Additive Migration from Plastics into Foods

A Guide for Analytical Chemists

T. R. Crompton

Smithers Rapra Technology Limited

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Smithers Rapra Technology Limited
A wholly owned subsidiary of The Smithers Group

Shawbury, Shrewsbury, Shropshire, SY4 4NR, United Kingdom
Telephone: +44 (0)1939 250383 Fax: +44 (0)1939 251118
http://www.rapra.net

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Preface

Plastics are now being used on a large scale for the packaging of fatty and aqueous foodstuffs and beverages, both alcoholic and non-alcoholic. This is evident for all to see on the supermarket shelves, namely margarine packed in polystyrene tubs, wine and beer in PVC bottles and meats and bacon in shrink-wrap film. As well as at the point of sale, foods are increasingly being shipped in bulk in plastic containers. Additionally, there is the area of use of plastics utensils, containers and processing equipment in the home and during bulk preparation of food in producing factories, at home and in restaurants and canteens.

Contact between plastics packaged commodities also occurs in the products of the pharmaceutical and cosmetics industries and similar considerations apply to these where direct contact occurs between the packed commodity and the container, this is likely that some transfer will occur of polymer additives, adventitious impurities such as monomers, oligomers, catalyst remnants and residual polymerisation solvents and of low molecular weight polymer fractions from the plastic into the packaged material with the consequent risk of a toxic hazard to the consumer. The actual hazard arising to the consumer from any extractable material is a function of two properties, namely, the intrinsic toxicity of the extracted material as evaluated in animal feeding trials (not dealt with in this book) and the amount of extracted from the polymer which enters the packed commodity under service conditions, i.e., during packaging operations and during the shelf life of the packaged commodity at the time of the consumption.

The principles covering the design of extraction tests proposed by various authorities are reviewed in Chapter 1. Chapters 2 and 3 review the types of polymers and elastomers, respectively, used in the packaging and the types of deliberately added or adventitious compounds that can occur in plastics and can be extracted into the packaged commodity.

The analysis of aqueous or fatty foods, beverages, food simulent liquids, pharmaceuticals and cosmetics which have been contacted with plastics either in extraction tests or during the shelf life of a packaged commodity presents many fascinating and all too difficult analytical problems. Thus, the substance to be determined usually occurs at extremely low concentrations and in complex matrix and several extracted substances may be present in the extraction liquid with mutually interfering effects on the analysis. For example, the extract of a polystyrene may contain an antioxidant, an ultraviolet stabiliser, antistatic agent, mineral oil and plasticiser.

Although the analyst may not be required to analyse for all of these substances it would be necessary to be aware of any interference effects that these substances may have on the determination of any particular component.

Chapter 4 to 11 discuss methods available for the determination polymer extractants of antioxidants, UV stabilisers, plasticisers, organotin heat stabilisers, organosulfur vulcanising agents, siloxanes and monomers and oligomers, respectively.

In order to give an idea of the care with which such methods have to be developed several detailed examples are given of previously unpublished methods developed in the Author's laboratories for the determination of particular types of extractables in extraction liquids, e.g., dilaurylthiodipropionate, Nonox CI, antioxidants and Ethylon (lauric diethanolamide).

The analysis of extraction liquids containing several extracted compounds is reviewed in Chapter 12. Next, there is the question of the analysis of additive breakdown either during polymer manufacture or upon contact with the packaged commodity or simulent liquid. Here there are two considerations, possible interference effects of breakdown products on the determination of the polymer migrant and the necessity to identify such breakdown products, as these too, must be considered from the toxicity point of view. These aspects are discussed in Chapter 13.

Chapter 14 reviews modern migration theory as it applies to polymer extraction tests. Currently theory is being developed which given certain basic parameters of the polymer-extractant system would enable extraction data to be predicted theoretically thereby obviating the need for lengthy extraction tests. Eventually it is hoped that such an approach in certain cases might be accepted by the governing authorities. Much more work is needed in this field.

The introduction of tailored polymer-based structures as packaging materials for foodstuffs has been increasing over the last decades. The main commercial appeal of the materials lies in their ability to offer a broad variety of tailor-made properties and yet to be cheap and easily processed. A large number of technologies have been put into place, i.e., multilayer structure, modified and equilibrium modified atmosphere packaging, active packaging and so on. The development of resins with high permeability properties for gases e.g., oxygen scavenging, and water and organic vapour is reviewed in Chapter 15.

Over the past decade, there have been considerable changes in European and Food and Drug Administration legislation regarding migration of polymer components into packaging commodities. This is discussed in detail in Chapter 16.

Finally, for completion, Chapter 17 reviews methodology for the determination of migrants in actual foodstuffs.

This book will be of interest to those engaged in the implementation of packaging legislation, including management, analytical chemists and the manufacturers of foods, beverages, pharmaceuticals and cosmetics and also scientific and toxicologists in the packaging industry.

Roy Crompton

June 2007

1 Additive Migration from Plastics into Packaged Commodities

1.1 Introduction

Plastics are now being used on a large scale for the packaging of fatty and aqueous foodstuffs and beverages, both alcoholic and non-alcoholic. This is evident for all to see on the supermarket shelf, namely margarine packed in polystyrene tubs, wine and beer in polyvinylchloride (PVC) bottles, and meats and bacon in shrink wrap film. As well as at the point of sale, foods are increasingly being shipped in bulk in plastic containers. Additionally, there is the area of use of plastics utensils, containers and processing equipment in the home and during bulk preparation of food in processing factories, at home and in restaurants and canteens.

Contact between plastics and package commodities also occurs in the products of the pharmaceutical and cosmetics industries and similar considerations apply to these. Where direct contact occurs between the packaged commodity and the container, it is likely that transfer will occur of polymer additives, adventitious impurities such as monomers, oligomers, catalyst remnants and residual polymerisation solvents and of low molecular weight polymer fractions from the plastic into the package material with the consequent risk of a toxic hazard to the consumer. The actual hazard arising to the consumer from any extractable material is a function of two properties, namely the intrinsic toxicity of the extracted material as evaluated in animal feeding trials (not dealt with in this book) and the amount of extracted from the polymer which enters the packed commodity under service conditions, i.e., during packaging operations and during the shelf life of the packaged commodity.

The principals governing the design of extraction tests proposed by various authorities are now reviewed.

1.2 Principles of Extractability Testing

The extractability of an additive or adventitious substance from a plastic can be determined by contacting the plastic for a specified time and temperature under standard test conditions with either the packed commodity or with a range of oily, alcoholic and aqueous extracts which simulate various types of packed commodities. At the end of the extraction test the extraction liquid or packaged commodity is analysed for extracted substances of interest by approved analytical techniques

However, low molecular weight additives frequently possess a high mobility in plastics materials and, in contrast to macromolecules, are capable of migrating from the packaging material into the packed product. The use of such substances in food packaging is, therefore, subject to strong legal controls. In order to decide whether a plastics packaging material complies with the requirements of the food law, two sets of questions should be considered. Concerning the plastics materials, one must ask whether the type to be used in contact with food is approved for packaging foodstuffs and whether it contains only approved additives in the allowed concentrations. The system, plastics plus foodstuffs to be packed, must also be considered, particularly the extent to which the individual plastics additives or their secondary products and plastics monomers migrate from the packaging material into the food and the extent to which low molecular polymer components similarly migrate.

The questions concerning the plastics can in most cases be answered by the manufacturer of the materials. For selecting some packaging materials, it is more important to answer the questions regarding the system - plastics plus foodstuff to be packed. The toxicity of plastics packages, particularly those kept in contact with food for a prolonged period or heated during the pasteurisation, sterilisation or preparation of the foodstuff is first of all determined by the extent to which the additives migrate into the packed foodstuff. It would be ideal if the migration of each additive into the packed material could be determined when the package has been filled and stored under normal conditions of use. This would ensure that no physiologically objectionable plastics material would be admitted and, on the other hand, that no suitable plastics material would be rejected because of a hypercritical assessment.

However, quantitative determination of the migrated additives in the heterogeneous foodstuff is extremely difficult. Therefore, natural migration must be simulated in model tests to determine the migrated or extracted additives in food simulants which can more easily be analysed. In this connection, the term ‘migration’ covers the transition of additives under storage conditions, (e.g., at and below 20 °C and 65% relative humidity) from packaging materials into packed foodstuffs or their simulants, while ‘extraction’ is the elimination of additives from a packaging material under extreme experimental conditions, (e.g., at 65 °C or at boiling heat) frequently with low boiling point liquids.

Both of the classes of substances mentioned previously, (i.e., additives and impurities) must be considered in polymer extractability investigations and the higher the