Analysis of Food Contaminants

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JOHN GILBERT

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Preface

In today's complex industrial environment the possibilities of occurrence of trace contamination of foods and beverages as well as the number of possible sources of contamination have significantly increased. Concern about low levels of exposure to contaminants, coupled with an improved analytical capability to detect smaller and smaller amounts of both organic compounds as well as inorganic elements, has generated a desire for surveillance of the food supply by both Regulatory authorities and manufacturing industry.

Sophisticated analytical techniques for monitoring trace contaminants have developed rapidly and the knowledge of 'what is present' in foods and beverages at low levels is far ahead of the necessary toxicology. Hence, although assessments of risk from contaminants in many cases are not possible, until such a judgement can be made it is still deemed important to continue surveillance. There are thus demands for large numbers of food and beverage samples to be analysed, and because of the 'sensitive' nature of contamination of something as important as 'our food' it is often necessary for positive results to be confirmed unequivocally. These demands are, however, against a worldwide background of 'cut-backs' and reductions in manpower both in Government service and in industry, with the result that automated techniques or rapid methods with low manpower commitments have become very attractive. Hence, methods which are highly specific and can be used on samples with a minimal preparation and clean-up are the methods of the future and hose receiving most attention in research laboratories active in method development for trace contaminants. This means that highly expensive instrumentation like mass spectrometers and plasma emission spectrometers, once the province

of the academically orientated research laboratories, are becoming used in more routine applications in surveillance work where the desired specificity can be more easily achieved and minimal time spent on sample preparation.

The aim of this book is to selectively choose a number of specialised techniques in trace analysis which are employed for food contaminants, where there have been important developments in recent years. Each of the techniques is described in simple terms for the non-specialist, and critically appraised by linking to one or more specific food contaminant problems giving key references for the reader who wishes to explore the potential of the methods in more depth.

The much neglected clean-up technique of size exclusion (gel permeation) chromatography is discussed and illustrated for a variety of problem areas as are immunological methods for drug residues in meat, both areas being more familiar to workers in biochemical and clinical fields, only recently becoming established in food science. Headspace gas chromatography has found wide application to trace analysis of foods and beverages and the chemiluminescence detector (TEA) is now widely used for nitrosamine monitoring, but both techniques are probably only well known to the specialists and their inclusion in this text should indicate their possibilities to a wider audience. High performance liquid chromatography is of course now a part of the instrumentation of most analytical laboratories but there have been recent developments in detectors and columns, and the advantages and limitations of these are discussed in relation to the important contamination area of mycotoxins. Recent advances in the measurement of inorganic elements is also covered, critically discussing both the neglected aspects of sample preparation through to recent innovations in instrumentation. Finally, the specialised confirmatory technique of mass spectrometry (selected ion monitoring) is discussed, once again for the non-spectroscopist attempting to outline the important features and how these may find application in the reader's own field.

It is hoped that this book will provide a starting point for the analytical chemist unfamiliar with some of the newer applications of techniques in food contaminant analysis. Also, others less familiar with the subject may gain an appreciation of the stimulating and challenging problems for the future in the analysis of trace contaminants in foods.

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Size Exclusion and Gel Chromatography: Theory, Methodology and Applications to the Clean-up of Food Samples for Contaminant Analysis

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SUMMARY

The application of size exclusion (gel permeation) chromatography (SEC) and gel chromatography (GELC) to the clean-up of food samples for trace analysis is reviewed. Gel chromatography is defined as the combination of exclusion with partition or sorption of solutes to the gel matrix. The theoretical basis of each mode of chromatography is considered with reference to the relationship between solute structure and retention. The influence of solvent choice upon the separation mechanism is discussed in terms of solubility parameter theory, and those solvent–solute and gel–solute interactions which may be expected to contribute to resolution in typical chromatographic systems are described in detail.

The practical aspects of setting up an SEC or GELC system are discussed with regard to the selection of gel and apparatus. Optimisation of chromatography is outlined and a full description of operating procedures is given to enable the analyst with little or no experience of SEC or GELC to establish a working system. High performance methods (HP-SEC) and automated instruments for high performance and low resolution chromatography are also described. The latter include both commercially available instruments and those which may be assembled in the laboratory using HPLC and other components. Finally, trace analysis applications of SEC, GELC and HP-SEC are discussed.

* The mention of individual manufacturer's products does not imply that they are endorsed or recommended by the UK Ministry of Agriculture, Fisheries and Food over other similar products not named.

1. INTRODUCTION

1.1. Objectives

Sample clean-up occupies probably a greater proportion of the time spent on trace level determination of organic species than any other aspect of analysis. This is particularly the case where a food matrix is involved because of the great number of potentially interfering compounds present. The advent of highly automated instrumental methods of analysis and the use of computers for subsequent data handling has exacerbated this problem.

Thus it is highly desirable that the process of sample clean-up should similarly be automated, releasing manpower for more productive tasks. There are some signs that progress is being made towards this end but we are still very much in the early stages of developing automated methods of clean-up. Typically, sample preparation entails a sequence of one or more steps, consisting of solvent extraction, liquid–liquid partition and column chromatographic separations of numerous kinds. It is the objective of this chapter to describe the application of size exclusion chromatography (SEC) and gel chromatography (GELC) to the isolation and analysis of low molecular weight (less than about 1000 daltons) organic compounds present in foods at trace level concentrations of 1 mg/kg or lower. A combination of review of theory and applications will be presented, together with a discussion of the methodology involved, in sufficient practical detail to permit an assessment to be made of the potential utility of either technique as part of the solution to individual clean-up problems.

Although the emphasis will be placed upon the advantages and disadvantages of automated GELC or SEC as a 'unit process' for incorporation into any scheme for sample clean-up, it should be recognised that both chromatographic modes have unique selectivities which can be of advantage even when the methodology has to be applied manually.

This combination of chromatographic methods has been chosen for review because SEC and GELC are essentially two aspects of one system. Many column liquid chromatography (LC) packings are structurally classified as gels; that is, they contain two interdispersed phases, one being a solid but porous matrix and the other a fluid such as an LC eluent. Aerogels (represented by silica gel) are rigid and their porosity is unaffected by applied pressure or removal of solvent. Xerogels, typified by the Bio-Beads (Bio-Rad Inc.) range of poly (styrene–

divinylbenzene) co-polymer beads and the Sephadex (Pharmacia) cross-linked dextrans, are much softer and will swell extensively when solvated with compatible liquids. They are liable to undergo significant changes in volume when equilibrated with a different solvent and their particle shape to deform under pressure. The internal solvent phase should be thought of as contained equally in the spaces around and between the interconnected matrix polymer chains rather than being confined to a system of discrete pores, such as exist in aerogels.

Either type of structure can separate molecules on the basis of size, as will be discussed in Section 2.1, and in many instances the gel matrix also participates in the separation mechanism (Section 2.2). SEC can be considered to be the limiting case of GELC where the matrix has no interaction with either solute or solvent. It should be noted that the term 'gel chromatography' is restricted here to those systems where separations are not due to SEC alone but to SEC in combination with adsorption or partition effects. Thus ion exchange and such well-defined phenomena as chelation are not considered explicitly, although the potential exclusion properties of the gel matrixes concerned should not be ignored.

One further motive for the compilation of this text is the current lack of a comprehensive single source of information for the analyst using either GELC or SEC as a tool for sample clean-up. SEC as applied to the separation of biological macromolecules or as a means for determining polymer molecular weight distributions has been extensively reviewed.[1–5] Possibly, because of a general tendency to consider exclusion chromatography as a technique useful only to polymer chemists or biochemists, the area of small molecule SEC (arbitrarily limited here to compounds with molecular weights of less than 1000 daltons) has been relatively neglected except by investigators concerned with elucidating the mechanisms operating in the separation of macromolecules. Again, the interface between GELC and SEC has been of interest to theoreticians but it has not before been considered with an emphasis on the practical requirements of sample clean-up. Among a number of publications of interest in this context is a review article by Walter and Johnson on the dimensional separation of low molecular weight compounds[6] which also employs the solubility parameter concept (Section 2.3) to examine the relationship between SEC and GELC.

Furthermore, although both SEC and GELC have been employed as complete or partial clean-up procedures for a wide range of com-

pounds in food or environmental samples, no single source of references is available. In many cases, the use of SEC or GELC is not mentioned in publication titles, key words or abstracts, and in consequence it has been difficult to obtain an overview of this application. Although it is possible to gain some appreciation of potential applications of these methodologies from literature compilations supplied by the manufacturers of gels and instrumentation, it seemed desirable to take this opportunity to present a more complete account of the range of applications reported in the area of clean-up of food and similarly complex samples for the analysis of contaminants and other trace level low molecular weight components.

1.2. Historical Development

Size exclusion chromatography is the preferred name[7] for the two independently evolved techniques of gel filtration (GF) and gel permeation chromatography (GPC). Other synonyms include molecular sieve and steric exclusion chromatography. GF and GPC differ essentially only in terminology. Gel filtration indicates the use of aqueous eluents to fractionate biological molecules, whilst in GPC organic solvents are employed to obtain molecular weight distribution and other information vital to the plastics and coatings industries. High performance variants of each have been developed in recent years and these will collectively be abbreviated as HP-SEC.

SEC is a form of chromatography where solutes are (ideally) separated solely upon the basis of differences in molecular 'size'. Gel chromatography employs the same range of column packings but with solvents chosen to introduce sorption, partition, hydrogen bonding and other effects into the separation in order to influence selectivity. Early workers attempting to develop 'pure' SEC soon realised[8] that these apparently confounding forces could be utilised to improve upon the inherently limited resolution of exclusion chromatography. Various aspects of the history of the development of SEC have been described by Synge,[9] Moore[10] and Anderson *et al.*[5] GF first became practicable following the introduction by Porath and Flodin in 1959 of the Sephadex cross-linked dextrans[11] and rapidly became indispensable to the study of peptides, proteins and other macromolecules. Matrixes compatible with organic solvents were reported by Vaughan[12] and Cortis-Jones[13] but these suffered from mechanical instability and other disadvantages. In 1964, however, Moore introduced the term GPC and

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