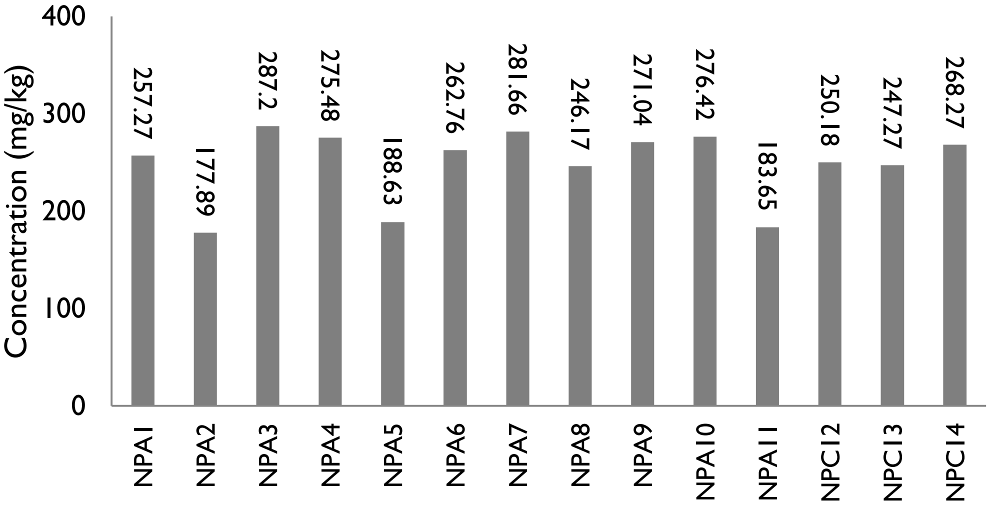

Figure 8.3 Bar chart illustrating antimony concentrations (mg/kg) in fourteen Nigerian PET bottles.

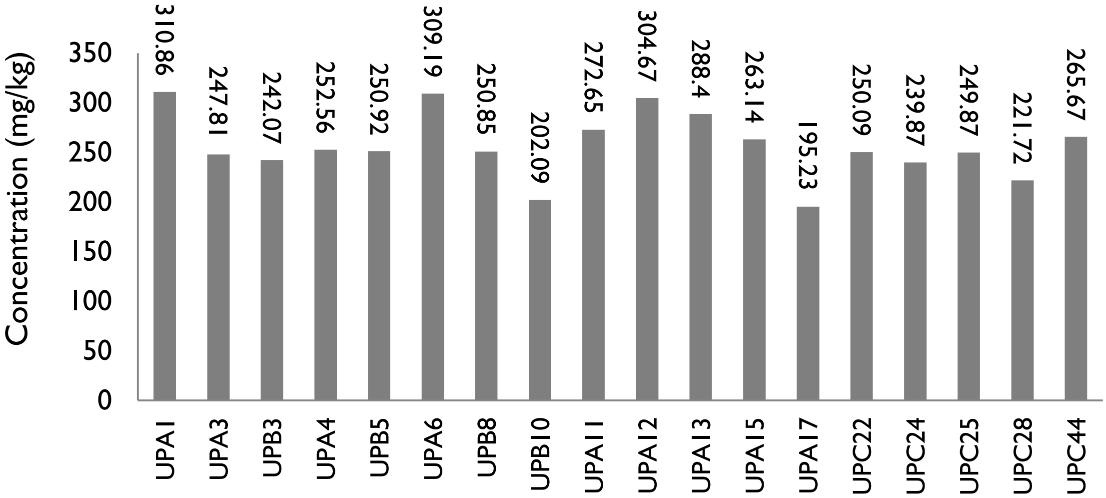

Figure 8.4 Bar chart illustrating antimony concentrations (mg/kg) in eighteen British PET bottles.

Antimony concentration in glass bottle materials was not determined as the method used for PET is not meant to be used with glass. As earlier mentioned however, Shotyk *et al* (2006) reported antimony concentrations of 7.6 and 10.1ppm from 2 glass bottles for bottling of water and cola drink respectively. The average antimony concentration in Nigerian and British PET materials are 250±40 and 260±30 mg/kg respectively. The antimony concentrations in PET from these two countries were shown to be not significantly different (Mann-Whitney U, U = 122, exact p = 0.896) implying the materials to be similar in terms of the amount of antimony catalyst added during synthesis. Additionally a Kruskal-Wallis test revealed the antimony concentration to be similar in bottles of different colours [bluish - mean = 248.19 mg/kg, colourless - mean = 265.12 mg/kg and green PET material – mean = 239.16 mg/kg) (χ^2 (2) = 2.33; p = 0.312] and in bottles having different contents [still water - mean = 271.60 mg/kg, sparkling water - mean = 236.48 mg/kg and soft drinks PET material – mean = 245.44 mg/kg) (χ^2 (2) = 4.7; p = 0.092].

8.5.6 Antimony in other plastics

As mentioned earlier bottle-related materials other than antimony are not expected to contain antimony in quantities that could leach into the bottle contents. Table 8.7 shows the antimony concentration found in plastic bottle caps, cap liners and two polyethylene potable water pouches from Nigeria. As can be seen from the Table the level of antimony found in these materials is very small in comparison to what is obtained in PET. This is expected as none of these plastic materials is manufactured using antimony as catalyst. The low levels of antimony in these samples provide evidence that the caps do not contribute in the migration of antimony into bottle and pouch contents. However, the levels of aluminium and titanium were found to be high in these samples. For the polypropylene and polyethylene-based polymers the levels of aluminium and titanium are most likely because of the use of Ziegler-Natta catalyst in their synthesis. Ziegler-Natta catalyst usually contains titanium and organoaluminum.

Table 8.7 Antimony in other plastics

Sample	plastic material	Sb (mg/kg)	Al (mg/kg)	Ti (mg/kg)
UPC24 plastic cap	PP	0.07	43.19	1.12
UPA6 plastic cap	PE	0.03	15.12	10.10
NGC13 plastic cap liner	unidentified plastic	0.03	97.53	13.24
UPC24 plastic cap liner	EVA/PP	0.01	146.08	20.47
NOA17 plastic pouch	PE	0.04	7.12	1.26
NOA18 plastic pouch	PE	0.03	42.86	3.44

8.6 Antimony and other trace metals in water and soft drinks

8.6.1 Analytical accuracy and precision

Analytical accuracy and precision for determination of antimony and other trace metals was monitored by analysis of TM-DWS.2 certified water reference material and by spiking at 1µg/L. The spikes cover germanium which is not contained in the reference material. From the results in Tables 8.8 and 8.9 analytical accuracy and precision were good.

Table 8.8 Recovery in spiked samples

Element	replicates	added (µg/L)	*found (µg/L)	recovery (%)	coefficient of Variation (%)
Sb	6	1.00	1.02±0.07	102.1	6.9
Pb	6	1.00	0.97±0.03	97.2	3.1
Cd	6	1.00	1.02±0.05	101.6	4.9
Ge	6	1.00	1.11±0.04	110.6	3.6
Zn	6	1.00	1.08±0.08	108.1	7.4
Co	3	1.00	1.025±0.007	102.5	0.7
Ti	3	1.00	0.98±0.03	98.2	3.1
Be	3	1.00	1.027±0.003	102.7	0.3
Al	3	1.00	1.05±0.05	105.4	4.8

*Mean and standard deviation

Table 8.9 Accuracy determination usingTM-DWS.2 certified water reference material

Element	replicates	certified (µg/L)	[1]found (µg/L)	recovery (%)	coefficient of Variation (%)
Sb	10	3.20±0.05[2]	3.4±0.3	105.3	8.8
Pb	15	7.8±0.1	7.9±0.3	100.4	3.8
Cd	15	4.20±0.05	4.26±0.19	101.4	4.5
Zn	15	379±3	377±4	99.4	1.1
Co	15	64.2±0.5	67.3±1.2	104.9	1.8
Ti	7	15.10±0.14	16±2	106.4	12.5
Be	15	13.40±0.14	14.3±0.4	107	2.8
Al	15	58.3±0.6	62.3±0.4	106.8	0.6

[1]Mean and standard deviation, [2]95% confidence interval

8.6.2 Antimony in water and soft drinks

The concentration of antimony in drinking tap water and 47 freshly purchased British bottled samples was determined (Table 8.14). Freshly purchased Nigerian samples could not be analysed due to sample storage and instrument availability. The antimony concentration in bottled water and soft drinks ranged between 0.033 and 6.61µg/L, with only one juice drink sample going above the EU maximum admissible concentration and US maximum contaminant level (5 and 6μg/L respectively) for antimony in drinking water (Table 8.12). In the works of Shotyk *et al* (2006), Shotyk and Krachler (2007) and Westerhoff *et al* (2008) the antimony concentration ranges reported for bottled water were 0.112 – 0.375 μg/L, 0.0089 – 2.57 μg/L and 0.095 – 0.521 μg/L respectively. In this work the average concentration in drinking tap water samples analysed at 3 different times was 0.27±0.015 μg/L. Only 5 out of the 47 analysed samples have antimony below the concentration found in the tap water. The concentration of antimony was shown to be similar in still and sparkling water using Mann-Whitney U test (U = 96, exact p = 0.896). However a significant difference was found between bottled water (regardless of type) and soft drinks (U = 61, exact $p < 0.01$). The same could be observed from the average concentrations in Table 8.10. The antimony concentration in the samples analysed can thus be summarised by the expression below.

Sb in tap water < Sb in bottled water < Sb in soft drinks

Table 8.10 Antimony in tap water, bottled water and soft drinks

Content type	number of samples	minimum (μg/L)	maximum (μg/L)	average (μg/L)	number above acceptable level
still water	19	0.04	2.10	0.89	
sparkling water	13	0.03	1.92	0.70	-
soft drinks	15	0.73	6.61	1.98	1
tap water	4	0.25	0.29	0.27	-

The average concentrations in water and soft drinks bottled in different bottle types is given in Table 8.11. The concentrations were found to differ (U = 61, exact p = 0.059) with contents in glass bottles showing lower concentrations than contents in PET.

Table 8.11 Antimony in PET- and glass-bottled contents

Bottle type	number of samples	minimum (μg/L)	maximum (μg/L)	average (μg/L)	number above acceptable level
PET	35	0.15	6.61	1.31	1
Glass	11	0.03	2.06	0.75	-

Table 8.12 Guidelines and standards for antimony and other trace metals in drinking water

Contaminant	EU Council directives 98/83/EC and 2003/40/EC	Britain The Water Supply (Water Quality) Regulations 2000	US Title 40 CFR part 141		WHO
	Maximum Admissible Concentration (µg/L)	Maximum Admissible Concentration (µg/L)	Maximum Contaminant Level (µg/L)	Secondary standards (guidelines) (µg/L)	Guideline values (µg/L)
Antimony	5 (5)	5(5)	6	-	20
Cadmium	5 (3)	5 (3)	5	-	3
Germanium	-	-	-	-	-
Zinc	-	-	-	5000	-
Aluminium	200	200	-	50 - 200	-
Beryllium	-	-	4	-	-
Titanium	-	-	-	-	-
Cobalt	-	-	-	-	-
Lead	10 (10)	25[2] (10)	15[1]	-	10

[1]Action level, [2]to change to 10µg/L after 25 December 2013, () maximum limit for constituents naturally present in natural mineral water at source

8.6.3 PET versus glass

To further study the relationship between bottling material and antimony concentration in bottled content 4 bottled water and 2 soft drinks bottled in both glass and plastic bottles were studied. A wilcoxon matched-pairs, signed ranks test showed that the difference between the median concentrations for contents bottled in PET (M = 1.231µg/L, SD = 0.543µg/L) and contents bottled in glass (M = 0.754µg/L, SD = 0.865µg/L) was significant beyond the 0.05 level (exact $p < 0.05$, two-tailed). In fact the glass to PET antimony concentration ration in sample UB8 is 1:33. The data in Figure 8.5 also shows the same picture. However the difference appears to be insignificant for the 2 soft drinks. It is not clear why the concentrations are higher in PET contents for bottled water but similar for both bottle types for the 2 soft drink brands. The most likely explanation is that most of the antimony in the soft drinks may have come from the drinks themselves rather the bottles. Cicchella *et al* (2010) and Reimann *et al* (2010) have also reported finding higher concentration of antimony in bottled water in PET than in similar brands in glass. However these researchers did not extend their studies to soft drinks. The lower antimony concentration in the water bottled in glass probably results from the lower antimony concentration observed in glass in comparison to PET as reported by Shotyk *et al* (2006).

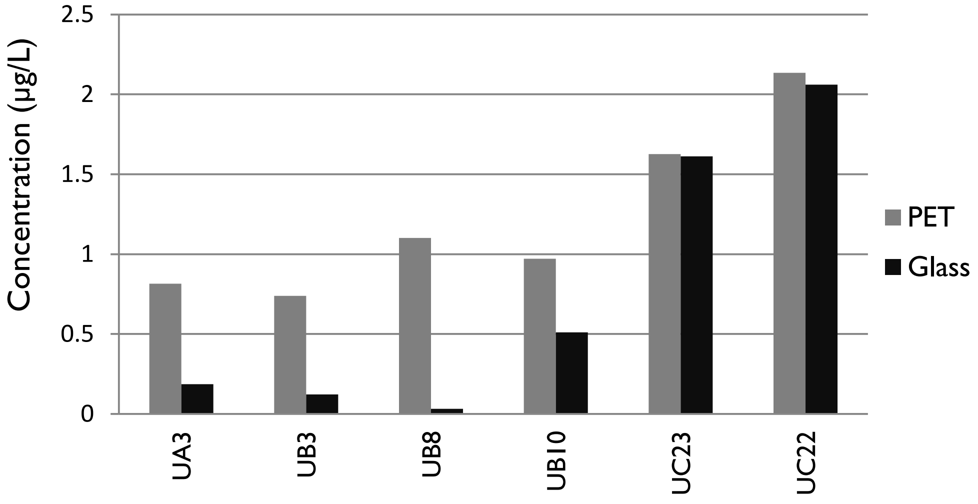

Figure 8.5 Bar chart illustrating antimony concentration in PET- and glass-bottled contents

8.6.4 Still versus sparkling water

In Subsection 8.6.2 the concentration of antimony in freshly purchased still and sparkling water samples were shown to be similar based on Mann-Whitney U test. In this Subsection wilcoxon matched-pairs, signed ranks test on similar still and sparkling water brands also showed the difference between the samples to be insignificant (exact p = 0.57, two-tailed). However in the work of Keresztes *et al* (2009) antimony concentration was reported to be higher in 3 sparkling water brands studied than in similar still water brands. From Figure 8.6 it can be seen that the results are mixed for the 9 paired samples in this study. It should be appreciated that freshly purchased British samples are not the best samples to be used to compare antimony migration from different containers or water types because the actual bottling dates for samples cannot be ascertained. With Nigerian samples however it is easy to know if samples are freshly bottled because bottling dates are usually embossed on bottles together with “Best before” dates.

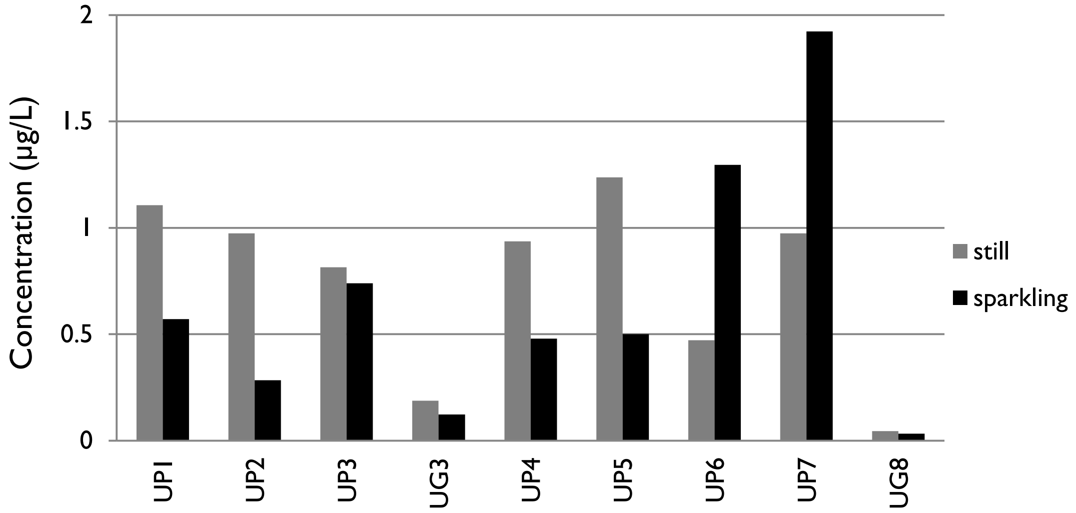

Figure 8.6 Bar chart illustrating antimony concentration in similar brands of still and sparkling water

8.6.5 Conductivity, pH and antimony concentration

In this study bottled water and soft drinks with higher conductivity tend to have higher concentration of antimony based on the results of Pearson's correlation (r(30) = 0.48; $p < 0.01$, $r^2 = 0.23$). According to Cohen (1988) an r value of around 0.10 denotes small (weak) relationship, around 0.30, medium relationship and around 0.50 or more, large (strong) relationship. The scatter plot is shown in Figure 8.7.

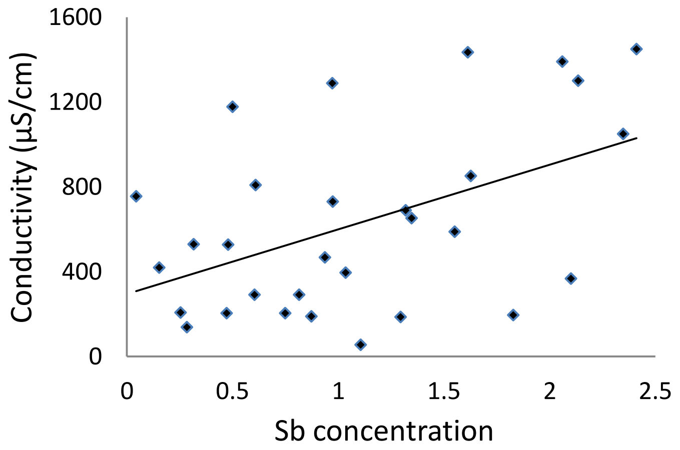

Figure 8.7 Relationship between conductivity and antimony concentration in bottle contents

From Figure 8.8 and the results of the Pearson correlation (r(23) = 0.14; p = 0.517, $r^2 = 0.02$) there is little or no relationship between pH and antimony concentration in freshly purchased samples. Reiman *et al* (2010) also reported observing an almost independent relationship between pH and antimony migration in an antimony leaching experiment.

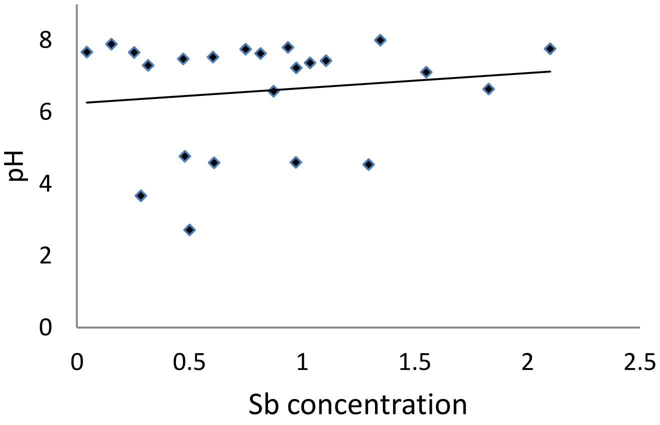

Figure 8.8 Relationship between pH and antimony concentration in bottle contents

8.6.6 Other trace elements in water and soft drinks

Concentrations of cadmium, germanium, zinc, aluminium, beryllium, titanium, cobalt and lead in bottled water and soft drinks are presented in Table 8.14. Summary statistics for the trace metals are presented in Table 8.13. Concentrations of all the elements were higher in soft drinks than in bottled and tap water as demonstrated in Table 8.11. The higher concentrations are believed to be as a result of the ingredients usually added to soft drinks but not to bottled water. Similarly concentrations of all the elements except antimony were higher in glass bottled contents than in PET bottled contents as demonstrated in the Table. The concentrations of lead, cadmium and beryllium are all within the EU MAC and/or US MCL. Guidelines and standards for cobalt, titanium, germanium and zinc in drinking-water have not been established. In the US secondary non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects in drinking water covers zinc and aluminium. The concentration of zinc in all the samples falls within the US MCL. The concentration of aluminium in 2 soft drinks is however greater than the British MAC. Concentration of titanium was found to be much higher in soft drinks than in bottled water. The concentration was found to be highest in cola drinks. Titanium in the form of titanium dioxide is a food additive approved for use in water-based flavoured drinks as stated in Codex Alimentarius' General Standard for Food additives online database (FAO/WHO 2010). It is reported to be used in powdered concentrate mixes for fruit beverage drinks in India at concentrations not exceeding 100mg/kg (Kuznesof, 2006). It is also used as a catalyst in the manufacture of PET to very small extent. Its presence at relatively higher concentrations in soft drinks in this study is believed to be as a result of its use as food additives in the soft drinks because it was identified in soft drinks bottled in glass, PET and other plastics at similar concentrations. In spite of its approved usage as food additive it has recently been reclassified by IARC from Group 3 (not classifiable as to its carcinogenicity to humans) to Group 2B (possibly carcinogenic to humans) based on inadequate evidence for its carcinogenicity in humans and sufficient evidence for its carcinogenicity by inhalation in experimental animals (IARC, 2010).

Table 8.13 Summary statistics for the measured trace elements

Element	Min (µg/L)	Mean (µg/L)					Median (µg/L)	Max (µg/L)	SD (µg/L)
		all	water	soft drinks	PET	glass			
Cd	< 0.02	0.40	0.29	0.67	0.36	0.62	0.07	4.41	0.82
Ge	< 0.02	0.21	0.16	0.35	0.21	0.24	0.09	1.14	0.29
Zn	< 0.13	14.91	2.64	41.95	7.72	34.00	2.89	160.49	32.18
Al	< 0.08	28.79	3.46	84.52	11.82	59.01	2.72	373.97	74.94
Be	< 0.003	0.03	0.01	0.07	0.02	0.05	0.004	0.39	0.06
Ti	< 0.16	141.6	2.32	447.78	115.42	224.84	2.46	1650.85	367.02
Co	< 0.01	0.32	0.16	0.66	0.23	0.52	0.16	1.43	0.38
Pb	< 0.03	0.51	0.31	0.95	0.32	1.06	0.21	3.89	0.72

Table 8.14 Concentration of antimony and trace elements in water and soft drinks

	Brand	Concentration (µg/L)								
		Sb	Cd	Ge	Zn	Al	Be	Ti	Co	Pb
1	UPA1	1.11	<0.02	<0.02	4.55	4.51	0.003	1.10	0.04	0.20
2	UPA2	0.87	0.02	<0.02	4.62	1.55	<0.003	1.75	0.05	0.61
3	UPA19	0.15	1.93	0.76	2.77	1.46	<0.003	2.22	0.08	0.18
4	UPA4	0.94	<0.02	0.93	2.89	3.42	0.013	1.92	0.03	0.14
5	UPA20	0.53	0.07	1.14	1.72	5.60	<0.003	2.12	0.06	0.08
6	UPA18	1.04	0.04	0.12	5.62	4.27	0.005	2.94	0.17	0.20
7	UPA17	1.83	<0.02	0.07	1.00	1.08	<0.003	5.69	0.01	0.15
8	UPA12	1.55	0.05	0.22	0.74	2.09	<0.003	2.43	0.29	0.13
9	UPA13	0.32	0.25	0.29	7.67	35.44	<0.003	13.76	0.18	0.26
10	UPA14	1.35	0.02	0.27	0.72	4.88	<0.003	2.49	0.11	0.60
11	UPA7	0.97	<0.02	0.12	0.94	0.29	0.008	2.15	0.20	0.62
12	UPA5	1.24	2.03	0.04	1.64	0.16	0.005	3.29	0.09	<0.03
13	UPA3	0.82	0.12	0.14	3.94	2.06	<0.003	2.03	0.13	<0.03
14	UPA6	0.47	0.35	0.03	4.08	1.96	<0.003	2.89	<0.01	<0.03
15	UPA15	0.75	0.78	0.06	0.54	2.72	<0.003	5.59	0.09	0.05
16	UPA16	2.10	1.12	0.16	0.18	1.43	0.004	5.58	0.08	0.03
17	UGC23	1.61	4.41	<0.02	3.38	15.66	<0.003	12.16	0.18	0.76
18	UGC22	2.06	0.09	0.14	3.99	14.99	0.07	1650.78	0.18	0.26
19	UPC22	2.14	2.40	0.32	4.14	6.39	0.066	1319.31	0.10	0.22
20	UPC23	1.63	0.81	0.07	1.19	5.17	0.045	16.89	0.15	0.22
21	UPC24	2.35	1.02	0.1	14.72	27.25	0.026	98.06	0.19	0.16
22	UPC25	1.32	0.05	<0.02	0.65	7.60	0.036	15.17	0.09	0.34
23	UPC26	2.41	0.09	0.12	12.50	2.18	<0.003	1255.41	0.50	0.49
24	UPB2	0.28	0.12	<0.02	11.44	1.44	0.053	1.47	0.09	0.62
25	UPB6	1.30	0.07	<0.02	2.00	3.56	<0.003	1.66	0.09	0.21
26	UPB4	0.48	<0.02	0.39	<0.13	0.94	<0.003	1.47	0.05	0.11
27	UPB3	0.74	0.38	<0.02	0.30	2.72	<0.003	1.18	0.12	<0.03
28	UPB10	0.97	0.10	0.05	<0.13	0.30	0.004	1.18	0.55	0.04
29	UPB5	0.50	0.04	<0.02	<0.13	0.09	<0.003	1.11	0.14	<0.03
30	UGB8	0.03	0.05	<0.02	0.98	4.48	<0.003	0.96	0.20	1.21
31	UGA8	0.04	1.29	<0.02	<0.13	1.50	<0.003	1.12	0.26	0.84
32	UGB10	0.51	0.19	0.06	0.53	1.85	<0.003	0.81	0.53	1.11
33	UGB9	0.61	0.04	<0.02	2.84	3.82	<0.003	1.27	0.46	0.35
34	UPB1	0.57	<0.02	<0.02	1.76	<0.08	<0.003	<0.16	0.50	0.12
35	UGB3	0.12	0.08	0.11	6.93	<0.08	0.02	1.25	0.11	0.04
36	UGA3	0.19	0.06	<0.02	2.90	<0.08	0.011	0.75	0.10	<0.03
37	UPB8	1.10	0.04	0.03	<0.13	<0.08	0.018	0.56	0.21	1.83
38	UPB7	1.92	0.04	<0.02	2.44	<0.08	0.022	1.06	0.16	0.43
39	UPA21	0.60	0.07	<0.02	6.58	<0.08	0.009	0.49	0.11	<0.03
40	UPC29	1.75	0.04	0.16	11.83	1.07	0.023	208.80	0.70	<0.03
41	Tap water	0.27	0.08	0.08	4.26	20.13	0.019	5.84	0.11	<0.03
42	UPC30	1.90	<0.02	0.57	57.51	20.44	<0.003	72.42	0.94	0.42
43	UGC31	0.98	<0.02	0.46	117.39	170.58	0.016	148.07	0.99	1.95
44	UPC32	1.08	0.34	0.45	34.93	172.85	0.187	909.29	0.54	1.01
45	UPC33	6.61	<0.02	0.46	63.97	88.36	0.06	76.10	1.39	1.41
46	UGC34	1.32	0.62	0.76	160.49	62.09	0.024	478.11	1.43	1.26
47	UOC35	1.75	0.12	0.57	68.10	299.35	0.066	278.25	1.24	1.80
48	UGC36	0.73	<0.02	0.98	74.41	373.97	0.391	177.96	1.30	3.89

8.7 Storage and antimony migration

As stated in Subsection 4.7.4 the longer the duration of contact between water, soft drinks or foods and the packaging material (PET, glass, etc), the higher the possibility of accumulation of migrants from the bottle in the water, soft drinks or foods. From Section 6.6 unopened bottles were found to be stored for as long as 1 year. In this study Nigerian and British brands of bottled water and soft drinks collected at different times (different bottling times) were studied to observe the influence of storage on antimony migration. All samples were stored at room temperature. The best way of studying migration is to observe changes of antimony concentration with time in the same sample. However in this work that was not possible due to instrument availability. It was found that the antimony concentration in 7 Nigerian samples stored for two months failed to reach 3µg/L (Table 8.15 and Figure 8.9). Yet for similar samples stored for 11 months the concentration has gone beyond the EU MAC in four of the 19 samples (two soft drinks and two bottled water). Eleven British samples were also analysed immediately after collection and after 19 months storage (Table 8.16 and Figure 8.11). For these samples the highest concentration achieved after 19 months is 2.95µg/L. The higher concentrations in Nigerian samples could probably be related to initial exposure to high tropical temperatures in Nigeria before purchase. In the Nigerian and British samples the highest percentage increases observed were 730 and 584% respectively. It must be noted that the samples with the highest percentage increases were not the samples with highest concentration as percentage increase depends on initial concentration and the amount of increase. In the work of Keresztes *et al* (2009) antimony concentration in two bottled water samples studied in similar way approached but failed to reach 1µg/L even after three years. Additionally according to Welle and Franz (2011) maximum migration levels caused by room-temperature storage of water in PET will not be expected to go higher than 2.5µg/L even after three years. However, the overall concentration of antimony as result of migration depends appreciably on the initial concentration and ambient weather conditions. For example (Niedzielski *et al*, 2001) has reported an antimony concentration of 1.25µg/L from a ground water sample. Additionally in this study and in the works of Westerhoff *et al* (2008) and Keresztes *et al* (2009) different PET materials have been shown to behave differently in terms of antimony migration.

Table 8.15 Change in antimony concentration (µg/L) with time in Nigerian samples

Brand	Storage period		% increase
	2 months	11 months	
NPA5	2.0	2.9	46
NPA2	0.3	2.6	730
NPA8	1.5	5.1	250
NPA4	0.9	1.2	31
NPA6	0.7	3.4	362
NGC16	1.4	5.1	258
NPC16	2.9	5.5	88
NPA1		2.6	
NPA3		2.5	
NPA7		1.7	
NPA9		3.4	
NPA10		4.9	
NPA11		5.1	
NPC12		1.2	
NPC13		2.1	
NGC13		4.4	
NPC15		1.6	
NGC15		2.0	
NPC14		3.4	
Mean	1.4	3.2	

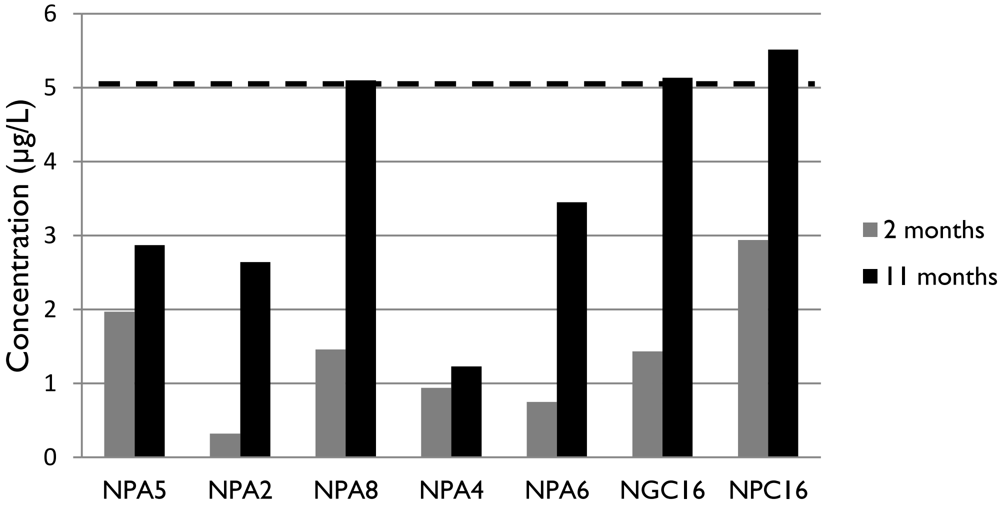

Figure 8.9 Bar chart illustrating change in antimony concentration with time in Nigerian samples (dotted line shows the EU MAC)

An interesting observation was made for samples NPC16 and NGC16, which are similar Nigerian soft drinks bottled in glass and PET. For these samples antimony and lead migration was observed from both the glass and PET bottles in a converse pattern (Figures 8.9 and 8.10). The initial and final concentrations of antimony were lower in glass content than in PET content. While the increase in antimony is less than 100% in PET it was over 200% in glass. Conversely the initial and final concentrations of lead were much higher in glass than PET. In fact the lead concentration in the 2 and 11 months old soft drinks were higher than the EU and British MAC for lead respectively. Also the lead concentration in another 2 month old Nigerian soft drink brand from the same bottling company approached the British MAC. The current British MAC for lead is 25μg/L up to 25th of December 2013 after which it should be reduced to 10μg/L based an EU directive. Some glass bottle materials have earlier been shown to leach antimony as vigorous as PET materials. In a report for antimony migration Reimann *et al* (2010) observed the highest antimony leaching value was from a glass bottle even though the median antimony concentration for the waters sold in PET bottles was 21 times higher than for the same water sold in glass bottles.

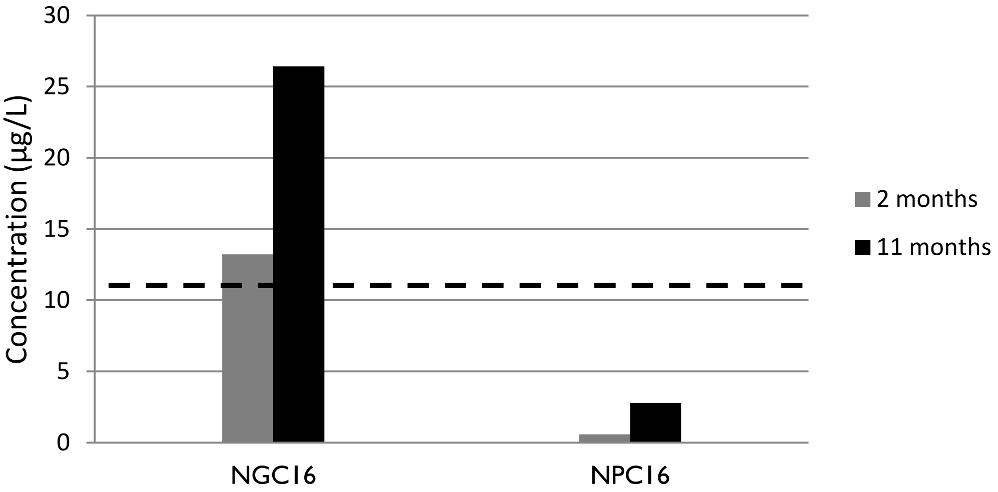

Figure 8.10 Bar chart illustrating change in lead concentration with time in a Nigerian soft drink sample bottled in glass and PET(dotted line shows the EU MAC)

Table 8.16 Change in antimony concentration (µg/L) with time in British samples

Brand	Storage period		% increase
	new	19 months	
UPA13	0.32	2.16	584
UPB10	0.97	2.88	196
UPB3	0.74	1.65	123
UPA3	0.82	2.76	239
UPB5	0.50	0.76	53
UPA17	1.83	3.77	106
UPB6	1.30	2.21	71
UPA12	1.55	2.95	90
UPB4	0.48	0.64	34
UPA15	0.75	0.82	9
Mean	0.93	2.06	

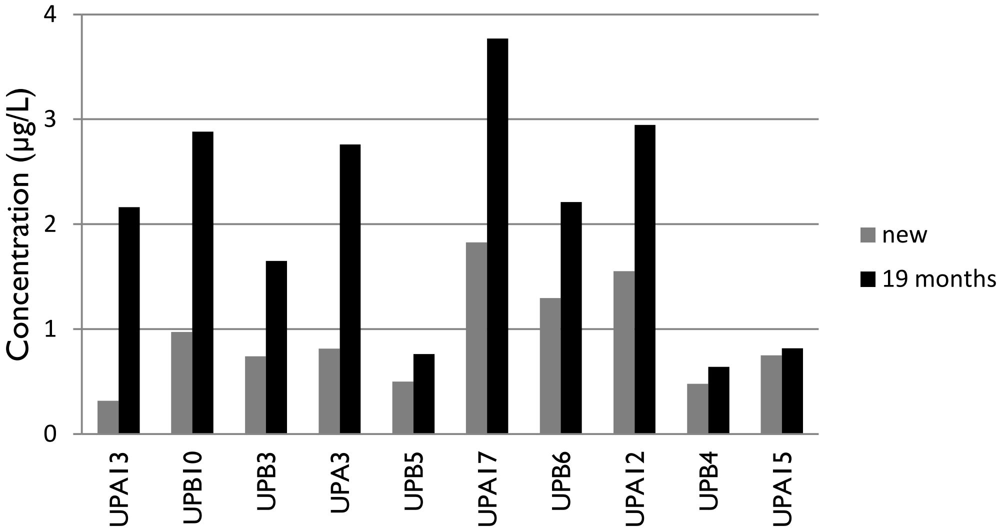

Figure 8.11 Bar chart illustrating change in antimony concentration (µg/L) with time in British samples

From the results in Chapter 6 79% of British respondents reported that bottled water and soft drinks were consumed within 7 days of purchase and 95% reported that they were consumed within 30 days. Only about 1% of respondents reported consuming contents in time periods greater than 3 months. Even in Nigeria where contents are consumed over a longer period of time (7 and 30 days by 50 and 85% of respondents) only about 6% of respondents reported consumption in time periods greater than 3 months. Consequently the likelihood of consuming soft drinks containing antimony above the current standard levels is very small. In case of lead the concentration going beyond the EU MAC after 2 months for bottles that were most likely reused several times is worthy of further investigation In Nigeria glass bottles are used more frequently in bottling the most popular soft drinks than PET bottles. Bottles are usually reused by the bottling companies but it is not known many times these bottles are put into reuse.

8.8 Water temperature elevation on exposure to sunlight

Experiments were carried out to determine the maximum water temperature achievable on exposure of bottled water to sunlight in Britain in the summer. The results of these experiments are presented in Figure 8.12. The experiments revealed that water in green bottles (PET or glass) displayed highest temperature gain while the water in colourless bottles displayed lowest temperature gain. The temperature gain for water in blue PET is midway between green and colourless PET. This observation is believed to be related to differences in absorption, transmission and reflection of light by the bottles of different colours. Water in PET heats up faster within the first 2 to 3 hours after that the water in glass heats up faster and thus becoming hotter. In general the experiments revealed that water temperature of up to 46°C is achievable if water in PET or glass bottles is exposed to brilliant sunlight on a clear British summer day and that a temperature of at least 40°C is sustained for up to 6 hours. Attempts to repeat the experiments for the purpose of monitoring antimony migration were unsuccessful because of bad weather.

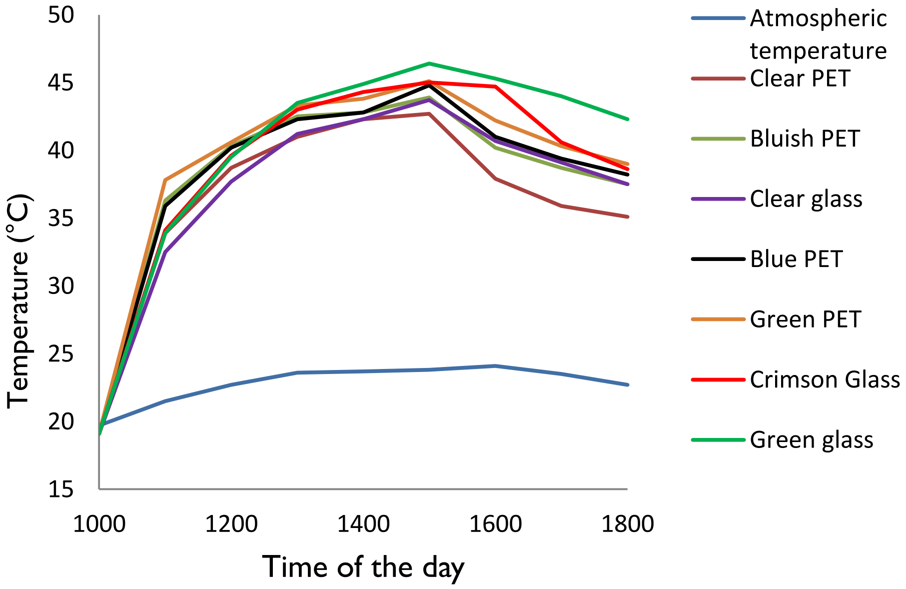

Figure 8.12 Sunlight-assisted bottled water temperature elevation

8.9 Antimony migration from PET and glass at elevated temperatures

The results in Section 8.9 confirms that water temperature of up to 46°C is achievable if water in PET or glass bottles is exposed to brilliant sunlight on a clear British summer day and that a temperature of 40°C or more can be sustained for up to 6 hours. In Nigeria a temperature of up to 58.3 °C was reported to be achievable on exposure of water in glass bottles for 2.5 hours from midday (Tukur *et al*, 2006). Consequently temperatures of 40 and 60°C were chosen for the purpose of assessing the antimony leaching propensity of eighteen PET bottles and two glass bottles over forty eight hours exposure time. To also see the behaviour of these materials at extreme non typical use conditions temperature of 80°C was included.

Typical results obtained showing the impact of exposure temperature and exposure time, on antimony migration are shown in Figures 8.13 and 8.14. As can be seen in Figure 8.13 the impact of temperature is not uniform over the temperature range studied even though the temperature increase is uniform. Also from Figure 8.14 a sharp rise in antimony migration is only observed from about 55°C for all the 3 exposure times. Keresztes *et al* (2009) reported observing a PET bottle material whose antimony migration rate was not affected by either exposure temperature or exposure time. However in this work the results obtained for all the ten samples studied at three exposure temperatures and three exposure times shows similar pattern as in Figures 8.13 and 8.14. The results for all the ten samples are shown in Figure 8.18. Figure 8.15 compares the migration propensity of two PET bottles and two glass bottles at 60°C. While the migration pattern is similar for the ten PET bottles (Figures 8.13, 8.14 and 8.18) the migration intensity differs. The reason for the difference in antimony migration intensity is probably related to the concentration of antimony in the PET materials.

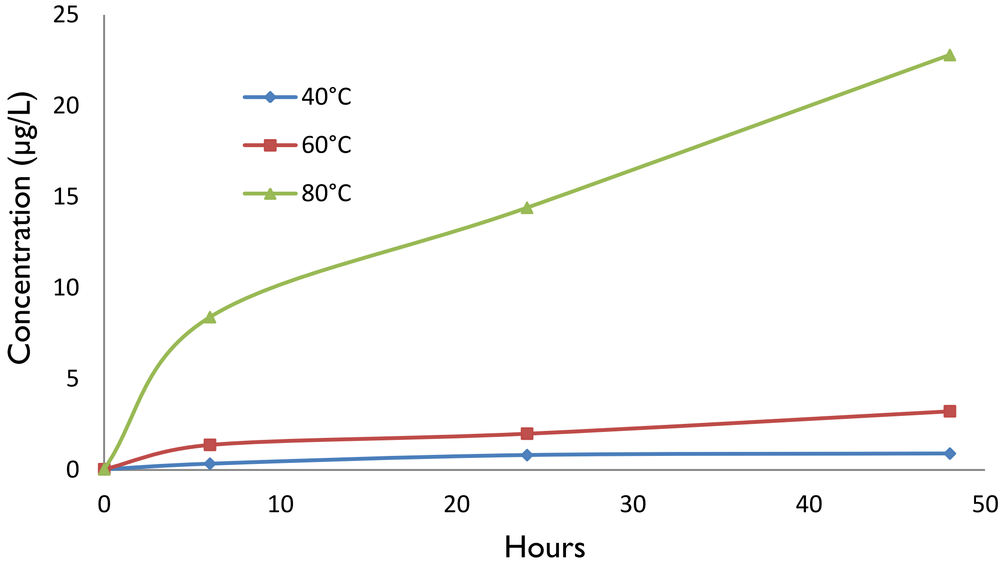

Figure 8.13 Impact of exposure temperature on antimony migration (sample UPA6)

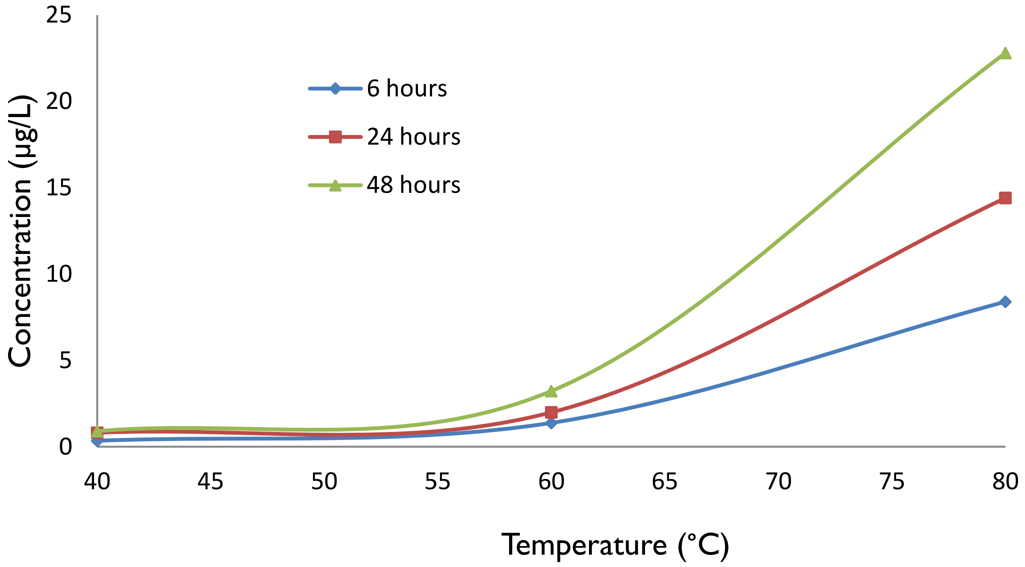

Figure 8.14 Impact of exposure time on antimony migration (sample UPA6)

As discussed earlier some glass bottles may leach as much antimony as PET bottles and in some cases even more. From Figure 8.15 it can be seen the two British glass bottles studied in the leaching test leaches very little antimony in comparison to the PET bottles. In fact for these bottles the leaching stopped after just 6 hours. These bottles appeared to behave in the same way as the PET bottle material reported by Keresztes *et al* (2009) as mentioned earlier. The migration of lead from these two British bottles has similar pattern and intensity as the leaching of antimony (Figure 8.16). In terms of antimony and lead leaching these bottles can be said to be clean in comparison to the

Nigerian glass bottle (NGC16) discussed in storage experiments (Section 8.7). Similar experiments should have been carried out using the Nigerian bottle. However the experiment was not carried out because only one NGC16 bottle sample was collected from Nigeria.

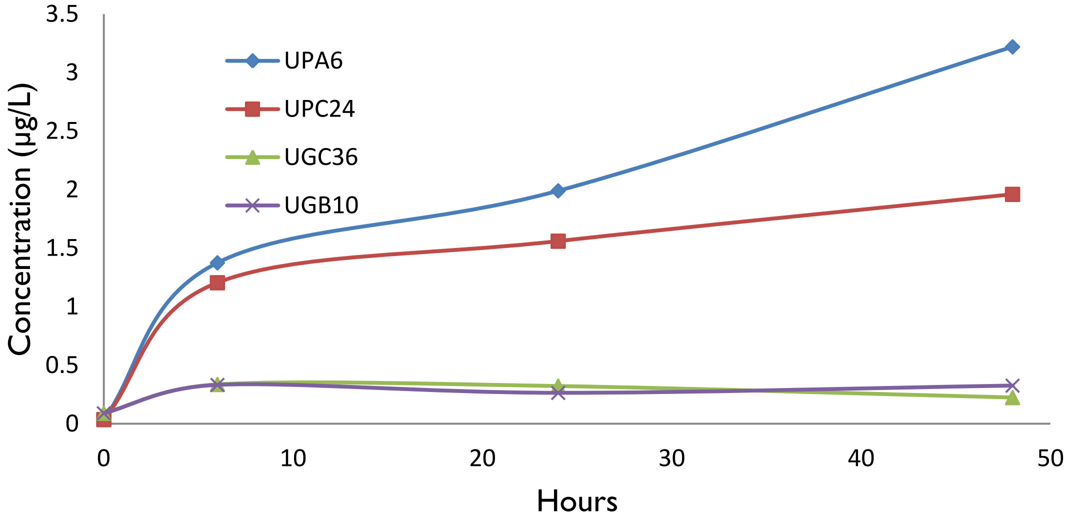

Figure 8.15 Comparison of antimony migration in 2 PET and 2 glass bottles at 60°C

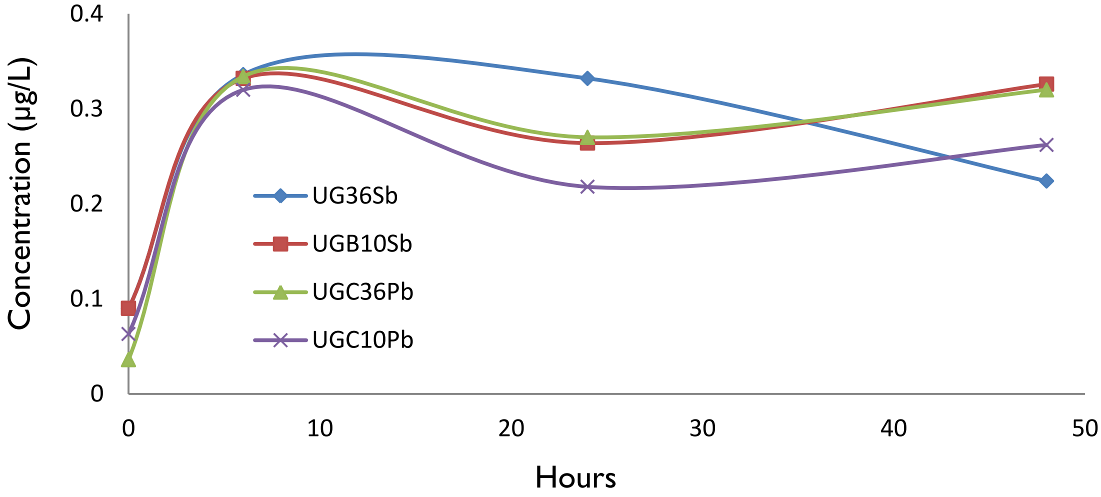

Figure 8.16 Lead and antimony migration in 2 glass bottles at 60°C

Figure 8.17 shows the antimony migration results at 60°C and 6 hours exposure time for all the twenty bottles studied. In addition to migration in deionised water migration into a soft drink was also assessed for ten out of the twenty bottles. Two PET bottles showing the highest levels of antimony migration are two still water bottles (UPA1 and UPA12) from France and Norway. Two PET bottles showing lowest level of migration at these conditions are for still water samples from Britain and Turkey (UPA4 and

UPA15). The quantity of antimony that migrated from these bottles is similar to the quantity from the two glass bottles. It is worth mentioning that even though these bottles released small amount of antimony relative to other bottles the antimony concentrations in the bottle materials is similar to average antimony concentration for the PET bottles analysed in this study. These bottles would probably behave in the same way as the PET bottle from the work of Keresztes *et al* (2009) as mentioned earlier. However because these bottles were studied only at 60°C for 6 hours it could not be ascertained with clarity as to whether they would have behaved in similar way. The migration pattern observed for bottles filled with soft drink is similar to the pattern observed for deionised water even though the final concentrations were higher.

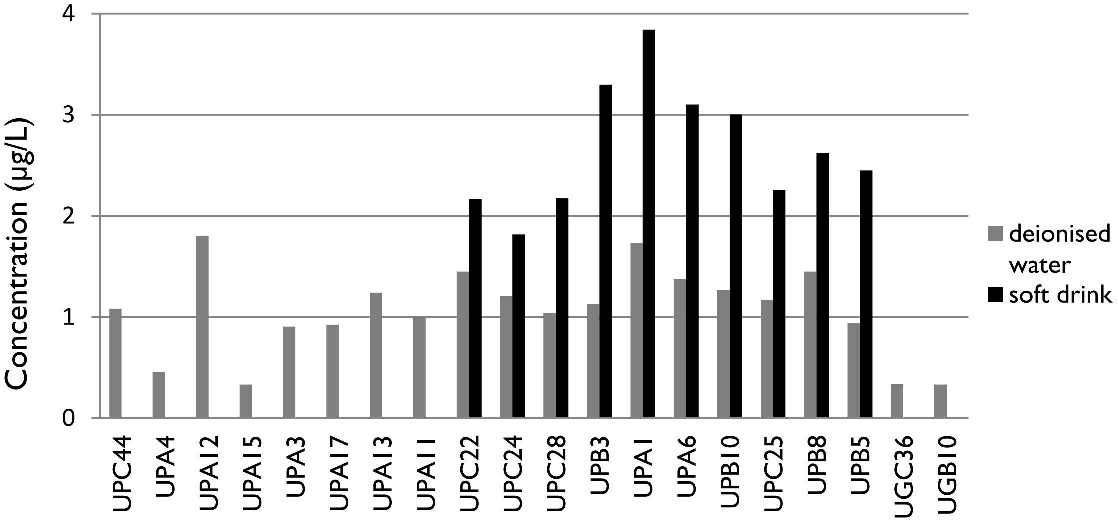

Figure 8.17 Bar chart illustrating antimony leaching propensity for 18 PET and 2 glass bottles at 60°C for 6 hours

The EU specific migration limit (SML) for antimony from PET bottle wall in foods and water and the EU maximum admissible concentration (MAC) of antimony into drinking water are 40µg/kg and 5µg/L respectively. Because the density of liquid water at 4°C is about 1kg/L it follows that the SML can also be presented as 40µg/L. In this study the release of antimony into deionised water and soft drinks at all the exposure conditions was lower than the EU SML (Figure 8.18). The implication of this is that all the studied PET and glass materials from both countries met the requirements of European Commission Directive 2002/72/EC on plastic materials and articles intended to come in contact with food. For all experiments at 40 and 60°C for up to the 48 hours maximum exposure time the antimony concentration remained below the EU MAC.

The highest concentration recorded at 60°C exposure for 48 hours was 4.08μg/L. However at 80°C for 6 hours the antimony concentration exceeded the EU MAC in 8 out the10 samples studied. At 80°C for 24 and 48 hours the EU MAC was exceeded in all the ten samples. The highest antimony concentration achieved is close to five times the EU MAC. Westerhoff *et al,* (2008) recorded antimony concentration of 14.4μg/L after exposing water in a PET bottle to a temperature of 80°C for 7 days. In this work the antimony concentration attained in some bottles after 24 hours of exposure at 80°C is similar to what was obtained by Westerhoff *et al,* (2008) after 7 days exposure as can be seen in Figure 8.18. But for other bottles antimony concentration could not reach the concentration reported by Westerhoff *et al,* (2008) even after 48 hours of exposure at 80°C. From these results it is clear that different bottle materials behave differently with regards to antimony leaching in water at elevated temperatures. Additionally it is likely that the experiments of Westerhoff *et al,* (2008) carried out for a fewer days would have achieved concentrations close to what they obtained for 7 days because antimony migration from PET generally decline with time as can be seen in Figures 8.13 and 8.15. Westerhoff *et al,* (2008) extrapolated the exposure durations required to reach the US Maximum Contaminant Level of 6μg/L for exposure temperatures of 60 and 80°C as 176 and 2.3 days respectively. This extrapolation is not applicable to all bottle materials because from Figure 8.18 it can be that seen for a particular bottle the antimony concentration was close to 5μg/L after just 48 hours of exposure at 60°C and for other bottles the US MCL was exceeded after 6 hours of exposure at 80°C.

As mentioned earlier bottled water temperatures at 40 and 60°C are temperatures that could be realistically encountered in PET bottle use or reuse in Nigeria and Britain. Consequently the risk of consuming water containing antimony above the EU MAC is removed for exposures within the time span studied. In solar water disinfection the minimum water treatment duration is 6 hours in sunny days and for days that are 50% cloudy. An important point worth mentioning is that in tropical developing countries like Nigeria it is still possible for bottled water to be exposed to the scorching tropical sun for several days in their life cycle. As the maximum exposure period used in this study is 48 hours it is not clear if the EU MAC could be exceeded after exposure at 60°C for several days.

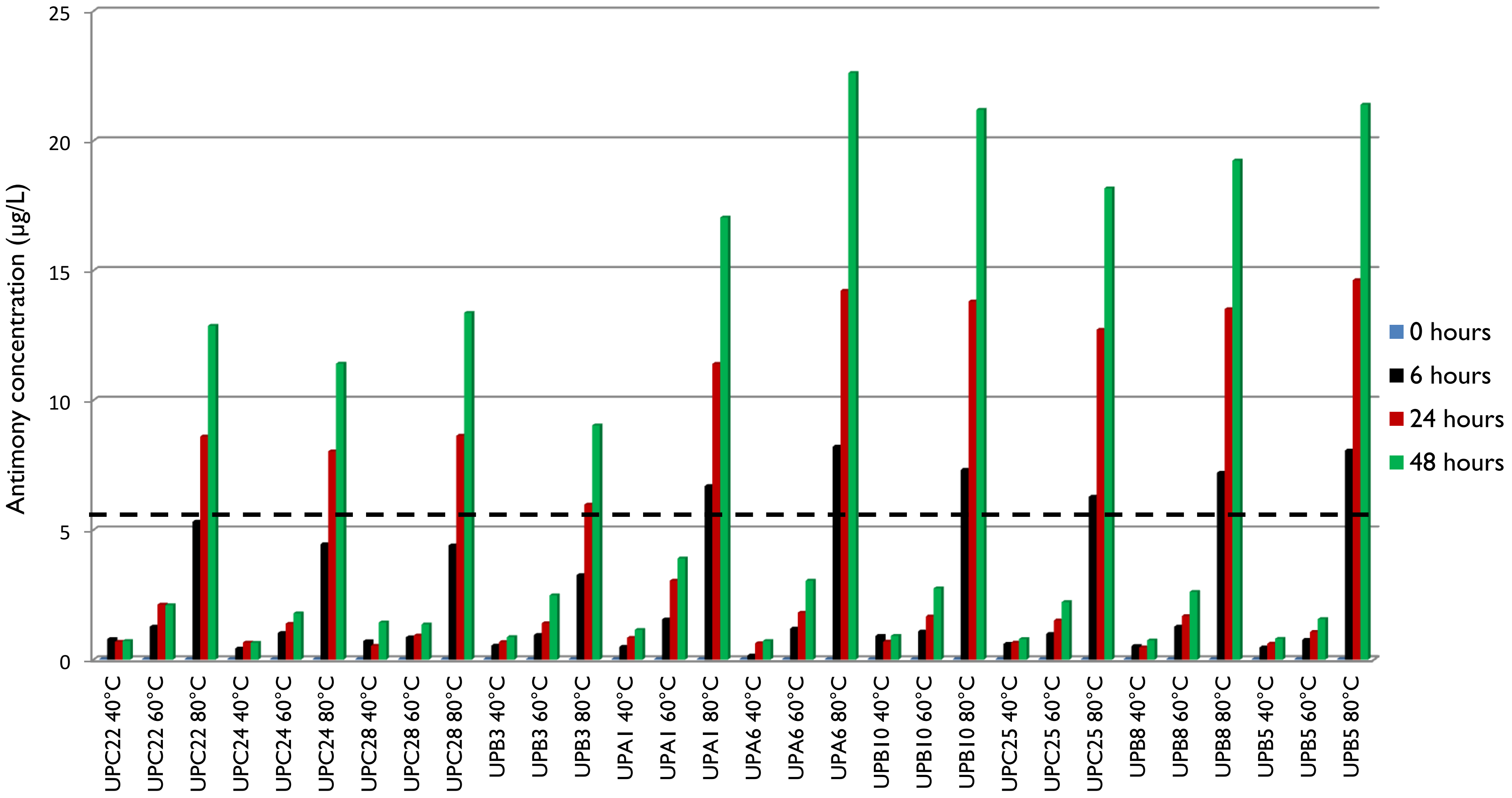

Figure 8.18 Bar chart illustrating antimony leaching propensity for 10 PET bottles at 40, 60 and 80°C for 6, 24 and 48 hours (dotted line shows EU MAC)

8.10 Dependency of antimony migration on its concentration in PET

The concentration of antimony used as catalyst in PET synthesis varies from 150 and 350mg/kg as mentioned earlier and as observed in this study. According to Fick's law the rate of diffusion in a given direction is directly proportional to the concentration gradient. Thus if antimony migration from PET follows the fickian diffusion kinetics the migration will be directly proportional to antimony concentration in PET at any given temperature. Experiments were carried out to assess whether there is any correlation between the concentration of antimony in PET and its migration in deionized water as explained in Sections 5.8. From the results in Table 8.17 it can be seen that at 60°C antimony migration follows the fickian diffusion kinetics for all exposure times. At this temperature antimony migration is directly proportional to the initial antimony concentration in PET for all the samples. For exposure at 40°C for 6 hours very high but negative correlation was observed implying that at these exposure conditions the higher the concentration in PET the lower the migration into the water. At 80°C the dependency is uniform but low for all exposure time. The low dependency at 80°C is probably indicates that different PET materials respond to the elevated temperature differently. Different PET materials could differ in their intrinsic viscosity and crystallinity.

Table 8.17 Dependency of antimony migration on its concentration in PET

Temperature	Exposure time (hours)	Pearson's correlation (r)
40°C	6	-0.75
	24	0.38
	48	-0.12
60°C	6	0.60
	24	0.65
	48	0.64
80°C	6	0.37
	24	0.23
	48	0.25

8.11 Dependency of antimony migration on PET bottle thickness

To assess whether there is any relationship between bottle thickness and antimony migration a digital calliper was used to measure the thickness of PET bottles for different content types from both Britain and Nigeria. The thickness statistics are shown in Table 8.18. Both *t* and Mann-Whitney U tests proved the thickness of the samples from the two countries to be statistically significantly different. The thinner bottles in Britain are not unrelated to the efforts in Britain to reduce packaging waste as reported by WRAP (2007). According to WRAP drinks sector contributes one-third of all packaging arising in the household waste stream. Bottles for carbonated drinks and sparkling water were also found to be thicker than bottles for still water in both countries most likely because of the greater need for them to be stronger for the purpose of withstanding the elevated pressures due to carbonation of contents.

Table 8.18 PET bottle thickness

	Nigerian bottle		British bottles		
	carbonated drinks	still water	carbonated drinks	still water	sparkling water
Average thickness (μm)	407	253	272	197	273
Maximum (μm)	462	350	302	253	340
Minimum(μm)	348	215	195	125	233

The thickness of British bottles was tested against their antimony migration ability at different temperatures. The results are presented in Table 8.19. During the first 6 hours of exposure at 40°C the relationship is weak, implying that thickness is not influencing migration. The absence of any relationship at this condition is most likely because migrating antimony is mainly from the outermost surface of the bottle wall. This can be further substantiated by the fact that for all temperatures rate of migration is highest within the first 6 hours (Figures 8.13 and 8.15). After 24 hours a direct proportionality can be observed between bottle thickness and antimony migration, implying that as thickness increases migration increases. The relationship became inverse after 48 hours of exposure. At 60°C positive but medium dependency was observed for all exposure times. At 80°C no relationship could be observed between bottle thickness and antimony migration. Again this could be due to different behaviours of different PET materials in response to elevated temperatures. Overall it can be said that antimony migration shows some dependency on bottle thickness at 40 and 60°C but not at 80°C.

Table 8.19 Dependency of antimony migration on PET bottle thickness

Temperature	Exposure time (hours)	Pearson's correlation (r)
40°C	6	0.13
	24	0.67
	48	-0.47
60°C	6	0.27
	24	0.39
	48	0.36
80°C	6	-0.02
	24	-0.03
	48	-0.04

8.12 Bottle aging and antimony migration

From the survey carried out in this study and information from the literature as much as 80% of respondents in Nigeria, Britain and United States reported being in the habit of reusing PET bottles. Also a few respondents reported reusing bottles for more than a year. The results for experiments carried out to assess the antimony leaching propensity of new and aged PET bottles are presented in Figures 8.19 and 8.20. The bottles labelled as aged were aged by filling and emptying with tap water on weekly basis over a period of one year. The bottles labelled aged 2 were treated in similar way except that after each emptying the bottles are scrubbed using bottle brush with mild detergent in hot water. In Figure 8.19 the three bottles from a French still water brand (UPA12) were filled with deionised and sparkling water and allowed to stand for 9 months. In Figure 8.20 the bottles were subjected to antimony migration test at elevated but realistic temperatures. Since the amount of antimony for migration is supposed to be depleted with sustained use of bottle it was expected that reused bottles will leach antimony to a lesser extent in comparison to new bottles. The results obtained agreed with the expected results. The greater concentration of antimony in sparkling water than in still water in Figure 8.19 should be in part due to higher initial concentration in sparkling water. In all the antimony migration experiments new bottles released more antimony into water than aged bottles and in all cases antimony concentration fell short of reaching the EU MAC for antimony in drinking water. An important point worth mentioning here is that only a proportion of antimony from the bottle wall is available for migration. According to Alt and

Haldimann (2008) only about 60% of the antimony in PET bottle wall is available for migration.

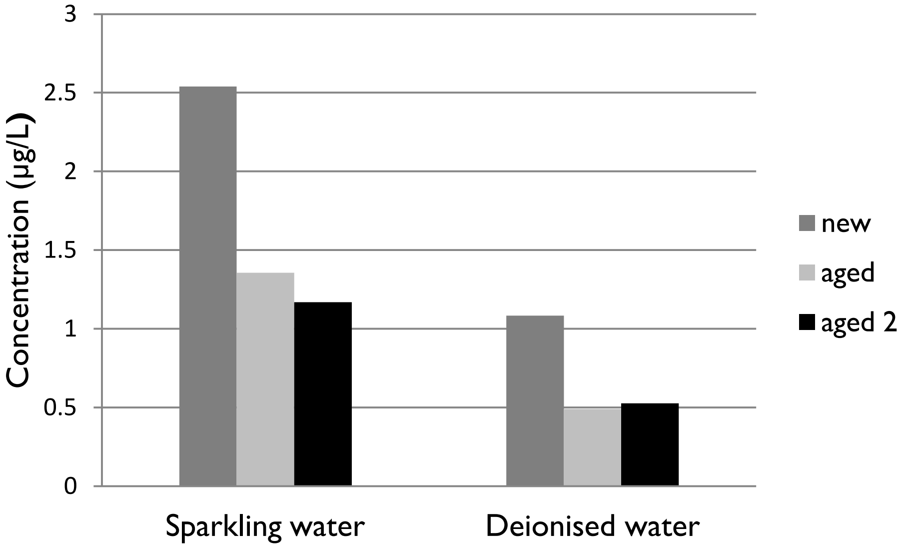

Figure 8.19 Bar chart illustrating antimony migration in new and one year aged PET bottles (UPA12) filled with deionised water for 9 months

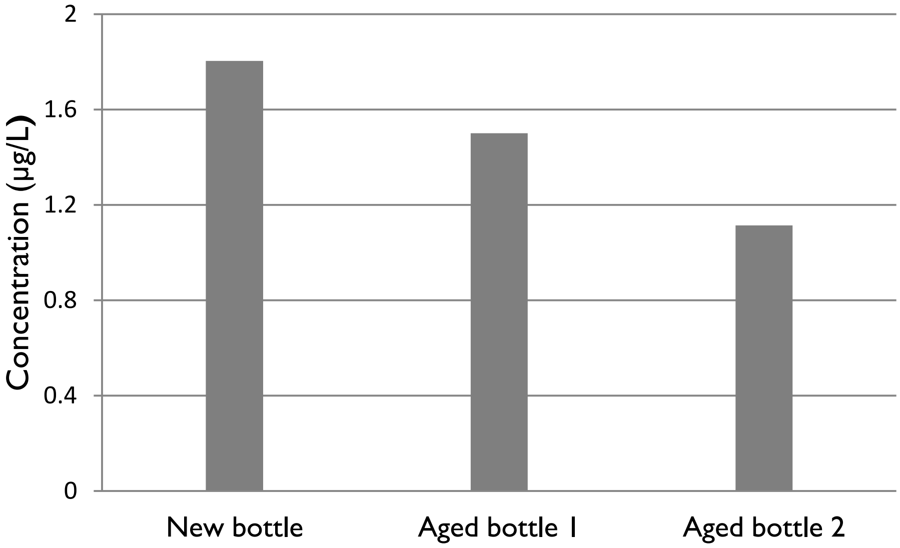

Figure 8.20 Bar chart illustrating antimony migration at 60°C in new and one year aged PET bottles (UPA12)

8.13 Water pH and antimony migration

In Subsection 8.6.5 antimony concentration in freshly purchased bottled water and soft drink was independent of pH. In this experiment a slight difference in antimony concentration was observed in three water samples of different pH stored in green sparkling water PET bottle (UPB5) over a period of 266 days. The results in Figure 8.21 confirmed that in stored water sample the lower the pH of the water the higher the migration of antimony.

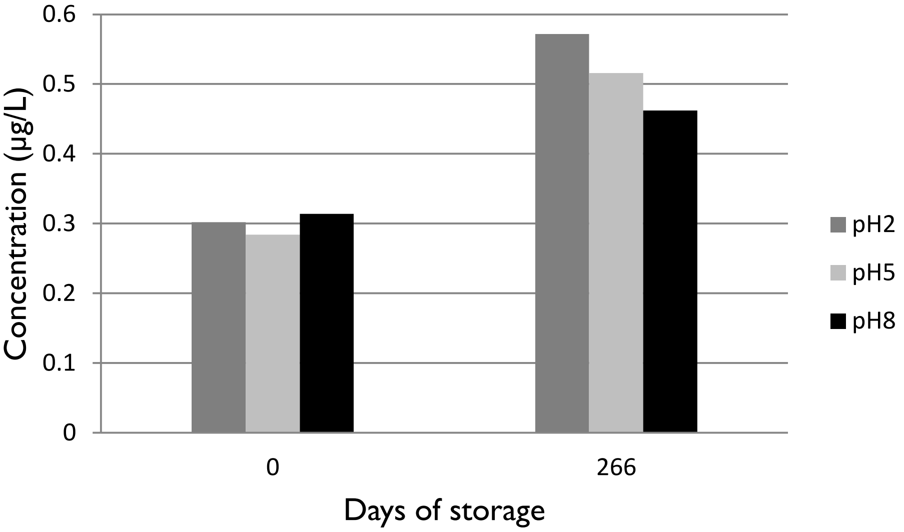

Figure 8. 21 Bar chart illustrating the dependency of antimony migration on water pH

8.14 Bottle size and antimony migration

From the survey results 2L and 500ml bottles accounted for 61% of the freshly purchased bottled water and soft drinks reported in places of residence of British respondents. Also close to 60% of bottles being reused are bottles with a volume of 500ml or less. Based on the results in their study Westerhoff *et al* (2008) hypothesized a possible relationship between antimony release in PET bottles and contact area to liquid volume ratio. Keresztes *et al* (2009) also observed a direct relationship between antimony concentration in bottle content and surface area to liquid volume ratio for 3 bottled water samples bottled at the same time in PET bottles of different volumes. Further study of this phenomenon at elevated temperatures using 5 clear still water bottles of the same brand (UPA3) but having different sizes gave the results in Figure 8.22. The results agree with the observation of Keresztes *et al* (2009) except for the smallest bottle. For all the bottles used the contact area to liquid volume ratio increases as bottle size decreased. While the antimony concentration in the biggest bottle was 2.22µg/L the concentration in the bottle next to the smallest one was beyond the EU MAC. These results confirmed the existence of an inverse relationship between bottle size and build-up of antimony in bottle contents. It is however worth mentioning that the migration temperature used is not typically encountered in normal bottle usage. So for all bottles of all sizes concentration of antimony will not be expected to go beyond the EU MAC if bottles are heated at realistic temperatures.

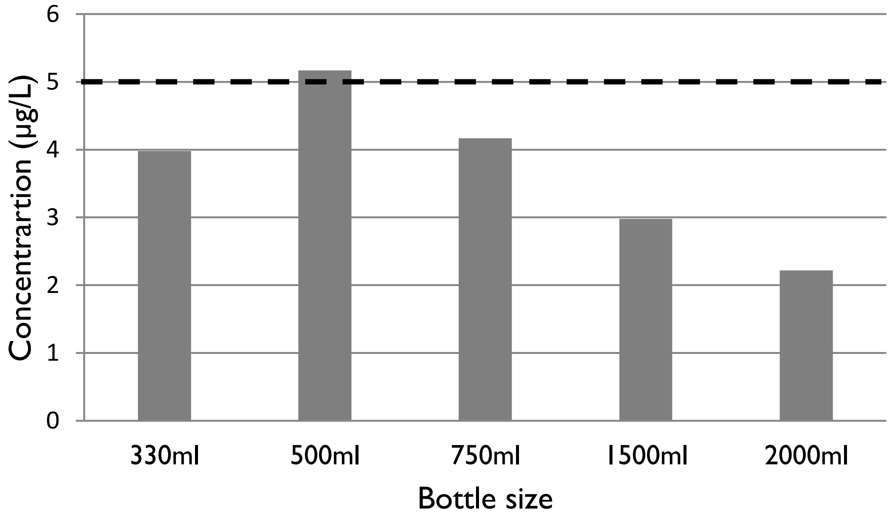

Figure 8.22 Bar chart illustrating migration of antimony into bottles of different sizes at 70°C (dotted line shows EU MAC)

8.15 Summary

The concentration of antimony and some trace metals in PET bottle materials and in bottled water and soft drinks from Nigeria and Britain were determined. Migration of antimony from PET and glass bottles at different conditions was also assessed. All Nigerian and British PET bottle materials contained antimony within the concentration range reported by industry sources implying the use of antimony catalyst in their synthesis. Antimony concentration in Nigerian and British PET materials were similar containing 250±40 and 260±30 mg/kg respectively. Antimony content in plastic bottle caps and cap liners was found to be too low to contribute in migration of antimony into bottled contents. A new method for PET digestion involving the hydrolysis of PET using domestic microwave oven has been described and validated.

Antimony concentration in British drinking tap water was 0.27±0.015 µg/L. The concentration ranged between 0.033 and 6.61µg/L in 47 freshly purchased British bottled water and soft drinks with only one sample going above the EU acceptable limit. While the concentration in still and sparkling water were similar the concentration in soft drinks was found to be higher than in bottled water regardless of type. The antimony concentration of liquids contained in PET was higher than in glass bottles. Bottled water and soft drinks with higher conductivity tend to have higher concentration of antimony, however little or no relationship exists between pH and antimony concentration in freshly purchased samples. But lower pH appeared to be associated with higher antimony concentration in storage experiments.

Concentrations of trace elements investigated (Cd, Ge, Zn, Al, Be, Ti, Co, Pb) were higher in soft drinks than in bottled and tap water. Similarly concentrations of all the elements except antimony were higher in glass bottled contents than in PET bottled contents. High levels of titanium were detected in soft drinks from both countries. The detected titanium is believed to be in the soft drinks as a result of its usage as food additive. Concentration of antimony in some Nigerian bottled water and soft drinks was above the EU MAC after 11 months of storage at room temperature. For 10 British bottled water samples the concentration remained below the EU MAC even after 19 months of storage. A Nigerian glass bottle for soft drink leached both antimony and lead above EU MAC after 2 months. However 2 British glass bottles subjected to antimony migration test at elevated temperatures demonstrated low level of antimony and lead migration.

Antimony concentrations in water exposed at 40, 60 and 80°C for up to 48 hours in PET and glass bottles remained below the EU specific migration limit for antimony from plastic materials and other articles intended to come in contact with food. At realistic temperatures of 40 and 60°C antimony concentration in the water remained below the EU MAC even after 48 hours of exposure but the concentration exceeded the EU MAC for most exposures at 80°C. Antimony migration into water was found to be directly proportional to the antimony concentration in PET and to bottle thickness for some exposure conditions. British bottles were generally thinner than

Nigerian bottles. Aged bottles leach lower amount of antimony than new bottles. Similarly larger bottles leach lower amount of antimony than smaller bottles.

Antimony concentration in freshly purchased bottled water and soft drinks and in migration experiments at realistic conditions are mostly within acceptable levels.

8.16 Conclusion

In this Chapter antimony concentration in PET bottle materials and in bottle contents were analysed. From the results most freshly purchased bottled water and soft drinks were found to be safe for consumption in terms of the content of antimony and the other trace elements analysed. The results also showed that extended storage of bottled water and soft drinks bottled in PET can lead to the concentration of antimony going above the safe limit. Exposure of water to PET at realistic temperatures did not result in antimony concentrations going above the safe limits. However exposure at atypical extreme temperatures resulted in antimony concentration in the water going above the safe limits.

CHAPTER 9: ACETALDEHYDE MIGRATION: RESULTS, DISCUSSION AND SUMMARY

9.1 Introduction

This Chapter presents the results obtained from the experiments explained in Section 5.9 of Chapter 5 (Methodology). The experiments quantified acetaldehyde in PET materials, drinking water from tap, freshly purchased bottled water and soft drink samples in PET bottles, glass bottles and other plastic bottles. The experiments also assessed migration of antimony under different conditions. The Chapter interprets and discusses the results in conjunction with the reviewed literature and the results in preceding chapters.

9.2 Calibration and retention time

The analysis of acetaldehyde in water and soft drinks and in PET materials was based on calibration curves as explained in Section 5.9. The curves for acetaldehyde determination in water, soft drinks and PET materials are presented in Figures 9.1, 9.2 and 9.3 respectively. The regression coefficients for all the curves were greater than 0.99, an indication of linearity and hence accuracy of response within the concentration ranges used. Retention time of acetaldehyde differed with the injection mode, in all cases the retention time was less than 1 minute. A typical acetaldehyde chromatogram is shown in Figure 9.4.

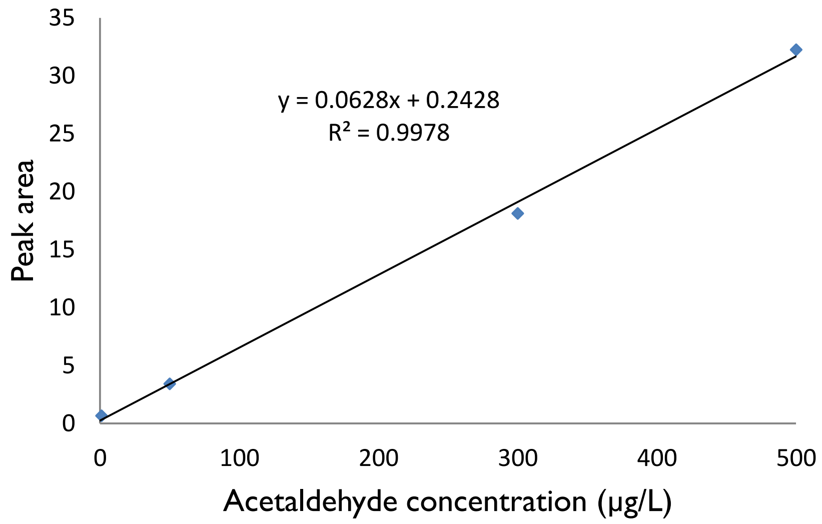

Figure 9.1 Calibration curve (splitless injection mode) for acetaldehyde in bottled water

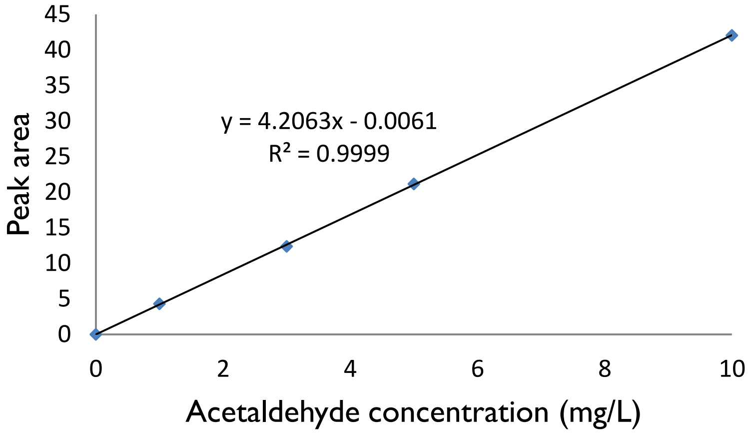

Figure 9.2 Calibration curve (split injection, 1:50 split ratio) for acetaldehyde in soft drinks

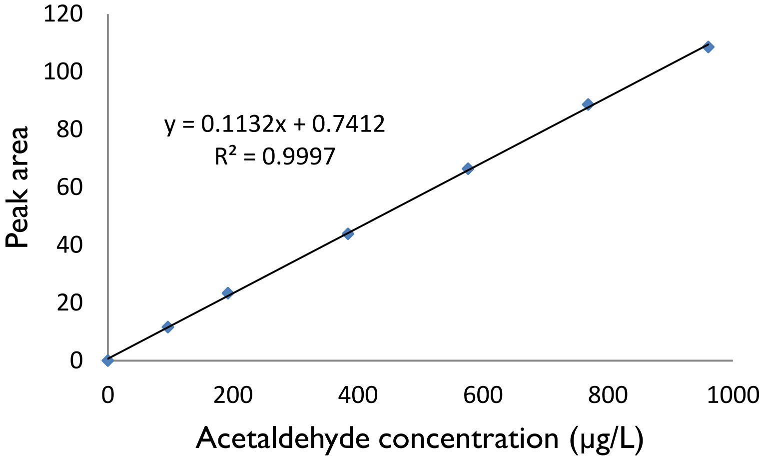

Figure 9.3 Calibration curve (split injection, 1:50 split ratio) for residual acetaldehyde in PET materials

Figure 9.4 Typical acetaldehyde GC-FID chromatogram (retention time: 0.5 minutes)

9.3 Limits of detection

The limits of detections for acetaldehyde in water and residual acetaldehyde in PET are presented in Table 9.1. The limits of detection are based on three times the standard deviations of analyte concentrations in 10 analyses of 10 µg/L acetaldehyde solution and acetaldehyde vapour at 8.64 µg/L.

Table 9.1 Limits of detection

	limit of detection (µg/L)
acetaldehyde in water	2.16
Residual acetaldehyde in PET	0.86

9.4 Accuracy and precision

Accuracy and precision for the determination of acetaldehyde in water and soft drinks were achieved by analysis of spikes of acetaldehyde at 50 and 100 µg/L (Table 9.1). Accuracy and precision for determination of residual acetaldehyde in PET was achieved by analysis of acetaldehyde vapour at concentration of 385.80 µg/L (Table 9.2). In all cases accuracy and precision were good as recoveries were around 100% and coefficients of variation were less than 15%.

Table 9.2 Accuracy and precision for acetaldehyde determination in water

	Spikes (µg/L)	
Added	50	100
Found	52.54	92.82
	51.20	101.48
	51.20	100.70
	50.77	105.14
	50.70	
	51.13	
	50.63	
	50.35	
	52.11	
	50.56	
Mean	51.12	100.04
standard deviation	0.70	5.18
Standard error	0.22	2.59
Coefficient of variation (%)	1.38	5.18
Recovery (%)	102.24	100.04

Table 9.3 Accuracy and precision for determination of residual acetaldehyde in PET

	Spike (µg/L)
Added	385.80
Found	394.21
	376.17
	385.60
	370.68
	382.07
Mean	381.75
standard deviation	9.00
Standard error	4.02
Coefficient of variation (%)	2.36
Recovery (%)	98.95

9.5 Sample coding

Similar sample coding was used as in Section 8.3.

9.6 Residual acetaldehyde in PET bottles materials

The concentration of residual acetaldehyde in freshly purchased British and Nigerian PET bottle materials is given in Table 9.4. Samples placed on the same rows in the Table are samples for similar soft drinks obtainable in both Britain and Nigeria. The minimum and maximum concentrations for British samples are 0.95 and 12.52 µg/g respectively. The total average and the average for still water, sparkling water and soft drinks PET materials for British samples are 4.76, 4.1, 1.55 and 6.7µg/g respectively. The average concentration for Nigerian soft drinks PET materials is 2.17µg/g.

As can be seen from Figure 9.5 and Table 9.4 the acetaldehyde concentration is higher in British soft drink PET materials than in the corresponding Nigerian PET materials. This difference is believed to be related to the concentration of acetaldehyde in the contents of the bottles. As will be discussed later acetaldehyde concentration was found to be much higher in a cola drink from Nigeria than in similar brand marketed in the UK. Additionally PET material has been shown in this study to have the ability to absorb acetaldehyde in solution. The average concentrations reported by Matsuga *et al* (2005) for Japanese, European and American bottles were 14.9, 7.8 and 12.3µg/g respectively. Comparison of the results obtained in this study with the results of Matsuga *et al* (2005) will imply that the residual acetaldehyde in PET bottle materials is lower in British and Nigerian bottles than in Japanese, European and American bottles.

Table 9.4 Residual acetaldehyde in fresh British and Nigerian PET bottle materials

British PET samples	Acetaldehyde concentration (µg/g)	Nigerian PET samples	Acetaldehyde concentration (µg/g)
UPC38	3.06		
UPC33	8.56		
UPC30	9.24		
UPC32	6.78		
UPC41	3.67		
UPC25	4.47	NPC14	2.61
UPC22	3.79	NPC13	1.29
UPC26	4.05	NPC16	2.54
UPC24	12.52	NPC12	2.72
UPC23	10.89	NPC15	1.69
UPA12	1.08		
UPB10	0.95		
UPA5	4.49		
UPB5	2.12		
UPA4	8.39		
UPB4	1.19		
UPA3	4.55		
UPB3	1.93		
UPA6	1.97		
UPB6	1.56		

It is however worth mentioning that Matsuga *et al* (2005) used a quantitation method different from the one used in this study and it is not known if quantitation method difference has any impact in determination of residual acetaldehyde in PET. The method used by Matsuga *et al* (2005) Involved simultaneous dissolution of PET in trifluoroacetic acid and derivatization of the acetaldehyde content with 2,4-dinitrophenylhydrazine followed by precipitation, solvent extraction with dichloromethane, evaporation, reconstitution in acetonitrile and analysis by HPLC. The acetaldehyde concentration range as reported by Linssen *et al* (1995) and Bashir *et al* (2002) were 1.1 – 3.8 and 0.3 – 0.8 µg/g respectively. It is unclear what method was used by Linssen *et al* (1995), however Bashir *et al* (2002) used a method differing slightly from the method used in this study. In order to generate greater surface area which will result in greater efficiency of extraction Bashir *et al* (2002) ground the PET after cooling in liquid nitrogen. While this method generate greater surface area for efficient desorption of acetaldehyde it also presents the risk of evaporation of the volatile acetaldehyde before the ground PET can be placed in vials.

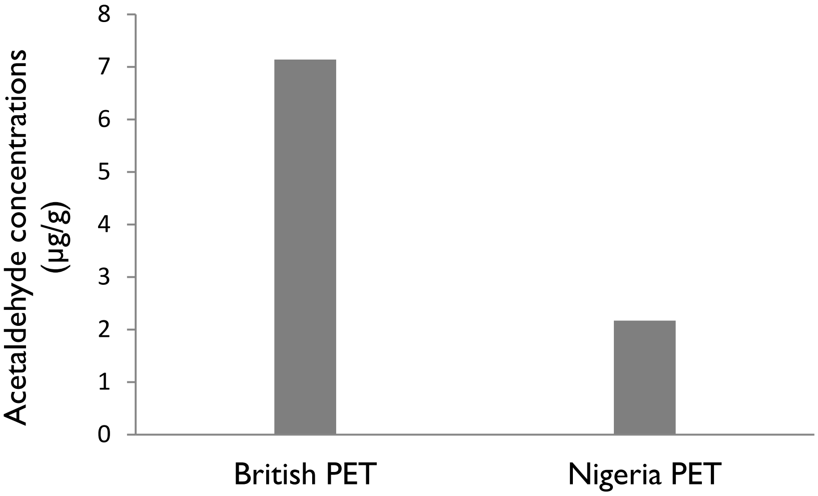

Figure 9.5 Average acetaldehyde concentration in British and Nigerian soft drinks PET materials

PET material for making containers for bottled water needs to contain lower amounts of acetaldehyde than material for making bottles for carbonated soft drinks because carbonated drinks can mask the taste and odour of acetaldehyde more than bottled water. As shown in Figure 9.6, the residual acetaldehyde content in PET differs for PET materials used for bottling of different contents. The acetaldehyde content was found to be higher in soft drinks PET followed by still water and sparkling water PET. The difference in concentration was found to be statistically significant using Kruskall-Wallis chi-square test ($p < 0.01$: χ^2 (3) = 9.351) and one-way ANOVA ($p < 0.05$, adjusted R^2 = 0.329). However Tukey's HSD range test revealed a statistically significant difference in acetaldehyde concentration between sparkling water PET and soft drink PET but not between still water PET and any of the 2 samples. As suggested earlier the higher concentration in soft drinks PET is believed to be related to the concentration in the soft drinks. The concentration difference between still and sparkling water PET is believed to be due to the higher acetaldehyde extraction ability in sparkling water than in still water.

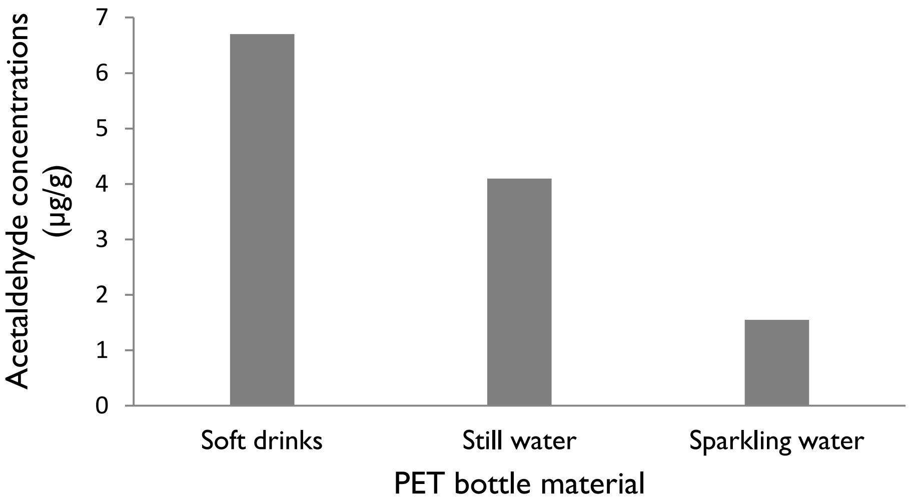

Figure 9.6 Average residual acetaldehyde in British PET bottles used for different soft drinks (n=10), still water (n=5) and sparkling water (n=5)

The concentration of residual acetaldehyde in 2, 13 and 26 months old Nigerian PET bottle materials is given in Table 9.5. The minimum and maximum concentrations are 0.46 and 3.09µg/g respectively. As for British samples the acetaldehyde concentration was found to be higher in soft drinks PET (mean = 1.5 µg/g) than in bottled water PET (mean = 0.83 µg/g). The difference was found to be statistically significant using Mann-Whitney U test (exact p = 0.009 U = 5). Change of acetaldehyde concentration in Nigerian PET with time is discussed in Subsection 9.6.

Table 9.5 Residual acetaldehyde in Nigerian PET

PET samples	Acetaldehyde concentration (µg/g)		
	2 months	13 months	26 months
NPA2	0.90	1.05	0.950
NPA6	0.87	0.46	
NPA8	1.63	0.60	
NPA4	0.97	0.63	
NPA5	1.64	0.64	0.60
NPA1		1.85	0.63
NPA11		0.51	
NPA9		0.93	
NPA10		0.69	
NPA3		1.06	
NPA7		0.68	
NPC14		1.10	
NPC13		1.63	
NPC16	3.09	1.67	
NPC12		1.53	
NPC15		1.56	

9.7 Bottle aging and acetaldehyde concentration in PET

As mentioned earlier, acetaldehyde is formed in PET by thermal degradation at temperatures above 160°C. As PET bottles are not typically exposed to such high temperature, the formation of acetaldehyde will not be expected to happen in PET bottle material after manufacture. As mentioned in Subsection 4.7.6. Nawrocki *et al* (2002) reported lower acetaldehyde concentration in one month old bottle material than in new bottle material. These authors also observed increases in the acetaldehyde content of bottled water with time. In addition, as will be discussed later outgassing of acetaldehyde has been observed from some PET bottles in this study. Based on these observations, the acetaldehyde content of PET bottle material will be expected to decrease with time rather than increase. Figure 9.7 compares the acetaldehyde contents of new and aged materials for two different brands of PET bottles. The samples UPB5 and UPA12 were aged for 266 and 368 days respectively. The aging period was selected in part because bottle reuse period of up to one year was reported by both British and Nigerian respondents in the survey carried out in this study. As explained in Subsections 5.9.10 the aging process was made to as much as possible imitates actual bottle reuse. Also while the bottles labelled as "aged bottle 1" were just rinsed with water before refilling, the bottles labelled "aged bottle 2" were scrubbed using brush with dilute solution of detergent in hot water prior to refilling.

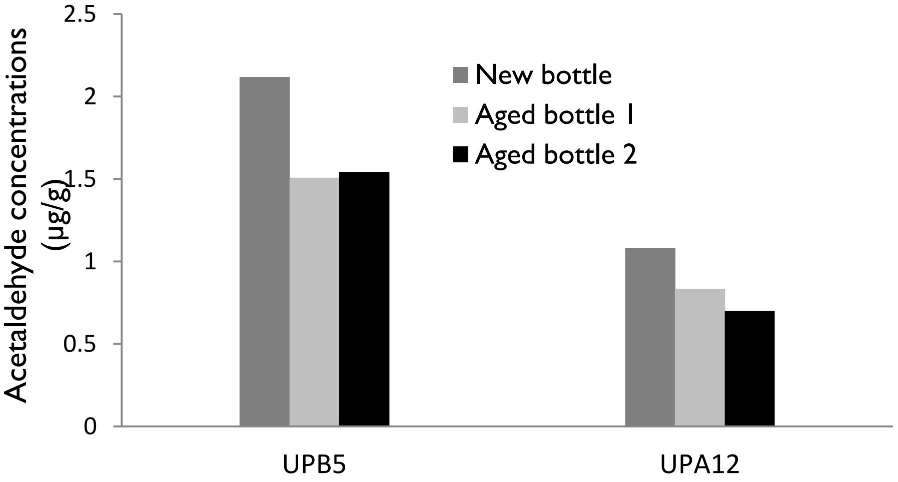

Figure 9.7 Acetaldehyde concentration in new and aged PET bottle materials

As expected, the results revealed that that the acetaldehyde content of PET material decreases as the bottle material ages. However the amount of decrease observed is lower than what was expected. This most likely implies that only the acetaldehyde in the upper layers of the PET material is available for diffusion under the aging conditions.

The results in Figures 9.8 and 9.9 further substantiate the observation made in Figure 9.7. In both cases the concentration of acetaldehyde in bottles allowed to remain with their contents for 13 months was plotted against the concentration of acetaldehyde in newer bottles. With the exception of NPA2 and NPC13, the concentration of acetaldehyde is higher in newer bottle materials than in bottle materials allowed to remain with contents for 13 months.

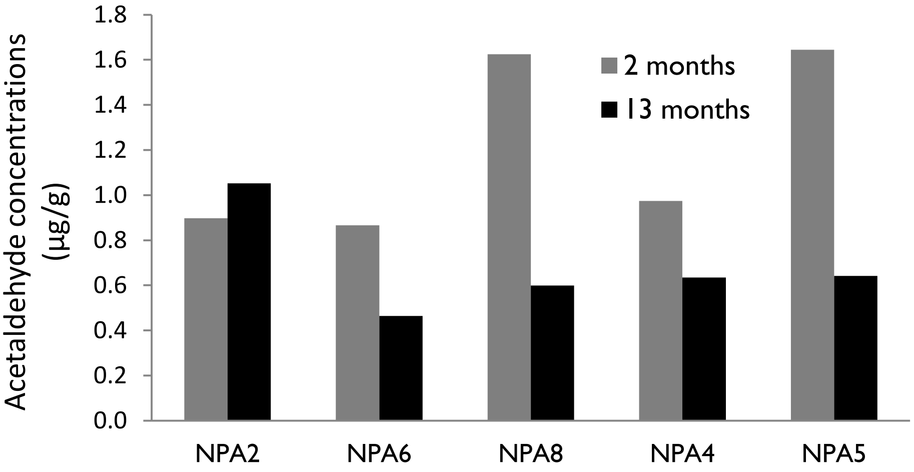

Figure 9.8 Change in acetaldehyde concentration in Nigerian bottled water PET with time

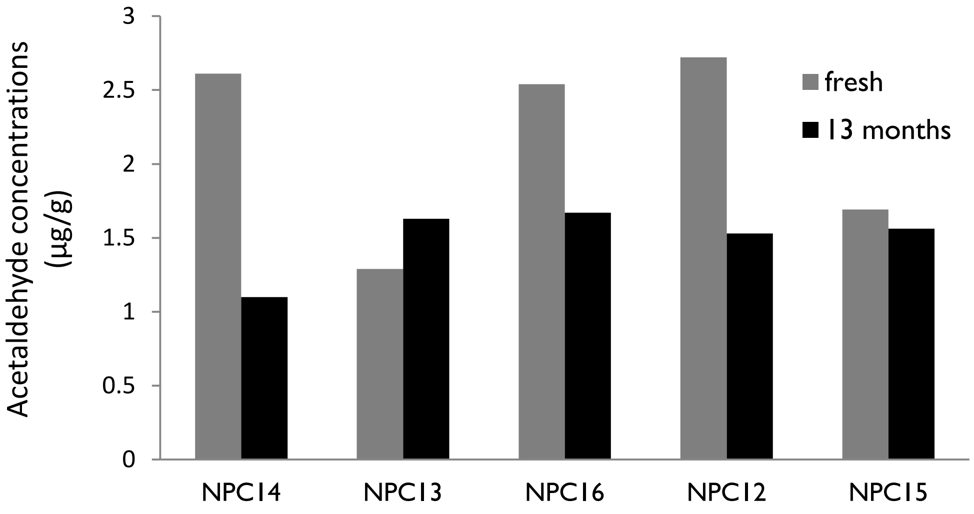

Figure 9.9 Change in acetaldehyde concentration in Nigerian soft drink PET with time

9.8 Bottle thickness and acetaldehyde concentration in PET

Bottle wall thickness was presumed to be positively associated with the concentration of residual acetaldehyde in PET. British PET bottles for water were used to test this hypothesis as newly collected samples were available and unlike PET bottles for soft drinks these bottles have not been in contact with liquids that may contain acetaldehyde. Pearson's correlation for the data showed strong statistically significant but negative correlation (r(8) = -0.823; p = 0.012. r^2 = 0.68). The r^2 value which is referred to as coefficient of determination gives the proportion of variability of thickness that can be explained by the linear relationship between the two variables being studied. In this case it implies that 68% of the total variation in bottle wall thickness can be explained by the linear relationship between concentrations of residual acetaldehyde and bottle wall thickness. The negative correlation implies that the thinner the bottle the higher the concentration of residual acetaldehyde. The scatter plot for the relationship is shown in Figure 9.10. The results obtained are clearly opposite to what was predicted. However as can be seen in Figure 9.6 and 9.11 the acetaldehyde concentration in the thicker sparkling water PET is lower than in the thinner still water PET. The acetaldehyde concentrations in the two materials were expected to be similar. The lower acetaldehyde content in sparkling water PET is in large part attributed to sparkling water's greater ability to extract acetaldehyde from PET bottle wall than still water. As stated in Subsection 4.7.3, carbonation of water was reported to enhance formation and/or migration of acetaldehyde from PET bottles into water.

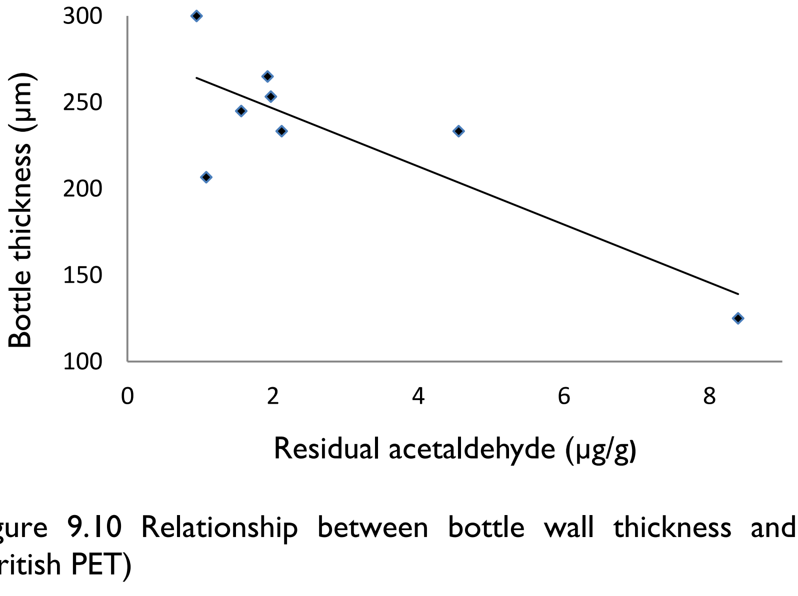

Figure 9.10 Relationship between bottle wall thickness and residual acetaldehyde (British PET)

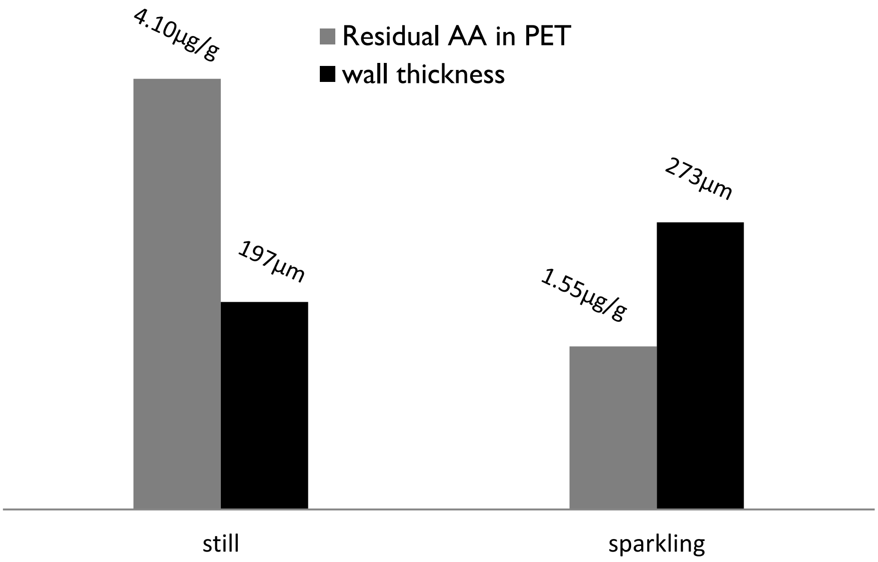

Figure 9.11 Bottle wall thickness and residual acetaldehyde in British still and sparkling water PET

To test the hypothesis using PET materials from still water only, Nigerian still water PET bottles that were allowed to stay with their contents for 13 months were used. Pearson's correlation for the data showed strong statistically significant positive correlation ($r(8) = 0.778$; $p = 0.005$. $r^2 = 0.60$). The scatter plot for the relationship is shown in Figure 9.12. The results obtained here proved that acetaldehyde concentration in bottle wall increases as the thickness of the wall increases.

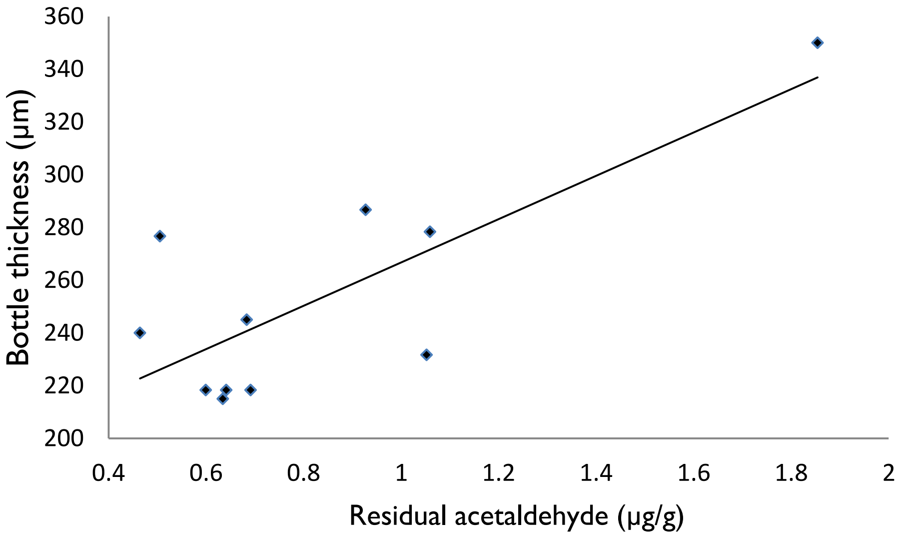

Figure 9.12 Relationship between bottle wall thickness and residual acetaldehyde (Nigerian PET)

9.9 Effect of carbonation on acetaldehyde quantitation

As explained in Subsection 5.9.7 experiments were carried out to ascertain whether the carbon dioxide in sparkling water and soft drink has any effect on acetaldehyde quantitation using headspace GC-FID. The results in Table 9.6 revealed that the quantitation of acetaldehyde in sparkling water and soft drinks is not affected by carbon dioxide content as the concentrations of acetaldehyde in both spiked still water and sparkling water are approximately equal.

Table 9.6 Effect of carbonation on acetaldehyde quantitation

Replicate samples	Peak area	
	Still water	sparkling water
1	3.45	4.73
2	4.33	3.45
3	4.64	4.12
Mean	4.14	4.1
Standard deviation	0.62	0.64

9.10 Acetaldehyde in water and soft drinks

Acetaldehyde has been documented to migrate from the PET bottle wall into the water and soft drinks (Nijssen *et al* 1996, Özlem 2008), yet acetaldehyde is also added to some soft drinks as a flavouring agent (Miyake and Shibamoto 1993, Food Safety Commission 2005, National Toxicology Program 2010). Concentration of acetaldehyde found in fresh British and Nigerian bottled water and soft drinks in this study are given in Table 9.7. In all cases the concentrations were within the range reported in the literature (Miyake and Shibamoto 1993, Sugaya *et al* 2001, Nawrocki *et al* 2002, Mutsuga *et al* 2006). The average concentrations found in this study in British fruit juices, carbonated soft drinks, sparkling water and still water are shown in Figure 9.13. The average concentrations based on packaging types are given in Figure 9.14. From Figure 9.13 it can be seen that acetaldehyde concentration is highest in fruit juices followed by soft drinks, sparkling water and still water. Acetaldehyde was found in soft drinks packaged in PET bottles as in soft drinks packaged in bottles made from glass and carton (Figure 9.14). This confirmed the origin of the acetaldehyde in soft drinks as the soft drinks themselves rather than migration from PET bottle. A juice carton is usually made up of layers of paper, polyethylene, and aluminium foil. Again as can be seen in Figure 9.14 and Table 9.7 acetaldehyde has not been detected in all bottled water in glass bottles. Similar results were reported in the work of Sugaya *et al* (2001). This provides evidence that the acetaldehyde detected in water bottled in PET originated from the PET materials.

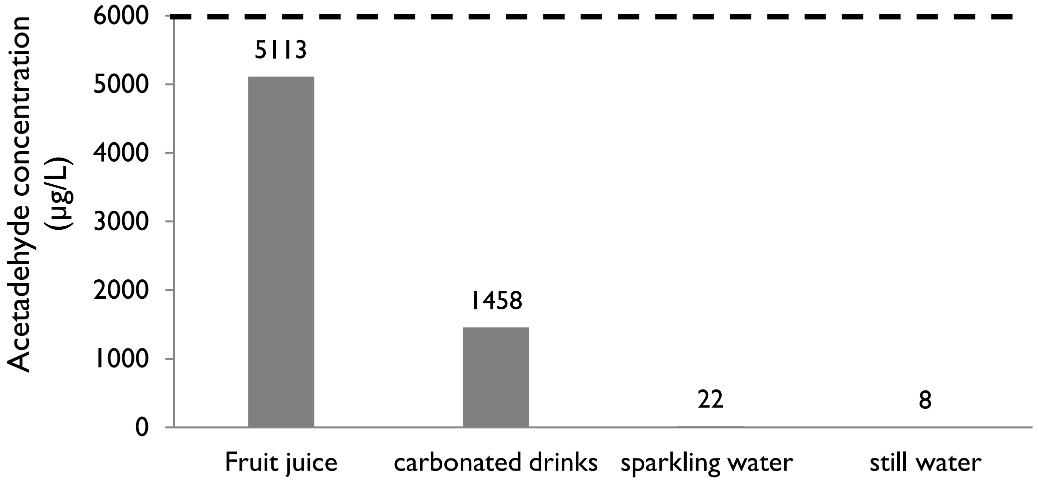

Figure 9.13 Average acetaldehyde concentrations by bottle content type (dotted line shows EU SML)

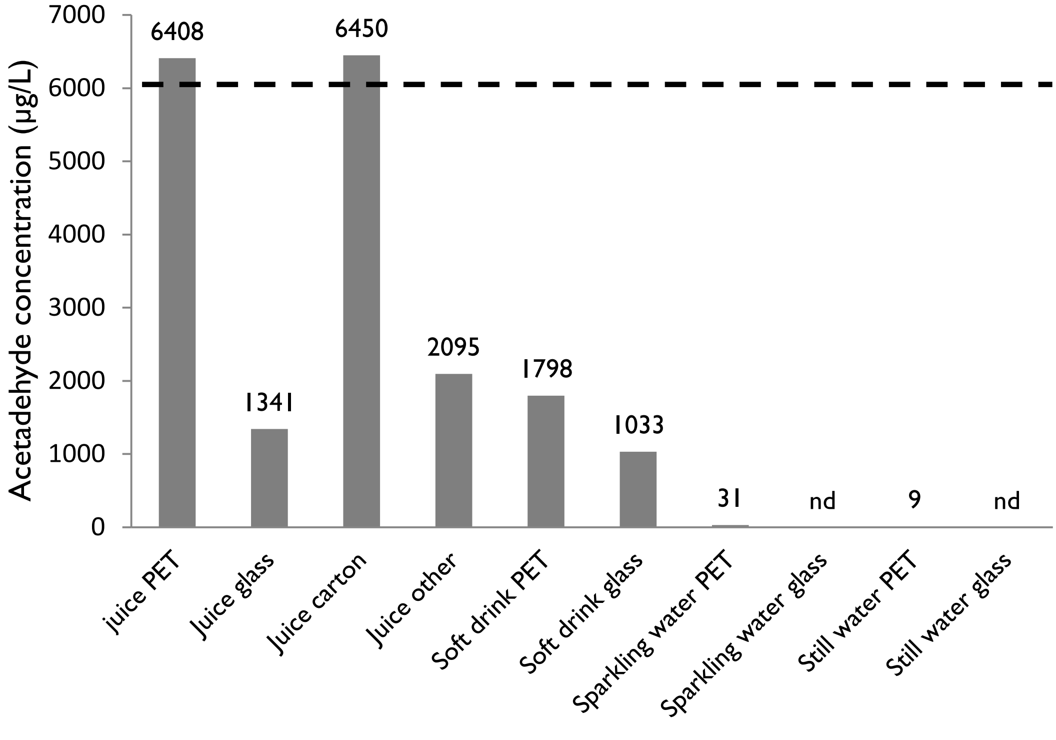

Figure 9.14 Average acetaldehyde concentrations by bottle content and packaging type (dotted line shows EU SML)

Table 9.7 Acetaldehyde concentration in British and Nigerian bottled water and soft drinks

Acetaldehyde concentration (μg/L)							
British bottled water		British soft drinks		Nigerian bottled water		Nigerian soft drinks	
UPB5	72.25	UPC37	3116.48	NPA5	nd	NPC16	178.38
UPB3	29.81	UPC38	9902.19	NPA8	6.4	NGC16	173.62
UPB6	29.33	UPC39	395.05	NPA6	16.43		
UPB4	54.65	UPC30	4952.19	NPA2	14.04		
UPB10	12.13	UPC33	330.76	NPA4	4.17		
UPB1	10.06	UPC40	14247.43				
UGB9	nd	UPC32	7145.05				
UGB3	nd	UPC41	3330.76				
UGB10	nd	UCC42	383.14				
UPA17	7.51	UCC43	12516.48				
UPA5	15.32	UGC34	187.9				
UPA7	nd	UGC36	1683.14				
UPA15	12.29	UGC31	2152.19				
UPA1	10.86	UOC35	2095.05				
UPA19	33.79	UPC40	14249.81				
UPA12	nd	UPC22	311.71				
UPA6	2.74	UPC24	4752.19				
UPA17	7.99	UPC25	1397.43				
UPA3	2.58	UPC26	597.43				
UGA8	nd	UPC23	1930.76				
UGA3	nd	UGC22	109.33				
		UGC23	3142.67				
		UGC26	599.81				
		UGC27	278.38				

nd – not detected

As mentioned earlier, guidelines and standards for acetaldehyde in drinking-water have not been established. Consequently acetaldehyde in bottled water and soft drinks can only be evaluated based on the EU specific migration limit (SML) for acetaldehyde from packaging into foods (6mg/kg), tolerable daily intake of acetaldehyde (0.1mg/kg body weight per day) and odour and taste threshold limits for acetaldehyde in drinking water. The EU specific migration limit (SML) for acetaldehyde from packaging into foods/water is 6mg/kg. In the case of water and soft drinks this is approximately equivalent to 6mg/L considering the fact that one litre of water at 4°C weighs 1Kg. It is worth mentioning that SML is meant only for assessing the safety of food packaging material in terms of contaminants migration. It is thus not a standard for assessing the concentration of contaminants in food or water. It will be used here for comparative purpose because it still refers to the concentration of contaminant that can be achieved in foods and water. Additionally, the SML was designed to ensure that exposure to acetaldehyde, as a result of intake of bottled water and soft drinks in PET bottles, is below the tolerable daily intake (TDI) for acetaldehyde. In this study the concentration of acetaldehyde found in 5 fruit juice samples was beyond the EU SML. An important question worth asking is on the significance of the acetaldehyde EU SML considering the fact that acetaldehyde can be added as flavouring agent in soft drinks at concentration greater that the SML.

The Panel on Dietary Reference Intakes for Electrolytes and Water (2011) set the daily recommended adequate intake for water for an adult man at 3.7 litres from all beverages and foods. According to their estimate about 80 percent of people's total water intake comes from drinking water and beverages with the other 20 percent coming from food. Thus 2.96 litre of the recommended water intake comes from drinking water and beverages. According to Ogden *et al* (2004) the average weight of an adult American is 86.1kg. If the 2.96 litre of water taken by an adult on daily basis is assumed to be totally in the form of soft drinks then the tolerable daily intake of acetaldehyde will be exceeded as a result of intake of 2 out of 9 carbonated soft drinks and 8 out of 15 fruit juices investigated in this study (Appendix 2). If only half of the daily intake comes in the form of the soft drinks the tolerable daily intake of acetaldehyde will be exceeded as a result of the intake of only 5 out of the 15 fruit juices investigated in this study (Appendix 2). The odour and taste threshold limit for acetaldehyde in bottled water is reported to be 20–40 µg /L (Nijssen *et al*, 1996; Schröder, 2001). From this it can be seen that the lower level of the threshold value was exceeded in 5 out of 26 bottled water brands analysed.

The average concentrations of acetaldehyde in Nigerian and British still water are basically similar as can be seen in Figure 9.15. However the concentration of acetaldehyde in a cola drink brand from Nigeria and Britain bottled in PET and glass bottles look different (Figure 9.16). The concentrations for samples from the same country are similar regardless of bottling material. The concentration in British samples is about three times the concentration in Nigerian samples. This most likely implies the use of different amounts of acetaldehyde in the production of this drink in the two countries.

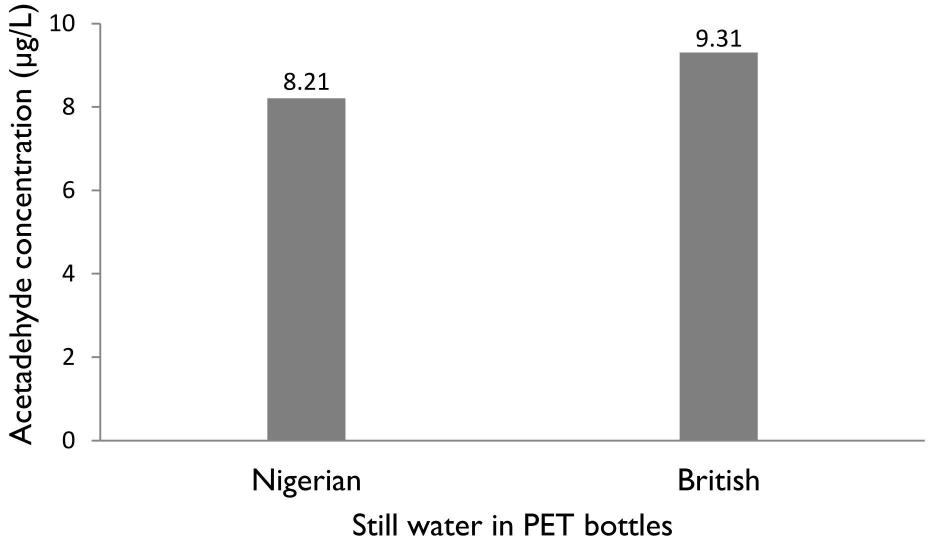

Figure 9.15 Acetaldehyde concentration in Nigerian and British still water

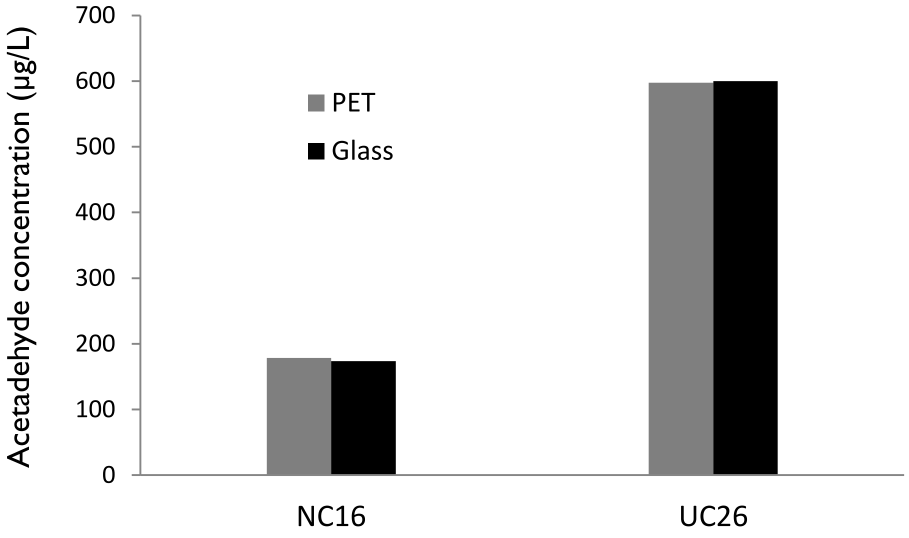

Figure 9.16 Acetaldehyde content in a cola drink brand from Nigeria and Britain bottled in PET and glass bottles.

Figure 9.17 shows the concentration of acetaldehyde in 5 British bottled water brands marketed as still and sparkling water. The concentration of acetaldehyde in all but one brand is higher in sparkling water than in the corresponding still water. As mentioned earlier, carbonation, which lowers the pH of sparkling water by raising the hydrogen ion concentration through formation of carbonic acid, enhances migration of acetaldehyde from PET bottles into water. The mechanism through which carbonation enhances the migration of acetaldehyde has not been determined. From these results it follows that bottled water pH will be positively correlated with acetaldehyde concentration.

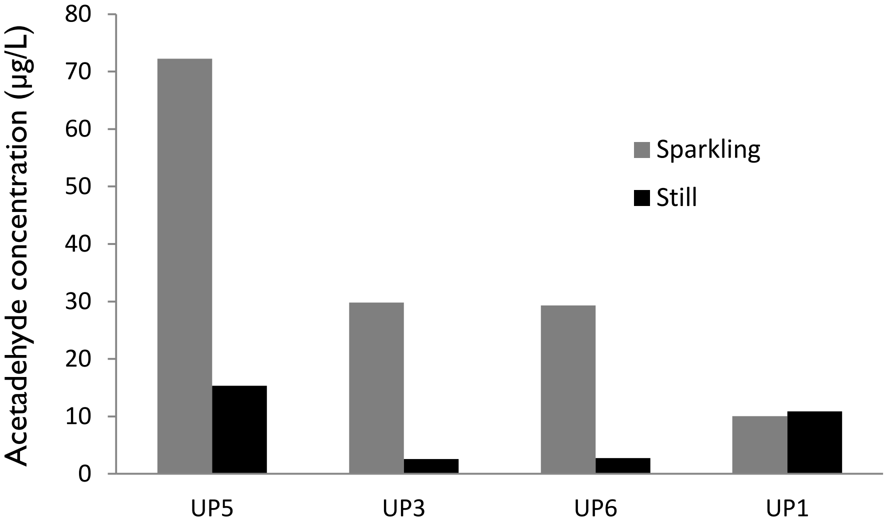

Figure 9.17 Acetaldehyde in 5 British brands of bottled water marketed as still and sparkling water

9.11 Conductivity and acetaldehyde concentration

High solute concentrations in aqueous samples decrease the solubility of polar organic volatiles in the sample matrix and promote their transfer out of the sample. This is the basis for addition of sodium chloride to samples in vials in the determination of acetaldehyde in water using headspace GC. As a result of this it was hypothesised that conductivity, which approximate the measure of total concentration of inorganic substances in water, will be inversely associated with acetaldehyde concentration in bottled water. Pearson's correlation showed strong statistically significant negative correlation between conductivity and acetaldehyde correlation in bottled water (r(9) = -0.722; p = 0.028. r^2 = 0.52). The scatter plot for the relationship is shown in Figure 9.18. The results obtained here proved that acetaldehyde concentration in bottled water decreases as water conductivity increases.

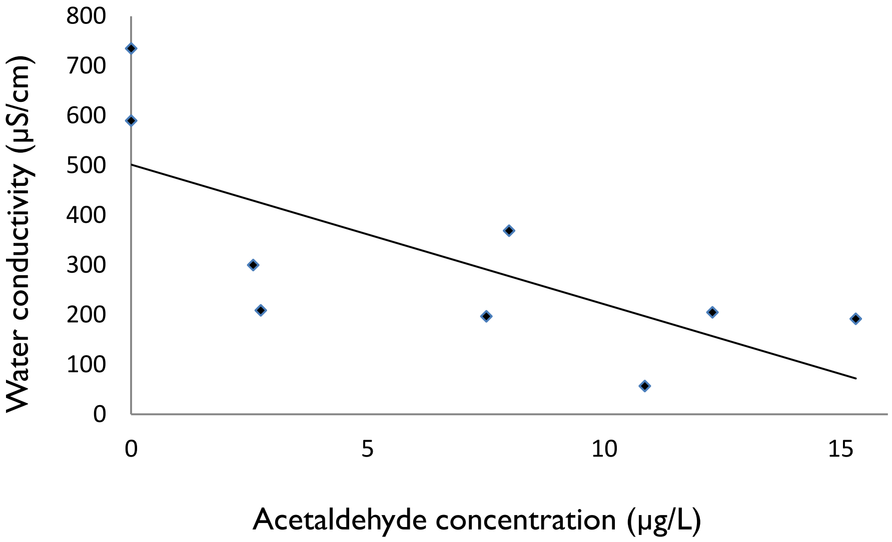

Figure 9.18 Relationship between conductivity and acetaldehyde concentration in bottled water

9.12 Storage and acetaldehyde migration into bottle contents

As stated in Chapter 6, purchased bottled water and soft drinks are mostly consumed within 30 days of purchase in both Nigeria and Britain. In both countries only a very small fraction of respondents reported consuming contents in periods greater than 3 months (Britain <1%, Nigeria 6%). Nevertheless storage period of up to one year has been reported. In this study bottled water and soft drinks were stored for up to 25 months at room temperature and the change in acetaldehyde concentration with time was studied. Table 9.8 and Figure 9.19 show the acetaldehyde content in fresh British bottled water samples and samples stored for 20 months. Table 9.9 shows the acetaldehyde content in fresh Nigerian bottled water samples, samples stored for 12 months and samples stored for 25 months. Figure 9.20 shows change in acetaldehyde concentration in a Nigerian soft drink stored for 12 months. From Table 9.8 and Figure 9.19 it can be seen that acetaldehyde concentration in 5 out of 8 samples dropped after 20 months storage. Acetaldehyde content increase in sample UPA3 but remain constant in sample UPB6. No acetaldehyde could be detected in both fresh and stored samples of brand UPA12. Unlike antimony which accumulates continuously in bottled content acetaldehyde migrating into content can be degraded by bacterial flora in the content as reported by Matsuga *et al* (2006). Heterotrophic bacteria may exist in British bottled water because the European Union Directive 2009/54/EC prohibited disinfection of natural mineral water. Acetaldehyde is not likely to be regenerated in the bottle material as regeneration usually occurs only at high temperatures. Nawrocki *et al* (2002) reported observing gradual increase in the content of acetaldehyde and formaldehyde in carbonated water over a period of 8–9 months followed by a decline. Additionally in this study acetaldehyde concentration has been shown to fall if acetaldehyde solutions are stored in polypropylene bottles (to be discussed later). Nawrocki *et al* (2002) associated the gradual decrease of aldehydes concentration they observed with the gradual loss of dissolved CO_2. The decrease in most of the British samples in this study is most likely related to depletion of the acetaldehyde content in the bottle material. The absence of acetaldehyde in both fresh and stored samples of brand UPA12 is probably related to bacterial content in the water as this PET material has residual acetaldehyde content comparable to other still water PET materials.

Table 9.8 Change in acetaldehyde content in stored British bottled water

Bottled water sample	Acetaldehyde concentration (µg/L)	
	fresh	20 months
UPB6	29.33	32.67
UPB4	54.65	26.3
UPB5	72.25	14.04
UPA19	33.79	17.7
UPA12	nd	nd
UPA3	2.58	6.24
UPA15	12.29	5.76
UPA17	7.99	3.21

nd – not detected

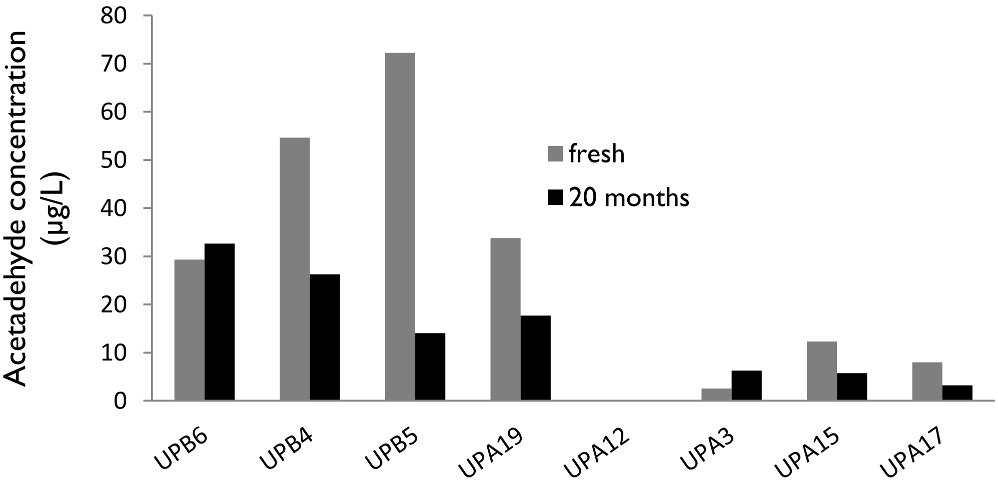

Figure 9.19 Change in acetaldehyde content in British bottled water stored for 20 months

Most Nigerian samples are table bottled water and even for spring water and natural mineral water a regulation similar to the European Union Directive 2009/54/EC may not be in existence. Consequently most Nigerian bottled water is disinfected. Increase in acetaldehyde concentration was therefore expected. However other factors that may determine the stability of acetaldehyde in the water include oxygen content and temperature. From Table 9.9 an increase in acetaldehyde concentration is observed with most samples. Importantly while the concentrations generally lie within the odour and taste threshold limit for British sparkling water the concentration failed to reach the lower border in British still water and in all Nigerian water samples.

Table 9.9 Change in acetaldehyde content in stored Nigerian bottled water

Bottled water sample	Acetaldehyde concentration (μg/L)		
	fresh	12 months	25 months
NPA1		7.35	5.92
NPA2	14.04	15.79	18.98
NPA3		3.69	
NPA4	4.17	7.19	
NPA5	nd	4.49	12.13
NPA6	16.43	3.85	
NPA7		4.81	
NPA8	6.4	10.38	
NPA9		nd	
NPA10		8.95	
NPA11		nd	

nd – not detected

From Figure 9.20 the concentration of acetaldehyde increased by 586% in the fresh Nigerian cola drink (NPC13) after storage period of 12 months. Özlem (2008) has reported similar observation after storing carbonated drink sample for 6 months. However the actual amount of acetaldehyde in the 28.59g bottle of 500ml capacity with a residual acetaldehyde concentration of 3.09μg/g is 88.4μg. Even if all the residual acetaldehyde migrate into the bottle content the concentration in the bottle content will only increase by 178.6 μg/L (about 100%). Unless acetaldehyde was being regenerated in the PET bottle material or from degradation of the soft drink the source of the increase could not be ascertained. The method used in acetaldehyde determination could not have been responsible for the increase, for it were it would have affected both fresh and stored samples to the same extent.

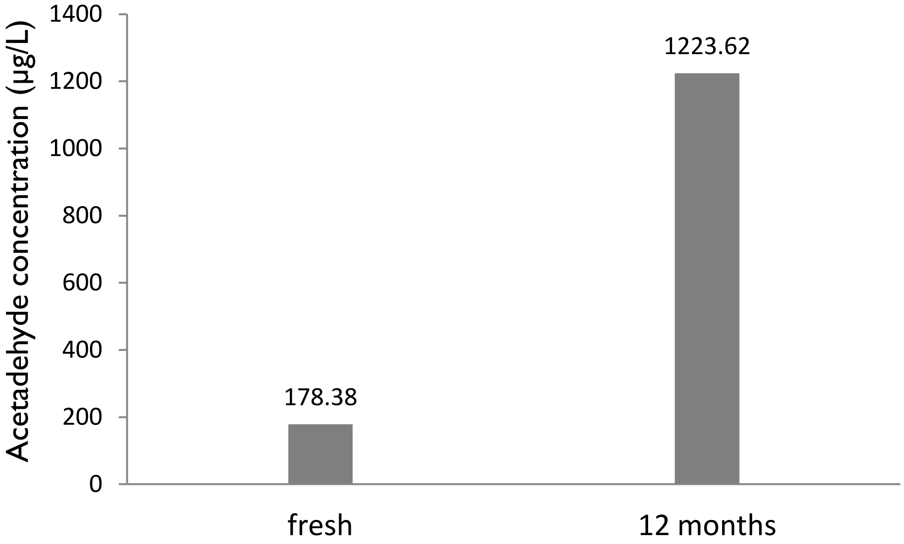

Figure 9.20 Change in acetaldehyde content in a fresh Nigerian cola drink brand (NPC13)

9.13 Acetaldehyde in PET materials and in bottle contents

For British water bottles as bottle wall thickness increases the acetaldehyde concentration in the wall matrix decreases (Section 9.8). This observation was in part attributed to sparkling water's greater ability to extract acetaldehyde from PET bottle wall than still water. Sparkling water is contained in bottles which are thicker than still water bottles. The results in Figure 9.21 provide further evidence in support of this argument. The Figure revealed that even though the acetaldehyde content is lower in the thicker sparkling water bottles than in the thinner still water bottles the acetaldehyde content is higher in sparkling water than in still water. From Figure 9.21 the mean acetaldehyde concentration in sparkling water is higher than the odour and taste threshold level for acetaldehyde in water To avoid the acetaldehyde concentration going above the odour and taste threshold in bottling of water, bottles with lower acetaldehyde contents should be used for sparkling water since sparkling water has greater ability to extract acetaldehyde than still water.

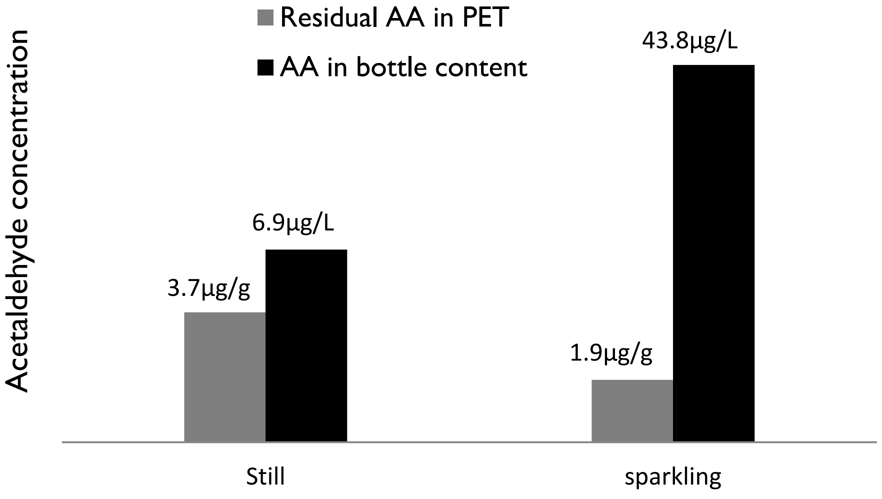

Figure 9. 21 Relationship between acetaldehyde concentration in PET and its presence in bottled water

9.14 Acetaldehyde outgassing from PET bottles

New plastics materials including those used in car interiors, shower curtains, and flooring initially outgas chemicals into the air which accounts for the distinctive smell associated with some of these products when new. Except for flavoured water chemicals other than carbon dioxide are usually not added to bottled drinking water. Consequently no additive-associated smell is expected to come from used PET bottles. In this study some used PET bottles were found to be releasing a gas with fruity smell which was suspected to be acetaldehyde vapour. To characterise and quantify the gas, bottles from 3 brands of bottled water were studied as explained in Subsection 5.9.11. The gas was confirmed to be acetaldehyde and the results obtained are shown in Figure 9.22. From the Figure it can be seen that sample UPB5 which is a green bottle for sparkling water releases acetaldehyde with the concentration increasing with time. A similar bottle aged for 266 days was not releasing acetaldehyde. Also 2 bottle samples used for still water (UPA12 and UPA15) were not releasing acetaldehyde. The residual acetaldehyde content for UPB5 and UPA12 is shown in Table 9.4. Even though UPB5 has higher residual PET than UPA12 the observation is believed to be more related to the usage of the bottle for sparkling water than with the residual acetaldehyde concentration. Since only 3 bottles were studied it cannot be said with certainty whether this phenomenon is more associated with sparkling water bottles than with still water bottles

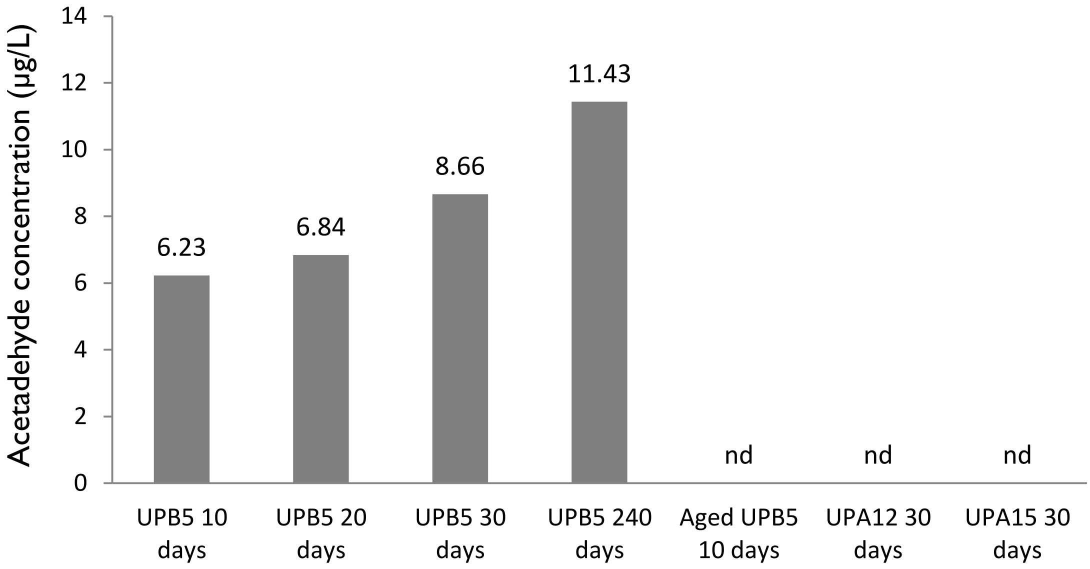

Figure 9.22 Outgassing of acetaldehyde from empty PET bottles (nd – not detected)

9.15 Acetaldehyde migration from water medium into PET

From the literature and results discussed earlier acetaldehyde has been established to migrate from PET bottle wall into the surrounding environment. To verify whether PET material could absorb acetaldehyde PET materials from samples UPB5 and UPA12 were soaked in acetaldehyde solutions of varying concentrations for 24 hours as explained in 5.9.12.

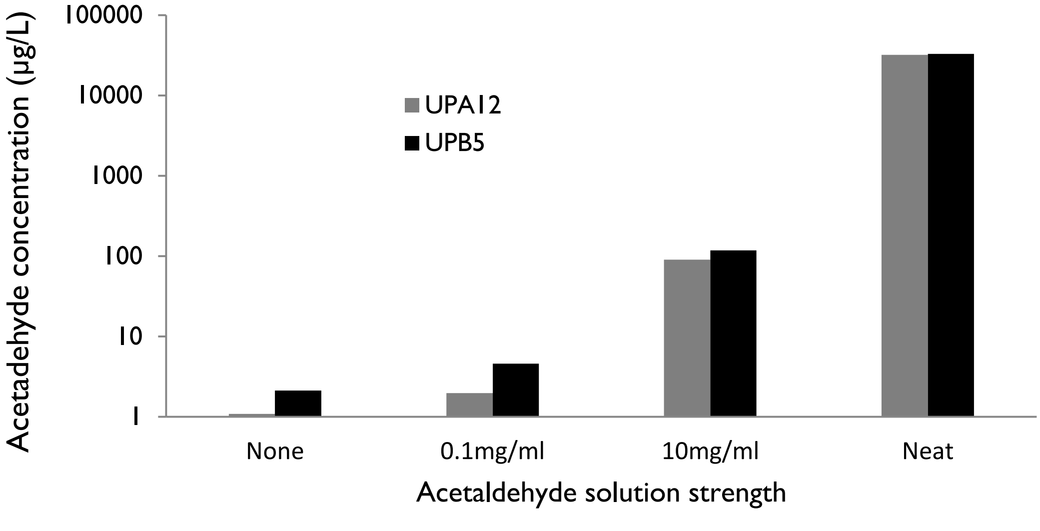

Figure 9.23 Absorption of acetaldehyde by PET

The results for these experiments are shown in Figure 9.23. From the results it can be seen that PET material can absorb acetaldehyde in solution and the amount absorbed increases with the concentration of the acetaldehyde solution. The results also revealed that at low concentrations the quantity of acetaldehyde absorbed varies directly with the concentration of the residual acetaldehyde. However at higher concentrations absorption pattern becomes similar. In the case of the two PET materials here at acetaldehyde concentration of 0.1mg/ml the absorption was about 100% of the concentration of residual acetaldehyde in each of the 2 materials. But the amount absorbed became roughly equal at acetaldehyde concentration of 10mg/ml and for neat acetaldehyde.

The lowest concentration used in this study (0.1mg/ml = 100mg/L) has been reported to be obtainable in some fruit juices. According to Food Safety Commission of Japan (2005) acetaldehyde is contained in fruit juices at concentrations as high as 230mg/L. In this study the highest concentration found was 14.25mg/L (Table 9.7). The implication of this finding is that PET materials from soft drinks and fruit juices cannot be used to assess actual residual acetaldehyde in PET since the materials could absorbed as much acetaldehyde from their contents as the residual acetaldehyde contained in them. As observed in this study the residual acetaldehyde concentrations found in soft drink and fruit juices bottles are higher than the residual concentrations in water PET bottles.

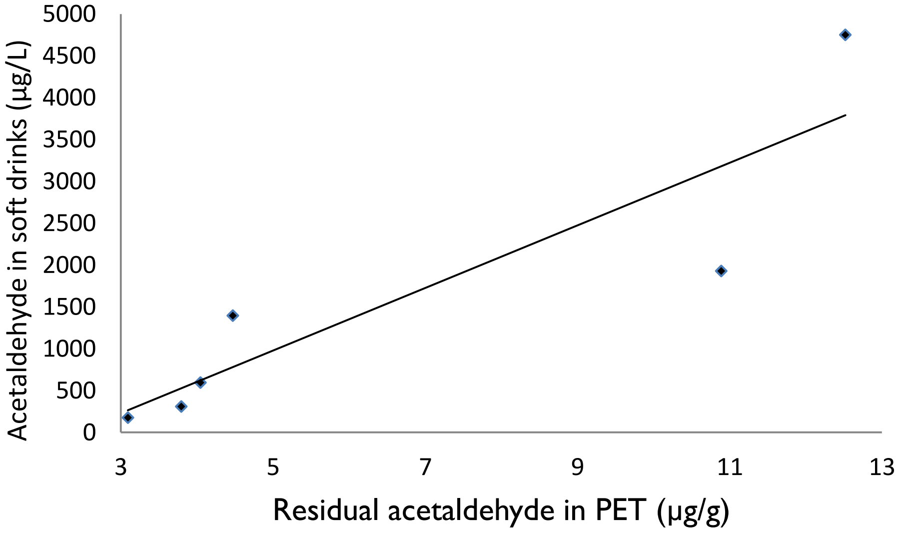

Figure 9.24 Relationship between residual acetaldehyde in carbonated drinks PET and the acetaldehyde concentration in the carbonated drinks

This is most likely as a result of acetaldehyde migration from soft drinks and fruit juices into the PET matrix. Further evidence giving some indication of acetaldehyde migration from content into PET is shown the scatter plot in Figure 9.24. In the Figure residual acetaldehyde in carbonated drinks PET has been shown to strongly correlate with the acetaldehyde concentration in the contents ($r(6) = 0.895$; $p = 0.016$. $r^2 = 0.802$). However for unknown reason no statistically significant correlation could be observed between the residual acetaldehyde in fruit juice PET and the acetaldehyde concentration in the fruit juices.

9.16 Stability of acetaldehyde with storage

Even though acetaldehyde is generated from PET bottle materials into bottle content it has also been reported to degrade in water (Nijssen *et al*, 1996). To study the stability of acetaldehyde in water three acetaldehyde solutions (50, 500 and 5000μg/L) in boiled and unboiled water in polypropylene bottles were stored in a refrigerator (about 5°C) and at room temperature (Subsection 5.9.13). The expectation was that acetaldehyde loss due to degradation and evaporation will be higher for acetaldehyde solution in unboiled water and water stored at room temperature. This is because the volatility of acetaldehyde dissolved in water increases as temperature increases and acetaldehyde stability in water increases in the absence of oxygen which is flushed out during boiling. Also according to Matsuga *et al* (2006) microorganisms in unsterilized water can remove acetaldehyde from the water by degradation. The expected pattern in terms of acetaldehyde reduction with time is given below:

$$\underset{\text{Decreasing acetaldehyde concentration with time}}{\underset{\xrightarrow{\hspace{6em}}}{\text{BF} < \text{BO} < \text{NBF} < \text{NBO}}}$$

B stands for “boiled”, F stands for “stored in refrigerator”, NB stands for “not boiled” and O stands for “stored at room temperature”.

For acetaldehyde at 50μg/L the concentration reduced to below detection limit for all storage conditions after 4 days. This finding agrees with the findings of Nijssen *et al* (1996) where acetaldehyde concentration was reduced from 100μg/L to less than 1μg/L within 8 days of storage. The results for solutions with higher acetaldehyde concentrations are given in Figures 9.25 and 9.26. For all unboiled solutions and boiled solution stored in refrigerator acetaldehyde concentration reduced gradually with time. Additionally for these samples the observation agreed to some extent with the expected results. For 500μg/L solutions lowest concentration was recorded in unboiled samples stored at room temperature, followed by unboiled sample stored in refrigerator and then boiled sample stored in refrigerator. For 5000µg/L solutions lowest concentration was recorded in unboiled samples stored at room temperature. However the concentration is similar for unboiled sample stored in refrigerator and boiled sample stored in refrigerator.

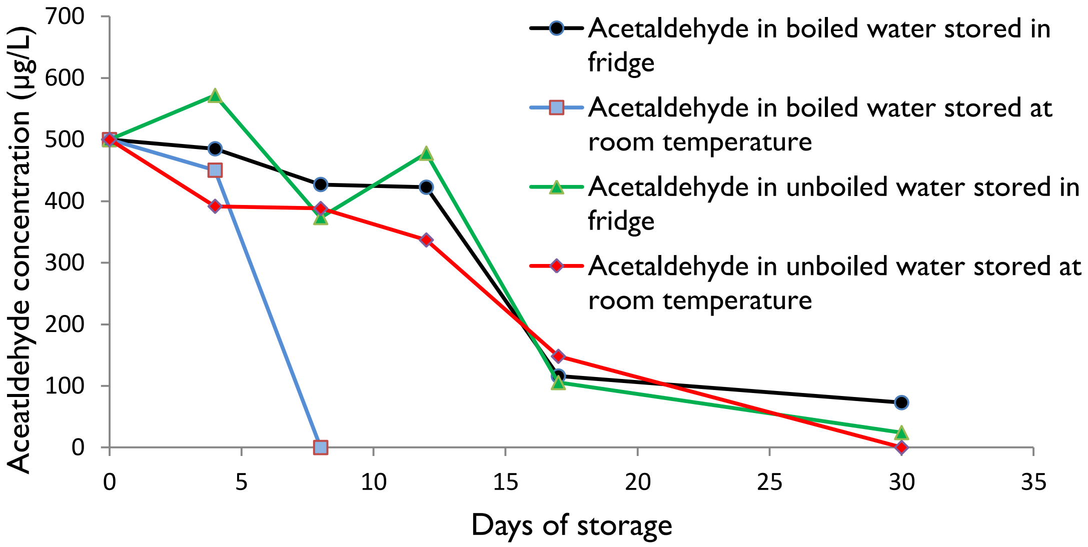

Figure 9.25 stability of 500µg/L aqueous acetaldehyde solution

At both concentrations (500 and 5000µg/L) boiled solutions stored at room temperature showed abrupt decrease in acetaldehyde. For these solutions the acetaldehyde concentrations reduced to levels below detection limit and 977.9µg/L after 8 and 12 days respectively. The reason why boiled samples stored at room temperature behaved in this manner remains a mystery. Nijssen *et al* (1996) earlier reported similar observation with glass bottles. According to these authors the rapid decrease in acetaldehyde in boiled water stored in glass bottles may be caused by the higher reactivity of the silicium oxides of the bottle wall. This is however not applicable to the observation in this research as polypropylene rather than glass bottles were used for the study. The observation may be related to greater solubility of oxygen in water than nitrogen. Due to the higher solubility of oxygen in water than nitrogen the ratio of oxygen to nitrogen is greater in water than the same ratio in air. As a result of boiling both oxygen and nitrogen are expelled from water. However as water cools the oxygen concentration rises faster than the less soluble nitrogen resulting in its transient higher concentration in proportion to nitrogen. Even though this should also happen in boiled samples stored in refrigerator, the rate of degradation may still be lower due to lower temperatures. The results of these experiments established that acetaldehyde concentration in water reduces if it is not been replenished.

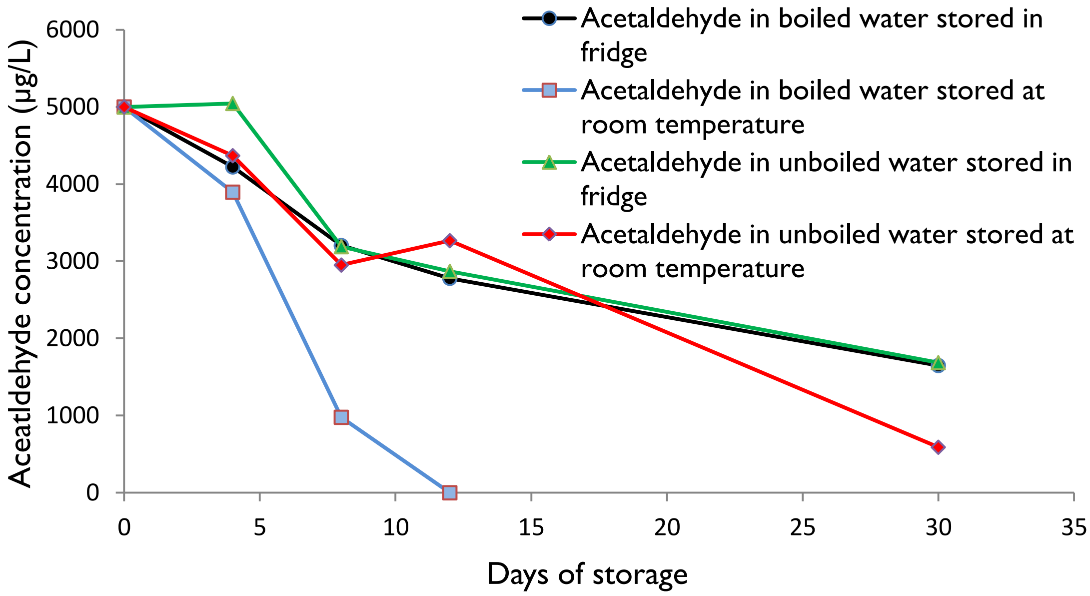

Figure 9.26 stability of 5000µg/L aqueous acetaldehyde solution

9.17 Summary

The concentration of residual acetaldehyde in PET bottle materials and the concentration of dissolved acetaldehyde in bottled water and soft drinks from Nigeria and Britain were determined. The influence of some parameters on the acetaldehyde concentration in PET materials and in bottle contents was also assessed. Accuracy and precision were good as recoveries were around 100% and coefficients of variation were less than 15% for all analysis types.

All Nigerian and British PET bottle materials contained residual acetaldehyde within the concentration range reported in the literature. The total average and the average for still water, sparkling water and soft drinks PET materials for British samples were 4.76, 4.10, 1.55 and 6.70 µg/g respectively. The average concentration for Nigerian soft drink PET materials was 2.17µg/g. Acetaldehyde concentration in PET material was found to decrease as the bottle material ages. The concentration was also established to be directly proportional to thickness of the bottle wall. Higher acetaldehyde concentration was observed in the thinner British still water bottles compared to the thicker sparkling water bottles. This observation was attributed to the sparkling water's greater ability to extract acetaldehyde from the bottle wall matrix than still water.

The average concentrations of acetaldehyde in fresh British fruit juices, carbonated soft drinks, sparkling water and still water were 5112.5, 1457.75, 21.8 and 7.84µg/L respectively. While acetaldehyde was detected in all fruit juices and carbonated drinks regardless of packaging, it was only detected in bottled water packaged in PET bottles. The average concentration in Nigerian still water and the concentration in a Nigerian carbonated cola drink are 8.21 and 176 µg/L respectively.

Acetaldehyde content of some soft drinks was found to be beyond the EU specific migration limit of acetaldehyde from PET bottles. The study also found that tolerable daily intake of acetaldehyde in human could be exceeded as a result of exclusive consumption of some fruit juices and carbonated soft drinks analysed. Additionally, the odour and taste threshold limit for acetaldehyde in bottled water has been exceeded in 5 out of 26 bottled water brands analysed. The presence of carbon dioxide in bottled water and soft drinks have no effect on acetaldehyde determination in those samples. Acetaldehyde concentration in bottled water showed an inverse proportionality to water conductivity. The concentration of acetaldehyde decreased in most British bottled water sample after storage for 20 months. Conversely an increase was observed in a Nigerian carbonated drink sample and most Nigerian still water sample after storage for 12 and 25 months.

Some empty bottles were established to have the ability to release acetaldehyde vapour continuously as was observed with a green sparkling water bottle. However a similar bottle aged for 266 days was not releasing acetaldehyde. Also two new still water bottles observed were not releasing acetaldehyde. It has also been ascertained that PET material do absorbs acetaldehyde when soaked in solution containing acetaldehyde at concentrations obtainable in soft drinks. Stability of acetaldehyde in water studies revealed that acetaldehyde dissolved in water diminishes with time even at low temperatures, so far as it is not been replenished.

9.18 Conclusion

In this Chapter acetaldehyde concentration in PET bottle materials and in bottle contents were analysed. From the results acetaldehyde concentration in bottled water is low and may only pose taste and odour problem to bottled water rather than been a safety concern. However acetaldehyde in soft drinks could pose safety problems as in some cases intake of acetaldehyde as a result of consumption of the soft drinks can exceed the tolerable daily intake of acetaldehyde in humans. Acetaldehyde concentration in water and in PET material has been shown to reduce with time. The decrease in acetaldehyde concentration in PET implies that aged PET bottles are safe for reuse.

CHAPTER 10: CONCLUSION AND FURTHER WORK

10.1 Introduction

This research aimed to assess the pattern and extent of antimony and acetaldehyde migration from British and Nigerian polyethylene terephthalate bottles into bottle contents under typical use and reuse conditions and to relate the migration patterns to current regulations and controls. This research aim was further subdivided into four objectives which were;

1. To examine the pattern and extent of bottled water and soft drink use and PET bottle reuse in Britain and Nigeria.
2. To assess the extent of antimony and acetaldehyde migration from PET into water and soft drinks under conditions representative of real use and reuse in Britain and Nigeria
3. Drawing on findings from 1 and 2, as well as existing regulations and controls to assess whether acceptable limits of chemicals in foods and water are being exceeded as a result of the chemical migrations
4. To generate recommendations about the extent to which existing regulations and controls might merit re-examination

The first objective was further divided into 3 sub-objectives namely;

i. To establish the pattern and extent of typical bottled water and soft drink use and PET bottle reuse including, the approximate proportion of individuals/ households using and reusing plastic bottles, bottled water and soft drinks storage periods prior to use, bottle sizes most often used and reused, bottle reuse periods, the number of bottles being used and reused by an individual or a household at any one time, etc.
ii. To determine public perceptions of the safety of reusing plastic containers to store drinking water, beverages, etc
iii. To find out factors influencing people's preferences with respect to reuse of plastic water containers

This Chapter reviews the steps taken through the entire research process, states how the approach in this research differed from the approaches in previous works, identifies the strengths and limitations associated with the research, and specifies the main findings of the research in relation to the objectives and the recommendations for action. The Chapter concludes by exploring potential areas for further research.

10.2 Main findings in relation to objectives

10.2.1 Survey on bottled water and soft drink use and PET bottle reuse

10.2.1.1 Pattern and extent of bottled water and soft drinks use and PET bottle reuse

British respondents use more bottled water and soft drinks than Nigerian respondents, however Nigerian respondents store unopened bottles for longer durations before use. An important implication of this observation is that attributes associated with consumption of bottled water and soft drinks will manifest differently in the two countries. For example risk of dental erosion, which has been associated with the consumption of soft drinks, may manifest more in Britain than in Nigeria. Conversely, the likelihood of exposure to chemicals migrating from bottle wall into contents may be more in Nigeria as a result of longer storage. Importantly, this study has established that storage of bottle contents prior to use, to periods beyond their "best before dates" is small in both countries. This also implies that for both countries the possibility of accumulation of chemicals beyond international standards is likely in only few cases where storage periods are extended.

Bottled water and soft drinks storage pattern in terms of storage places are similar in both countries. Unrefrigerated storage in the summer will not have much implication in Britain and other temperate countries in terms of temperature elevation of bottle content. In Nigeria where ambient temperature can approach 40°C, storage outside the refrigerator can result in the elevation of temperature of bottle contents. This issue can even be more interesting if North African and some Middle Eastern countries, which are usually hotter than Nigeria, are considered. As mentioned earlier elevation of temperature enhances leaching of chemicals from PET bottle wall into the contents.

In spite of the lack of information on bottle reuse in the literature the results in this study together with the earlier results from the US shows that PET bottle reuse is high and practised to the same extent in both developing and developed countries. These results are interesting in that reuse was initially hypothesised to be much higher in developing countries than in developed countries. This study showed that PET bottles are reused for longer periods in Nigeria than in Britain. A similar extent of reuse in both countries with longer reuse duration in Nigeria than in Britain is believed to be due to greater bottle availability in Britain. Reuse of a larger number of bottles for storage of drinking water in Nigerian places of residence than in British places of residence probably results from the lower availability of drinking tap water and lower consumption of bottled water in Nigeria.

10.2.1.2 Bottle reuse, safety perception and safety debate

Perception of bottle reuse as an unsafe practice by respondents from both countries gives some indication about the extent of this concern in both developing and developed countries. A small proportion of British respondents believe that cancer causing chemicals migrate from PET bottles into contents. The extent to which chemical migration risk is overstated by the media and internet is believed to have some influence on the bottle reuse safety perception observed in this study. The greater concern about chemical migration and risk of cancer from bottle reuse in Britain than in Nigeria could be connected to greater health/environmental awareness in Britain than in Nigeria. In particular greater access to internet is believed to play an important role.

The level of safety concern from both reusing and non-reusing respondents in both countries was found to be similar. The similar levels of safety concern imply that safety concern is not an important determinant of bottle reuse. It cannot be ascertained why the existence of this perception is not affecting the extent of bottle reuse.

10.2.1.3 Factors influencing bottle reuse

The most important factors this study identified as affecting bottle reuse are convenience associated with PET bottle reuse, saving money, concern for environment, bottle age and original use of bottle. Economic status and climate for a country did not show significant relationship with the proportion of people reusing PET bottles; however these two factors may have some influence on reuse duration and also the number of bottles being reused in households. For British respondents the single most important motivation for reusing bottle is the desire to preserve the integrity of the environment followed by the need to save money. For the Nigerian respondents convenience associated with reuse of PET bottle was the most important motivating factor followed by the need to save money. The emergence of environmental concern as the most important factor influencing reuse in Britain is a reflection of greater global environmental awareness in developed countries than in developing countries.

10.2.2 Antimony and acetaldehyde in PET and their migration into bottle content

The second objective assesses the extent of antimony and acetaldehyde migration from PET into water and soft drinks under typical use and reuse conditions. The concentration of antimony and acetaldehyde in PET and other materials related to bottling was initially assessed. This is because antimony and acetaldehyde can only migrate into contents if they are present in the PET materials. This was followed by assessment of their concentrations in freshly purchased bottled water and soft drinks samples to establish baseline concentrations for fresh samples. Migration was assessed under typical use and reuse conditions and also under some extreme conditions.

In this study only the bottle material in the form of PET was found to contain antimony in quantities that could leach into the bottle contents. Plastic bottle caps and cap liners were eliminated as source of antimony that can migrate into bottle content. Bottle caps and cap liners were not expected to contain antimony as they are not manufactured using antimony catalyst. All Nigerian and British PET bottle materials contained antimony within the concentration range reported by industry sources confirming the use of antimony catalyst in their synthesis rather than germanium, titanium, cobalt, manganese, magnesium or zinc-based catalysts. Antimony was found in some soft drinks bottled in glass; however, antimony content in glass materials was not quantified.

Antimony was detected in all fresh soft drinks and bottled water samples. The antimony concentration in fresh soft drinks samples was higher than in bottled water. This difference is in large part believed to be due to presence of antimony in the constituent materials used for making soft drinks. Bottled water and soft drinks with higher conductivity tend to have higher concentrations of antimony, however little or no relationship exists between pH and antimony concentration in freshly purchased samples. But lower pH values (acidic) appeared to be associated with higher antimony concentration in storage experiments. Concentrations of the trace elements investigated (Cd, Ge, Zn, Al, Be, Ti, Co and Pb) were higher in soft drinks than in bottled water and tap water. Similarly concentrations of all the elements except antimony were higher in glass bottled contents than in PET bottled contents. High levels of titanium were detected in soft drinks from both countries. Titanium is believed to be in the soft drinks as a result of its usage as food additive.

An increase in antimony concentration with time was observed in storage experiments in PET bottles. Similarly, increase in antimony concentration was observed in temperature exposure experiments in PET bottles. Glass bottles demonstrated much lower release of antimony in comparison to PET bottles. Release of lead was observed from a Nigerian glass bottle. Antimony migration into water was found to be directly proportional to the antimony concentration in PET and to bottle thickness for some exposure conditions. Aged bottles leach lower amounts of antimony than new. Similarly larger bottles leach lower amount of antimony than smaller bottles.

Glass materials and plastics other than PET identified in this study were not expected to release acetaldehyde. However, none of these materials were analysed for acetaldehyde. All Nigerian and British PET bottle materials contained residual acetaldehyde within the concentration range reported in the literature. Acetaldehyde concentration in PET material was found to decrease as the bottle material ages. A phenomenon explaining this was observed in the form of acetaldehyde outgassing from some PET bottles. The concentration in PET materials was also established to be directly proportional to thickness of the bottle wall. Higher acetaldehyde concentrations were observed in the thinner British still water bottles compared to the thicker sparkling water bottles. This observation was attributed to the sparkling water's greater ability to extract acetaldehyde from the bottle wall matrix than still water. Higher acetaldehyde concentrations were found in soft drinks PET materials than in other PET materials. It was suspected and confirmed that soft drink PET materials absorbs acetaldehyde from the soft drinks. The implication of this finding is that PET materials from soft drinks and fruit juices cannot be used to assess actual residual acetaldehyde in PET since the materials could absorbed as much acetaldehyde from their contents as the residual acetaldehyde contained in them.

Acetaldehyde was detected in all fruit juices and carbonated drinks regardless of packaging type. However acetaldehyde was detected only in bottled water packaged in PET bottles. Concentration of acetaldehyde in soft drinks was so high that it could only be attributed to the use of acetaldehyde as flavouring agents in the soft drinks. Acetaldehyde concentration in bottled water decreases with increase of water conductivity.

The concentration of acetaldehyde decreased in most British bottled water sample after storage for 20 months. Conversely an increase was observed in a Nigerian carbonated drink sample and most Nigerian still water sample after storage for 12 and 25 months. Studies of the stability acetaldehyde in water revealed that the concentration of acetaldehyde dissolved in water diminishes with time even at low temperatures, if acetaldehyde is not been added from another source.

As mentioned earlier the most important concern in bottle reuse is the safety of the bottles with regard to release of chemicals into contents. This study has confirmed that age of bottle decreases the concentration of antimony and acetaldehyde in bottle wall and their leachability from the bottle wall into the content. This is attributed to depletion of the migrants in the bottle wall matrix as a result of migration.

10.2.3 Migration in relationship to usage pattern and existing regulations

This component of the objective seeks to draw on from findings from the first and second objective, existing regulations on chemical migration and literature to assess whether acceptable limits of chemicals in foods and water are being exceeded as a result of the chemical migrations.

10.2.3.1 Antimony and other trace elements in fresh samples

The EU maximum admissible concentration for antimony is 5µg/L (European Commission, 2003; EPA, 2010). The EU specific migration limit (SML) for antimony from PET into foods is 40µg/kg of food (EFSA, 2004). Since one litre of water weighs approximately one kilogram (Lide, 1990), the SML for water can be presented as 40µg/L. Detectable levels of antimony were found in tap water and all the 47 freshly purchased British bottled water and soft drinks samples analysed. However the concentration exceeded the EU maximum admissible concentration only in one fruit juice sample from a PET bottle. The concentration found in the fruit juice was 6.6µg/L. Concentrations were below the EU SML in all samples. The concentrations of lead, cadmium and beryllium are also all within the EU MAC and/or US MCL. Guidelines and standards for cobalt, titanium, germanium and zinc in drinking-water have not been established. In the US secondary non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects in drinking water covers zinc and aluminium. The concentration of zinc in all the samples falls within the US MCL. The concentration of aluminium in two freshly purchased British soft drinks is however greater than the British MAC.

10.2.3.2 Antimony in samples exposed to different conditions

Concentration of antimony in some Nigerian bottled water and soft drinks was above the EU MAC after 11 months of storage at room temperature. For 10 British bottled water samples the concentration remained below the EU MAC even after 19 months of storage. A Nigerian glass bottle for soft drink leached both antimony and lead above EU MAC after 11 months. Lead concentration in the contents of the same glass bottle was above EU MAC after 2 months of storage. However 2 British glass bottles subjected to antimony migration test at elevated temperatures demonstrated low level of antimony and lead migration. Antimony concentrations in water exposed at 40, 60 and 80°C for up to 48 hours in PET and glass bottles remained below the EU specific migration limit for antimony from plastic materials and other articles intended to come in contact with food. At realistic temperatures of 40 and 60°C antimony concentration in the water remained below the EU MAC even after 48 hours of exposure but the concentration exceeded the EU MAC for most exposures at 80°C.

10.2.3.3 Acetaldehyde in fresh samples

In the absence of guidelines and standards for acetaldehyde in drinking-water, acetaldehyde in bottled water and soft drinks was evaluated based on the EU specific migration limit (SML) for acetaldehyde from packaging into foods (6000µg/kg), tolerable daily intake of acetaldehyde (0.1mg/kg body weight per day) and odour and taste threshold limits for acetaldehyde in drinking water. For water and soft drinks the SML for acetaldehyde can be approximated to 6000µg/L given that one litre of water at 4°C weighs 1kg. In this study the concentration of acetaldehyde found in 5 soft drinks samples was beyond the EU SML. An important question worth asking is on the significance of the acetaldehyde EU SML considering the fact that acetaldehyde can be added as flavouring agent in soft drinks at concentration greater than the SML. If the 2.96 litre of water taken by an adult on daily basis is assumed to be totally in the form of soft drinks then the tolerable daily intake of acetaldehyde will be exceeded as a result of intake of 2 out of 9 carbonated soft drinks and 8 out of 15 fruit juices investigated in this study. If only half of the daily intake comes in the form of the soft drinks the tolerable daily intake of acetaldehyde will be exceeded as a result of intake of only 5 out of the 15 fruit juices investigated in this study. The odour and taste threshold limit for acetaldehyde in bottled water is reported to be 20–40 µg/L (Nijssen *et al*, 1996; Schröder, 2001). From this it can be seen that the lower level of the threshold value was exceeded in 5 out of 26 bottled water brands analysed.

10.2.3.4 Acetaldehyde in samples exposed to different conditions

The concentration acetaldehyde decreased in most British bottled water sample after storage for 20 months. An increase was observed in a Nigerian carbonated drink sample and most Nigerian still water sample after storage for 12 and 25 months. Importantly while the concentrations generally lie within the odour and taste threshold limit for British sparkling water the concentration failed to reach the odour and taste threshold limit in British still water and in all Nigerian water samples. Acetaldehyde concentration increased by 586% in the fresh Nigerian cola drink after storage period of 12 months. However the concentration still failed to reach the EU SML for acetaldehyde. Acetaldehyde could increase in bottled water and soft drinks with storage. Nevertheless, based on the residual acetaldehyde found in PET in this study and in the literature and also the level of migration observed, acetaldehyde increase in bottled contents will not reach concentrations at which tolerable daily intake of acetaldehyde can be exceeded as a result of consumption of the bottled contents. For bottled water the observed increase is only of importance in terms of the acetaldehyde odour and taste threshold limit in water.

10.2.4 Re-examination of existing regulations and controls

The fourth objective explores the extent to which existing regulations and controls might merit re-examination. Acetaldehyde associated with alcoholic beverages (derived from the alcoholic beverages and from their metabolism in the body) has been concluded to be carcinogenic to humans (Group 1) in a recent IARC review of human carcinogens. In this study acetaldehyde has been identified in soft drinks at concentrations higher than the European Union specific migration limit for acetaldehyde from food packaging materials into foods and that the tolerable daily intake of acetaldehyde could be exceeded as a result of intake of some soft drinks.

Consequently the absence of international guidelines for acetaldehyde in water and foods is in need of reassessment.

10.3 Other findings

In addition to addressing the primary objectives of the research, the research has other findings which were not anticipated.

10.3.1 Use of PVC as cap liner in Nigeria

The characterisation of materials associated with bottling is a secondary issue not initially targeted by the research. However as the research involves working with all bottle materials having contact with bottle contents it became worthwhile to characterize them. The characterisation exercise has revealed useful information relating to use of different materials in bottling in the two countries of interest. The characterisation has revealed the use of EVA/PP copolymer and plasticised PVC as bottle cap lining material for glass bottles by the same multinational bottling company in Britain and Nigeria respectively. While EVA/PP has not been associated with any health risk, plasticised PVC is a plastic material associated with health risk issue.

10.3.2 New PET digestion method

In the course of determination of antimony in PET and other bottling materials a new simpler method of PET material digestion was developed. The developed method has the potential to make the procedure for determination of antimony simpler and cheaper because the procedure requires a microwave oven for household use rather than purpose-built laboratory microwave digestion system.

10.3.3 Material minimization in PET bottle manufacture

The research has revealed the use of bottles with thinner walls in Britain than in Nigeria. The minimization of bottle wall thickness translate into utilisation of fewer raw materials to make bottles and generation of less waste associated with bottled water and soft drinks. Thicker bottle walls in Nigeria may also facilitate the longer re-use periods associated with this country.

10.3.4 Elevation of water temperature on sunny summer day

The research has shown the temperature elevation pattern in bottle contents exposed to sunlight and the maximum temperatures that could be attained by bottle contents on exposing bottles with the contents to brilliant sunlight on a British summer day. As mentioned earlier migration of chemicals from bottles into contents is directly associated with temperature.

10.4 Implication of results

10.4.1 Plasticized PVC cap linings in Nigeria

The ban on the use of 6 phthalates including DEHP at concentrations greater than 0.1% by mass in the manufacture of plastic toys and childcare article, the consideration of a bill in the State of California in the US for banning of use of PVC in consumer packaging and the efforts to eliminate PVC from products and packaging by major corporations is a clear indication of potential for harm associated with use of PVC (usually made up of 30 – 40% plasticizers), especially in consumer packaging. As said earlier phthalates were reported to be associated with allergies in children, decrease in anogenital distance among male infants exposed before birth, inducement of less male typical play behaviour in boys and other manifestations related to mimicry of human hormones. In developing countries like Nigeria regulations guiding the use of materials in packaging may either be non-existent or where they exist enforcement may be poor. In many situations local and multinational companies, which are profit-oriented organisations, exploit the situation to use materials that have potential to cause harm in consumers. The use of PVC cap lining in Nigeria but not in Britain by the same multinational company is believed to be one of such situations where the poor enforcement of safety regulations is being exploited. The National Agency for Food and Drug Administration and Control (NAFDAC) is the Nigerian agency vested with the task of safeguarding public health by ensuring that only the right quality drugs, food and other regulated products are manufactured, imported, exported, advertised, distributed, sold and used. The PVC cap lining issue in Nigeria will need to be investigated by NAFDAC and appropriate actions need to be taken.

10.4.2 Antimony and other trace elements in bottled water and soft drinks

The detection of antimony and the other trace elements in all freshly purchased British bottled water samples at concentrations below the regulatory limits corroborate on the safety of the water brands for use as drinking water with regard to antimony and the other trace elements investigated. The same cannot be said of freshly purchased Nigerian samples as these were not analysed. Antimony in freshly purchased fruit juice has been found to exceed the regulatory standards in this works and in earlier works. The worrisome aspect of this finding is that the high concentrations were found in freshly purchased samples. By implications if these samples are to be allowed to stay longer in the bottles, especially in the tropical countries like Nigeria where ambient temperatures are generally high, the antimony concentrations will be even higher as a result of migration. Findings like these raise questions about the effectiveness of monitoring activities by the agencies in charge of food safety. Actions need to be taken to ensure that antimony in fruit juices and other bottled products remain within the regulatory standard from bottling to consumption for the purpose of safeguarding the health of consumers.

The detection of titanium at a concentration approaching two parts per million in soft drinks is not necessarily alarming considering the fact titanium dioxide is an approved substance for use as food additive in water-based flavoured drinks and other foods. However as titanium dioxide dust, taken into the body by inhalation, has recently been reclassified by the International Agency for Research on Cancer (IARC) from Group 3 (not classifiable as to its carcinogenicity to humans) to Group 2B (possibly carcinogenic to humans), the use of titanium dioxide as food additive will need greater scrutiny in future.

Elevation of antimony and lead content to levels above the regulatory limit after long term storage of bottled water and soft drinks in PET and glass is not a serious issue since most of these bottled water and soft drinks are not typically stored for long periods before consumption in both Britain and Nigeria. However the elevation of lead to concentration above the EU MAC in a Nigerian soft drink brand after 2 months of storage in refillable glass bottle (most likely reused several times for bottling) will need greater scrutiny from the regulatory authorities. Reuse of refillable glass bottle for soft drink bottling is an environment-friendly behaviour. So the most important issue here is not the reuse of the glass bottle but the chemical composition of the bottle. NAFDAC in Nigeria needs to act to ensure that refillable glass bottles used in bottling do not contain high levels of lead or other chemical substances that can cause harm to consumers through migration into contents.

The antimony migration behaviour of the new and aged PET bottles studied at the realistic temperatures of 40 and 60°C demonstrated the safety of using the bottles with regard to antimony migration at the said temperatures. This is good news considering the fact that drinking water being purified by SODIS in tropical developing countries has not been reported to heat up above 60°C. Consequently treating drinking water by SODIS in bottles will not elevate the antimony concentration to levels above the regulatory limits even for bottles reused over a long period of time. As explained earlier SODIS is a low-cost drinking water disinfection technology with a great potential to improve the health of people without access to safe drinking water. Even though exposure of water or soft drinks in PET bottle at temperature of 80°C is associated with release of antimony several times above the accepted limit, this exposure situation is not typically encountered. The likelihood of encountering this situation become even lower considering the fact that at such temperatures deformation in bottle shape can start to manifest as the result of the elevated temperature. However in developing countries like Nigeria where PET bottle is reused in very many ways exposure at 80°C can still not be completely ruled out. So for situations like this the regulatory authority needs to inform the people reusing bottles to be aware of the risk associated with reusing the bottles at such high temperatures.

10.4.3 Acetaldehyde in bottled water and soft drinks

Acetaldehyde was found in freshly purchased bottled water in PET bottles but not in glass bottles. However the concentration was so low that it is only relevant to odour and taste of the bottled water rather than to the safety of consumption of the water. Acetaldehyde concentration in some freshly purchased soft drinks exceeded the EU specific migration limit for acetaldehyde from food packaging material into packaged food (6mg/kg). The SML was established based on the tolerable daily intake level of 0.1mg/kg. Maintaining the concentration of acetaldehyde below the SML is meant to assure that exposure remains under the Tolerable Daily Intake. For the sake of safety this study recommends that the amount of acetaldehyde that can be added to soft drinks as flavouring agent should be below the specific migration limit (SML) for migration of acetaldehyde from PET bottle into bottle contents. For the purpose of preventing the acetaldehyde concentration from going above the odour and taste threshold limit in sparkling water in PET bottles, bottles with low acetaldehyde contents should be used for bottling sparkling water since sparkling water has greater ability to extract acetaldehyde than still water.

10.5 Research strengths and limitations

Unlike previous studies in the field of chemical leaching from water and soft drinks containers this research attempted to approach the problem by exploring and linking the two different but complementary aspects of the problem namely, the pattern and extent of bottle use and reuse and the chemical migration, which to appreciable extent depends on the former. Fusion of the two aspects conferred some uniqueness to the research in allowing the problem of migration to be visualised from the perspective of the actual bottle handling. For example the research has found that single PET bottles are reused for as long as one year but that bottles subjected to actual reuse condition for as long as a year release less antimony and acetaldehyde than new bottles. In other words reused bottles are safer to use than new bottles. As advantageous as this approach may be it is still associated with some difficulties. For example the two aspects of the research belong to two different fields (social science and physical science) with different skills requirement on the side of the researcher and also different supervision requirements.

As in all research works some issues were encountered that affected the achievement of some of the objectives in this research. Some of these limitations are discussed below

- The survey, which was meant to reveal the pattern and extent of bottled water and soft drink use and PET bottle reuse in the general population, considered university environments only, as that was the most feasible strategy to adopt. Surveying the general population, even though more challenging would have provided truer information on the general population.
- Due to practical issues, the survey was only piloted in a UK context. Had a pilot been conducted in Nigeria, apparently inaccurate reporting of bottle sizes might have been avoided (see section 6.4 and 6.11).
- In spite of the importance of determining the concentration of the analytes of interest in freshly purchased samples, the concentration of antimony could not be determined from freshly purchased Nigerian samples due to sample storage and instrument availability limitations.
- The research aimed to determine the concentration of antimony in both bottling materials and in bottle contents. However antimony content in glass

bottle materials was not measured as the methods used in this research were not designed to quantify antimony in glass. Quantifying antimony in glass bottle materials would have been useful in that antimony has been reported to be used as fining agent in the manufacture of bottle material and in this research it has been found in similar quantities in some soft drink brands bottled in both glass and PET.

- The best way to assess the migration of both antimony and acetaldehyde with time is to measure them in a freshly purchased sample and then measure them in the same sample after desired storage period. This research assessed migration with time by concurrently measuring the migrating chemicals in a sample stored for a desired storage period and in a fresh sample. The method involving one-sample could not be used due to instrument availability limitations. While the two-sample method can reveal chemical migration, it is not as reliable as the method using single samples as some differences could arise in samples of different batch.

10.6 Further work

While this research attempted to address the questions in the research objectives, other question have arisen as a result of the research work. The most important of these question are listed here as a basis for future work

- In Nigeria the water packaged in plastic pouches accounts for 68 percent of total commercial water and is consumed by the low-income group as stated in the literature review. This type of packaged water was not fully investigated in this study because the plastic packaging for the water is not PET plastic. Notwithstanding studies will be needed to see how the consumption of this type of water affects the extent of use of bottled water in Nigeria.
- Antimony and acetaldehyde in freshly purchased soft drink samples evidently originate from both migration from bottle walls and from the soft drinks themselves, their ingredients or the processes associated with their of production. A study will be needed to ascertain the origin of these chemicals in soft drinks to see whether the manufacturing processes used and/or the ingredients will need to be reviewed.

- In this study outgassing of acetaldehyde was observed in some empty bottled water PET bottles but not in others. This observation was believed to be related to the presence of sparkling water in bottles. However, since only three bottles were observed, the reason behind the observed outgassing could not be ascertained with certainty. It will be worthwhile to investigate this previously unreported phenomenon.
- In this study an increase of 586% in the acetaldehyde concentration was observed after storage of a cola drink for a period of 12 months. Özlem (2008) has reported a similar observation. However both in this work and in the work of Özlem (2008) the acetaldehyde increase could not be accounted for from the migration of the residual acetaldehyde in PET material. In other words migration of all the residual acetaldehyde in the PET material could not elevate the level of acetaldehyde to the concentrations observed. Studies are needed to ascertain the source of this increase, i.e. whether it is as a result of degradation of some components in the soft drinks or from the degradation of the PET material.
- For the sake of standardisation studies comparing the different methods available for determination of antimony and residual acetaldehyde in PET will need to be carried out. These studies will reveal whether the methods have similar effectiveness. For determination of antimony the microwave digestion-ICP-MS carried out in this study will need to be compared with laser ablation-ICP-MS, Instrumental Neutron Activation Analysis and energy dispersive X-ray fluorescence spectroscopy. For determination of acetaldehyde the headspace-GC-FID used in this study can be compared with the methods described by Bashir *et al* (2002) and the method described by Matsuga *et al* (2005) which Involved simultaneous dissolution of PET in trifluoroacetic acid and derivatization of the acetaldehyde content with 2,4-dinitrophenylhydrazine followed by precipitation, solvent extraction with dichloromethane, evaporation, reconstitution in acetonitrile and analysis by HPLC. The method of Bashir (2002) is similar to the method used in this study. The two differ in that rather than introducing the PET material directly into the headspace vial, in the method of Bashir (2002) the PET is cooled in liquid nitrogen and ground.
- Because glass bottles were not the main interest in this study, only few were assessed for chemical migration. Considering the finding made in this study with

regards to migration of antimony and lead from some glass bottles, and the fact that antimony and arsenic are in some cases used as fining agent in glass manufactures, glass bottles from different countries will need to be investigated for migration of antimony, lead and arsenic. A further justification for a research like this lies in the fact that in Nigeria use of refillable glass bottles is very common in the soft drink bottling industry. Among other issue a research like this will need to investigate is the relationship between the age and frequency of refill of a bottle and migration of chemicals.

- The phthalate plasticizer in the Nigerian PVC cap lining was not characterised in this study. Chromatographic studies to characterise the plasticizer are worth carrying out. Studies assessing the extent to which the plasticizer can migrate into the soft drinks are also worthwhile.

Overall, this investigation has pushed forward knowledge about how PET bottles are used in practice and the implications this has for exposure to migrant chemicals leaching from bottle walls.

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Appendix I Survey questions

RESEARCH SURVEY

Preamble: I am a researcher looking on how **clear plastic bottles** are **used** and **reused**. **Clear plastic bottles** are the bottles used for bottling water and many soft drinks.

1. Do you drink water or drinks bottled in **clear plastic bottles**?

Still water	Yes ○	No ○
Sparkling water	Yes ○	No ○
Bottled drinks	Yes ○	No ○

If you do not drink bottled water or bottled drinks in clear plastic bottles proceed to question 11

Unopened bottled water/bottled drinks in clear plastic bottles

2. How many **unopened** bottles containing bottled water and/or drinks do you have presently at your residence? If you do not have any bottle put *None*. If you do not know put *Don't know*.

Still water ______ Sparkling water_______ Bottled drinks_______

If you do not have unopened clear plastic bottles at your residence proceed to question 7

3. What size(s) are the **unopened** bottles? (250ml, 500ml, 750ml, 1L, 2L, 3L, *don't know, etc*)

Still water ________ Sparkling water__________ Bottled drinks__________

4. For how long are the **unopened** bottles in your possession? ___________________

5. What was the longest time an **unopened** bottle remained unopened in your possession? ________

6. Where are the **unopened** bottles stored? ___________________________

Opened bottled water/bottled drinks in clear plastic bottles (original content)

7. How many **opened** bottles containing bottled water and/or drinks do you have presently at your residence? If you do not have any bottle put *None*. If you do not know put *Don't know*.

Still water ______ Sparkling water_______ Bottled drinks_______

If you do not have opened bottled water or bottled drinks at your residence proceed to question 11

8. What size(s) are the **opened** bottles? (250ml, 500ml, 750ml, 1L, 2L, 3L, *don't know, etc*)

Still water _________ Sparkling water_________ Bottled drinks__________

9. Where are the **opened** bottles stored in winter? ___________ In summer? ______________

Please turn over

Appendix I Survey questions (continued from page 210)

10. What was the longest time an opened bottle lasted before the content was used up? If you do not know put *Don't know* ____________________

Clear plastic bottles filled with drinking water (from tap, etc) or other drinks (Bottle reuse)

11. Do you **reuse** empty clear plastic bottles to store drinking water or other drinks at you residence?
Yes ○ No ○ If yes how many bottles are you **reusing** at present? _________

If you are not reusing clear plastic bottles to store drinking water or other drinks at your residence proceed to question 15

12. A single empty plastic bottle may be **reused** repeatedly to store drinking water or other drinks. Approximately how many times have you refilled the clear plastic bottle(s) you are presently **reusing** in your residence? _________________

13. For approximately how long have you **reused** the bottle(s) you are currently using for the purpose of storing drinking water or other drinks? _____________________

14. What are the sizes of the bottle(s) you **reuse** for storing drinking water or other drinks? (250ml, 500ml, 750ml, 1L, 2L, 3L, *etc*) _____________________

15. Do you **reuse** clear plastic bottle(s) to store drinking water while on the move? Yes ○No ○

16. Do you **reuse** clear plastic bottle(s) to store drinking water while at work? Yes ○ No ○

17. If yes to question 15 and/or 16, for how long have you **reused** the bottle(s) you are currently using for the purpose of storing drinking water or other drinks
at work? _____________. while on the move?_____________.

18. Have you ever chosen not to consume water or drinks stored in a **reused clear plastic bottle** because you think it is unsafe? Yes ○ No ○

19. If yes to question 18, in what way do you think it is unsafe? _________________________

20. Apart from safety, are there other factors that have influenced your choices about **reusing** clear plastic bottle? Yes ○ No ○ If yes list them____

21. Country of origin ________________

22. Gender _________________

23. Age: 19 and below ○ 20-29 ○ 30-39○ 40-49 ○ 50-59○ 60+○

24. Status: Member of staff ○ undergraduate ○ MSc student ○ Research student○ other student ○

Appendix 2 Acetaldehyde intake from soft drinks

Sample	Acetaldehyde concentration (μg/L)	Acetaldehyde in 2.96 litres of sample	Mean weight of male adult	daily intake (mg/kg)*	daily intake (mg/kg)**
UPC37	3116.48	9.22	86.1	0.11	0.05
UPC38	9902.19	29.31	86.1	0.34	0.17
UPC39	395.05	1.17	86.1	0.01	0.01
UPC30	4952.19	14.66	86.1	0.17	0.09
UPC33	330.76	0.98	86.1	0.01	0.01
UPC40	14247.43	42.17	86.1	0.49	0.24
UPC32	7145.05	21.15	86.1	0.25	0.12
UPC41	3330.76	9.86	86.1	0.11	0.06
UCC42	383.14	1.13	86.1	0.01	0.01
UCC43	12516.48	37.05	86.1	0.43	0.22
UGC34	187.9	0.56	86.1	0.01	0.00
UGC36	1683.14	4.98	86.1	0.06	0.03
UGC31	2152.19	6.37	86.1	0.07	0.04
UOC35	2095.05	6.20	86.1	0.07	0.04
UPC40	14249.81	42.18	86.1	0.49	0.24
UPC22	311.71	0.92	86.1	0.01	0.01
UPC24	4752.19	14.07	86.1	0.16	0.08
UPC25	1397.43	4.14	86.1	0.05	0.02
UPC26	597.43	1.77	86.1	0.02	0.01
UPC23	1930.76	5.72	86.1	0.07	0.03
UGC22	109.33	0.32	86.1	0.00	0.00
UGC23	3142.67	9.30	86.1	0.11	0.05
UGC26	599.81	1.78	86.1	0.02	0.01
UGC27	278.38	0.82	86.1	0.01	0.00

*if all water intake is in the form of soft drinks

**if half of water intake is in the form of soft drink the other half as water