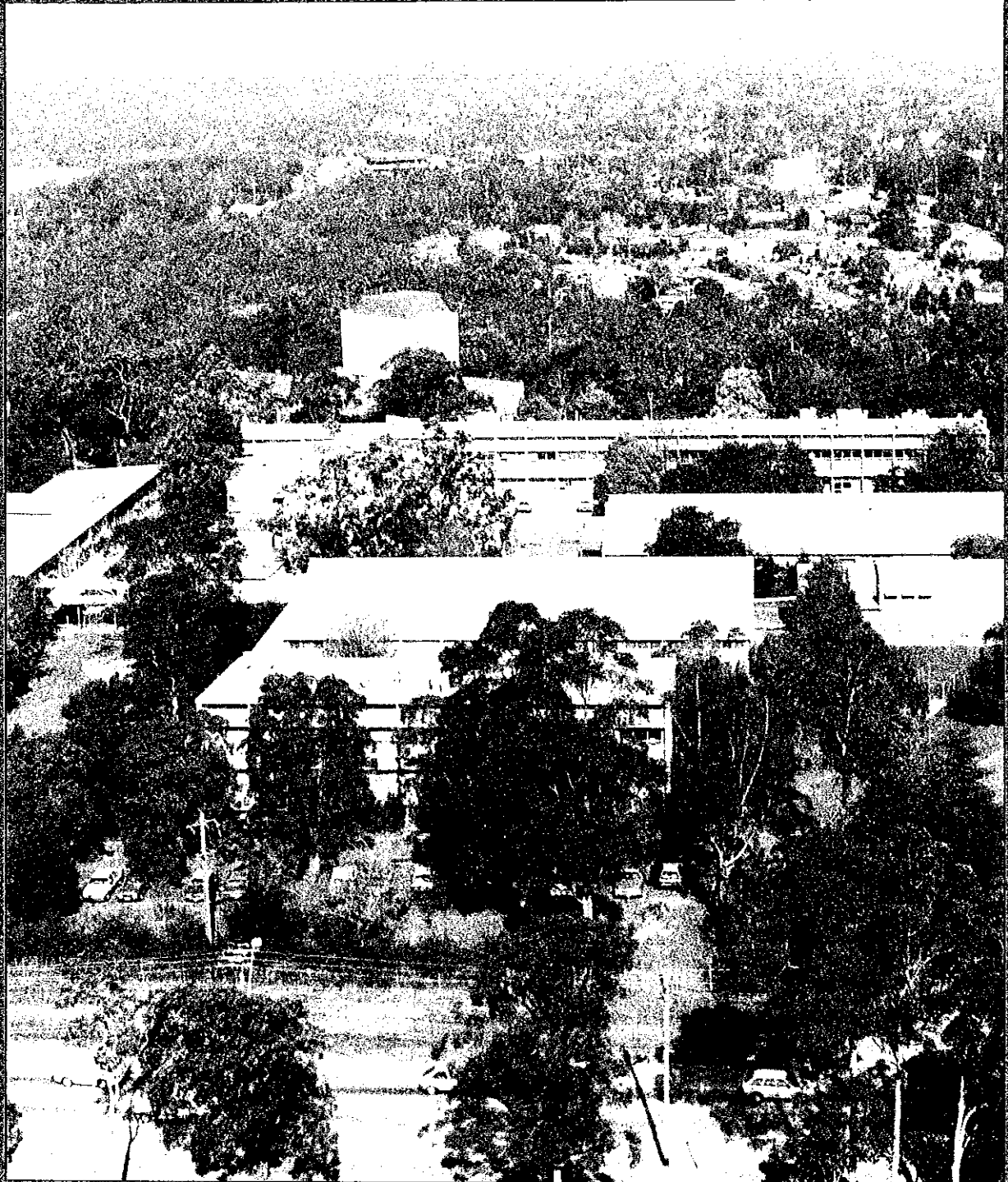


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# Supercritical fluid extraction – new technology for the food industry

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Extraction under supercritical conditions depends on the ability of the supercritical fluid to selectively dissolve differing amounts of low molecular weight substances. The application of supercritical fluid extraction to a range of foodstuffs is reviewed, with particular reference to deodorization and fractionation. Specific food processing applications are discussed such as coffee decaffeination, hop extraction, essence removal and oil fractionation. Impediments to commercialization and process potential are considered.

## Introduction

Before considering the implications of supercritical extraction technology for the food industry, it is first appropriate to consider the principles behind this new process. At the heart of the process is the use of a gas under specified conditions to fractionate the product concerned. It is necessary to consider some of the factors influencing the behaviour of gases under various conditions to understand the basics of supercritical extraction.

Much of the work discussed herein is based on three particularly useful review articles, those of Rizvi *et al.* (1986a,b) and Brogle (1982). Figure 1 (after Rizvi *et al.* 1986a) shows a typical pressure temperature phase relationship for a pure material, and indicates some of the relationships between phase transformation processes. The essential conditions for the liquefaction of gases was discovered in 1869, as the result of studies on the effect of pressure on carbon dioxide. It was found that there was a temperature (31.1°C) above which it could not be liquefied, no matter what pressure was applied. Below this temperature pressures of 75 atm were sufficient to liquefy the gas. Further investigation has shown that this characteristic of a critical temperature exists for all gases. The maximum temperature at which a gas may be liquefied (above which it cannot exist as a liquid) is known as the *critical temperature*, and the pressure required to cause liquefaction at that temperature is known as the *critical pressure*. This is also the highest vapour pressure the liquid

can exert. The volume occupied by one litre of the substance at the critical temperature and pressure is known as the *critical volume*. Note that the word "vapour" is used to refer to a gas when its temperature is below the critical temperature, and it can be condensed to a liquid by pressure alone. It should be noted that the transition between liquid and vapour generally occurs sharply. However, as the critical temperature is approached, the transition is less clear.

A supercritical fluid is one which is above its critical pressure and critical temperature. In general, supercritical fluids exhibit characteristics between those of liquids and gases. High solvent power is generally shown as a result of the high density of the fluid, whilst penetrating power is excellent because of its high diffusivity and low viscosity. Some typical values of physical properties of a liquid, gas and supercritical fluid are shown in Table 1.

The characteristics of supercritical fluids depend of their physical conditions, temperature and pressure in particular. Alteration of these parameters results in significant changes of viscosity, diffusivity and density. Such changes can be utilized to increase the extraction efficiency of this technology. As the solubility of solutes in supercritical fluids depends very heavily on the density (and thus the temperature and pressure) of the solvent, selective extraction of various components under differing physical conditions can be achieved. It should also be

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TABLE 1

Typical physical properties associated with different fluid states

State of fluid	Density (g/cm <sup>3</sup> )	Diffusivity (cm <sup>2</sup> /s)	Viscosity (g-cm/s)
Gas			
P = 1 atm, t = 15-30C	(0.6-2) × 10 <sup>-3</sup>	0.1-0.4	(1-3) × 10 <sup>-4</sup>
Liquid			
P = 1 atm, t = 15-30C	0.6-1.6	(0.2-2) × 10 <sup>-5</sup>	(0.2-3) × 10 <sup>-2</sup>
Supercritical			
P = P <sub>c</sub> , T = T <sub>c</sub>	0.2-0.5	0.7 × 10 <sup>-3</sup>	(1-3) × 10 <sup>-4</sup>
P = 4P <sub>c</sub> , t = T <sub>c</sub>	0.4-0.9	0.2 × 10 <sup>-3</sup>	(3-9) × 10 <sup>-4</sup>

from Rizvi *et al.* (1986a)

noted that the selectivity of the process increases as the temperature or pressure of the supercritical fluid approaches supercritical conditions. Solubility varies with molecular weight for solutes of similar structure. Basically, the solvent power of a supercritical

fluid increases with density at a given temperature, and with temperature at a given density.

Small amounts of added entrainer — a compound of intermediate volatility — can dramatically affect solubility and selectivity, extending the flexibility of supercritical fluid extraction. Typical entrainers include methanol and acetone.

By comparison with supercritical fluid extraction, it should be noted that classical solvent extraction has two main disadvantages. Firstly, in classical solvent extraction, the solvents must be removed after extraction, which is energy intensive, and this process may degrade the product. Secondly, it is often not possible to completely remove the solvent, which may result in undesirable contamination of the product. Such problems are of particular concern in food processing.

### Solvent selection

For food applications there are a number of aspects in solvent selection to be considered. These include toxicity, miscibility, cost,

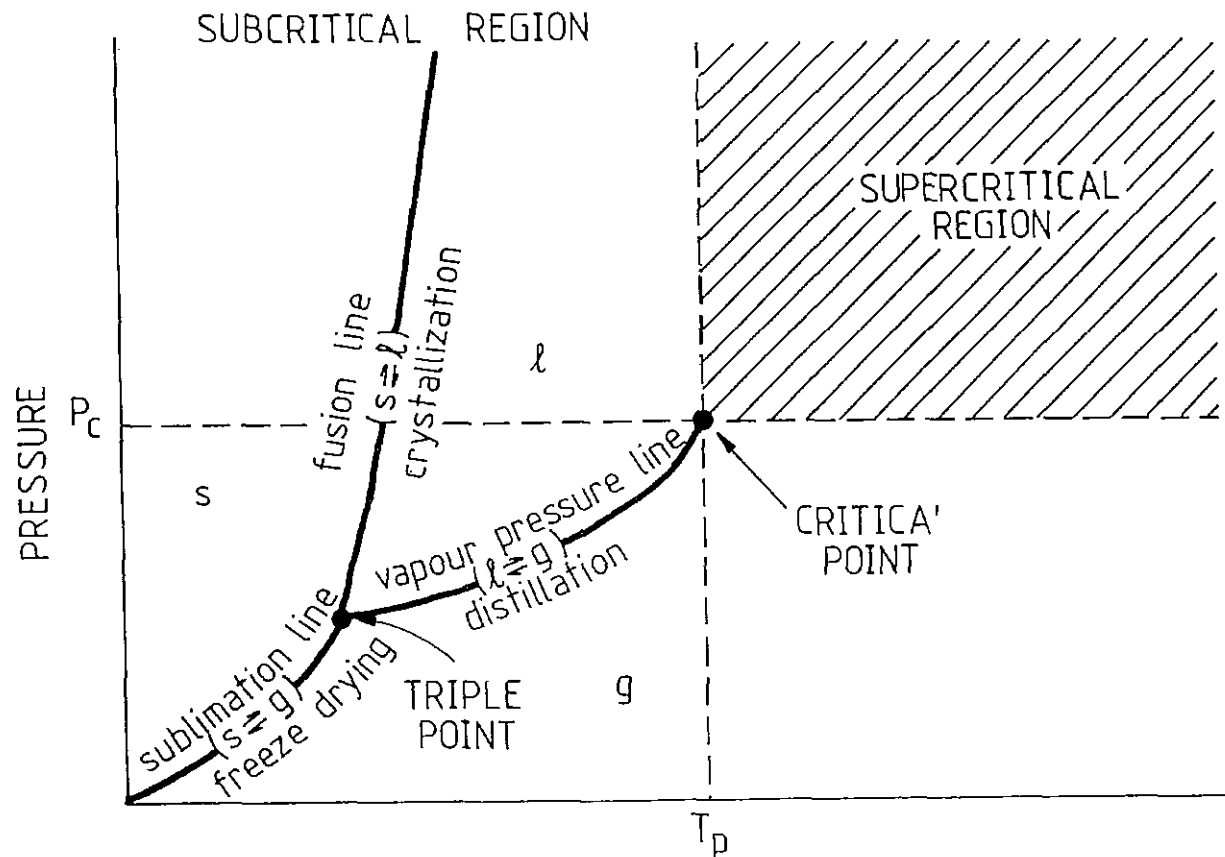


Fig 1. Phase diagram for a pure compound, showing phase transition relationships (after Rizvi *et al.* 1986a)

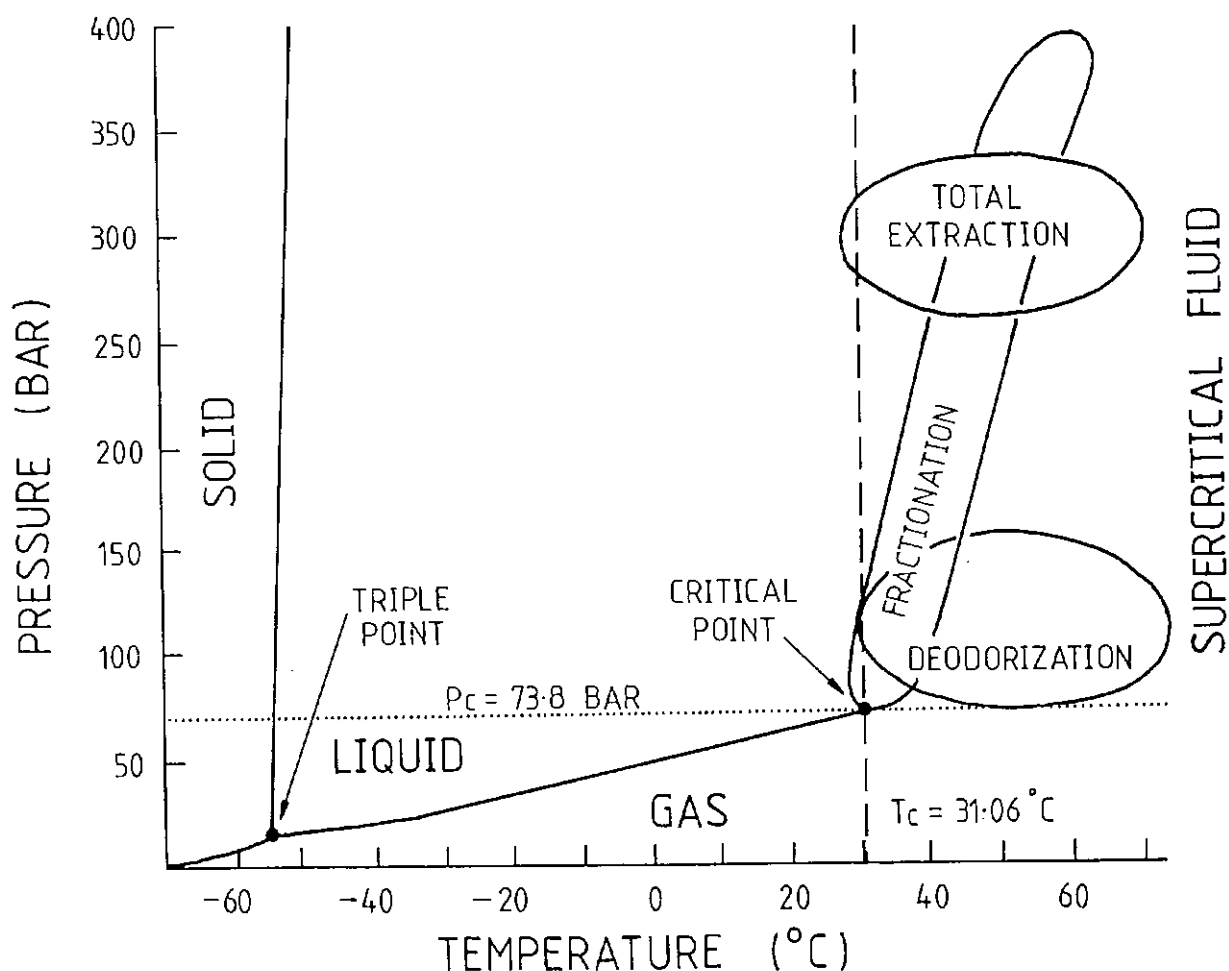


Fig. 2 Physical states of carbon dioxide at various temperatures and pressures, illustrating regions used for food processing applications (after Rizvi *et al.* 1986b)

availability, critical temperature, and reactivity. Of the various supercritical fluids studied, only carbon dioxide, ethane, ethylene and some fluorinated hydrocarbons meet the necessary requirements and are currently of interest to the food industry.

The primary factor involved in solvent selection must be its ability to dissolve the solute, but so far little information on this topic has yet appeared in the literature. As a rough guide, it has been suggested that the difference in solubilities between the liquid and the supercritical states of a fluid is about one order of magnitude, which may be taken as a starting point for feasibility studies.

Carbon dioxide is the solvent of choice for food applications for the following reasons:

- (i) carbon dioxide can be readily separated from any solute
- (ii) carbon dioxide has low viscosity and high diffusivity, is non-toxic and causes no environmental problems
- (iii) carbon dioxide is not inflammable, and is inexpensive (Brogle 1982)

However, the use of carbon dioxide in supercritical fluid extraction does have significant limitations. These include:

- (i) only low molecular weight compounds (under about 500 Daltons) are readily soluble in supercritical carbon dioxide
- (ii) polar organics are generally only soluble if the molecular weight is very low — amides, ureas, urethanes and azo compounds show very poor solubility

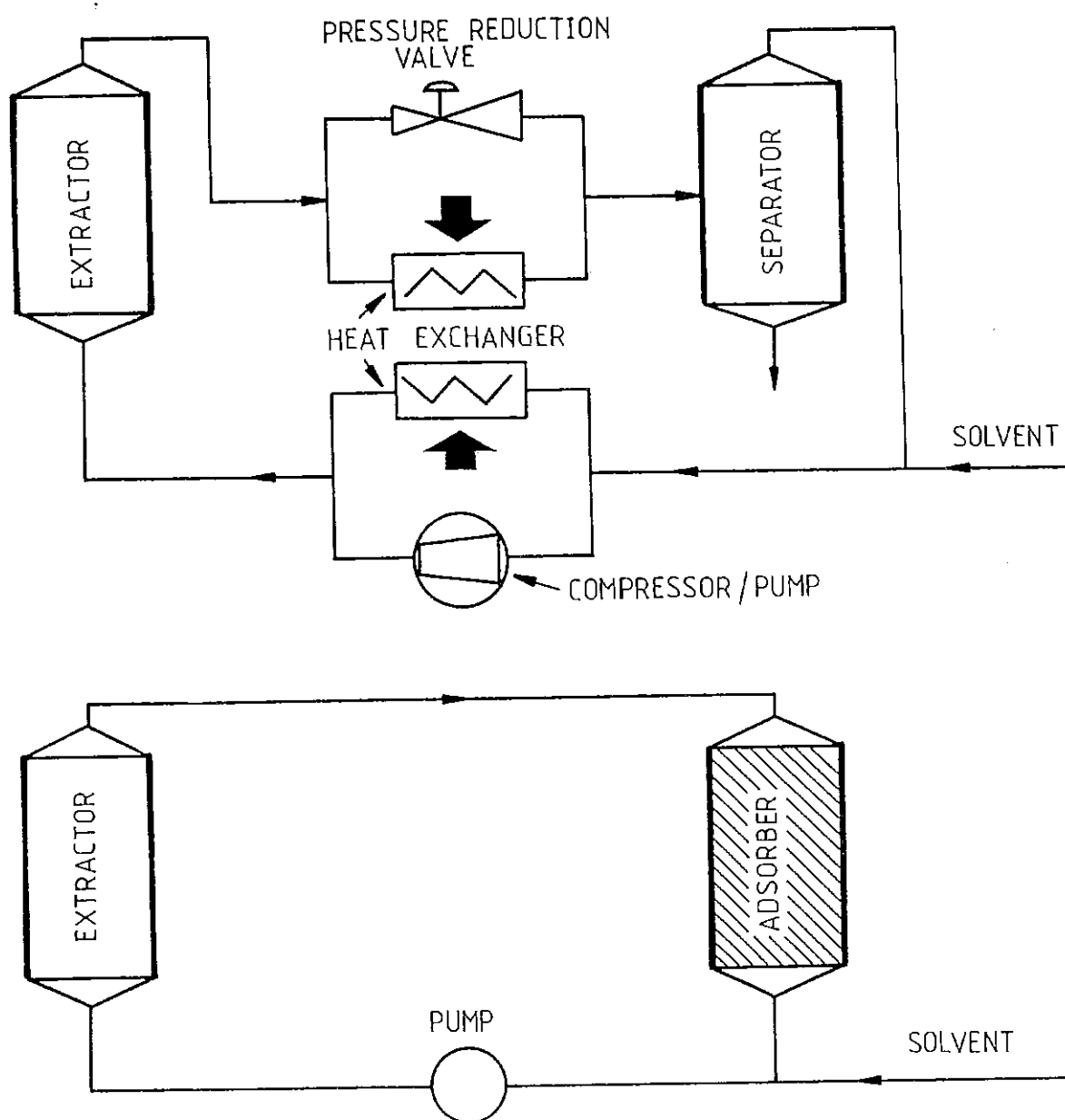


Fig. 3. Process schematic for supercritical fluid extraction equipment;  
 Upper — pressure and temperature controlled system for solute recovery;  
 Lower — an adsorption system for solute removal.

- (iii) fatty acids and triglycerides show poor solubility
- (iv) chlorophyll, amino acids, fruit acids and inorganic salts are insoluble.

### Methodology

The physical attributes of carbon dioxide, and their relationship to extractive procedures under supercritical conditions, are shown in Figure 2 (Rizvi *et al.* 1986b). In general, an increase in pressure results in increased solubility but decreased selectivity. Variations on extraction procedures are outlined below:

- (i) Complete extraction  
In general, this requires maximum operating pressure and temperature. Maximum operating temperature possible will generally depend on the chemical and physical nature of the substrate, whereas maximum pressure will generally depend on equipment design.
- (ii) Fractionation  
This may be carried out via a series of passes under differing conditions of temperature and pressure. For these purposes, entrainer incorporation may have very beneficial effects.
- (iii) Deodorization  
In general, conditions for deodorization are less stringent than those for total extraction or fractionation as only removal of the more soluble components is generally required.

Four major components are required for supercritical extraction. These are: a solvent compressor/pump; an extractor; a temperature/pressure controller; a separator or adsorber. Other control equipment such as pumps, regulators and flow meters, is also necessary. There are at least three configurations suitable for supercritical extraction.

In the first, temperature is manipulated to remove the desired component. The extraction vessel is charged and supercritical fluid introduced at the temperature of maximum solubility. The resultant solution is passed through a heat exchanger, and the temperature adjusted to minimize the solute's solubility in the supercritical phase. The solute is collected in the separator, and the solute-depleted supercritical fluid recompressed and recycled.

In the second form, pressure is used to perform the separation. In this case, the solute-rich fraction is reduced in pressure, and the

solute separated. Again the solvent may be recycled after recompression. Use of this methodology is constrained by the cost of pressure adjustment. (To overcome this the use of a turbine to reduce pressure and to recycle the energy derived during this process has been suggested).

The third configuration uses a fixed-bed process involving isobaric and isothermal conditions. Solutes are removed from the matrix by adsorption in a fixed material such as activated carbon. A schematic diagram of the three processes is shown in Figure 3 (after Rizvi *et al.* 1986b).

Although there are at present few full scale commercial operations utilizing the supercritical extraction process, there is much current interest in its applications. A number of companies are offering bench and pilot scale equipment for process assessment. These include Newport Scientific of Maryland, USA and the Flow Control Division of Milton Roy

**TABLE 2**  
**Applications of supercritical extraction in foods**

Process	Raw Material
Decaffeination	Coffee, tea
Deodorization	Vegetable oils Animal fat and oil Brewers yeast
Aroma recovery	Spices Hops Tobacco Coffee Apples
Oil recovery	Soy beans Peanuts Sunflower Rapeseed Corn germ Coconut Cocoa Lemon Olives
Oil refining	Fatty acid removal Hydrogenation Separation
Fractionation	Cod liver oil Fatty acid esters
Glyceride mixtures	

(after Rizvi *et al.* 1986)

Co., of Pennsylvania. On a larger scale, Xytel Corporation of Illinois has been involved in the design of a number of bigger units for commercial assessment.

### Food processing using supercritical extraction

Scientists have been studying supercritical fluid extraction for food process applications for more than two decades. Table 2 (Rizvi *et al.* 1986) outlines some of the applications considered to date.

At present, there are two major uses for supercritical fluid extraction within the food industry. These are:

#### (i) Decaffeination of coffee

Since 1978, a major supercritical fluid extraction plant has been operating in West Germany for the removal of caffeine from coffee beans. The beans are soaked in water to increase the selectivity of the process towards caffeine. The caffeine is recovered from the supercritical solvent by scrubbing with water, which is later decompressed and distilled to recover the caffeine. This process eliminates the expensive depressurization and recompression procedures otherwise required. Caffeine levels are reduced from about 0.7% to 0.02% without any effect on flavour or aroma. Alternative methods developed used activated charcoal to absorb the caffeine.

#### (ii) Recovery of hops extract

These extracts are used to give beer its characteristic flavour. Conventional extraction processes use organic solvents such as methylene chloride, which must be very effectively removed to reduce their residual levels. Supercritical extraction offers therefore considerable benefits in terms of assured product quality. Single stage extraction is used, which yields a stream containing 99% of the desired product (Vollbrecht 1982).

Construction of a 5000 tonnes p.a. extraction plant was under way in West Germany in 1982. The following reasons were put forward for selection of supercritical extraction methodology rather than the use of liquid carbon dioxide for the process:

- Supercritical fluid extraction involves higher pressures, and thus supercritical fluid extraction equipment can also be used at lower pressures for liquid carbon dioxide extraction.
- Supercritical fluid extraction is capable of extracting a wider range of solutes than liquid carbon dioxide.
- Process conditions for supercritical fluid

extraction were deemed easier, rather than the stepwise extraction procedure required by liquid carbon dioxide.

- There were no additional cost benefits resulting from the use of liquid carbon dioxide, and it was decided that the more flexible supercritical process was preferable.

It is interesting to note that studies on supercritical extraction in the perfumery industry (Calame and Steiner 1982) have suggested that the process is expensive, except when dealing with large quantities of material, such as in the decaffeination of coffee. Further, it was reported that the costs of classical extraction processes and supercritical fluid extraction were similar where there was a large amount of concentrated extractable material, but that supercritical fluid extraction costs rose sharply where dilute materials were involved.

Many other applications have been suggested for supercritical fluid extraction within the food industry. These include:

- (i) Fat extraction from potato chips and similar snacks. Potato chips contain about 40% fat, about half of which may be readily removed by supercritical fluid extraction (Anon 1981).
- (ii) Recovery of "spent" cooking oil. Spent oil takes on a deep colour, and contains large quantities of free fatty acids and peroxides. Supercritical extraction may be used to improve its quality significantly.
- (iii) Fat fractionation  
This is a major area of interest.

Suggested applications include:

- (a) Coconut oil has been fractionated into five components using supercritical extraction. Lactones and the low molecular-weight fatty acids responsible for the characteristic flavour of coconut oil have been isolated in the first fraction, and could be used as flavour concentrates rather than the whole oil. Similar results have been reported in studies on cocoa butter.
- (b) Schaap, Straatsma and Escher (1986) have reported on the extraction of anhydrous milk fat using supercritical extraction fluid technology. These workers reported that triglycerides with a low acyl number can easily be extracted, and the operations carried out with high selectivity. Free fatty acids are

also easily extracted, but peroxides are not concentrated in the extract. It has also been reported (Urbach 1987) that the aroma compounds extracted from anhydrous milk fat have useful applications in the baking industry.

- (c) Fractionation of butter fat into fractions containing mostly short and long-chain triglycerides (Kaufman *et al.* 1982).
- (d) Manufacture of low cholesterol butter (Fujimoto *et al.* 1987). Similar studies on the modification of butter oil to lower the cholesterol level and improve spreadability of butter were reported by Shiskikura *et al.* (1986) and Arul *et al.* (1987).
- (iv) Extraction of oils from Antarctic krill (Yamaguchi *et al.* 1986)
- (v) Production of defatted soybean products by supercritical extraction (Friedrich and Eldridge 1985)
- (vi) Cotton seed oil extraction (List, Friedrich and Pominski 1984).

Thus the technology can be used to fractionate (as in oil and fat processing), to extract to improve the perceived quality of the extracted material (as in treatment of spent cooking oil or in the extraction of cholesterol), or to extract to utilize the extract (as in perfumery or in the extraction of concentrated flavours).

### Future developments

There are a number of impediments to the commercial acceptance of this technology by industry.

- (i) The process is essentially a batch operation at present and thus inappropriate to many applications. However, it is understood that a number of companies are examining the feasibility of continuous operation. This will improve the potential applications of the process considerably.
- (ii) Costs are still high, and scale-up problems in transferring results from bench-top applications to full scale are considerable. In general, both capital and operating costs of supercritical extraction are higher than conventional processes, and clear economic advantages must be demonstrated if the technology is to be commercially viable.

The high capital involvement tends to preclude utilization of the technology by smaller companies.

- (iii) Patents are held in many areas of the world covering applications such as flavour extraction, oil extraction, fractionation, decaffeination, production of hops extract and deodorization using supercritical technology. Potential users should be aware of these patents to ensure that infringement does not occur.

In spite of these drawbacks, supercritical fluid extraction does offer the industry new technology and the opportunity to develop new value-added products. Continuing engineering developments will no doubt improve the capacity of existing equipment, and, should continuous equipment be developed, there is no doubt that commercial applications will expand. The technology is in the very early stages of development, and little is understood at this stage about selection of optimum operating parameters in the extraction of a multi-component mixture. A better understanding of the process is needed, at both the theoretical and practical levels if this technology is to benefit the food industry in general.

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# Rapid dry matter maturity test for kiwifruit by microwave

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The dry matter content of kiwifruit, measured before or after ripening, increases with the maturity of the fruit. The official method for determining dry matter of fruit uses an air oven and vacuum oven to dry blended samples of fruit. Preparation of the sample is tedious, and the drying procedure takes two days, making this method unsuitable for regulatory purposes. This paper describes the use of a microwave oven for the determination of dry matter content, as a measure of the maturity of kiwifruit. The determination takes less than one hour, including the simplified preparation of the sample.

## Introduction

Kiwifruit production in Australia has increased considerably over the last ten years and will continue to do so as new plantings come into full bearing. Australian growers face strong competition from the well-organised New Zealand industry that is able to market fruit for nine months of the year by using long-term storage technology. The Australian industry does not store kiwifruit long-term, most fruit being marketed during the harvest season common to both countries when fruit is plentiful and prices are low.

In New Zealand the level of soluble solids at harvest (i.e. unripe) is used as the measure of maturity. Fruit are not harvested until the soluble solids reach 6.25%. Inspection must take place on the farm as the soluble solids start to rise only a few hours after harvest.

Preliminary studies carried out at the CSIRO Food Research Laboratory, aimed at improving the marketing of Australian-grown kiwifruit, showed that some fruit was acceptable to a panel of tasters long before the level of soluble solids reached the New Zealand maturity standard. This finding suggested that Australian fruit has an early season advantage for both export and domestic marketing.

A detailed study was then made over two seasons (1984/85), measuring chemical and physical attributes as well as the eating quality as determined by a taste panel (Scott *et al*, 1986). In both seasons, and for three varieties, eating quality was found to be directly related to the dry matter content and also to the soluble solids of the fruit when ripe but poorly

related to the soluble solids content at harvest. Furthermore, most of the fruit was acceptable up to six weeks earlier than indicated by the New Zealand maturity test.

The percentage soluble solids in ripe fruit was not only an excellent measure of maturity, it was also a simple test to perform. However, as it takes at least five days to ripen kiwifruit, the test is not suitable for regulatory purposes.

It did not matter whether measurements for dry matter were taken at harvest, after storage or after ripening as the test was always a good measure of quality. The dry matter test can therefore be performed at any stage during marketing and is not limited to on-farm use as is the New Zealand test. There was only one drawback to the use of dry matter as a maturity index: measurement of dry matter by the official method requires extensive sample preparation and the drying procedure takes two days.

The present study was carried out to determine whether microwave drying could be used in place of the official method as a rapid method for determining dry matter content of kiwifruit.

## Materials and methods

Fruit of two cultivars, Hayward and Dexter, were harvested from two growing regions in NSW: Sydney Hills district and Coffs Harbour. Fruit was harvested every two weeks beginning in February, and continuing until May. These harvests began with obviously immature fruit and continued until fruit were well past

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commercial maturity. Three methods of determining maturity were compared: dry matter by standard oven drying, dry matter by modified preparation and microwave, and percent soluble solids in ripe fruit.

Fruit at harvest (i.e. unripe) were used for the measurement of dry matter, although some tests on semi-ripe and ripe fruit were also performed to observe the effect of an increasing sugar content caused by fruit ripening.

#### *Dry matter — oven drying*

Ten unripe fruit from each harvest were peeled and blended, and a sample taken for analysis of dry weight as a percentage of fresh weight. Samples were partially dried in an air oven at 70°C before vacuum oven drying (AOAC 1980, method 22.018). The method of sample preparation and analysis was identical with the method used in the 1984-85 study (Scott *et al.* 1986).

#### *Dry matter — microwave*

##### *Sample preparation*

Various methods of sample preparation were evaluated for dry matter determination by microwave, and the results were compared with

blending peeled whole fruit. The easiest and quickest method was to cut thin (approx. 2 mm) equatorial slices from the middle of the fruit. Each slice weighed between two and three grams.

Preliminary tests showed that the dry matter varied along the length of the fruit, but the middle few slices gave an average reading for the whole fruit. One middle slice taken from each of ten unripe fruit was then used to give an average dry matter reading for the ten fruit.

#### *Drying*

A large domestic microwave oven (National NE 7870) was used for the experimental work. The power output of this oven on the "low" setting was determined, using Australian Standard AS 2895-1986, as 240 watts. With this power setting it was always possible to dry the samples of unripened fruit to constant weight. Constant weight was defined as no further loss in weight (two decimal places) after a further 10 minutes heating.

The average percentage dry weight for each sample of fruit was determined by weighing the middle slice from each of ten fruit onto two glass petri-dishes with lids, (i.e. 5 slices per

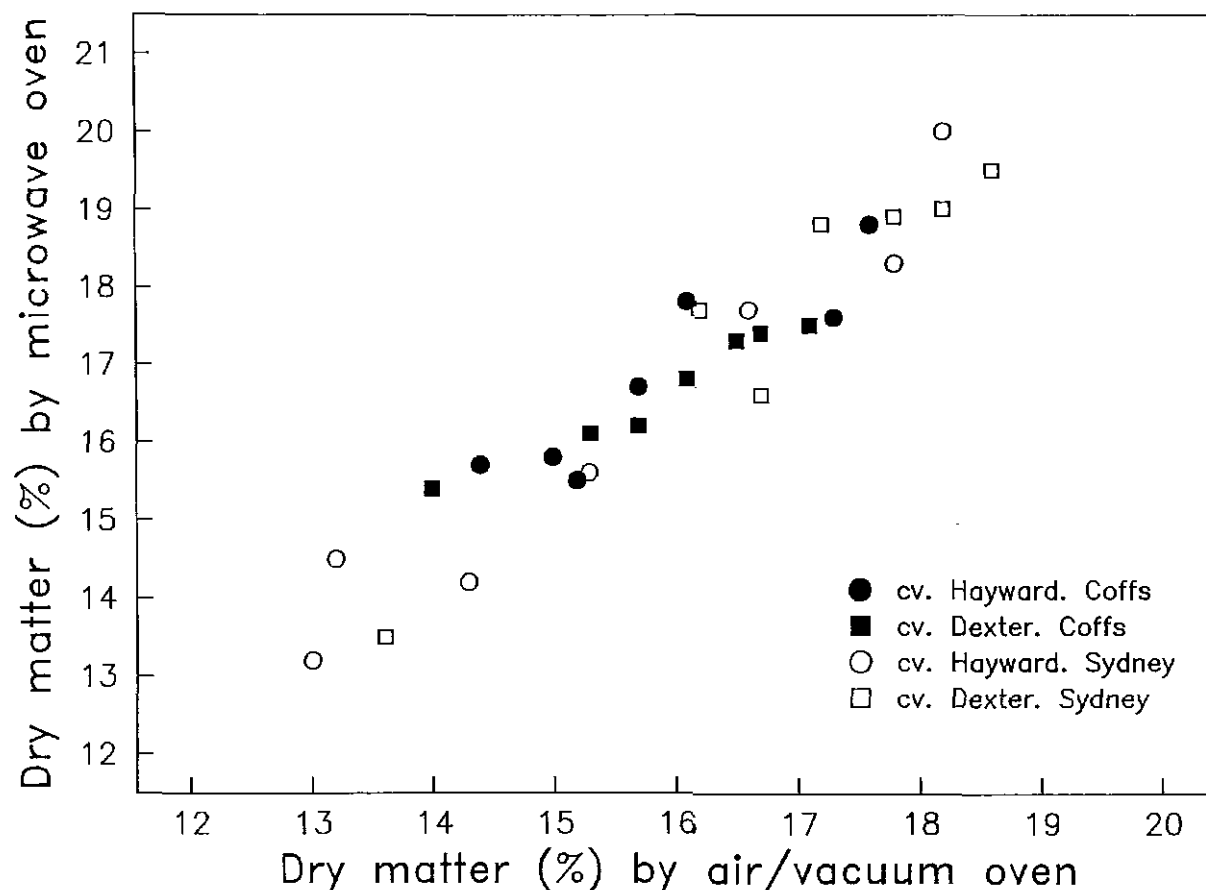


Fig. 1. Percentage dry-matter of unripe kiwifruit: microwave oven versus air/vacuum oven.

dish, total weight 10-15 g per dish). Either two petri-dishes (one sample) or four petri-dishes (two samples) were placed inside the microwave oven and heated on low power until constant weight was reached. After 20 minutes heating, the samples were removed, the lids were immediately placed on the petri-dishes and the samples were weighed while still warm. The dishes were then returned to the microwave oven for further 10 minute periods until constant weight was reached.

#### *Soluble solids when ripe*

Ten fruit from each harvest were ripened by exposure to ethylene (10 uL/L) for five days at 20°C. The total soluble solids in each ripe fruit was measured by cutting the fruit in half and squeezing two drops of juice from each half onto a refractometer prism. An average figure for ten fruit was calculated.

#### **Results and discussion**

The relationship between dry matter by air/vacuum oven and dry matter by microwave

oven is shown in Figure 1. The correlation is highly significant ( $r = 0.95$ ,  $n = 28$ ,  $P < 0.001$ ), and the relationship can be expressed by the equation:

$$Y = 1.05X$$

where Y = Dry matter (%) by microwave oven  
X = Dry matter (%) by air/vacuum oven

Therefore a dry matter content of 15% by oven drying will be equivalent to a dry matter content of 15.8% by microwave.

These results confirm that a microwave oven can be used to determine quickly and accurately the dry matter content of unripened kiwifruit. The microwave technique is applicable to fruit of any maturity, from very immature fruit to fruit harvested well after current commercial maturity.

The microwave technique is also applicable to semi-ripe fruit with a soluble solids as high as 10%. Some browning of the samples occurs on heating, but constant weight is still achieved, and the resulting dry matter correlates well with that obtained by drying in

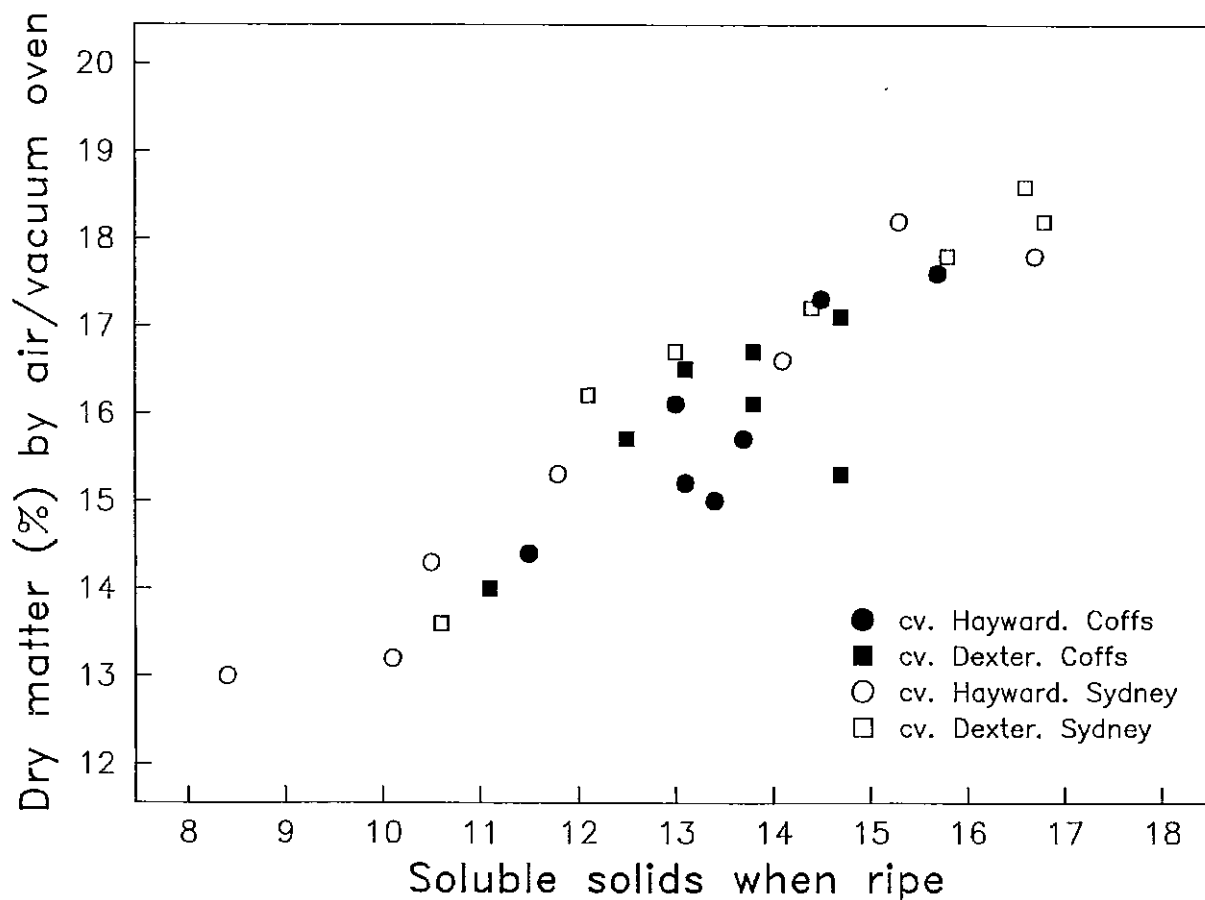


Fig. 2. Percentage dry-matter of unripe kiwifruit by air/vacuum oven plotted against percentage soluble solids or ripe fruit.

an air/vacuum oven. The dry matter content of fully-ripe fruit cannot be determined by microwave as the higher level of sugar causes the samples to burn.

The relationship between dry matter at harvest and soluble solids in ripe fruit was found to be highly significant ( $r = 0.92$ ,  $n = 28$ ,  $P < 0.001$ ), (Figure 2) and similar to that obtained in the 1984 and 1985 seasons. This result confirms that either test can be used to indicate harvest maturity and that the tests are interchangeable. A grower can therefore monitor the maturity of his crop by ripening a small sample of fruit every week and determining the soluble solids content when

ripe. At the terminal markets or prior to export the maturity can be quickly checked by dry matter if required. The microwave technique is recommended for general use and as a regulatory tool for determining kiwifruit maturity.

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# Oat Bran

## Does oat bran lower plasma cholesterol . . . and, if so, how?

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*'Oats — A grain which in England is generally given to horses, but in Scotland supports the people':  
Dr Samuel Johnson*

That oats can lower plasma cholesterol has been known for at least the past quarter of a century. The effect seems to have been first reported by de Groot and colleagues in 1963. Since then, there have been a number of feeding trials carried out with oats and oat products, using animal and human subjects. This work has consistently demonstrated that oats have the ability to lower plasma cholesterol concentrations — hence the current enthusiasm for oats and oat bran.

Is this enthusiasm justified? The evidence that oats and oat bran can lower plasma cholesterol is strong and convincing. However, oat bran is a highly variable material and the daily intake needed for there to be any likely health benefit is substantial — perhaps more suited to horses than people!

### What is oat bran?

Oat bran, like the more familiar wheat bran, is the outer part of the grain (but not the husk). It is, though, a very different material from wheat bran. It separates less cleanly from the grain and contains a much higher proportion of the starchy endosperm. Oat bran is also a much more variable material than wheat bran. Its composition depends on the milling procedure and varies from mill to mill and probably from batch to batch — at present there is almost no reliable comparative analytical information available. The compositions of a representative oat bran and wheat bran are compared in the Table. The oat bran contains considerably more starch and less dietary fibre than the wheat bran. Oat bran does, though, contain a higher proportion of water soluble fibre and this appears to be an important factor in its cholesterol-lowering activity. The relative amounts of protein, fat and moisture are not very different.

### The evidence for cholesterol-lowering activity

#### *Experiments with animals*

Cholesterol lowering activity of whole oat meal and various oat fractions has been studied in chicks fed hypercholesterolaemic diets (Fisher and Griminger 1967). Whole oat meal and oat hulls significantly reduced the birds' plasma cholesterol concentrations, with hulls being the more effective. Purified oat starch and the oat oil were totally ineffective, suggesting that the active principle is present in the bran. A more recent set of experiments with chickens confirmed that rolled oats can substantially lower plasma cholesterol (Prentice *et al.* 1982). A reduction of 25% was reported with a 9% reduction in plasma triglycerides.

Several studies using rats have produced similar results (Chen and Anderson 1979; Chen *et al.* 1981; Kritchevsky *et al.* 1984). Oat bran effectively lowered total plasma cholesterol and increased the ratio of HDL to LDL cholesterol.

#### *Experiments with humans*

The early experiments of de Groot *et al.* (1963) included a study in which a group of healthy men were given 120 g rolled oats daily, incorporated into bread. Plasma cholesterol concentrations were measured weekly for three weeks before the experiment, for the three weeks of the experimental period and for three weeks afterwards. The mean concentration fell from 6.49 mM to 5.76 mM during the test period (a fall of 11%) and in the following two weeks rose again to 6.36 mM.

The effect of feeding whole rolled oats has more recently been reinvestigated by Judd and Truswell (1981). The rolled oats (125 g/day) were substituted for breakfast cereals and wheat flour in the metabolically controlled diets of ten subjects. The experimental period

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was three weeks. They found a small decrease in LDL cholesterol (8%), too small to be statistically significant. HDL cholesterol and triglyceride concentrations were unchanged.

Kirby, *et al.* (1981) have carried out a well controlled experiment in which they fed oat bran at 100 g/day to a group of hypercholesterolaemic men. The mean LDL cholesterol concentration fell by 14% during the ten days of the experiment ( $p < 0.05$ ) and the HDL cholesterol concentrations again remained unchanged. A more recent experiment has confirmed these results (Anderson *et al.* 1984). In a group of hypercholesterolaemic men, again fed oat bran at 100 g/day, the mean LDL cholesterol concentration fell by 23% and the HDL cholesterol concentration by 5.6%. In this case the experimental diet was continued for three weeks.

### Mechanisms?

Chen *et al.* (1981) fed rats a variety of oat products with results suggesting that the cholesterol-lowering activity of oat bran is due to the presence of a water soluble gum — a  $\beta$ -glucan hemicellulose. The isolated gum was more effective than oat bran in lowering plasma cholesterol. Two possible mechanisms have been proposed: (1) Increased faecal excretion of cholesterol (in the form of neutral sterols and bile acids) (Kirby *et al.* 1981; Kritchevsky *et al.* 1984). (2) Suppression of endogenous cholesterol synthesis (Chen *et al.* 1981). This second proposed mechanism is based on the fact that oat gum is extensively fermented by the microorganisms in the large bowel producing volatile fatty acids — acetate, propionate, butyrate — which enter the blood stream and suppress cholesterol synthesis (Anderson and Bridges 1981). Illman and Topping (1985), using rats, have examined these two mechanisms and concluded that the increased concentrations of VFA in the blood in response to feeding oat bran are too low to influence cholesterol synthesis. They found substantially increased faecal excretion of bile acids and neutral sterols in response to the oat bran and concluded that this was the most likely cause of the cholesterol lowering effect.

### How much oat bran is required for a significant effect?

Unfortunately there is as yet no definite answer to this question. The experiments of Kirby *et al.* (1981) demonstrated a convincing and useful lowering of plasma cholesterol by feeding 100 g/day of oat bran. In contrast, in Judd and Truswell's experiments, in which they fed

125 g/day of rolled oats, the effect was small and not statistically significant. Rolled oats would contain about 33% bran (Shukla 1975) so the 125 g/day fed by Judd and Truswell would be equivalent to about 46 g/day of oat bran.

Another indication comes from an experiment in which volunteers were given 60 g/day of oat bran or oat meal (Van Horn *et al.* 1986). At this level there was a small decrease in plasma cholesterol, but only 3%.

Going to still lower daily intakes, 16-18 g/day of oat bran appears to be totally ineffective. In an experiment designed to investigate effects on transit time and faecal bulk, Hojgaard, *et al.* (1980) found that oat bran given at 12 and 18 g/day had no effect on faecal bile acid excretion (believed to be the mechanism by which the cholesterol-lowering effect occurs). Thus it seems that a substantial dietary intake of oat bran is required for it to effectively reduce plasma cholesterol concentrations — at least 60 g/day and probably close to 100 g/day. This would be equivalent to a generously heaped metric cupful.

Another complication is the variability in the chemical composition of oats. The active component seems to be the  $\beta$ -glucans and the content of this has been reported to range from 2.2 to 4.2% of the dry grain (Aman and Graham 1987).

### Conclusions

There is good evidence from animal and human studies that oat bran can effectively lower plasma cholesterol concentrations. This is in marked contrast to wheat bran, and dietary fibre in general, which seem to have little or no effect on plasma cholesterol concentrations (Oakenfull and Topping 1987).

TABLE 1  
Comparative compositions of representative samples of wheat bran, oat bran and rolled oats (g per 100g)

	Oat bran	Wheat bran	Rolled oats
Protein	20.1	14.1	15.3
Fat	6.0	5.5	6.0
Starch	38.4	23.0	57.6
Water	10.0	8.3	10.0
Dietary fibre:			
soluble	10.5	2.8	4.8
insoluble	11.7	39.9	4.8
total	22.2	42.7	9.6

The only forms of fibre which have been convincingly demonstrated to have a cholesterol lowering effect are the water soluble gums, such as pectin and guar. Oat bran seems to fall into this category. It contains a water soluble  $\beta$ -glucan which appears to behave similarly to pectin and guar.

However, the dietary intake of oat bran required, on its own, for effective and useful lowering of plasma cholesterol concentration (say 10-20%) seems to be substantial — at least 60 g/day and probably close to 100 g/day (a generously heaped metric cup). How oat bran would interact with other dietary strategies to lower plasma cholesterol remains totally unknown, but there is no reason for not recommending oat bran (and other oat products) as part of a cholesterol lowering diet.

It is important to bear in mind, though, that oat bran is a highly variable material. Consequently different types of oat bran and different oat products are likely to be highly variable in their effectiveness. Much more research is needed. The fact remains, though, that there is strong and convincing evidence that oat bran can lower plasma cholesterol levels.

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# The 'Laminate Film' method for measuring odour transmission rates through food packaging films

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## Introduction

The use of plastic films as barriers in packaging applications has led to many problems with oxygen and water vapour permeation from the atmosphere into food products. Furthermore, monomers, plasticizers and other ingredients in plastic films can migrate into the food; taints can be transmitted through the packaging materials from outside, and food odours can be lost from inside the package. New ways of measuring water vapour and oxygen transmission through packaging films using polymer film detectors have proved particularly successful because of their simplicity, (see for example Holland *et al.* 1980, 1981 and Holland and Santangelo 1982, 1984) and somewhat similar "laminate film" procedures will be described for measuring the permeation of higher molecular weight diffusants.

In the laminate method for oxygen and water vapour, the oxygen in the air or the water vapour in a humidity cabinet are the permeant sources; they are applied to one face of a test film, the other face of which is in intimate contact with a "collector" film, containing a reactive absorbent for oxygen or water. The reaction leads to a colour or U.V. absorbance change in the collector film with time, proportional to the amount of permeant which has diffused through the test film. This change is measured directly on the double film laminate by a spectrophotometer (if the test film is transparent) or on the separated collector film otherwise. It is necessary to use a cell with a sealing gasket to prevent ingress of gas between layers when an appreciable partial pressure difference occurs between the inside of the laminate and the air. This cell is not necessary for low volatility permeants.

For materials such as odorants a further refinement is possible; for compounds which are rather less volatile than water, a "supply" film containing the compound absorbed into the polymer can be used as a source, and a trilayer laminate system can be assembled. The laminate can be assembled and disassembled with little loss of permeant, and simple layering

of the films under tension or pressure is sufficient for sealing (see Fig. 1).

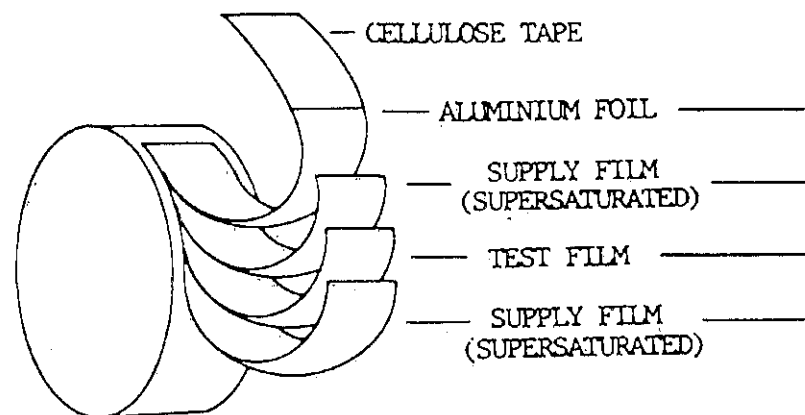
To measure the permeation rate of an odorant such as vanillin, a supply film containing vanillin can be laid on top of the test film, which in turn is laid on top of the collector film. As vanillin strongly absorbs in the U.V. a reactive collector is not required. For materials without a suitable spectrum, the collector film can be weighed on a microbalance at intervals, with somewhat lower sensitivity, or a suitable reactive system devised. All the above methods are examples of the transmission (or permeation) method of measuring diffusion where the usual gas or liquid supply and collector systems are replaced by a completely solid state system. A feature of transmission measurements is the lag time, the time before permeant appears in the collector after application on the test film face; after some time, a steady state linear transmission can usually be measured.

A second not heretofore considered possibility for measuring the parameters required for permeability measurements (the permeability is the product of the diffusion coefficient and the solubility of the permeant in the polymer), is the sorption technique. In this case supply films are applied to both faces of the test film, which is also the collector film, and permeant uptake can be measured as before. The solubility is measured at the equilibrium point where the test film absorbs no more permeant; the absorption rate of permeant is not linear with time, but can be used for calculating the diffusion coefficient. Most importantly, there is no lag time, and diffusion measurements can begin at the first reading. Hence in the sorption technique we have a supply/test/supply laminate, compared to supply/test/collector for transmission measurements; in both cases the layers are separated at each reading; usually only the collector (or test) film is monitored, but in principle any layer could be measured.

The permeability equations for volatile materials are usually expressed in terms of pressure differences across test films, as

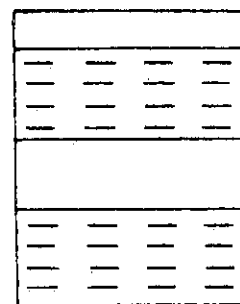
*CSIRO Food Res. Q.* 1988, 48, 40-46

# FILM ARRANGEMENT : ODOUR PERMEABILITY MEASUREMENT

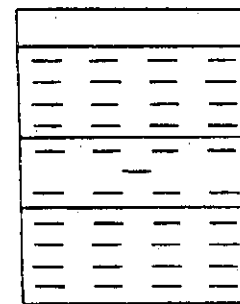


GLASS CYLINDER

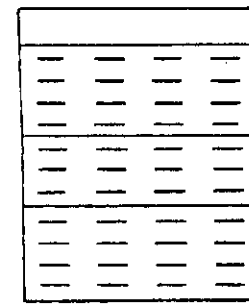
## SORPTION METHOD



INITIAL FILM  
CONTACT

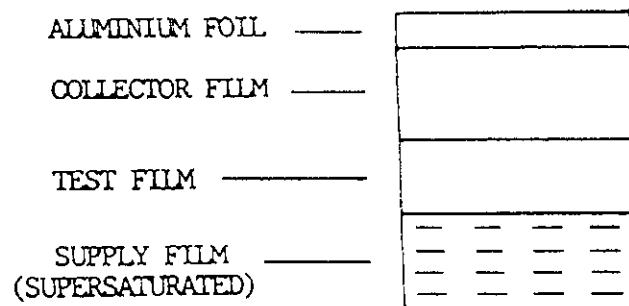


DIFFUSION INTO  
TEST FILM

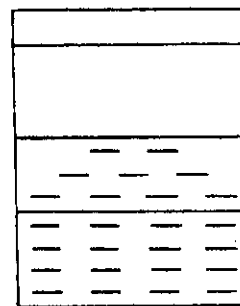


SATURATION OF  
TEST FILM

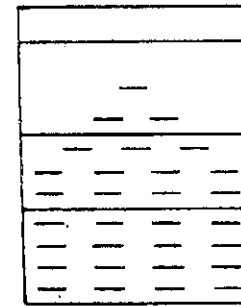
## TRANSMISSION METHOD



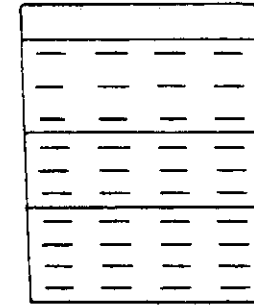
LAG  
TIME



DIFFUSION INTO  
TEST FILM



DIFFUSION INTO  
COLLECTOR FILM



SATURATION OF  
COLLECTOR FILM

pressures are conveniently measured. With the laminate method concentration differences provide the driving force for diffusion, and it can be shown that this is indeed the correct and simplest way of expressing permeability. This of course is quite compatible with the practical situations where ingredients often diffuse into or out of packaging materials at liquid or solid food contact points rather than through the headspace. In any case, from a thermodynamical point of view, a saturated solution source is equivalent to a saturated vapour, as they are in equilibrium with each other.

### Theory

In the transmission technique the lag time is required to calculate the diffusion coefficient; if the permeant appears in the collector very rapidly, it may be desirable to use multiple thicknesses of test film to obtain a more accurate value of the lag time. The lag time though, can easily be weeks or months, in which case a sorption method may be preferred. The reason for such difficulties is seen by considering the equation for the lag time  $t$ ;

$$x^2 = 6Dt,$$

where  $D$  is the diffusion coefficient or constant, and  $x$  is the "average" (root-mean-square) distance a molecule undergoing a "random walk" travels in time  $t$ . If  $x$  is doubled, for example, the lag time is four times as long, and if the diffusion coefficient has values as small as  $10^{-12}$  cm<sup>2</sup>/sec, a ten micron thick film will experience a lag time of  $1.7 \times 10^5$  sec; hence the transmission technique with thick "as received" films may not always be feasible, but if transmission can be set up, and linear steady state transmission occurs, the steady-state flow rate ( $F$ ) is given by (Crank and Park)

$$F = D'(c_1 - c_2)/l$$

where  $l$  is the thickness of the test film and  $c_1$  is the permeant concentration of the supply film,  $c_2$  the measured concentration in the collector film.  $D'$  is the permeability coefficient for the test film; the ratio  $D/D'$  is equal to the relative solubility of the permeant in the two phases. The partition coefficient (relative solubility) can be obtained from equilibrium measurements between supply and test films. Note that for solid and liquid phases the dimensions of the permeability coefficients are the same as for the diffusion coefficients, as there are no pressure terms. For the sorption

technique, data is usually plotted in the form  $t^{1/2}/1$  versus  $M_t/M_\alpha$  where  $M_t$  is the amount of permeant absorbed in the test film at time  $t$ , and  $M_\alpha$  the equilibrium amount. This graph is usually linear for a considerable part of the reaction, and the diffusion coefficient is either found from the gradient of the initial part — (Crank and Park)

$$M_t/M_\alpha = 2.257 (Dt)^{1/2}/l$$

or from the relationship

$$D = 0.04919/t_{1/2}/l^2$$

where  $t_{1/2}$  is the time when the reaction is half finished. Note that  $M$  may be difficult to obtain from a sorption measurement on, say, a thick film, for reasons similar to those in the transmission method, but other methods of measuring the solubility are usually available. (Increasing concentrations of permeant can be cast with the test polymer until opalescence appears in the film).

### Preparation of supply and collector films

Both supply and collector films should be cast from polymers which are highly permeable and good solvents for the permeants; this is to eliminate concentration gradients within the collector or supply films which will distort the ideal concentrations across interfaces. Such gradients can be a problem even in the gaseous phase (as in the standard dish method for measuring water vapour permeation), but convection or flow will act to reduce the effect. This of course is not possible in polymer systems, where the only method of eliminating the gradient is to have a much higher permeability in the collector and supply films. Fortunately this can usually be done, and both supply and collector films can then be cast rather thicker than the test film to maximise the amount of permeant that can be measured.

Ethyl cellulose, and particularly PS099 (Petrarch systems), a silicone/polycarbonate block copolymer, are many times more permeable than most other films, at least to common gases, and on this basis they have been chosen as substrates for a variety of organic permeants. The silicone material unfortunately, has some U.V. absorbance, but is insensitive to minor humidity fluctuations which can make gravimetry a problem. The first two methods used for preparing supply films were to condition a suitable highly permeable polymer over an odorant until the desired concentration was reached, or to cast a film from the odorant and polymer dissolved in a solvent. The latter procedure became preferred if the saturated vapour pressure of the permeant was low. In the first method, for

low vapour pressure odorants, the distance between film and odorant, and the use of a vacuum were critical factors in transferring appreciable amounts of the vapour to the film in a reasonable time.

A much more rapid procedure is to use saturated (or supersaturated) cast films to sandwich the film to be treated. Transfer is generally much faster than by the vapour method, which explains why rapidly diffusing solid systems can be weighed etc. in the air without appreciable loss. Saturated (but not supersaturated) films can be made by this method. In a similar way partition coefficients (relative solubilities), can be measured by contact equilibration of two different film materials.

For most methods of measuring permeability it is desirable that the supply concentration does not change appreciably. A thick, highly permeable, high concentration film could be used. Even more efficient is the use of supersaturated films where undissolved solid or liquid trapped in the supply polymer provides a reservoir of material to keep the supply film at saturation point (assuming the trapped material dissolves as rapidly as it migrates to the test film).

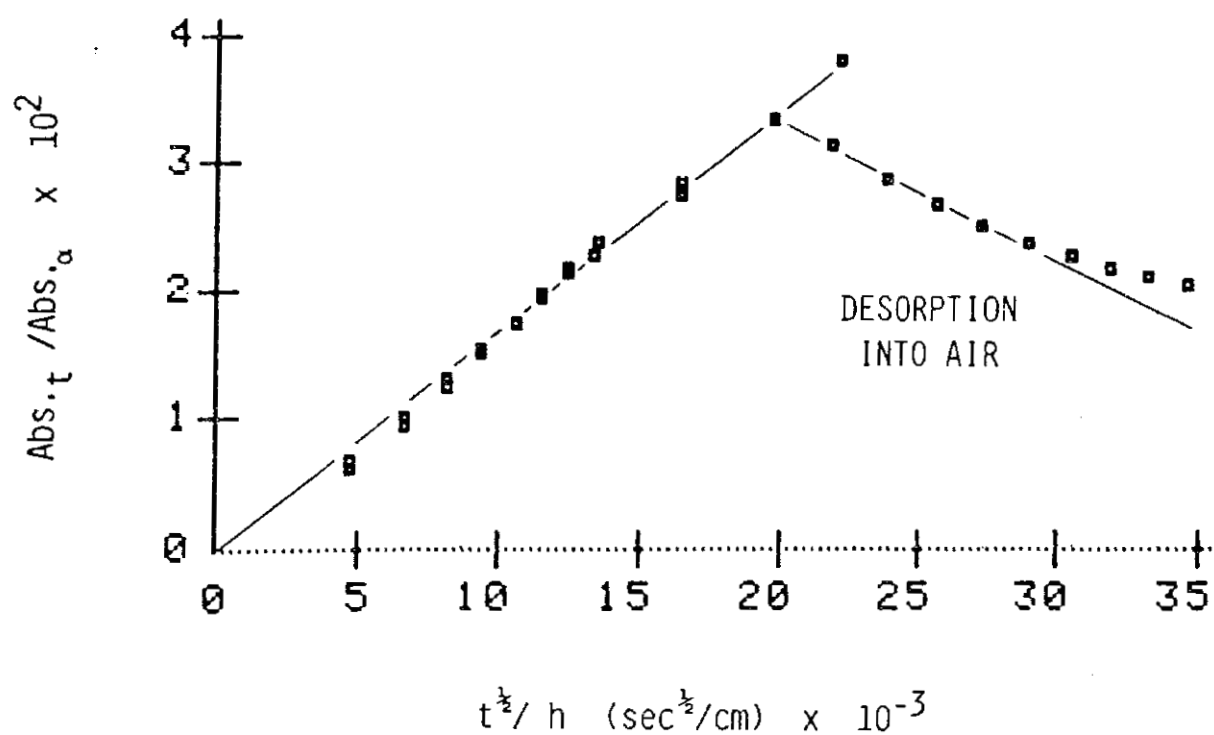
### Measurement of transmission

In Figure 1 the arrangement of films on a cylindrical base is shown. The usual film area is a few square centimetres. All the films except the one measured are attached by adhesive tape to a common area on (say) a beaker. The order is as described earlier — supply/test/supply for the sorption method, supply/test/collector for transmission measurement. Thin aluminium foil is used to seal the laminate by preventing loss of permeant from the top surface; the foil is stretched tightly over the laminate and is itself attached firmly by means of another adhesive tape to the beaker surface. A small amount of permeant can possibly escape through the edges, which could also be sealed; however for many odorants this does not seem to be necessary at the accuracy obtainable. The film to be measured is slotted into and removed from its correct space at intervals, and during the exposure period it forms part of the laminate. It may be a matter of concern whether the contact between films has to be intimate to ensure good transfer. The laminate can hardly compare with commercial laminate films with regard to contact, and entrapped air must certainly be present. For volatile materials,

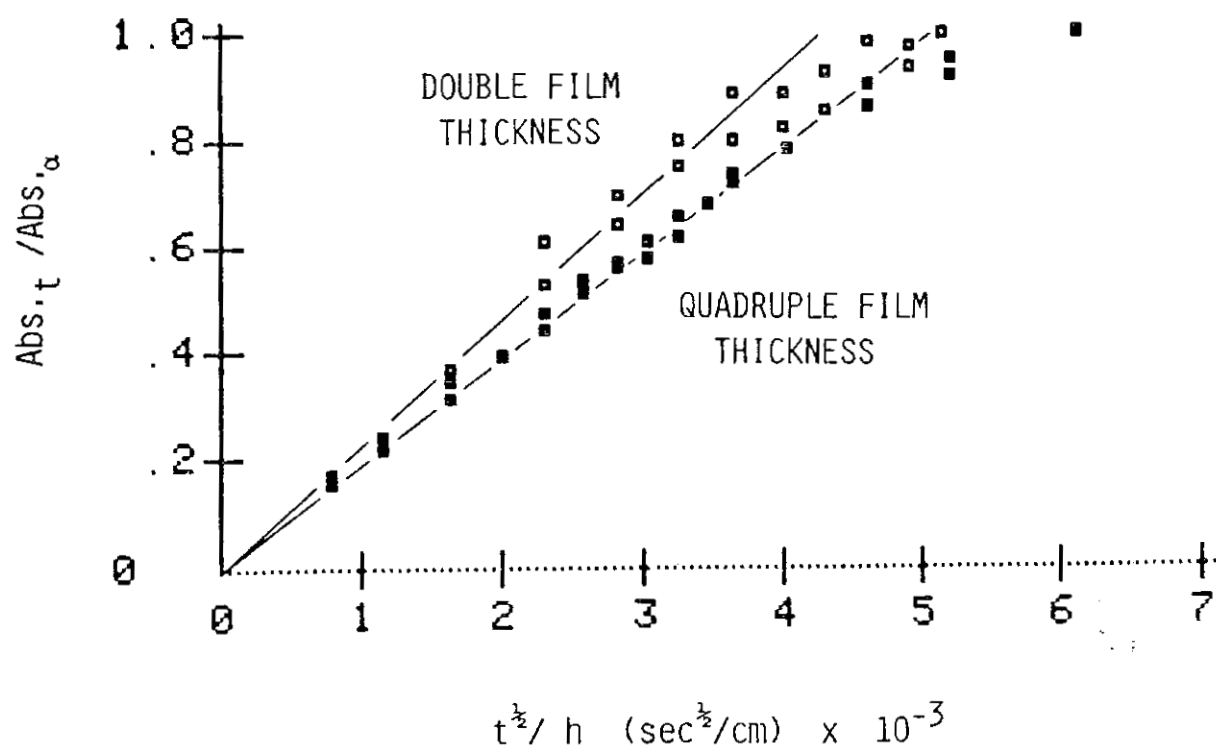
TABLE 1  
Permeation values for NYLON 11, LDPE and PS099

Test Film	Thickness h cm	Diffusion Co-efficient D cm <sup>2</sup> /sec	Saturation Solubility C <sub>1</sub> g/cm <sup>3</sup>	Partition Co-efficient P.C. = C <sub>1</sub> /C <sub>2</sub> moles/L	Permeability Co-efficient P' = P.C. (D) cm <sup>2</sup> /sec	Flux Area F = D.C <sub>1</sub> /h g/cm <sup>2</sup> .sec	
NYLON 11	4.0x10 <sup>-3</sup> (40μm)	5.65x10 <sup>-13</sup>	8.82x10 <sup>-2</sup>	5.80x10 <sup>-1</sup>	2.13	1.20x10 <sup>-12</sup>	1.25x10 <sup>-11</sup> 4.48x10 <sup>-4</sup>
L.D.P.E.	5.8x10 <sup>-3</sup> (58μm)	7.79x10 <sup>-9</sup>	3.30x10 <sup>-4</sup>	2.17x10 <sup>-3</sup>	7.96x10 <sup>-3</sup>	6.21x10 <sup>-11</sup>	4.43x10 <sup>-10</sup> 1.60x10 <sup>-2</sup>
SUPPLY FILM				C <sub>1</sub>			
PS099	8.5x10 <sup>-3</sup> (85μm)	1.87x10 <sup>-9</sup>	4.14x10 <sup>-2</sup>	2.72x10 <sup>-1</sup>	1.00	1.87x10 <sup>-9</sup>	

# SORPTION-VANILLIN/NYLON 11



# SORPTION-VANILLIN/LDPE



contact is not essential (though large air gaps should be avoided — see discussion above;) the reason is that diffusion coefficients in air are about ten thousand times larger than in liquids or polymers. Surprisingly, even for non-volatile materials inefficient contact between films (a few percent perhaps) does not necessarily lead to markedly reduced transfer between films (Berg). The reason is that the transmissions between contact “apertures” between laminate films is not proportional to the area but to the radius of the apertures. Diffusive flow is quite different from bulk flow, and it can be shown that contact of the right type (small apertures, but widely spaced) leads to very efficient transfer. In any case the reproducibility of measurements under a range of contact conditions can be used to verify transfer efficiency.

### Measuring the permeation of vanillin through two packaging films

PS099 containing vanillin was used as a supply film (cast with excess ( $\sim 1$  M) vanillin), and the sorption technique was used on duplicate films in both cases. The unplasticized test film were nylon 11 (40  $\mu\text{m}$  thick) and low density polyethylene (LDPE, 58  $\mu\text{m}$  thick); all measurements were made at 25°C. Vanillin has a strong absorbance at 275 nm, ( $\epsilon = 10233$ ) and as in nylon this peak soon becomes unmeasurably high and the final solubility was obtained by microgravimetry. This procedure took several weeks before saturation, even though initial readings were taken at six minute intervals. A desorption technique was also used (Fig. 2) in which an air desorption graph (diverging line at the top), measured at twelve minute intervals, is also displayed. Corrections for sampling times in the spectrophotometer or microbalance can be made from such curves, but are negligible if the sorbing time is longer than a few minutes. In Figure 3 the much more rapid LDPE data is displayed. Packs of two and four films had to be used to provide convenient time intervals (six minutes), and more accurate initial rates, for the LDPE data.

### Results and discussions

Notice the agreement in the duplicate data in Figure 2 and Figure 3. In Figure 3 the duplicate samples for the quadruplicate film appear to give more consistent agreement and are used for the data table. The vanillin solubility in these films, as mentioned, was very low relative to nylon; fortunately because of the large extinction even low concentrations were easily measured spectrophotometrically;

gravimetric measurement would probably be too insensitive unless a transmission technique were used. Unfortunately, sorption graphs are not very illuminating, and the data obtained from the following table can be interpreted as follows. (See Table 1 for numerical values).

#### *Diffusion coefficients*

The lag times calculated for LDPE (or PS099) are very short; vanillin is detectable almost immediately through LDPE. Nylon packaging, on the other hand, can be expected to have lag times comparable to shelf life.

#### *Saturation solubility*

In contrast to the above, nylon is an excellent solvent for vanillin (compared to LDPE) and can be expected to extract this odour from food quite efficiently (depending on the relative partition).

#### *Partition coefficients*

These show the relevant efficiencies of vanillin extraction by the various films.

#### *Flux transmission rate*

Using saturated supply films, the maximum transmission rates are given in terms of g/unit area/unit time. Note that if the concentration gradient in the test film is known as well as the concentration on either side, the diffusion coefficient of the test film can be found. Reducing the concentration gradient will reduce the transmission loss, but knowledge of the entire food/package film system may be required to estimate odour loss.

### Permeability coefficients

These allow different films and different diffusants to be compared. The multiplicity of units used in gas permeability work can be standardized to the values given here (v. Yasuda (1975)  $D' = 82.96$  P (measured in Barrers at 25°C)). The permeability coefficient  $D'$  is the flux transmitted through a one centimetre thick film under unit concentration gradient. Note that the supply film used here is thirty times more permeable than polyethylene, and therefore should be adequate for the role. Secondly, LDPE is more permeable than nylon, though by no means as much as might be expected from their relative lag times (diffusions). The flow rate through nylon, though delayed, is not inappreciable in the steady state.

If a vanillin flavoured food were placed in two impermeable containers, one lined with nylon film, and the other with LDPE, serious

“scalping” of the odour could be expected by the nylon liner but not by the LDPE. The reason is that nylon is a very effective barrier material in the short term at least, this is largely because vanillin is being absorbed by the film, and still presumably lost from the product. In the reverse direction, nylon might be an excellent barrier material against many taints, as these would be held up for a long time before they contacted the food. Hence a knowledge of the diffusion and solubility of compounds as well as the transmission rate, simplifies the search for a suitable packaging film.

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# THE HEALTHY DIET PYRAMID

