Chapter 1

INTRODUCTION

1.1 Introduction

Plastics have become a part of life today. There is no sphere of human activity in which plastics have not made their entry, ranging from agriculture, chemical industry, packaging, space exploration or even for off-shore drilling. One of the most popular plastic materials is Polyethylene Terephthalate (PET). It can be used in many applications, especially for food packaging, bottled water and soft drinks (ILSI Europe Report Series, 2000). The increase use of PET in daily life raises an important question of contaminations by the migrants of PET into these food and drinks.

1.1.1 Polyethylene Terephthalate

Polyethylene Terephthalate (PET) is a plastic material which has found increasing applications within the packaging field, especially for bottling gaseous drinks and mineral waters. Moreover, PET containers are now finding even wider applications as packaging for beers, wines, spirits and edible foods, as food trays for use in conventional and microwave ovens (Monarca, 1994).

PET is a kind of polyester material, a linear thermoplastic consists of repeating units (Figure 1).

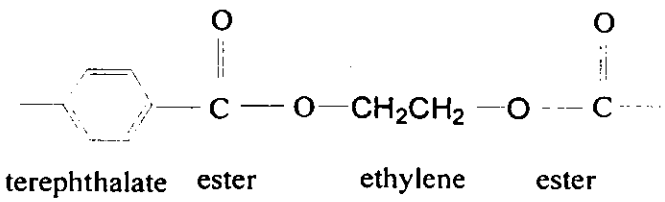

Figure 1 Polyethylene Terephthalate monomer

PET (sometime PETE) is formed from the intermediates, pure terephthalic acid (PTA) and ethylene glycol (EG) (Figure 2).

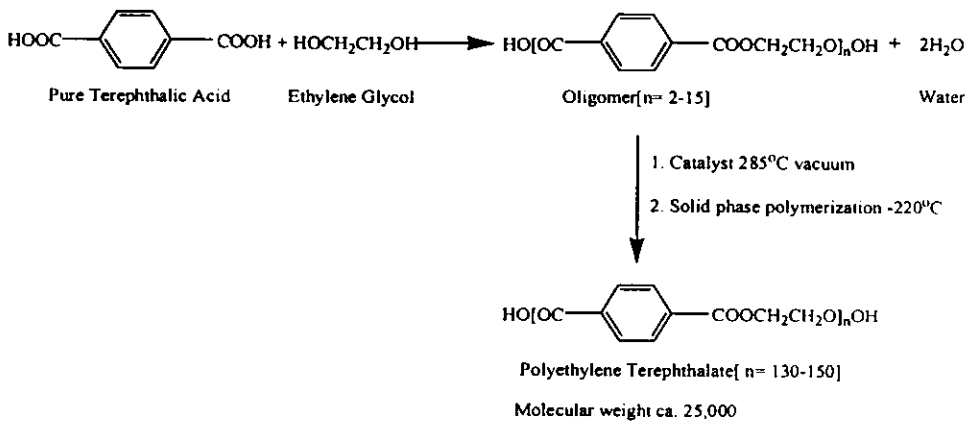

Figure 2 Chemistry of PET formation

The main reasons for its popularity are the properties of glass-like transparency coupled with adequate gas barrier properties for retention of carbonation. It also exhibits a high toughness: weight property ratio which allows light weight, large capacity, safe, unbreakable containers. Its chemical inertness, together with other physical properties, has made it particularly suitable for food packaging applications (ILSI Europe Report Series, 2000). The three major packaging applications of PET are as containers (bottles, jars and tubs), semi-rigid sheet for thermoforming (trays and blisters) and thin oriented films (bags and snack food wrappers).

PET bottles and jars are manufactured by the process of injection stretch blow moulding (Figure 3), a process developed specifically to maximize the beneficial properties of PET. Selection of the optimum blowing temperature is vital to achieve the best balance of properties. Impact resistance, transparency, stiffness, gas barrier properties and creep are all optimized during this part of the operation (ILSI Europe Report Series, 2000).

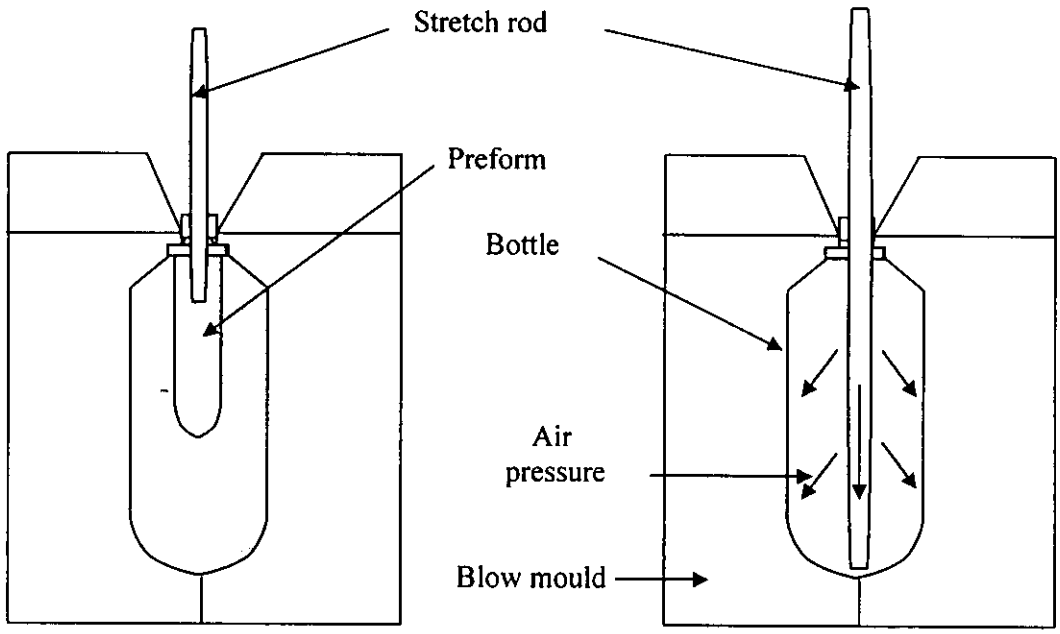

Figure 3 Stretch blow moulding of a PET bottle (ILSI Europe Report Series, 2000)

During the high temperature processing of PET, *e.g.* injection moulding, when the shearing is too high, degradation reaction generate by products, which can leach out, either by evaporation if they are volatile, or by diffusion into the liquid content after bottling (ILSI Europe Report Series, 2000). A total of 19 migrants from commercial amber PET bottle wall have been identified by gas chromatograph equipped with mass selective detector (GC/ MS) analysis. The majority of compounds appeared to be intermediate reaction products or residual monomers of their dehydration and transesterification products. Fatty acid and commonly used plasticizer were also identified (Kim, 1990).

Among the volatile products, acetaldehyde (CH_3CHO) is the most dominant. It is formed during thermal degradation of PET, when the polymer is molten, that is, from thermochemical reactions (Figure 4). Acetaldehyde is able to migrate from the PET polymer into liquid media. Using a static headspace gas chromatographic method, acetaldehyde was found in carbonate mineral water and lemonade, ranged between 1.1 and 7.5 mg L^{-1}, while the contents of acetaldehyde in the PET packages

ranged from 1.1 to 3.8 μg g^{-1} (Linssen, 1995). Acetaldehyde was also identified in tap water and commercial mineral water in Japan ranged between non detectable and 260 μg L^{-1}, by head space gas chromatography mass spectrometry (Sugana, 2000).

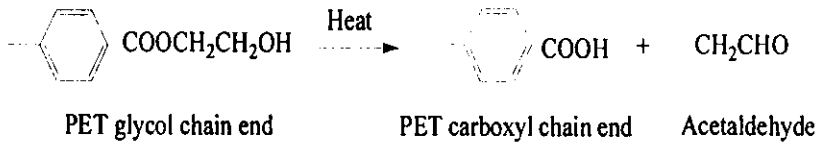

Figure 4 Acetaldehyde formation

Migration of acetaldehyde from PET depended on the temperature. At 40 °C, it reached a constant level after 4 days which was about 10% of the residual value of acetaldehyde (6.3 mg kg^{-1}) and at 60 °C this level was raised up to 50 % (Eberhartlinger, 1990).

Since high level of acetaldehyde can add to or change the taste of foods (ILSI Europe Report Series, 2000), and is a probable human carcinogen (EPA, 1987), therefore, it is very important to control the amount of acetaldehyde from PET uses in food packaging. The presence of acetaldehyde in foods from the use of plastic packaging has been regulated internationally for many years. In 1998, the EU SCF (European Scientific Committee for Food) specified a Tolerable Daily Intake (TDI) for acetaldehyde of 0.1 g kg^{-1} body weight, equivalent to a migration limit for acetaldehyde of 6 mg kg^{-1} bottle weight (EU SCF, 1998).

1.1.2 Acetaldehyde

Acetaldehyde is a simple, naturally occurring organic chemical found in many ripe fruits, *e.g.* apples, grapes and citrus fruits (up to 230 ppm). It is produced during fermentation of sugar to alcohol and is a natural constituent of butter, olives, frozen vegetables and cheese. It forms in wine and other alcoholic beverages after exposure to air (up to 140 ppm). It even occurs as an intermediate in the decomposition of sugars in body, hence, can be found as traces in blood. Acetaldehyde is listed as an approved additive and is used to enhance citrus flavors helping to create natural, fruity tastes and fragrances (Furia and Crosby, 1980). As a flavor ingredient it can be found

in ice creams, sweets, baked goods, chocolates, rum and wine (ILSI Europe Report Series, 2000).

Acetaldehyde is a colorless, volatile liquid with a pungent suffocating odor with a reported odor thredshold at 0.09 mg m^{-3}. It is a highly flammable and reactive compound that is miscible in water and most common solvents (EHC 167, 1995 and OSHA, 1988). Its vapor is an irritant of eyes, nose, and throat. Inhalation of high concentrations may cause drowsiness, dizziness, and unconsciousness. Ingestion of acetaldehyde may cause drowsiness, dizziness, unconsciousness, kidney damage, and respiratory problems. The onset of respiratory symptoms may be delayed. Eye contact with acetaldehyde may cause erythema and burns. Repeated skin contact may result in dermatitis which can be caused either by primary irritation by sensitization (NIOSH/ OSHA, 1981)

The International Agency for Research on Cancer (IARC) reports that acetaldehyde is an animal teratogen, mutagen, and carcinogen. IARC also reports that there is inadequate evidence of carcinogenicity of acetaldehyde to humans. IARC states that in the absence of adequate human data, it is reasonable to treat chemicals for which sufficient evidence of animal carcinogenicity exists as if they were carcinogenic to humans (IARC, 1984).

Analytical methods are available for the detection of acetaldehyde in air (including breath and water). The principal method is based on the reaction of acetaldehyde with 2, 4-dinitrophenylhydrazine and subsequent analysis of the hydrazone derivatives by high pressure liquid chromatography or gas chromatography (EHC 167, 1995).

Levels of acetaldehyde in ambient air are generally averaged at 5 $\mu g\ m^{-3}$ and in water are generally less than 0.1 $\mu g\ L^{-1}$. Analysis of a wide range of foodstuffs in the Netherlands showed that the concentrations, are generally less than 1 mg kg^{-1}, and are occasionally ranged up to several 100 mg kg^{-1}, particularly in some fruit juices and vinegar (EHC 167, 1995).

Acetaldehyde also comes out during thermal degradation of PET in bottle processing and can migrate and change the taste of foods and drinks (ILSI Europe Report Series, 2000), therefore, it is necessary to control the amount of acetaldehyde from PET uses in food packaging. A conventional technique uses to analyze

acetaldehyde residue in PET bottle is a 24-hour airspace gas chromatography equipped with flame ionization detector (Airspace acetaldehyde test, 1999). However, in the softdrink industry at presence, the high demand of the market makes it necessary to fill the soft drinks only a few hours after the bottles were blown. Thus, an alternative, more rapid technique is needed for the analysis.

This work focused on the development of sample preparation of acetaldehyde residue analysis in PET bottle using gas chromatography equipped with flame ionization detector that used consuming less time than the conventional technique.

1.1.3 Background

1.1.3.1 Acetaldehyde

Chemical formula:	C_2H_4O
Chemical structure:	CH_3-CHO
Common name:	acetaldehyde
Common synonyms:	ethanal; acetic aldehyde; acetylaldehyde; ethylaldehyde; diethylacetal; 1,1-diethyoxy ethane

1.1.3.2 Physical and chemical properties of acetaldehyde

Physical and chemical properties of acetaldehyde are shown in Table1.

Table 1 Physical and chemical properties of acetaldehyde (Hagemeyer, 1978 and IPCS/CEC, 1990).

Physical property	Acetaldehyde property
Color	Colorless
Relative molecular weight	44.1
Boiling point at 101.3 kPa	20.2 °C
Melting point	-123.5 °C
Octanol/ water partition coefficient as log P_{ow}	0.63
Flash point, closed cup	-38 °C
Autoignition temperature	185-193 °C
Explosion limit of mixture with air	4.5-60.5 vol% acetaldehyde
Vapor press at -50 °C	2.5 kPa
0 °C	44.0 kPa
20.16 °C	101.3 kPa
Specific gravity(20/4)	0.778
Relative vapor density	1.52
Refractive index 20/D	1.33
Dissociation constant at 0 °C, K_a	7.0×10^{-15}
Solubility	miscible in water and most common solvents

1.1.3.3 Conversion factors

1 mg acetaldehyde m^{-3} air = 0.56 ppm at 25°C and 101.3 kPa (760 mmHg)

1 ppm = 1.8 mg acetaldehyde m^{-3} air

1.2 Literature reviews

Acetaldehyde has been identified in different matrix such as air, blood, tissue, water and food, *e.g.*, beverage, breast milk, beer and wine. In air, acetaldehyde is formed in the atmosphere in a variety of ways. It is generated by oxidation of non-methane hydrocarbons (Grosjean, 1982), oxidation of alcohol, by products of fermentation (IARC, 1985), waste disposal from petroleum refining, coal processing, production of incomplete combustion of plastics and polycarbonate and polyurethane foams (US EPA, 1975, Hagen, 1967 and Boettner *et al.*, 1973).

The determination of acetaldehyde in air was mostly based on the reaction of acetaldehyde with 2, 4-dinitro-phenylhydrazine (2, 4-DNPH) and the subsequent analysis of the hydrazone derivatives to gas chromatography equipped with different detector such as flame thermal detector (FTD), flame ionization detector (FID), or High Performance Liquid Chromatography (HPLC) with spectrophotometric detection.

Jarke *et al.* (1981) investigated the amount of acetaldehyde in air by collecting the analyte in a tube containing thermal stable organic polymer based on 2, 6-diphenyl-*p*-phenylene oxide and analyzed with HPLC. The lower detection limit was 0.9 $\mu g\ m^{-3}$ and only used 2 L of sample. This method was suitable for analysis of indoor and outdoor air. For automobile exhaust analysis Lipari and Swarin (1982) collected the sample in a midget impinger containing 2, 4-DNPH in acetonitrile with perchloric acid as catalyst. The collected acetaldehyde was analyzed using HPLC with spectrophotometric detection. However, this system provided higher (18 $\mu g\ m^{-3}$) detection limit than the previous one. Aoyama and Yashiro (1983) decreased the detection limit to 0.09 – 0.45 $\mu g\ m^{-3}$ using silica gel treated with 2, 4-DNPH to adsorb acetaldehyde that was subsequently detected by a GC-FTD. This analysis was suitable not only for automobile exhaust but also smog.

In addition to the above collecting materials, depended on the sampling site, time and level of acetaldehyde, acetaldehyde in air was also collected by 2, 4 DNPH coated Sep- Pak cartridge, acidified with HCl (Tejada, 1986), 2, 4- DNPH coated on Chromosorb P (Binding *et at*, 1986), annular denuders coated with 2, 4-DNPH (Possanzini *et al.*, 1987), and midget bubblers containing Girard T solution (US NIOSH, 1987). These were all subsequently analyzed by HPLC with

spectrophotometric detection. Among these the lowest detection limit was 32 mg m^{-3} (US NIOSH, 1987). An improvement in detection limits (0.1 μg L^{-1} and 12 ng per cartridge) was obtained by Watanabe (1988) using Chromosorb 104 tube with GC-FID and Grosjean (1991) using the DNPH-coated on $C^{-1}8$ cartridge with HPLC-UV detection.

Acetaldehyde can also be detected in blood and tissue, of a person that has consumed alcoholic beverage. These beverages contain ethanol which is metabolized to acetaldehyde by alcohol dehydrogenase (ADH) (IARC, 1988). Determination of acetaldehyde in blood was mostly focused on the improvement of sample preparation to give a good detection limit and less interference from other proteins. Eriksson *et al.* (1982) reduced artificial formation of acetaldehyde in blood by precipitated protein with perchloric acid before analyzed acetaldehyde by GC headspace analysis. The detection limit of this work was 4.4 μg per 100 μl sample. Pezzoli *et al.* (1984) and Di Padova *et al.* (1986) tried to reduce the detection limit by adding butyraldehyde as an internal standard to blood. First, the sample was deproteinized followed by derivatization with 2,4-DNPH, extraction of derivative compound and analysis using HPLC-UV detection. Using these techniques, the detection limit could be obtained at 4.4 ng per 2 mL sample (Pezzoli *et al.*, 1984) and 0.9 ng per 0.5 mL sample (Di Padova *et al.*, 1986).

In 1987, Peterson and Polizzi designed an experiment suitable for clinical use by liquid-liquid extraction for separation of acetaldehyde in plasma and haemolysate then analyzed the extractant using HPLC with fluorescence detection. The sample size for the analysis was 1 mL plasma or red blood cell haemolysate. In the same year Ung- Chhun and Collins (1987) designed a microassay with negligible interference that could reduce the sample size to 50 – 100 μl using reaction of blood with 1, 3-cyclo-hexanone in the presence of ammonium ion and propionaldehyde as internal standard. In another method Miyake *et al.* (1998) investigated acetaldehyde in blood by reacting blood sample with cysteamine, extracted the derivative with dichloromethane and subsequently analyzed by gas chromatography with fuse silica capillary column and nitrogen- phosphorus detector. The quantities of acetaldehyde found in blood ranged from 2.04 μmol mL^{-1} to 14.8 μmol mL^{-1} with the lower detection limit of acetaldehyde 7.1 pg mL^{-1}. Lynch *et al.* (1983) determine

acetaldehyde in both blood and tissue by the reaction of blood and methanolic solution of 2, 4- DNPH and dinitrophenyl-[^{14}C]-formaldehyde as an internal standard. Acetaldehyde adduct was identified using HPLC and confirmed by GC- MS. This method was suitable for assessment of aldehyde levels in clinical and experimental studies of ethanol metabolism and alcoholic beverage with low detection limit (4.4 μg L^{-1}) and small sample size (1 mL of blood and 1 g of tissue).

In water, acetaldehyde is a by product from the interaction of aqueous free chlorine and/or ozone with natural organic matter in water (Cancho, 2001). Acetaldehyde contamination can also be from the migration of component of plastics container which come out during moulding process (Monarca, 1994 and Nawrocki, 2002). This source can cause contamination in food uses plastic packaging. Acetaldehyde in beverage, beer and wine can also come from oxidation of alcohol.

For natural water, acetaldehyde level should be very low because it has a high vapor pressure and some transfering to air from water and soil can be expected (EHC 167, 1995). However, there were some works that determined the volatile organic compounds (Spingarn *et al.*, 1982) and carbonyl compounds (Facchini *et al.*, 1986) in water sample which could be detected small amount of acetaldehyde.

In drinking and mineral water, acetaldehyde has been identified. Sugana *et al.* (2000) analyzed aldehydes in both tap and commercial mineral water in Japan using headspace GC-MS with high sensitivity. Acetaldehyde concentration ranged from non detectable to 260 μg L^{-1} was found. While Cancho *et al.* (2001) used pentafluorobenzylhydroxylamine derivatization and solid phase micro-extraction for aldehydes analysis in drinking water where acetaldehyde concentration was found to be 0.8 μg L^{-1}. In Poland, acetaldehyde in bottled water was identified using *0*- (2, 3, 4, 5, 6 – pentafluorobenzyl) hydroxylamine (PFBOA) derivatization coupled with gas chromatograph equipped with electron capture detector (Nawrocki *et al.*, 2002). The concentration was found to be more than 100 μg L^{-1}.

Acetaldehyde has also been detected in a variety of foods (US NRC, 1981, 1985; Horvath *et al.*, 1983; Feron *et al.*, 1991), though few quantitative data are available. Acetaldehyde concentration in foods, including fruits, juices, vegetables, milk products, bread, eggs, fish, meat, and alcoholic beverages, were generally less than 1 mg kg^{-1}, but occasionally ranged up to several hundred mg kg^{-1}, particularly in

some fruit juices and alcoholic beverages. In vinegar, a maximum value of 1060 mg kg^{-1} was reported (Maarse and Visscher, 1992). For slurry food samples, Priego-Lopez *et al.* (2002) used pervaporation to remove volatile species (acetaldehyde and acetone) from the sample such as yogurt, actimel and different kind of juices where acetaldehyde was found ranged from 3 - 9 $\mu g\ L^{-1}$.

In alcoholic beverages, such as beer and wine, acetaldehyde has also been identified (Okamoto *et al.*, 1981; Piendl *et al.*, 1981; Jones *et al.*, 1986). Levels in 18 English beers ranged from 2.6 to 13.5 mg L^{-1} (Delcour *et al.*, 1982). Levels of 0.2 to 1.2 mg L^{-1} were found in wine samples in Japan (Okamato *et al.*, 1981), while Margeri *et al.* (1984) reported levels of acetaldehyde in wines ranging between about 30 and 80 $\mu g\ L^{-1}$.

Acetaldehyde has also been found in carbonate mineral water and lemonade in PET bottle ranged between 1.1 and 7.5 mg L^{-1}, while the contents of acetaldehyde in PET packages ranged from 1.1 to 3.8 $\mu g\ g^{-1}$(Linssen *et al.*, 1995). To investigate the migration of acetaldehyde into soft drinks at different temperature, Eberhartlinger *et al.* (1990) studied the migration from PET at 40 °C and 60 °C. At 40 °C acetaldehyde reached a constant level after 4 days which was about 10% of the residual value of acetaldehyde (6.3 mg kg^{-1}). At 60 °C this level was raised up to 50 %. In this work the bottle was cut into pieces and melted in order to studying the migration. Another technique for acetaldehyde in PET bottle analysing was a 24-hour airspace analysis (Airspace acetaldehyde test, 1999). This technique needed 24 hours to allow the migration of acetaldehyde from PET bottle wall into the bottle then analyzed the gas sample in the bottle using GC-FID. The technique has many advantages such as simple, no solvent is needed and no decomposition of the sample. However, it needs a long sample preparation time (24 hours) and is not suitable for the present bottled industry where the bottles are filled only a few hours after they are made.

1.3 Objective

The objective of this work was to develop an appropriate sample preparation technique and investigated the qualitative and quantitative analysis of acetaldehyde residue in PET bottle using gas chromatography-Flame ionization detector (GC-FID). This was then applied for a quantitative analysis of acetaldehyde that migrated from Non Refillable PET bottles.