Review

Contamination in food from packaging material

Oi-Wah Lau[a,*], Siu-Kay Wong[b]

[a]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong*
[b]*Government Laboratory, Homantin Government Offices, Kowloon, Hong Kong*

Abstract

Packaging has become an indispensible element in the food manufacturing process, and different types of additives, such as antioxidants, stabilizers, lubricants, anti-static and anti-blocking agents, have also been developed to improve the performance of polymeric packaging materials. Recently the packaging has been found to represent a source of contamination itself through the migration of substances from the packaging into food. Various analytical methods have been developed to analyze the migrants in the foodstuff, and migration evaluation procedures based on theoretical prediction of migration from plastic food contact material were also introduced recently. In this paper, the regulatory control, analytical methodology, factors affecting the migration and migration evaluation are reviewed. © 2000 Elsevier Science B.V. All rights reserved.

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Contents

*Corresponding author. Fax: +852-26-035-315.
E-mail address: oiwahlau@cuhk.edu.hk (O.-W. Lau).

1. Introduction

Packaging makes food more convenient and gives the food greater safety assurance from microorganisms, biological and chemical changes such that the packaged foods can enjoy a longer shelf life. As a result, packaging became an indispensable element in the food manufacturing process. In order to meet the huge demand of the food industry, there was a remarkable growth in the development of food packaging in the past decades. Now, more than 30 different plastics are being used as packaging materials. Also, different types of additives, such as antioxidants, stabilizers, lubricants, anti-static and anti-blocking agents, have been developed to improve the performance either during processing and fabrication or in use of these polymeric packaging materials. Nevertheless, concern about the wholesomeness and safety of foods has increased dramatically recently. Most concern usually focuses on food additives, both those added intentionally to the foods and those ending up in the food from the packaging material or processing equipment. In the area of packaging material, plasticiser migration from food contact materials into food had raised many concerns in communities since the early eighties. This was attributed to the demonstrated carcinogenic effect in rodents and potential estogenic effect in humans as revealed by toxicology studies of several commonly used plasticisers [1,2]. Such incidence indicated that the packaging could itself represent a source of contamination through the migration of substances from the packaging material into food. Hence, regulatory authorities around the world have recognized that it is necessary to control such contamination, and many have enacted extensive legislation. On the other hand, a large amount of research regarding the migration of volatiles, additives, monomers, and oligomers from plastic packaging materials into food were conducted. However, analysis of the migrant in the foodstuff or simulant can be very expensive and time-consuming because of the low concentrations of migrated substances found in the foodstuff and the complexity of the food matrix. In an effort to overcome these difficulties, new migration evaluation procedures based on theoretical prediction of migration from plastic food contact material were introduced recently. In this paper, the regulatory control, analytical methodology, factors affecting the migration and finally, the migration evaluation are reviewed.

2. Regulatory control

In order to protect consumers from the migration of harmful substances from packaging to foodstuff, CEC (Commission of the European Communities) Directives have been implemented for plastics packaging materials within the European Communities. The first relevant CEC Directive was issued in 1976 on the approximation of the laws of the Member States related to the subject [3]. Apart from harmonized legislation, the directives proposed analytical test methods to enable limits in the Directives to be respected. In 1980, the Commission Directive laid down the first Community method of analysis for the official control of vinyl chloride monomer level in food packaging materials [4]. In general, the Directives introduced limits upon the overall migration from plastics into food and food simulants. In addition, specific migration limits or composition limits for free monomers in the final article have been set for some monomers [5]. Currently, the limit

for overall migration was set at 10 μg/dm^2 or 60 mg/kg of food simulant. It also includes the lists of permitted monomers together with the restrictions which apply to specific monomers.

In the USA, the structure of the regulations for food packaging material is much more complex. The regulations encompass both the basic polymer resins used in food packaging and the adjuvants, which are added to a polymer in the process of manufacturing the final food package. Regulations frequently contain specifications for the resin, such as residual monomer content. In addition, limits are sometimes placed on specific migration. More often, the regulations for polymeric resins limit global migration from the packaging. The time/temperature/solvent conditions for the short-term extraction tests used to test compliance are also spelled out in the regulation [6]. Furthermore, in the Federal Register of 17 July 1995, the US Food and Drugs Administration (FDA) established a 'threshold of regulation' process. This process was proposed for determining when the extent of migration to food is trivial that safety concerns would be negligible. Based on this regulation, pre-market approval by FDA is currently required for food packaging materials to be used in the USA [7].

However, food packaging has not received much attention within the Codex Alimentarius Commission supported by the Food and Agriculture Organization of the United Nations and the World Health Organization. In the Codex Alimentarius, it specifies that packaging should not transmit to the food product substances beyond the limits acceptable to the official agency having jurisdiction. The Codex Alimentarius contains guide-line levels for vinyl chloride monomer and acrylonitrile in food [8].

3. Analytical methodology

Analytical methods are important because they are the keys in studying the migration of packaging components from the package or food-contacting material into the food. They are also required by regulatory agencies who are responsible for ensuring public safety by monitoring foods for excessive and potentially harmful levels of contaminants from the packaging. Furthermore, methodology is required to establish databases to evaluate changing residue levels as well as to calculate dietary intakes. Indeed, in the literature, most of the related analytical work was reported with one of the following objectives:

(a) to identify the potential migrants or contaminants in the food contact packaging materials and access their toxicological potency,

(b) to determine levels of residual monomers or additives in food contact materials and in foods with which they had been in contact,

(c) to identify the factors affecting the migration of contaminants from the packaging into foodstuff, and

(d) to estimate the maximum likely intake of the contaminants resulting from the food contact usage.

The analytical procedures typically involve sample preparation, extraction, cleanup and a final determination step. Some of the commonly used analytical methods that have been applied to determine different types of packaging migrants, grouped as plastic additives, monomers and oligomers and contaminants, are discussed as follows.

3.1. Additives in polymeric packaging

In order to improve the performance either during processing and fabrication or in use of the polymeric packaging materials, a wide variety of additives were developed and used. Additives such as plasticisers, antioxidants, light stabilizers, thermal stabilizers, lubricants, anti-static agents and slip additives are all commonly encountered in various types of polymeric packaging materials.

3.1.1. Plasticisers
Among the additives used to modify the properties of polymeric packaging materials, the plasticisers had raised much concern in the communities from the hygienic point of view. Butyl stearate, acetyltributyl citrate, alkyl sebacates and adipates are types of plasticisers commonly used with low toxicity. However, restrictions had been brought on the use of phthalate plasticisers due to its potential carcinogenic and estogenic effect as revealed in some toxicological studies [2,9]. Recently, it was also reported that phthalates might impair human fertility [10]. As a response, the EC Scientific Committee for

Food (SCF) had established tolerable daily intakes (TDIs) for the phthalates [11]. Survey on the occurrence of phthalate esters and other types of plasticisers in a large variety of packaging and food had also been conducted in the UK, Canada and Hong Kong [12–15].

In order to provide a highly specific gas chromatographic detection of plasticisers of phthalates, adipates, sebacates and acetyltributyl citrate in the presence of complex food matrix, the technique of stable isotope dilution gas chromatography–mass spectrometry was proposed [16–23], where deuterated or ^{13}C-labelled analogues of the migration species are employed as internal standards. As both labeled and unlabeled components behave identically thereafter and thus, during subsequent extraction and cleanup from the foodstuff, the internal standard will compensate throughout for recovery losses. Normally, a size-exclusion chromatography (SEC) clean-up step using the Bio-Beads SX3 was required to remove lipid matrix in fatty food prior to GC–MS determination [24]. The unlabeled analyte and the internal standard co-elute in one GC peak, but because of their mass difference they can be separately and simultaneously measured (Fig. 1). For example, adipates and phthalates were determined by monitoring m/z 139 and 149 respectively, while also monitoring m/z 143 and 153 for deuterated ($[^2H_4]$) adipates and phthalates respectively. The quadruple in use in the above analysis was the most commonly used type of mass spectrometer. However, Lau and Wong reported that the precision and sensitivity in the determination of plasticisers in foods could be improved by employing ion trap type of mass spectrometer [25]. Sweep co-distillation clean-up procedure, a new sample pre-treatment technique, was employed for the phthalates analysis in fatty food [26]. This technique has been used exclusively for the clean-up of fat samples for pesticide residue analysis [27]. Kondyli et al. reported an indirect method for the study of the migration of phthalates and adipates from poly(vinylchloride) (PVC) films into ground meat. The ester plasticisers were determined indirectly after extraction, saponification and quantitation of their alcoholic constituents using gas chromatography [28].

3.1.2. Thermal stabilizers

Apart from plasticisers, thermal stabilizers are the most abundantly used additive in plastics. Generally, epoxidized seed and vegetable oils such as soybean oil (ESBO) are widely used in a range of food-contact plastics heat stabilizers, lubricants and plasticisers as well. Materials such as poly(vinyl chloride), poly(vinylidene)chloride and polystryrene frequently contain epoxidized oils at levels ranging from 0.1 to 27% [29]. Their toxicity is affected by their purity since the residual ethylene oxide is quite toxic. In pure epoxidized oils, the toxicity decreases with increasing molecular mass (i.e. with decreasing solubility) [30].

Different from phthalates or adipates, direct isotope dilution GC–MS analysis of ESBO is not feasible due to its polydisperse nature and low volatility, however, ESBO analysis is possible based on the degradation of the triglyceride to its constituent fatty acid components using ^{13}C-labelled epoxidized triolein as internal standard [31,32]. Transmethylation under basic conditions converts the triglyceride to its component fatty acid esters. These fatty acid methyl esters are derivatized to form 1,3-dioxolanes [33], which are then amenable to direct GC–MS analysis. Analysis was conducted by monitoring m/z 396 and 367 for the dioxolane derivative of methyl epoxy-stearate, while also monitoring m/z 397 and 368 for the ^{13}C-labelled internal standard. This method has sensitivity and precision similar to other isotope dilution procedures. However, Han et al. recently proposed a simple gas chromatographic method for the detection of ESBO in packaging materials, where EBSO was first extracted with toluene. The toluene extract was then shaken with 25% (w/w) tetramethylammonium hydroxide in methanol for 10 min, water was added and the toluene layer dried with anhydrous sodium sulphate. The methyl esters of mono-, di- and triepoxyoctadecanoic acid produced were determined with a wall-coated open tubular (WCOT) Ultimetal HT SimDist CB column (5 m×0.5 mm I.D.) with a 0.15 μm film of stationary phase and operated with temperature programming from 100 to 240°C at 10°C/min. Helium was used as carrier gas and the analytes were detected with flame ionization detection (FID) [34].

3.1.3. Slip additives

Fatty acid amides are used as slip additives in a variety of plastics used for packaging, such as
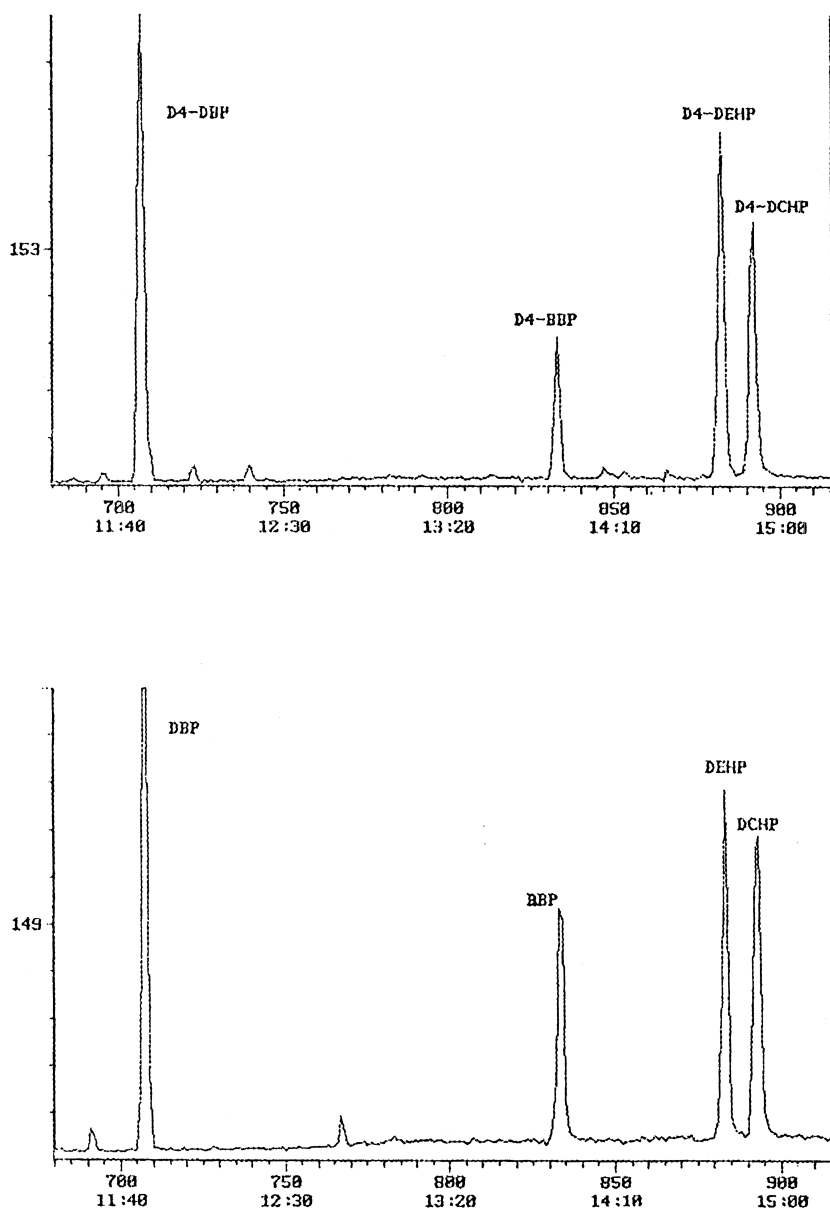
Fig. 1. GC–MS Spectrum of phthalates (scan of m/z 149) and their deuterated analogues (scan of m/z 153) (from Ref. [25]).

polyolefins, polystyrene and polyvinyl chloride. Slip additives are added to plastic formulations where they gradually tend to bloom to the surface imparting useful properties including lubrication, prevention of films sticking together, and reduction of static charge. Although the toxicological data of this type of compound have yet to be collected, migration

studies on them from plastics into fatty food simulants had been conducted. For the determination of fatty acid amides, such as oleamide, stearamide, erucamide, stearyl erucamide and oleyl palmitamide, solvent extracts were pumped through Sep-Pak cartridge and the eluent discarded. The analytes were then eluted with acetone and the solvent evaporated.

The residues were reconstituted in propan-2-ol, and the analytes were finally quantified by capillary gas chromatography with FID [35].

3.1.4. Light stabilizers

Light stabilizers are used to improve the long term weathering characteristic of plastics, especially polyolefins. Polymeric hindered amines (HALS), such as Tinuvin 622 and Chimasorb 944, are commonly used in polyolefins as light stabilisers. The determination method involves dissolution of the polyolefin, followed by precipitation and extraction with sulphuric acid to separate the cycloaliphatic nitrogen-containing HALS from other additives such as antioxidants and lubricants. The extracts are then qualitatively and quantitatively determined by pyrolysis gas chromatography. It was observed that not only the polymeric, but also the monomeric HALS gave characteristic pyrolysis patterns [36].

3.1.5. Antioxidants

Under the exposure of UV light and in the presence of air, polymer may undergo degradation through oxidation mechanism. To slow down such oxidation process, antioxidants are added to stabilize the polymer by preferentially degrading themselves. A list of compounds commonly used for that purpose is shown in Table 1.

Generally, they are all efficient antioxidants. Hygienic acceptability of the substituted phenols had been assessed from their structures, and most of them were found to be non-toxic and have good stabilization effects. However, these arylsubstituted phosphites are considered as toxic [37]. Neverthe-

less, some of them are found in the positive lists of many countries, often accompanied by strict purity requirements. This is due to the trisubstituted derivative being much toxic than the mono- and disubstituted ones. Triphenyl phosphite can be included among highly toxic substances. For higher derivatives of mono- and dihydroxybenzophenones and the benzotriazoles, their toxicity is not high. However, they are still under the tests for possible genetic effects. Their uses as antioxidants in packaging materials are only allowed if the respective packaging material is not in contact with fat-containing foodstuffs.

Reversed-phase liquid chromatographic methods were widely used to determine antioxidants in polyolefins packaging materials [38–42]. However, more and more applications of supercritical fluid chromatographic (SFC) techniques were proposed for the analysis in the early nineties [43–45]. A comparison between HPLC and SFC methods for the determination of antioxidants and light stabilizers in packaging materials was also made [46]. Bücherl et al. proposed a rapid analytical method for the determination using SFE coupled with supercritical fluid extraction (SFE) and mass spectrometry. The idea of such coupling was to make use of the extraction and separation power of SFE–SFC for these antioxidants, which are thermolabile and have high molecular weights, and to combine with the powerful identification abilities of a mass spectrometer that can work over a wide mass range and with high resolution [47]. A SFE–SFC–MS system is displayed in Fig. 2, and a typical SFC–MS chromatogram of polyolefin is also shown in Fig. 3.

Table 1
List of compounds used as antioxidant in polymer

| Common name	Chemical name	M_r
Tinuvin P	2-(2′-Hydroxy-5′methyl-phenyl)benzotriazole	225
Tinuvin 326	2-(5-Chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methylphenol	315
Tinuvin 770 DF	Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	481
Tinuvin 234	2-[2-Hydroxy-3,5-bis(1-methyl-1-phenyl)phenyl]benzotriazole	447
Chimasorb 81	2-Hydroxy-4-*n*-octyloxybenzophenone	326
Irganox 1076	Octadecyl-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate	530
Irganox 1330	(1,3,5-Trimethyl-2,4,6-tris(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate	774
Irganox 1010	Pentaerythrityl-tetrakis-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate	1176
Irgafos 168	Tris-(2,4-di-*tert.*-butylphenyl) phosphite	646
Irgafos P-EPQ	Tetrakis(2,4-di-*tert.*-butylphenyl)-4,4′-biphenylene diphosphonite	1034
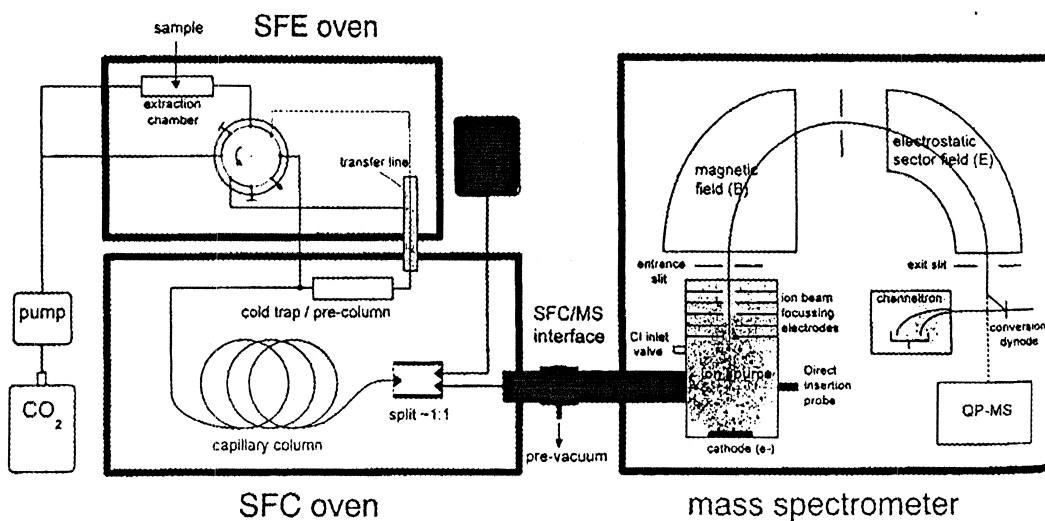
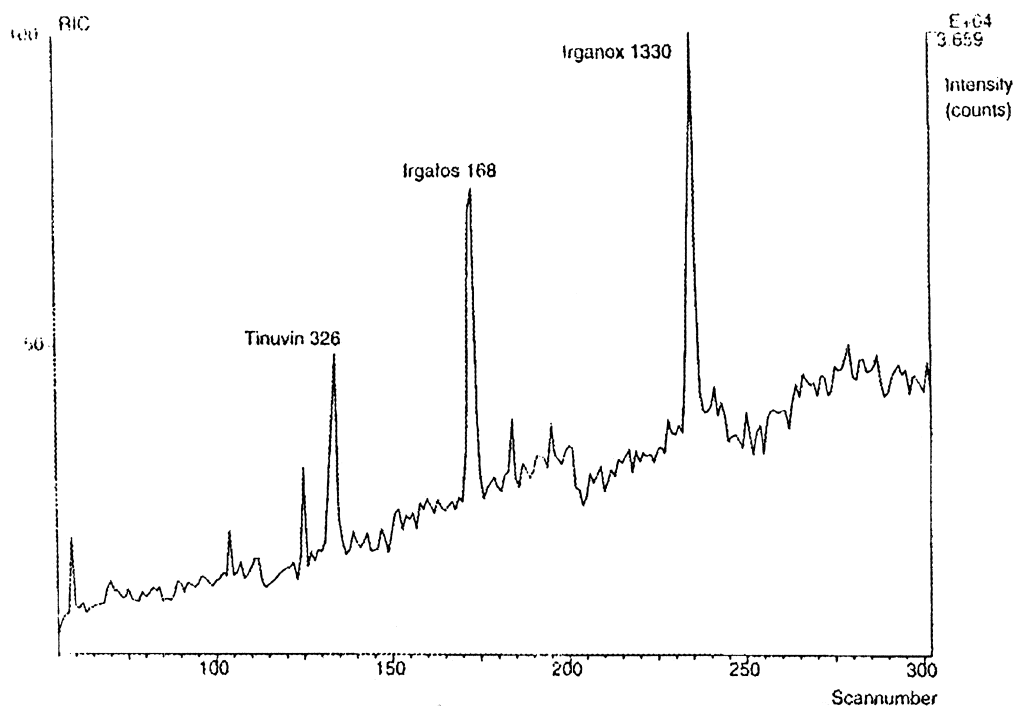Fig. 2. SFE–SFC–MS System (from Ref. [47]).

Fig. 3. Typical SFC–MS chromatogram of Polyolefin (from Ref. [47]).

3.2. Monomers and oligomers

Monomers are reactive substances, with respect to living organisms, and hence more or less toxic. Therefore, hygiene regulations usually restrict the content of residual monomers in the starting materials, plastics, and articles made thereof. Their toxicity and respective analytical methodology are being discussed as follows.

3.2.1. Styrene

Despite the acute toxicology of styrene is not high, its metabolism involves phenyloxirane, which is a mutagenic compound [48,49]. Further, styrene may effect sensory properties at very low levels: 200–500 ppb in yogurt, and 40–730 ppb in water [50,51]. Although reversed-phase liquid chromatographic method had been reported for the determination of styrene in foodstuff [52], headspace gas chromatographic method was the most widely used technique for the analysis so far [53–60]. Usually, the set-up was coupled with a purge and trap injector to improve the sensitivity of detection, and a mass spectrometry detector was employed to enhance the specificity of the analysis.

3.2.2. Vinyl chloride

Since vinyl chloride monomer is highly toxic [61,62], monomer levels in PVC food packaging material are closely controlled. Both the residual monomer content of the polymer and migration levels to foods or food simulants are also regulated [4,63]. Just as in the cases of styrene monomer, gas chromatographic headspace methods were widely used to determine the residual vinyl chloride in food packaging and foods [64–68]. Recently, a migration study on the vinyl chloride tetramers was also reported [69]. These oligomers do not share the RCH=CHCl structural features of the vinyl chloride monomer and therefore does not raise an immediate alert with respect to toxicity by analogy with the monomer. Nevertheless, as organochlorine compounds, the migration of these oligomers is still of interest. They were extracted from packaging materials and beverage with hexane followed by gas chromatographic determination with electron capture detection.

3.2.3. Bisphenol A diglycidyl ether

Epoxy resins of the bisphenol A type, such as Bisphenol A diglycidyl ether (BADGE), are the starting materials for cold-cured epoxy resins. The degree of toxicity of epoxy compounds depends mainly on the fractional concentration of unreacted epoxy groups. The epoxy compounds are alkylating agents and they have rather specific cytotoxic actions in tissues with high rates of cell division. Such epoxy resins are used in a great number of applications, e.g. as coatings on food cans and food storage vessels. Because of their toxicity, it is necessary to control the unreacted products to prevent their migration into food. Indeed, a survey of BADGE in canned foods has been conducted recently [70]. In the past decades, BADGE or related oligomers were mainly determined by liquid chromatography using UV detection [71]. However, fluorescence [72–74] or mass spectrometry [75,76] could provide a more sensitive and specific method for the detection of BADGE at very low levels.

3.2.4. Isocyanate

Within the food packaging industry, isocyanates are used in polyurethane polymers and adhesives. As isocyanates are considered as toxic compounds and their health effects are well-documented [77,78], their use in the manufacture of plastic materials and articles intended to come into contact with foods are regulated by EC Directive [5]. Residual levels in the finished plastics must not exceed 1.0 mg/kg expressed as –NCO. Twelve isocyanates are currently permitted for use in food-contact materials. Several methods have been published that detail the analysis of isocyanate in polyurethane prepolymer [79–82]. These methods rely on various derivatization reagents to improve chromatographic resolution and provide a convenient chromophore. The most successful derivatization reagent is 9-(methylaminomethyl)anthracene (MAMA), and the reaction scheme is shown in Fig. 4. The urea derivatives formed, which are fluorescent, are analyzed by reversed-phase LC with fluorescence detection.

3.2.5. Caprolactam

Polyamides, commonly known as 'nylons', are one type of food packaging material used to contain
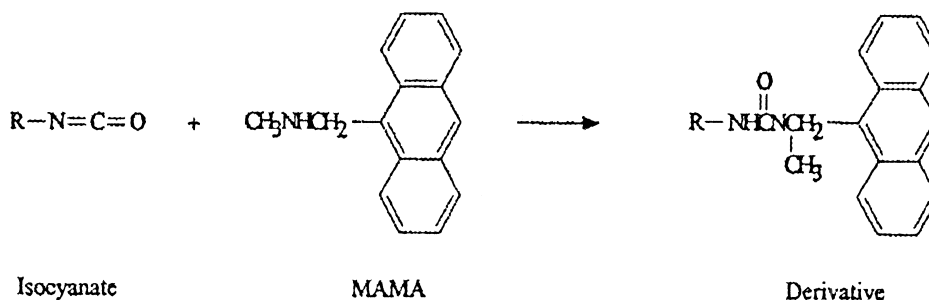
Fig. 4. Reaction scheme for the derivatization of isocyanates with 9-(methylaminomethyl) anthracene (MAMA) (from Ref. [82]).

food during cooking. There was evidence showing that relatively large amounts of nylon 6 oligomers and residual caprolactam, monomer of nylon, could migrate into boiling water [83]. Although caprolactam is not especially toxic on oral administration, it may cause minor protracted effect on thermo-regulation and disagreeable bitter taste in foods [84].

Residual oligomers and caprolactam in nylon food packaging were determined by a dissolution and precipitation procedure, and were quantified by HPLC with UV detection at 210 nm [85].

3.2.6. Polyethylene terephthalate oligomer

Polyethylene terephthalate (PET) is a copolymer of ethylene glycol with either terephthalic acid or dimethyl terephthalate. It is commonly used as packaging material for beverages and edible oils. As it will not thermally deform below about 220°C, PET is also used in the form of trays and dishes for microwave and conventional cooking. However, PET is known to contain small amounts of low mole-culear weight oligomers ranging from dimer to pentamer. These cyclic compounds were found with levels ranging from 0.06 to 1.0% depending on the type of PET.

HPLC method has been employed to determine the migration levels of oligomers from PET [86]. Adsorption and gel permeation chromatography are also used with a view to separating and monitoring the individual oligomers [87,88]. Castle et al. proposed another method involving the conversion of all the oligomers present in a food extract to the monomer terephthalic acid followed by GC–MS single-ion monitoring. Despite the disadvantage that oligomers are measured as total levels together with

any monomer that may be present, this method could achieve good specificity and precision [89,90].

3.3. Contaminants

Apart from additives and monomer residues present in the packaging materials, other sources of food contamination were also reported. Decomposition products from additives or monomers will also migrate into the foodstuffs under appropriate conditions. Through direct contact with foods, residues of chemicals that were used in the processing of packaging materials may lead to contamination. Surrounding environment could also act as a source of contaminant too. Some typical examples are shown below.

3.3.1. Decomposition product

Diphenylthiourea is a kind of thermal stabilizer used in the manufacturing of PVC film. Beckmann and Niebergall reported that diphenylthiourea and its decomposition products including isothiocyanatobenzene, aniline and diphenylurea were detected in the food packaging material and the food as well. The compounds are determined by HPLC on a Nucleosil amine column, with dichloromethane–ethanol as the mobile phase [91].

3.3.2. Benzene and other volatiles

Komolprasert et al. reported that benzene might migrate into food from contaminated PET bottles [92]. In 1994, a survey was conducted by the UK Food Safety Directorate to measure benzene in plastic food packaging and the migration into food [93]. For the determination of the benzene level, dynamic headspace gas chromatography was the

widely used technique [94] (Fig. 5). The food sample, mixed with deuterated benzene as the internal standard, was heated for 30 min. in a sealed vial at 250°C. The headspace gas was analysed by GC–MS in selected-ion monitoring mode (m/z 78 for benzene and m/z 84 for the internal standard). A similar headspace extraction was also applied to determine the levels of residual solvents in food packaging printed film [95].

It was also demonstrated that benzene and alkylbenzene could be generated from several types of food contact plastics in high temperature applications [96,97]. Risch and Hotchkiss [98] developed a specific methodology to evaluate volatile compounds produced during microwave cooking. A closed system was designed to cryogenically trap volatile compounds produced (Fig. 6). The cryo-trap consists

of a vessel packed with glass wool to facilitate the trapping of volatile compounds. Following the purging during microwave heating, the trap is transferred to a traditional purge and trap system where the compounds are analyzed by GC–MS [98].

3.3.3. Environmental contaminants

The levels of naphthalene vapour in air were found to increase in places exposed to paint and naphthalene-based moth repellant. Lau et al. [99] observed that, in an environment containing a considerable amount of naphthalene, the naphthalene concentration in milk drinks contained in low density polyethylene (LDPE) bottles increased with storage time. The effect of naphthalene vapor in air on the level of contamination in milk was then studied, where napthalene in the milk and that in the LDPE
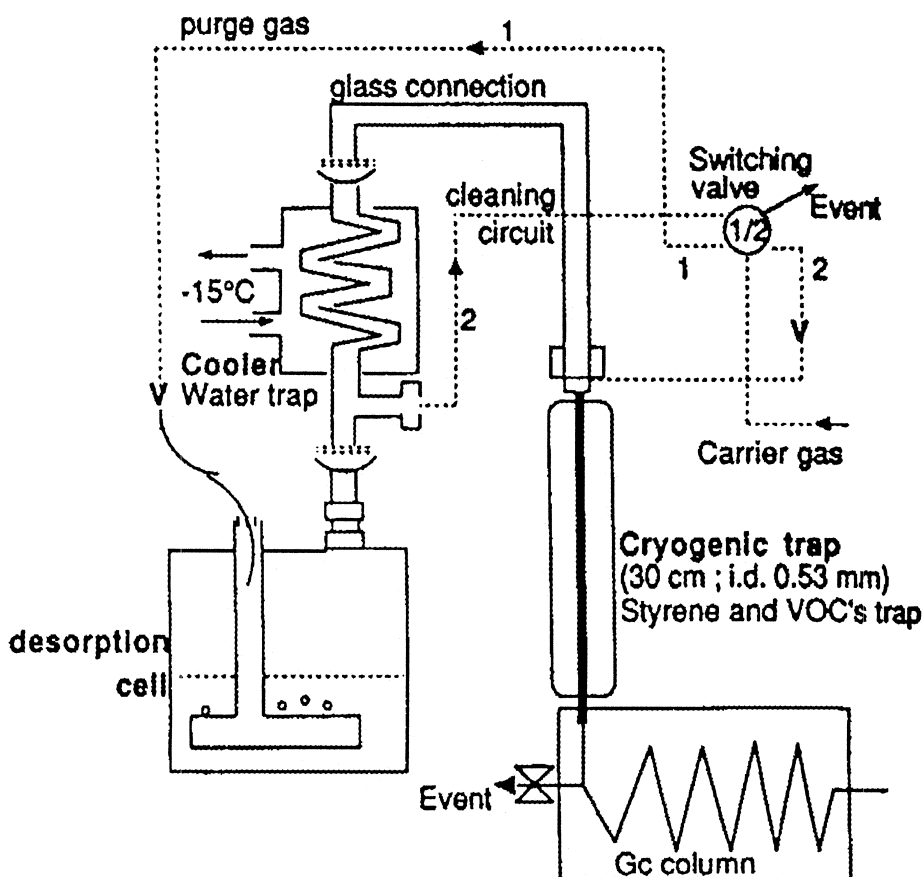

Fig. 5. Set-up for the dynamic headspace analysis of styrene and other volatile organic compounds (from Ref. [94]).
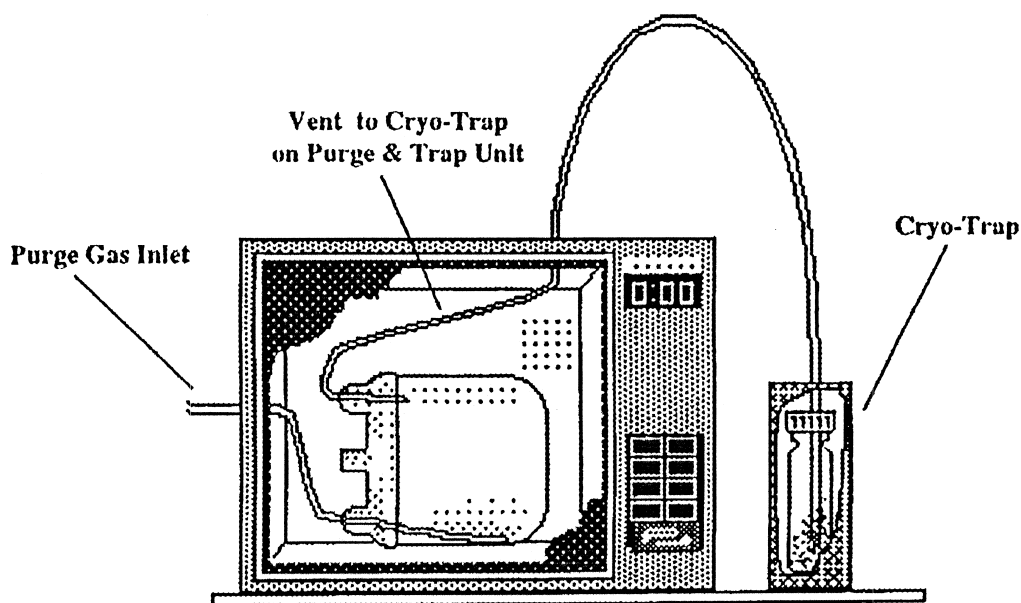
Fig. 6. Closed system designed to cryogenically trap volatile compounds produced during microwave oven cooking (from Ref. [97]).

packaging material were determined by GC after extraction into heptane using a Dean–Stark apparatus. It was concluded that naphthalene in air could be absorbed by the LDPE packaging and then migrated into the milk which it contained [99]. A mathematical model was developed to describe the migration of naphthalene from the atmosphere into milk and was validated. Also, the extent of naphthalene migration was found to increase with the fat content of milk [100].

3.3.4. Processing agents

Hydrogen peroxide is commonly used as a sterilization agent for polypropylene and polyethylene aseptic food packaging. Castle et al. developed a method to evaluate the migration levels as well as the effects of hydrogen peroxide sterilization on the migration characteristics of polypropylene and polyethylene materials [101].

3.3.5. Other contaminants

Dioxins could be found in PVC polymers as a contaminant and also in paperboard treated with bleaching agent. Recently, a survey of PVC food packaging for dioxins has been conducted. Eight samples of PVC food packaging were analysed and

the concentrations were shown to range from 2.6 to 6.9 ng TEQ/kg of PVC, and the estimated maximum concentration of dioxins present in food due to migration was 0.07 ng TEQ/kg [102].

4. Factors affecting migration

The migration of additives or contaminants from polymeric food packaging to food may be separated into three different, but inter-related, stages: diffusion within the polymer, solvation at the polymer-food interface, and dispersion into bulk food.

4.1. Diffusion within the polymer

At this stage, the migration of additives or contaminants is controlled by diffusion, which is a macroscopic manifestation of a random walk or Brownian motion of individual migrant molecules within the polymer lattice. This mode of molecular transport has been shown in most cases to obey Fick's laws of diffusion [103]:

Fick's first law: $F = -D_p \cdot \dfrac{\delta C_p}{\delta x}$ (1)

Further, if the diffusion coefficient is independent of concentration,

Fick's second law:
$$\frac{\delta C_p}{\delta t} = D_p \cdot \frac{\delta^2 C_p}{\delta x^2} \qquad (2)$$

where F is the rate of transport per unit area of the polymer, D_p is the diffusion coefficient of migrant in the polymer, C_p is the migrant concentration in the polymer, x is the space coordinate measured normal to the polymer–food interface, and t is the elapsed time, and these are the parameters that may affect the rate of migration according to the above equations at this stage.

For contaminants coming from the surrounding environment, such as naphthalene or other volatile organics, Lau and Wong reported that the rate of migration is also related to the glass transition temperature of the polymer, T_g. This is due to the fact that polymer with T_g lower than room temperature, such as polyethylene and polypropylene, has a larger permeability for organic vapours compared with those with T_g higher than room temperature, such as polystyrene and PVC [104].

Furthermore, the rate of migration was found to vary with the thickness of the polymer packaging. However, the rate reached a constant value from a particular thickness onwards. This was defined as the limiting thickness, d_g, which was found to vary with the nature of the polymer. For example, in the polyolefin polymer, d_g decreases in the order LDPE→HDPE→PP [105].

4.2. Solvation at the polymer–food interface

At this stage, the migrant moves by way of solvation into the food. If the migrant partitions well into the food, i.e. more soluble in the food than in the polymer, the migrant concentration profile is smooth and continuous in this region, which facilitates the rate of migration into the food. On the other hand, if the migrant partitions poorly into the food, the migrant concentration profile may be discontinuous in this region, which retards the rate of migration into the food. That is the reason why the problem of food contamination is more serious in fatty foods than in aqueous foods, as most of the polymer additives and contaminants are fat-soluble. Lau and

Wong reported that the extent of migration of adipates from PVC cling film into cheese varied expontentially with the fat content of the cheese samples [23].

4.3. Dispersion into bulk food

At this stage, just beyond the interface between the polymer and the food, the solvated migrant molecules diffuse away from the interface and move into the bulk food. The migration at this stage as well as that for the previous two stages are driven mainly by entropy, a measure of randomness. Limm and Hollifield demonstrated that mixing could increase the migration into food because mixing enhances kinetically migrant solvation by removing solvated migrant from the interface thus reducing reprecipitation [106]. However, the migrant solubility and diffusion coefficient are the prime factors governing the dispersion of migrant into food, thus affecting the rate of migration as a whole.

5. Examples of predictive migration modelling

An estimate of the exposure to additives or contaminants in the diet is determined by combining migration data with information on the uses of food packaging that may contain the additives or contaminants. Traditionally, migration data were obtained from migration tests performed by using food-simulating liquids such as water, edible oils, ethanol–water solutions. However, these tests are quite time consuming and expensive. In an effort to overcome the inherent difficulties associated with migration tests, researchers suggested the use of predictive migration modeling to estimate the extent of migration.

In general, studies have shown that migration is controlled by diffusion through the polymer according to Fick's law and diffusion follows Arrhenius behavior with temperature. Hence, the extent of migration should be predictable, at least theoretically. Indeed, quite a number of mathematical models have been established for such purposes.

The simplest model, Eq. (3), was provided by Crank to predict the extent of migration from polymer into the extraction solvent [103].

$$M_t = 2C_{P0}\sqrt{\frac{D_p t}{\pi}} \qquad (3)$$

where M_t is the total migrant from the polymer in time t, C_{P0} is the initial migrant concentration in the polymer and D_P is the diffusion coefficient of the migrant in the polymer. Eq. (3) assumes that the solvent is well mixed and never saturated with migrant, and the polymer is sufficiently thick for the migrant concentration at the mid-plane to remain at its original value C_{P0}. Baner et al. expressed the model in the form as:

$$C_{F,t} = \frac{A}{m_F} \cdot \rho_P C_{P0}\sqrt{D_P t} \qquad (4)$$

where $C_{F,t}$ is the estimated concentration, ρ_P is the density of the plastic material, D_P is the migrant diffusion coefficient and (A/m_F) is the package surface area. However, the actual diffusion coefficient was usually not known and was estimated by the empirical correlation given by Eq. (5).

$$D_P = 10^4 \exp(A_P - aM_r - bT^{-1}) \qquad (5)$$

where the coefficient A_P accounts for the effect of the polymer on diffusivity, M_r is the substance's relative molecular weight, T is the temperature in Kelvin, and a and b are correlation constants for molecular weight and temperature effects on diffusion respectively. As the results indicated a tendency of over-estimation of the actual migration, the model was mainly used to estimate the maximum migrant concentration in a polymer (QM) and its specific migration limit (SML) as stated in the relevant EC directive [107].

Till et al. modified Eq. (3) to make it applicable to real case where the solvent (food) phase are immobile [108]. As such, migration into this phase must occur by diffusion. Thus, a solvent phase diffusion coefficient of the migrant has to be included in the model as follows:

$$M_t = 2C_{P0}\sqrt{\frac{2D_p t}{\pi}} \cdot \left[\frac{\beta}{(1+\beta)} \right] \qquad (6)$$

where

$$\beta = K\sqrt{\frac{D_s}{D_p}} \qquad (7)$$

and K is the equilibrium partition coefficient and D_S represents the diffusion coefficient of the migrant in the immobile solvent (food). Mercer et al. applied this model to predict DEHA migration from PVC cling-film into a variety of foods. They estimated the value of K and measured diffusion coefficients in a food-simulating solvent. However, results from the model failed to agree well with the levels actually determined [109].

Starting from the Fick's second law, Lau and Wong derived another model, Eq. (8), for similar situations [110].

$$M_t = \frac{2\sqrt{D_s t} \cdot KC_{P0}}{1 + K\alpha} \left[\frac{1}{\sqrt{\pi}} - ierfc\left(\frac{L}{2\sqrt{D_p t}} \right) \right] \qquad (8)$$

where $\alpha = (D_s/D_P)^{1/2}$ and $ierfc(x)$ is the complementary error function.

The value of K and diffusion coefficients were estimated from data from control experiments using mathematical optimization techniques. Despite the final equation was quite complex, the predicted results agreed with the actual migrant levels determined to within 22%.

Recently, it was suggested that recycled plastics could be re-used safely in food packaging applications by indirect contact behind a barrier layer made from virgin food contact approved plastic material. However, controversial discussion about such a functional barrier concept is still going on. To predict the extent of migration across functional barrier layers into foodstuffs, Franz et al. derived a model based on Crank's equation [111].

$$M_t = \frac{2}{\sqrt{\pi}} \cdot \left[C_P \cdot (1 + \tfrac{b}{d}) - C_B \cdot \tfrac{b}{d} \right] \\ \cdot \rho_P \sqrt{D_P}(\sqrt{\theta_r + t} - \sqrt{\theta_r}) \qquad (9)$$

where b is the thickness of the barrier layer, d is the thickness of the recycled plastic layer, C_B is the migrant concentration in the barrier layer, θ_r is the lag time of the migrant across the barrier layer and ρ_P is the density of the recycled plastic layer.

For cases in which the contaminants come from the surrounding environment, Lau and Wong proposed a model as shown below to predict the extent of migration.

$$M_t = C_{sat}\gamma_{air} \cdot \sqrt{\frac{Dt}{\pi}}$$
$$\cdot [1.33\beta t - 0.54(\beta t)^2 + 0.15(\beta t)^3 + ...] \qquad (10)$$

where β is the kinetic factor, C_{sat} is the saturated migrant concentration in the packaging material when exposed to saturated migrant vapour, γ_{air} is the ratio of migrant concentration in air to that of the saturated migrant concentration in air. The model was found applicable to fit the actual experimental data of naphthalene migration from air into milk contained in low density polyethylene bottles [112].

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