FOOD SAFETY, PLASTICS AND SUSTAINABILITY Materials, Chemicals, Recycling

and the Circular Economy







Food Safety, Plastics and Sustainability

Scrivener Publishing

100 Cummings Center, Suite 541J Beverly, MA 01915-6106

Publishers at Scrivener Martin Scrivener (martin@scrivenerpublishing.com) Phillip Carmical (pcarmical@scrivenerpublishing.com)

Food Safety, Plastics and Sustainability

Materials, Chemicals, Recycling and the Circular Economy

Johannes Karl Fink Montanuniversität Leoben, Austria





This edition first published 2023 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA © 2023 Scrivener Publishing LLC

For more information about Scrivener publications please visit www.scrivenerpublishing.com.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

Wiley Global Headquarters

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 978-1-394-17456-0

Cover image: Pixabay.com Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Con	tents
-----	-------

Pr	Preface		xi
1	Foo	d Safety	1
	1.1	Food Security	2
	1.2	Migration of Substances from Packaging	3
		1.2.1 Modeling of Migration	4
		1.2.2 Sample Pretreatment Methods	6
		1.2.3 Special Chemicals	7
		1.2.4 Safety of Recycled HDPE and PP	11
	1.3	Food Safety and Hygiene	12
		1.3.1 Sensors for Amine Detection	13
	1.4	Impact of Microplastics on Humans and the Environment	14
		1.4.1 Polychlorinated Biphenyl Compounds	17
		1.4.2 Polycyclic Aromatic Hydrocarbon Compounds	17
		1.4.3 Organochlorine Pesticides	21
		1.4.4 Carcinogens	30
	1.5	Methods of Food Packaging	42
	1.6	Recycling Safety	58
	Refe	rences	58
2	2 Regulations		67
	2.1	European Strategy for Plastics	67
	2.2	Basic Principles of Packaging	68
	2.3	Colorants and Optical Brighteners	68
	2.4	Non-intentionally Added Substances in Food Contact	
		Material	69
		2.4.1 Analysis Methods	71
	2.5	Recycling	74
		2.5.1 Recycled Plastics in Food Packaging	74
		2.5.2 Planning and Decision-Making Process	76
		2.5.3 Mechanical Recycled Plastics	76

vi Contents

	2.6	Stand	lards	77
		2.6.1	Gloves	78
		2.6.2	Specifications for Compostable Plastics	78
		2.6.3	Containers for Packaging of Liquid Foodstuffs	79
		2.6.4	Williams-Landel-Ferry Equation	79
	Refe	erences		80
3	Test	ting M	ethods	83
	3.1	Risk .	Assessment	84
	3.2	Antir	nicrobial Packaging	84
	3.3	Food	Colorants	96
			Milk Freshness Testing	101
		3.3.2	Meat Freshness Testing	102
		3.3.3	Fish Freshness Testing	103
	3.4	Stand	lards	103
		3.4.1	Odor and Taste Transfer from Packaging Film	106
		3.4.2	Annealed Aluminum and Aluminum-Alloy Foil	
			for Food Contact	106
		3.4.3	Detection of Leaks in Packages	107
		3.4.4	Changes in Sensory Attributes	111
		3.4.5	Irradiated Food Contact Materials	112
		3.4.6	Oxygen Headspace Analysis	114
	Refe	erences		114
4	Foo	d Pack	aging	121
	4.1	Auto	mated Method	121
	4.2	Multi	ilayer Packaging	126
	4.3	Flexil	ble Packaging	127
	4.4	Multi	component Package	129
		4.4.1	Barrier Films	134
	4.5	Chlor	rine Dioxide Gas-Releasing Package	140
	4.6	Susta	inable Food Packaging	142
	4.7	Venta	ible Food Packages	142
		4.7.1	Ventable Microwave-Safe Food Package	142
		4.7.2	Self-Venting Microwave-Safe Food Package	143
		4.7.3	Smart and Active Food Packaging	143
	4.8	Packa	ages for Pourable Food	146
	4.9	Food	Storage	149
		4.9.1	Trays	149
		4.9.2	Storage Container	151
		4.9.3	Storage System	154

	4.10	Specia	l Materials for Food Packaging	156
		4.10.1	Film-Forming Biodegradable Classes	156
		4.10.2	Cytotoxicity	158
		4.10.3	Microwavable Food Packaging Materials	160
			Film-Forming Materials	161
		4.10.5	Antimicrobial Biodegradable Food Packaging	164
		4.10.6	Multilayer Films for Food Packaging	170
		4.10.7	Bilayer Film with Dihydromyricetin	170
	Refe	rences		174
5	Mat	erials		191
-	5.1		composites	191
		5.1.1	PVC/Ag Nanocomposites	192
		5.1.2	Montmorillonite Clays	193
			Graphene Nanoplates	197
			Carbon Nanotubes	197
			Micro- and Nanoplastics	197
	5.2		lymers	198
		-	Proteins	199
		5.2.2	Gelatin	203
		5.2.3	Storage Polymers in Bacterial Cells	207
		5.2.4		208
		5.2.5	Starch	209
		5.2.6	Dry Heating Treatment	210
		5.2.7	Thermoplastic Starch	210
		5.2.8	Modified Starch	211
		5.2.9	Starch-Based Foams	212
		5.2.10	Residual Starch from Potato	213
		5.2.11	Cellulose	213
		5.2.12	Biodegradable Polymer Reinforced with Cellulose	
			Nanocrystals	214
		5.2.13	Cellulose Nanofibrils	221
		5.2.14	Chia Seeds	224
		5.2.15	Poly(lactic acid)	226
		5.2.16	Poly(hydroxyalkanoate)s	227
		5.2.17	Poly(hydroxybutyrate)	229
		5.2.18	Poly(caprolactone)	230
	5.3	Micro	plastics	231
		5.3.1	Microplastics in the Environment	232
		5.3.2	Microplastics in Food	233

		5.3.3	Microplastics in Agroecosystems	234
			Release of Microplastics	235
	5.4		e-Use Materials	235
	5.5	Edibl	e Films	236
		5.5.1	Poly(saccharide)s	236
			Cellulose	238
	Refe	rences		239
6	Add	itives		255
	6.1	Chem	nical Additives	255
		6.1.1	Hazardous Metal Additives	259
	6.2	Math	ematical Models	262
	6.3	Evalu	ation of Models	264
			c Additives by Swelling	264
	6.5		Acid Amide	277
			Plasticizers	277
			Antioxidants	277
			Monomers and Oligomers	278
			Light Stabilizers	278
			Slip Additives	278
			iorinated Compounds	279
			Materials in Plastics	284
	6.8	Aflato		284
			Sorbents for Aflatoxin	285
			ation of Additives from Plastics into Food	286
			ne Environments	287
		Surfa		288
	6.12		ng-Out Agents	289
		6.12.1	Determination of Food Stimulants	289
		6.12.2	2 Determination of Biogenic Amines	289
			3 Liquid-Liquid Microextraction	290
		6.12.4	Determination of Aromatic Amines	292
	Refe	rences		296
7	Арр	licatio	ons	303
	7.1		e-Like Coatings	303
	7.2		tional Food Applications	306
		7.2.1	Fructan	306
		7.2.2	Zogale	306
		7.2.3		307
		7.2.4	Mulberry Plants	309

		7.2.5	Citrus Seeds	310
		7.2.6	Vine Tea	310
		7.2.7	Anti-Stress Drugs	316
		7.2.8	Microalgae	318
		7.2.9	Phenolics	318
		7.2.10	Liposomes	319
		7.2.11	Diacylglycerol Functional Oil	319
	7.3	Preve	ntion of Oxidation	320
			Photo-oxidation	320
		7.3.2	Lipid Oxidation	322
			Natural Antioxidants	322
			Extraction Methods for Natural Antioxidants	330
	7.4		ocyclic Aromatic Amines in Prepared Food	339
	7.5	Radia	tion-Curable Compositions	341
	7.6	Antin	nycotics	344
	Refe	erences		347
8	Rec	ycling		357
	8.1	• •	fication of the Materials	359
		8.1.1	Spectroscopic Methods	359
			Real Time Mass Spectrometry	359
			Optical Identification	360
			Chemical Safety Aspects	361
			Migration of Contaminants	364
			Migration of Plasticizers	366
		8.1.7	•	366
	8.2	Recyc	ling Methods	367
		8.2.1	Delamination	367
		8.2.2	Separation	369
		8.2.3	Mechanical Recycling	369
		8.2.4	Selective Dissolution	372
		8.2.5	Dissolution-Reprecipitation Technique	372
			Compatibilization	374
			Feedstock Recycling	374
		8.2.8	Closed-Loop Recycling	375
		8.2.9	Supercritical Ethanol	377
	8.3		Consumer Polyolefins	377
		8.3.1	Predictive Models	377
		8.3.2	Safety Concerns	378
		8.3.3	Multilayer Composites	380
		8.3.4	Recyclability Enhancement of Food Containers	384

x Contents

8.4 Plastic Waste Generation		384
8.5 I	Recycled Plastics in Food Contact	385
8	3.5.1 Improving Safety and Quality	385
References		385
Index		391
Acron	lyms	391
Chem	icals	394
Gener	al Index	404

Preface

This book focuses on plastics for food safety and materials and chemicals, methods and applications of these polymers.

The book begins with a chapter about food safety. Here, food security and the issues of migration of substances from packaging into the corresponding food are discussed.

Then, in the next chapter, regulations, standards, and specifications are detailed. Furthermore, in another chapter, testing methods, such as risk assessment, freshness testing of food, and food colorants are discussed.

In the chapter entitled "Food Packaging," the methods that can be used for these issues are given. Also, materials, special uses, and finally, methods for recycling are given.

The subsequent chapters and their subject matter are:

Chapter 1: Food Safety Chapter 2: Regulations Chapter 3: Testing Methods Chapter 4: Food Packaging Chapter 5: Materials Chapter 6: Additives Chapter 7: Applications Chapter 8: Recycling

The text focuses on the literature of the past decade. Beyond education, this book will serve the needs of industry engineers and specialists who have only a passing knowledge of the plastics and composites industries but need to know more.

How to Use This Book

Utmost care has been taken to present reliable data. Because of the vast variety of material presented here, however, the text cannot be complete in all aspects, and it is recommended that the reader study the original literature for more complete information.

The reader should be aware that mostly US patents have been cited where available, but not the corresponding equivalent patents in other countries. For this reason, the author cannot assume responsibility for the completeness, validity or consequences of the use of the material presented herein. Every attempt has been made to identify trademarks; however, there were some that the author was unable to locate.

Index

There are three indices: an index of acronyms, an index of chemicals, and a general index.

In the index of chemicals, compounds that occur extensively, e.g., 'acetone,' are not included at every occurrence, but rather when they appear in an important context.

Acknowledgements

I am indebted to our university librarians, Dr. Christian Hasenhüttl, Margit Keshmiri, Friedrich Scheer, Christian Slamenik, Renate Tschabuschnig, and Elisabeth Groß for their support in literature acquisition. I also want to express my gratitude to all the scientists who have carefully published their results concerning the topics dealt with herein. This book could not have been otherwise compiled.

Last, but not least, I want to thank the publisher, Martin Scrivener, for his abiding interest and help in the preparation of the text. In addition, my thanks go to Jean Markovic, who made the final copyedit with utmost care.

> **Johannes Fink** Wiener Neustadt, January 6, 2023

1

Food Safety

With the world's growing population, the provision of a safe, nutritious and wholesome food supply for all has become a major challenge (1). To achieve this, effective risk management based on sound science and unbiased information is required by all stakeholders, including the food industry, governments and consumers themselves. In addition, the globalization of the food supply requires the harmonization of policies and standards based on a common understanding of food safety among authorities in countries around the world. With some 280 chapters, the *Encyclopedia of Food Safety* provides unbiased and concise overviews which form in total a comprehensive coverage of a broad range of food safety topics, which may be grouped under the following general categories (1):

- 1. History and basic sciences that support food safety,
- 2. Foodborne diseases, including surveillance and investigation,
- 3. Foodborne hazards, including microbiological and chemical agents,
- 4. Substances added to food, both directly and indirectly,
- 5. Food technologies, including the latest developments,
- 6. Food commodities, including their potential hazards and controls,
- 7. Food safety management systems, including their elements and the roles of stakeholders.

The Encyclopedia provides a platform for experts from the field of food safety and related fields, such as nutrition, food science and technology and environment, to share and learn from state-of-the art expertise with the rest of the food safety community (1).

Plastic plays a significant and growing role in modern day society, delivering many benefits, particularly in food safety and preservation, and can help to reduce food waste (2).

Advances in packaging can not only reduce losses but also improve food quality and safety. To offer the best food protection the FAO suggests that a packaging solution could include more, but better packaging, rather than less packaging.

A novel approach for food safety, which integrates a statistical study and subjective discussion, was adopted to review the recent advances in the environment and food safety (3).

Here, a scientometric-based statistical study was conducted based on 4904 publications collected from the Web of Science Core Collection database. It was found that the research on the environment and food safety grew steadily from 2001 to 2020. The statistical analysis of most-cited papers, titles, abstracts, keywords, and research areas revealed that the research on the environment and food safety was diverse and multidisciplinary.

In addition to the scientometric study, strategies to protect the environment and ensure the safety of food were critically discussed, followed by a discussion on the emerging research topics, including emerging contaminates, e.g., microplastics, rapid detection of contaminants, e.g., biosensors, and environmentally friendly food packaging materials, e.g., biodegradable polymers (3).

1.1 Food Security

Plastic pollution arising from food systems is driving policies for reduction, removal, reuse and recycling (4).

A systematic scoping review was used to describe the extent, range and nature of published evidence since 2000 on seven major plastic types used at any point within food systems.

The majority of the publications focus on the agricultural production; relatively fewer publications relate to retail, household and food waste disposal plastics (4).

Some plastic types were more frequently linked to certain outcomes than others: Poly(ethylene) and poly(propylene) (PP) were frequently explored in relation to effects on the nutrient or bacterial content of crops and food (n = 445 and 274, respectively), but only one study considered the effects of PP (commonly used in infant feeding bottles) on the presence of plastics or associated chemicals in the human body.

Among the studies that looked at plastics and chemicals in the human body, as well as human health states and/or physiological changes, the most commonly explored types were unspecified plastics, miscellaneous plastics and poly(ethylene terephthalate) (PET). Despite finding evidence of each major plastic type in our sample, a lack of chemical specification of the plastic exposures was very common (4).

1.2 Migration of Substances from Packaging

The usage of new food packaging materials has increased the number of occurring hazards due to the migration from packaging material to the packaged food (5). Although polymers have mainly monopolized the interest of migration testing and experimentation, recent studies have revealed that migration also occurs from traditional materials generally considered to be safe, such as paper, carton, wood, ceramic, and metal. The regulations and the directives of the EU tend to become stricter in this respect.

The emphasis is on reaching a consensus in terms of food simulants and testing conditions for migration studies. Furthermore, the list of hazardous monomers, oligomers, and additives continues to be augmented in order to ensure that the consumer safety is in current agreement with the hazard analysis critical control points (HACCP), which is continuously gaining ground (5).

Food and beverages can be very aggressive chemical milieu and may interact strongly with materials that they touch (6). Whenever food is placed in contact with another substance, there is a risk that chemicals from the contact material may migrate into the food. These chemicals may be harmful if ingested in large quantities, or impart a taint or odor to the food, thereby negatively affecting the food quality. Food packaging is the most obvious example of a food contact material. As the demand for prepackaged foods increases, so might the potential risk to consumers from the release of chemicals into the food product.

Chemical Migration and Food Contact Materials reviews the latest controls and research in this field and how they can be used to ensure that food is safe to eat.

In a monograph, the regulation and quality control of chemical migration into food are discussed (6). Then, the latest developments in areas such as exposure estimation and analysis of food contact materials are reviewed. Finally, specific chapters on major food contact materials and packaging types are presented, such as recycled plastics, metals, paper and board, multilayer packaging and intelligent packaging.

The large number of synthetic materials that are used for the manufacture of packages makes the evaluation of the food package interactions complicated (7).

Different parameters, such as the nature of the food of interest, the type of food package contact, the time and temperature of contact, the packaging materials used, the properties of the migrating substances, as well as the amount of potential migrants contained in the packaging materials, can drastically affect the migration rate and the extent of migration.

Due to the extreme variety of foods used, several food simulants have been suggested and applied for testing the migration phenomenon under various laboratory conditions (7). The use of many of those simulants is defined by national and international legislation. The main migration phenomena, which are related to the most commonly used packaging materials, have been detailed (7). In the study, it was clearly demonstrated that the complexity of the migration phenomena requires more research to establish internationally accepted risk management procedures and standardized testing methods.

1.2.1 Modeling of Migration

The potential for the use of migration modeling for studying polyolefin packaging materials, such as low-density and high-density poly(ethylene) and poly(propylene), was summarized and demonstrated with practical examples (8). For these polymers, an upper limit of migration into foodstuffs can be predicted with a high degree of statistical confidence. The only analytical information needed for modeling in such cases is the initial concentration of the migrant in the polymer matrix.

For polyolefins of unknown origin or newly developed materials with new properties, a quick experimental method has been described for obtaining the characteristic matrix parameter needed for the process of migration modeling.

For easy handling of both the experimental results and the diffusion model, a user-friendly software has been developed. An additional aim of the described method is the determination of the migrant partition between polymer and food or food simulant and the specific contribution of the migrant molecular structure on the diffusion coefficient. For migration modeling of packaging materials with multilayer structures, a numerical solution of the diffusion equation is described. This procedure has also been applied for modeling the migration into solid or high-viscosity foodstuffs (8).

The permeation through and diffusion/migration from highdensity poly(ethylene), poly(butylene), poly(propylene) and crosslinked poly(ethylene) films was investigated experimentally with three different methods to determine diffusion coefficients in these polyolefins for a series of additives, their degradation products and other organic substances in the 20°C to 60°C temperature range (9).

The experimental methods used were dynamic permeation through additive-free polymer films, kinetic desorption from additivated films into water and kinetic migration from additivated into additive-free polymer films. It was found that in general the temperature dependence of the obtained diffusion coefficients was well represented by the Arrhenius law.

Some of these results also suggested that the contact of the polyolefins with water had an influence on the magnitude of the diffusion coefficients and on their apparent activation energy of diffusion (9).

The migration of phthalate from PET bottles containing non-alcoholic beer was done by performing an adaptive neuro-fuzzy inference system analysis (10).

The data showed that the storage temperature, contact surface and storage period correlate with the rate of migration. The migration of phthalate increases with storage duration gradually and reduces under different temperatures and contact surface. Moreover, increased temperature and storage duration resulted in an increase in migration level ranging from 0.6 $\mu g l^{-1}$ to 2.9 $\mu g l^{-1}$ (10).

The study used an adaptive neuro-fuzzy inference system analysis architecture, which consists of three inputs (temperature, surface and storage period), Gaussian-bell membership functions for each input variable and one output layer, which represent the migration level. The validation and training models showed an excellent match between the experimental and predicted values of adaptive neuro-fuzzy inference system analysis.

The analysis of the model showed that adaptive neuro-fuzzy inference system analysis is a powerful tool for predicting phthalate migration from bottles containing non-alcoholic beer (10).

1.2.2 Sample Pretreatment Methods

An excessive absorption of migrating substances from food contact materials can affect human health. Thus, it is essential to analyze the migration of contaminants from food contact materials (11).

However, comprehensive analysis has been challenged by low concentration of migrating substances and manifold and complex matrix interference of food contact materials. Therefore, appropriate sample pretreatment methods should be applied before instrumental detection, which is essential to improve the analytical efficiency, sensitivity, and reliability.

The development of sample pretreatment methods for the analysis of migrating substances from food contact materials has been reviewed in the past decade (11). To extract volatile and semi-volatile substances, headspace extraction, headspace solid phase microextraction, and a purge and trap technique are discussed here.

For non-volatile substances, solid-liquid extraction and field-assisted extraction are usually used to extract them from food contact materials; while liquid-liquid extraction, solid phase extraction, and their corresponding microextraction techniques play important roles in the enrichment process (11).

Also, new progress in the development of sample pretreatment methods of food contact materials was summarized, covering new devices, specific adsorbents, and sample preparation methods for rapid detection (11).

1.2.3 Special Chemicals

1.2.3.1 Styrene

Poly(styrene) (PS) is extensively used in diverse forms for packaging of many food products such as meat, dairy and bakery products. There is a potential migration of styrene monomer from PS packages into the foods which are in contact with them (12).

The representative styrene migration from PS packaging material into the corresponding foods was detailed. Also, the addressed parameters affecting the styrene migration were discussed. The analytical methods for detecting the styrene monomer in food products and PS packaging materials was also covered in the study. The possible safety and health issues related to the styrene monomer migration were also covered.

The quality of PS packaging materials in terms of their styrene monomer residue level and the storage conditions of foods can greatly affect styrene migration. Also, the food characteristics, such as fat content and pH, can significantly affect the migration of styrene. Although styrene is considered a nontoxic compound, its migration into foods can downgrade sensorial properties as well as result in health problems. In some cases, the presence of styrene in foods can cause carcinogenic, hematological, cytogenetic, and neurotoxic issues (12).

A sensitive, accurate and fast headspace-solid phase microextraction-gas chromatography-tandem mass spectrometry (HS-SPME-GC-MS/MS) method was developed and validated for the determination of styrene in various food matrices. The mean recovery ranged from 90% to 116% with a relative standard deviation of =11% (13).

This method was used for the determination of the concentration of styrene in 23 foodstuffs packed in PS containers, as well as the levels of styrene migrating into various foods (water, milk, cheese or cream) from 14 tableware or kitchenware articles made of styrene plastics. All samples were collected from the Greek market in 2020.

The concentrations of styrene in the packaged foods ranged from 0.4 to 160 $ng g^{-1}$, with the highest concentration found in a meat product packed in a foamed PS tray. It is worth noting that 56% of PS packaged dairy products and desserts had a styrene concentration of higher than $10 ng g^{-1}$. Particularly high levels of styrene that have

not previously been reported, of up to $46 ng g^{-1}$, were found in dairy products for children. The highest level of styrene migration from tableware or kitchenware articles, 89 $ng g^{-1}$, was observed when disposable cups from foamed PS were filled with milk at 70°C for 2 h (13).

1.2.3.2 Bisphenol A

Bisphenol A is mainly used in the production of poly(carbonate), a material with high durability and strength. This chemical is also used in the production of epoxy resins, applied in the coating of metal surfaces in contact with food. Moreover, it is employed in thermal paper (14).

Bisphenol A has been widely reported by the media, being the aim of diverse scientific studies, since it is a xenoestrogen with a chemical structure identical to that of β -estradiol, which allows it to interact with human estrogen receptors. These compounds are shown in Figure 1.1.

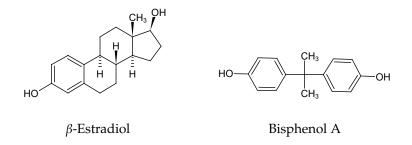


Figure 1.1 Xenoestrogens.

Bisphenol A monitoring is essential to avoid a potential health risk of the population. The European Union has recently updated the specific migration limit for bisphenol A at $0.05 mg kg^{-1}$ of food.

Regarding the levels of migration determined in different types of food contact materials, it was found that, despite the great majority of studies showing positive samples, none of them exceeded the value of specific migration limit established by the European Union at the time of the studies (14).

1.2.3.3 Benzophenone

Benzophenone may be present in cartonboard food-packaging materials as a residue from UV-cured inks and lacquers used to print on the packaging (15). It may also be present if the cartonboard is made from recycled fibers recovered from printed materials.

A method has been developed to test for benzophenone in cartonboard packaging materials and to test the migration levels in foodstuffs.

Here, the packaging material is extracted with a solvent containing d10-benzophenone as the internal standard. Foods are extracted with solvent containing d10-benzophenone and the extract is defatted using hexane. The extracts are analyzed by gas chromatography (GC)-mass spectroscopy (MS). d10-Benzophenone is the deuterium labeled benzophenone. It is shown in Figure 1.2.

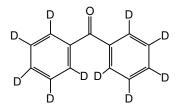


Figure 1.2 d10-Benzophenone.

For the analysis of food, the limit of detection was $0.01 \ mg \ kg^{-1}$ and the limit of quantification was $0.05 \ mg \ kg^{-1}$. The calibration was linear from $0.05 \ mg \ kg^{-1}$ to $20 \ mg \ kg^{-1}$. The method for food analysis was validated in-house and it also returned satisfactory results in a blind check-sample exercise organized by an independent laboratory.

The methods were applied to the analysis of 350 retail samples that used printed cartonboard packaging. A total of 207 (59%) packaging samples had no significant benzophenone (<0.05 $mg dm^{-2}$). Seven (2%) were in the range 0.05 $mg dm^{-2}$ to 0.2 $mg dm^{-2}$, 60 (17%) were from 0.2 $mg dm^{-2}$ to 0.8 $mg dm^{-2}$ and 76 (22%) were from 0.8 $mg dm^{-2}$ to 3.3 $mg dm^{-2}$.

A total of 71 samples were then selected at random from the 143 packaging samples that contained benzophenone, and the food it-

self was analyzed. Benzophenone was detected in 51 (72%) of the foods. Two food samples (3%) were in the range 0.01 $mgkg^{-1}$ to 0.05 $mgkg^{-1}$. A total of 29 (41%) were from 0.05 $mgkg^{-1}$ to 0.5 $mgkg^{-1}$, 17 (24%) were from 0.5 $mgkg^{-1}$ to 5 $mgkg^{-1}$ and three (4%) food samples exceeded 5 $mgkg^{-1}$. The highest level of benzophenone in food was 7.3 $mgkg^{-1}$ for a high-fat chocolate confectionery product packaged in direct contact with cartonboard, with room temperature storage conditions and with a high contact area:food mass ratio. When the mass fraction of the migration of benzophenone was calculated for the different contact and storage regimes involved, the attenuation effects of indirect contact and of low temperature storage were cumulative. Thus, there was a sixfold reduction in migration for indirect contact compared with direct contact, a sixfold reduction for chilled/frozen storage compared with ambient storage, and 40-fold reduction for the two contact conditions combined (15).

1.2.3.4 Perfluorochemicals

Perfluorochemicals are widely used in the manufacturing and processing of a vast array of consumer goods, including electrical wiring, clothing, household and automotive products. Furthermore, relatively small quantities of perfluorochemicals are also used in the manufacturing of food contact substances that represent potential sources of oral exposure to these chemicals (16).

The most recognizable products to consumers are the uses of perfluorochemicals in non-stick coatings (poly(tetrafluoroethylene) (PTFE)) for cookware and also their use in paper coatings for oil and moisture resistance. Recent epidemiology studies have demonstrated the presence of two particular perfluorochemicals, perfluorooctane sulfonate and perfluorooctanoic acid, in human serum at very low part per billion levels. These perfluorochemicals are biopersistent and are the subject of numerous studies investigating the many possible sources of human exposure. Among the various uses of these two chemicals, perfluorooctane sulfonate is a residual impurity in some paper coatings used for food contact and perfluorooctanoic acid is a processing aid in the manufacture of PTFE used for many purposes, including non-stick cookware.

Very little information is available on the types of perfluorochemicals that have the potential to migrate from perfluoro coatings into food. One obstacle to studying the migration is the difficulty in measuring perfluorochemicals by routine conventional analytical techniques such as GC/MS or LC-UV. Many perfluorochemicals used in food contact substances are not detectable by these conventional methods. As liquid chromatography-mass spectrometry (LC/MS) develops into a routine analytical technique, potential migrants from perfluoro coatings can be more easily characterized. In a study, data is presented on the types of perfluorochemicals that are used in food packaging and cookware. Additionally, research is presented on the migration or potential for migration of these chemicals into foods or food-simulating liquids.

The results from migration tests show $mg kg^{-1}$ amounts of perfluoro paper additives/coatings transfer to food oil. Analysis of PTFE cookware shows residual amounts of perfluorooctanoic acid in the low $\mu g kg^{-1}$ range. Perfluorooctanoic acid is present in microwave popcorn bag paper in amounts as high as 300 $\mu g kg^{-1}$ (16).

1.2.4 Safety of Recycled HDPE and PP

An analytical protocol was set up and successfully applied to study the food safety of recycled high-density poly(ethylene) (HDPE) and PP crates (17). A worst-case scenario was applied that focused not only on overall migration and specific migration of accepted starting materials but also on migratable degradation products of polymers and additives that may be formed during mechanical recycling.

The analytical protocol was set up to cover a wide variety of possible migrants. Identification and semi-quantification were possible for almost all migrants that increased significantly with increasing mechanical recycling steps for both the HDPE and PP crates.

It was concluded that the analytical protocol was suitable to study the influence of (multiple) recycling on the food safety of plastic materials. The protocol can be applied to other plastic foodcontact materials and provides valuable information on the food safety of the recycling process and the resulting recycled foodcontact materials in addition to challenge testing (17).

1.3 Food Safety and Hygiene

Food hygiene is the conditions and measures necessary to certify the safety of food from production to consumption. Food can become contaminated at any point during slaughtering or harvesting, processing, storage, distribution, transportation and preparation.

All conditions and measures that are required during production, processing, storage, distribution and preparation of food to ensure that it is safe, wholesome and fit for human consumption were defined in 1984 by the World Health Organization (WHO).

A lack of requisite food hygiene can lead to foodborne diseases and death of the consumer. Foodborne illness has been associated with improper storage or reheating (50%), food stored inappropriately (45%) and cross contamination (39%). Proper food preparation can prevent most foodborne diseases.

More than 200 known diseases can be transmitted through food (18). Some of these diseases are collected in Table 1.1.

Disease or Agent		
Bacterial	Bacterial	
Bacillus cereus Brucella spp. Clostridium perfringens Listeria monocytogenes Salmonella, nontyphoidal Staphylococcus Vibrio vulnificus	Botulism, foodborne <i>Campylobacter</i> spp. <i>Escherichia coli</i> <i>Salmonella typhi</i> <i>Shigella</i> spp. <i>Vibrio cholerae</i> <i>Yersinia enterocolitica</i>	
Parasitic	Parasitic	
Cryptosporidium parvum Giardia lamblia Trichinella spiralis	Cyclospora cayetanensis Toxoplasma gondii	
Viral	Viral	
Norwalk-like viruses Astrovirus	Rotavirus Hepatitis A	

Table 1.1 Known diseases (19).

Hazard analysis and critical control points is a systematic preventive approach to food safety from biological, chemical, and physical hazards in production processes that can cause the finished product to be unsafe and designs measures to reduce these risks to a safe level. Food hygiene and safety usually refer to contamination with microorganisms or microbes.

1.3.1 Sensors for Amine Detection

Biogenic amines are good indicators of food freshness because they are products of microbial fermentation (20). In the process of food spoilage, microbes break down amino acids via deaminization to generate ammonia, and via decarboxylation to generate biogenic amines such as cadaverine, putrescine, spermidine, spermine, and others. These amines are shown in Figure 1.3.

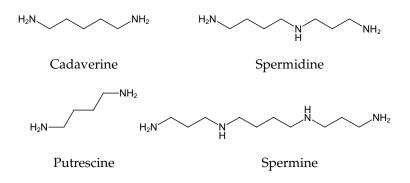


Figure 1.3 Biogenic amines.

These biogenic amines not only signal food spoilage, but also have an adverse impact on human health and physiological functions. Thus, monitoring biogenic amines in food is important both because the chemical species can have toxic effects, and because they signify food spoilage by microbes. When compared to time-temperature indicators, which only respond to temperature changes, a system detecting the presence of biogenic amines offers a more direct method of monitoring food safety and hygiene.

Aggregation-induced emission (AIE) active chemosensors exhibit a change for UV-vis absorption and become non-luminescent upon protonation (20). Upon deprotonation, the chemosensors revert to their original absorption and emission. This deprotonation process can be triggered in the presence of amines, and specifically, biogenic amines. So, the chemosensors can detect amine species, e.g., biogenic amines produced during food fermentation, quickly and with a high sensitivity.

As chemicals, 1,2-dihydroquinoxaline derivates can be used (20, 21).

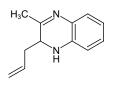
Some derivates are shown in Table 1.2 and Figure 1.4.

Table 1.2 1,2-Dihydroquinoxaline derivates.

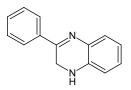
Compound
3-Methyl-2-prop-2-enyl-1,2-dihydroquinoxaline
3-Methoxy-6-(trifluoromethyl)-1,2-dihydroquinoxaline
2-Phenyl-1,2-dihydroquinoxaline
3-Phenyl-1,2-dihydroquinoxaline
3-Phenyl-1,2-dihydroquinoxaline-2-carboxylic acid
3-Methyl-2-propan-2-yl-1,2-dihydroquinoxaline
5-[6-[4-(Trifluoromethyl)phenyl]pyrimidin-4-yl]oxy-
1,2-dihydroquinoxaline
5-Bromo-3-[4-(trifluoromethyl)phenyl]-1,2-dihydroquinoxaline
3-[Chloro(phenyl)methyl]-1,2-dihydroquinoxaline
3-(1H-Indol-3-yl)-1,2-dihydroquinoxaline
6-Chloro-1,2-dihydroquinoxaline
3-(3-Nitrophenyl)-1,2-dihydroquinoxaline
Ethyl 7-amino-3-ethoxy-6-(trifluoromethyl)-1,2-dihydroquinoxaline-
2-carboxylate
8-Amino-2-ethyl-5-(hydroxymethyl)-1,2-dihydroquinoxaline-
6-carboxylic acid
2,3-Dimethyl-1,2-dihydroquinoxaline
2-Chloro-3-(5-chloro-1H-pyrazol-3-yl)-1,2-dihydroquinoxaline
2-Bromo-5-[6-[4-(trifluoromethyl)phenyl]pyrimidin-4-yl]oxy-
1,2-dihydroquinoxaline

1.4 Impact of Microplastics on Humans and the Environment

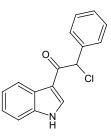
Micro- and nanoplastics have the potential to be transferred between trophic levels and, therefore, the risk characterization and the assessment of dietary exposure to them constitutes a current challenge for food safety alongside the study of the role of plastics as vectors of other contaminants and pathogenic microorganisms (22).



3-Methyl-2-prop-2-enyl-1,2-dihydroquinoxaline



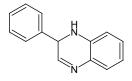
3-Phenyl-3-Phenyl-1,2-dihydroquinoxaline



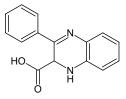
3-(1H-Indol-3-yl)-1,2-dihydroquinoxaline



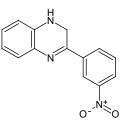
6-Chloro-1,2-dihydroquinoxaline



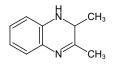
2-Phenyl-1,2-dihydroquinoxaline



3-Phenyl-1,2-dihydroquinoxaline-2-carboxylic acid



3-(3-Nitrophenyl)-1,2-dihydroquinoxaline



2,3-Dimethyl-1,2-dihydroquinoxaline

Figure 1.4 1,2-Dihydroquinoxaline derivates.

16 FOOD SAFETY, PLASTICS AND SUSTAINABILITY

The risk posed by microplastics to humans and the environment, has become a hot topic (23). The concern is focused not only on the effect of microplastics as such but also on additives and chemical contaminants absorbed by microplastics that may be released and negatively affect animals and environmental health. Despite several works having been written on this topic, a number of knowledge gaps still should be filled to enable a correct risk assessment of this important issue. For example, the relevance of microplastics for food safety has not yet been fully established and scientific results aimed at establishing a possible health risk for contaminants associated with microplastics are rather controversial. The risk assessment of microplastics in foodstuff is still at a very early stage and very few studies on the monitoring of microplastics in foodstuff and their effects on human health are available. Additionally, it is difficult to compare results from different studies as methodologies and study designs are not uniform. For this reason, it is not always possible to reach some definitive conclusion (23).

Studies have shown high concentrations of chemical contaminants that adsorb microplastics from the surrounding environment (24).

The compounds are listed in Table 1.3.

Compound	Amount in pallets/[$ng g^{-1}$]
Polycyclic aromatic hydrocarb	ons 52.1 – 17,023.6
Polychlorinated biphenyl	0.9 – 2285.8
Organochlorine pesticides	0.4 - 13,488.7
UV filters	0 - 37,740.3
Brominated diphenyl ethers	0 – 180.58
Organophosphorus flame retain	rdants 20.0 – 378.0
Compound A	mount in fragments/[$ng g^{-1}$]
Polycyclic aromatic hydrocarb	ons 35.1 – 8725.8
Polychlorinated biphenyl	1.6 – 772.5
Organochlorine pesticides	0.4 – 3778.8
UV filters	3.7 – 2169.3
Brominated diphenyl ethers	0.06 - 3923.9
Organophosphorus flame retain	rdants 22.6 – 7013.9

Table 1.3 Contaminants in microplastics (24).