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# JOURNAL OF FOOD TECHNOLOGY

## Institute of Food Science and Technology (U.K.)





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# Radiation preservation of food—the current status

S. A. GOLDBLITH

## Introduction

Radiation preservation of foods represents man's first directed approach toward the development of a new method of preservation since Appert's discovery of canning over 160 years ago. It also represents perhaps the greatest amount of research and development funding that has ever been spent on a new method of preservation.

Research directed toward the use of radiation for the preservation of foods began in 1945—25 years ago—and intensive efforts were initiated in the 1950's through the U.S. Atomic Energy Commission and the U.S. Army Quartermaster Corps programs, programs at the Low Temperature Research Station in England, at the Federal Research Centre for Food Preservation in Karlsruhe, Germany, and elsewhere in Europe. These programs, particularly in the U.S.A., have had 'their ups and their downs'—being in favour and then thrown backward because of governmental decision at a fairly high level.

It is probably fair to say that in the U.S.A., only the keen interest and active support of the Joint Committee on Atomic Energy of the U.S. House of Representatives and of the U.S. Senate have kept alive government funding to this day. (As this paper is being written, March 1970, there is a hue and cry going on in the Department of Defense which once again threatens the U.S. Army program.)

If one were to guess at the amount of *government* (U.S. Army and U.S. Atomic Energy Commission) funding in the U.S.A. alone on the radiation preservation of foods programs since 1950, it would probably be upward of $50 million! Perhaps another $10 million has been spent by industry and other governmental agencies.

It is the purpose of this article not so much to review the past as to present the present status and future prognostication of this field. This is being done primarily from an American point of view because of the writer's personal experience.

In order to understand the possible future of this method of preservation, one must understand the reasons for the 'ups and downs' in U.S. Government funding of this field. When it was first presented in 1953 by the U.S. Army, it was felt to be a 5-year program to prove the feasibility of the process. It soon became apparent that neither 5 years nor the originally budgeted moneys were sufficient to see this program of radiation *sterilization* of foods through to a logical conclusion.

In 1959, the U.S. Atomic Energy Commission began a feasibility study leading

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toward the radiation *preservation* of selected foods—marine products and fruits primarily. This program has been active since 1960 but is now beginning to die out (as is the Army program). We need to examine why.

*The wholesomeness of irradiated foods*

In 1963, the U.S. Food and Drug Administration approved the radiation sterilization of bacon (15 February, 1963). This was a great milestone and was a tremendous impetus to this field. In 1968, however, in the course of evaluation by the U.S. Food and Drug Administration of a petition requesting a regulation for radiation-sterilized ham, the petition was denied; and, moreover, the regulation permitting the radiation sterilization of bacon was revoked (24 August, 1968). This was done because the original feeding and toxicological data on irradiated bacon were being used for the ham petition, and on a thorough review of the *entire* sets of original data on the feeding studies of irradiated bacon, sufficient questions were raised by the U.S. Food and Drug Administration to question whether the wholesomeness of the product had been proven. In fact, scientists in the U.S. Food and Drug Administration claimed that the radiation-sterilized bacon had produced unexplained tumors in rats fed these products and that the treated bacon was not safe.*

This action by the U.S. Food and Drug Administration obviously had a negative effect on the radiation treatment of foods throughout the entire world and in the U.S.A., particularly in the agencies responsible for funding the programs.

To this should be coupled an additional negative input, that of possible mutagenic effects in irradiated-autoclaved sugars as postulated by Holsten, Sugii & Steward (1965).†

As a result of the U.S. Food and Drug Administration's action on the irradiated ham petition, the U.S. Army has undertaken to set up a new wholesomeness program on irradiated ham. It should be recalled that the original wholesomeness studies on irradiated bacon were carried out in the mid-1950's using techniques of the 1940's and re-evaluated by scientists in the late 1960's! Thus a new protocol is being set up on the wholesomeness of radiation-sterilized ham and will include thermally processed ham as one of the controls. Whether this program will be funded so that it will be carried out still remains to be seen at the time of preparation of this manuscript.

The U.S. Atomic Energy Commission has had studies performed on the wholesomeness of irradiated strawberries, and it is hoped that the report will be completed shortly so that the data may be submitted for a petition on the use of radiation to

* The use of feeding data on irradiated bacon for the ham petition was based on the assumption that the products are similar in composition, cure, etc.

† It is not the purpose to debate herein the judgment of the U.S. Food and Drug Administration nor the validity of the data and arguments of Holsten *et al.* This has been presented elsewhere (Goldblith, 1970). The author is only presenting historical milestones pertinent to the present status of radiation treatment of foods.

extend the storage life of strawberries by treatment with 150,000 rad. In addition to feeding studies on strawberries, extended long-term, multi-generation feeding studies are being conducted on bananas (irradiated to delay ripening) and on papayas (to destroy insects for quarantine control). The final series of products being studied by the U.S. Atomic Energy Commission involves marine products but as yet no definitive feeding studies have been carried out on these.

In the course of the U.S. Army sterilization program, some twenty-one foods have been fed to two species of animals over extended periods with data obtained on reproduction efficiency and growth, histopathology, etc. It is the considered opinion of the Office of the Surgeon General that taken in their totality, these studies show radiation to be safe and wholesome with no toxicological problems.

Obviously, the U.S. Food and Drug Administration disagreed with these conclusions insofar as the studies on irradiated bacon were concerned. Thus there has arisen the need for a new set of studies on the feeding of irradiated ham based on revised protocols drawn up which use the methodology available at the present time and incorporate the many lessons learned over the past 2 decades. In the meantime, extensive animal feeding studies are being carried out on selected foods and feedstuffs in other parts of the world. When all of these data are in, we should have a much more solid basis for evaluation of the wholesomeness of radiation-sterilized foods.

I have dwelt at some length on the safety and wholesomeness aspects of irradiated foods for a reason that is germane to this paper. One cannot attempt to prognosticate the future of irradiation insofar as foods and feeds are concerned without a realization of the pragmatic influence that the events of the past 8 years vis-à-vis wholesomeness have had on the present climate insofar as the use of ionizing energy for food preservation is concerned. The decision of the U.S. Food and Drug Administration with regard to bacon, in particular, and the work of Holsten *et al.* have done much to dampen the ardour of governmental programs outside of the U.S.A.

In general, one can answer such criticisms only from a laboratory podium. Thus we see the reason for developing the new protocol on feeding of irradiated ham. Thus, too, we see the reason for the U.S. Atomic Energy Commission initiating extensive studies to ascertain the nature of the degradation products of irradiated sucrose in work undertaken by Dr Jack Schubert at Pittsburgh University; and to verify the possibility of mutagenic effects, they have initiated extensive work at the Oak Ridge National Laboratories. Within 6 months to a year, we should have a definitive reply to whether the allegations of Holsten *et al.* are founded on fact.

I propose herein to evaluate the prospects of ionizing energy with this background, using several categories. These are:

1. Radappertization
2. Radurization
3. Radicidation
4. Miscellaneous.

*Radappertization*

In my judgment, I rank radappertization at the lowest possible level in terms of more immediate probability of use. I do so not for technological reasons but because:

1. I believe the wholesomeness problem will be a long time in resolving.
2. I doubt seriously whether commercially it is of as great interest as some of the other uses which are discussed below.

Just a few more remarks here as to the wholesomeness aspects. In the midst of the arguments between the U.S. Food and Drug Administration and the Surgeon General's Office of the Department of the Army as to the wholesomeness of irradiated ham (the latter deeming irradiated-sterilized ham to be safe and wholesome, and the former, the U.S. Food and Drug Administration, concluding that some of the data were *not* acceptable as proof of wholesomeness), a crisis developed as to what constitutes a proper method of evaluating an irradiated food for safety evaluation. This argument has been due to the fact that one cannot often feed excessive quantities of certain foods (non-irradiated as well as irradiated) to animals, thus not permitting the challenge of exaggeration—upon which our whole concept of safety evaluation of chemical additives is based. Although suggestions have been made by some scientists that chemical tests be used as alternatives to animal studies, this meets with the most obvious objection of not knowing what to look for! Thus we really are not certain that we have available today a method which will provide data to permit a definitive conclusion as to the wholesomeness of an irradiated product.

As to potential lack of commercial interest, I believe this to be due, in part, to the wholesomeness problems just discussed; and, in part, because in Western society we have highly acceptable thermally processed and frozen foods, thus we have little need for radiation-sterilized foods for commercial use.

Technologically, using low temperatures of processing, highly acceptable irradiated products have been produced in studies carried on by the U.S. Army Natick Laboratories. As a matter of fact, these studies, involving several thousands of evaluations, have shown not only radiation-sterilized ham and bacon to be highly acceptable items but also chicken, pork, beef, shrimp, and codfish cakes as well.

Thus, there is acceptance of the products by the military consumer. What is needed is a resolution of the wholesomeness-testing dilemma.

For the above reasons, in terms of commercial usage, I place radappertized foods in the lowest possible category.

*Radurization*

Radurization of certain foods, i.e., the extension of storage life of these foods using substerilizing doses to destroy the bulk of the non-spores (dosages of under 1 megarad) followed by storage at refrigeration temperatures above freezing, offers distinct com-

mercial possibilities as well as, in my judgment, better hope for resolution of the wholesomeness question. The latter statement is dictated primarily by the simple fact that dosages of one-tenth to one-fifth of that needed for sterilization are used, concomitantly with much less production of secondary side effects.

Those products which would appear to offer the greatest possible potential for radurization appear to be fin fish such as cod and haddock; shrimp; strawberries; and papayas.

In the case of fin fish, studies both in the United Kingdom (at the Low Temperature Research Station and at Wantage) and in the U.S.A. (under U.S. Atomic Energy Commission sponsorship) have shown the products to be highly acceptable and with positive commercial benefit. Treatment with doses of about 100–200 Krad will increase the storage life of fish, at wet ice temperatures, several weeks, thus opening up in the U.S.A. a considerable inland market not now receiving fresh fish. The entire economic analysis of the radurization of fish has been made in an excellent cost benefit study under U.S. Atomic Energy Commission sponsorship and shows that for the U.S.A., at least, the benefits outweigh radiation processing costs by roughly fourteen to one (Anon, 1967).

One of the concerns of governmental regulatory agencies in respect to the radurization of seafood has been the possible outgrowth of *Clostridium botulinum* Type E. Extensive experiments with fin fish fillets inoculated with a massive number of spores ($10^6$ per gram) have shown this fear to be groundless with cod and haddock. In the case of fish with more fat, such as ocean perch, the fish must be kept at wet ice temperatures (32–33°F), a condition which would normally be met by commercial handling practices.

In the U.S.A., at any rate, the future of the radurization of seafood is dependent on carrying out the necessary multi-generation animal feeding studies to satisfy the Food and Drug Administration. Whether these studies will be carried out depends on whether funding will be made available to the Atomic Energy Commission which, at the moment, appears dubious. Thus if radurization of seafoods is to become an accomplished commercial fact, it probably will occur first in some country other than the U.S.A., hopefully in the United Kingdom which has done so much of the basic as well as applied research in this area.

With respect to fruits, the most likely candidate for radurization is strawberries. Doses of about 150,000 rad can extend the storage life of strawberries significantly and thus offers great commercial potential. Animal feeding studies on strawberries have been carried out under U.S. Atomic Energy Commission sponsorship and have just been completed (March 1970). It is hoped that a petition asking for a regulation permitting the use of ionizing energy for the radurization of strawberries may be submitted to the U.S. Food and Drug Administration within the next few months. There is no question but that in the U.S.A., at least, the radurization of fresh strawberries offers great economic and commercial benefit.

*Radicidation*

As urbanization increases, world trade increases and our food supply becomes more complex, there is increasing need for removal of pathogenic organisms from food and animal feedstuffs. In particular, salmonellosis has become an increasingly important problem that must be solved.

Radiation treatment at doses of under $0{\cdot}75 \times 10^6$ rad has been suggested to remove the salmonellae in frozen chicken, in eggs, and in animal feedstuffs. With eggs, the off-flavour problem can be minimized if not eliminated by the use of thermal energy and ionizing energy in a complementary fashion (Licciardello, 1964; Grim & Goldblith, 1965). In the case of animal feedstuffs, work in The Netherlands and in the United Kingdom, in particular, has shown the efficacy of ionizing radiation in destroying the salmonellae in fish meal, bone meal, and other animal feedstuffs, such as horse meat (Thornley, 1963).

Since there is increasing world trade in animal feedstuffs due to an increasing need for protein for animals, the problem of salmonellosis has become particularly important. To date there is no means other than ionizing energy that would appear to offer as great a potential for destroying salmonellae, and thus breaking the cycle and improving the health of man. This ionizing energy can do without seriously impairing the nutritive value of the products as is the case with thermal sterilization.

Because ionizing energy can achieve meaningful results in improving the public health of man, I place radicidation at the top of the list in terms of potentiality and immediacy. This, in spite of the fact that there have been no wholesomeness (animal feeding) studies in the U.S.A. Studies that have been carried out in The Netherlands have shown the animal feedstuffs to be wholesome and free of toxic substances. In this respect, I believe that countries other than the U.S.A., particularly The Netherlands and the United Kingdom, are likely to be among the first to adopt such a method thus utilizing ionizing energy to improve man's well-being.

There are those (Erdman, Thatcher & MacQueen, 1961a, b) who feel that sub-sterilizing doses may result in the development of mutants that are much more radiation resistant. My own feeling, substantiated by work in our laboratories (Licciardello *et al.*, 1969), is that such a fear is groundless, as it takes re-exposure of selected survivors to the extent of at least 6 cycles in order to finally obtain meaningful radiation resistant mutants—a condition hardly ever likely to be reached in practice.

*Miscellaneous*

In this category, come such processes as the use of radiation in low doses ($\sim$ 25,000 rad) to get rid of insects—for example, deinfestation of papayas—for quarantine control. The U.S. Atomic Energy Commission in conjunction with the Department of Agriculture of the State of Hawaii has done much to show the feasibility of this process, and animal feeding studies are now under way. If wholesomeness can be proven, it is

highly likely that such a process can prove to be economic, useful in terms of improving the public health, and thus be adopted as a positive force for good by the public health authorities of the world.

The use of radiation for destruction of insects in grain and for prevention of sprouting in tubers has been known for some time. In spite of the technological feasibility of the process, there is little indication that it will be adopted commercially, unless there is a marked change in attitude of either industry or of government in the countries where insect infestation of grain is a particular problem.

There are no doubt many other potential applications of ionizing energy that have been suggested with other foods and which I have omitted herein. This is primarily because I feel that the probability of these other suggested applications becoming commercial is far less than those discussed above or that these uses are simply relatively unimportant economically.

*Radiation sources*

Finally, some mention should be made of radiation sources. If and when radiation processes are approved by the regulatory authorities, there will be need for both penetrating radiations (Cobalt-60 gamma rays and high-energy X-rays) and the relatively non-penetrating electrons. Each type will find its own niche dependent on the process and on economics. There is no question that electrons are much cheaper than X-rays or $\gamma$-rays per kw of ionizing energy. However, multitudinous factors must be evaluated and integrated, and the answers are not easily arrived at but rather require a detailed analysis of the many variables comprising any situation. The important consideration is to realize that several radiation sources do exist and are available and that a detailed feasibility analysis is needed of any situation to determine the ideal source for any specific use.

## Conclusion

There are other aspects of radiation processing not covered herein such as packaging, etc., but I feel that the all-controlling factor governing the potential use of ionizing energy in food processing is the wholesomeness aspect, and therefore space has been devoted to this aspect at the expense of other considerations. Radiation can serve as a positive force *pro bono publico*, and it is for this reason that I have given the relative probability of successful use first to radicidation, then radurization, and finally radappertization.

If breakthroughs are needed to make radiation processing a commercial reality, I believe such breakthroughs to be not in the area of radiation processing but rather in the field of wholesomeness testing. This is the key to all new food processes of the future and particularly innovations in food additives and in radiation processing. While it is true that the proof of safety of a new process depends on the innovator, we cannot help but

ask the question whether thermally processed foods could withstand the testing to which radiation-processed ham has been subjected? If there is doubt that thermally processed products could withstand such rigorous testing after over a century and one-half of commercial use, we need to re-examine our entire philosophy of wholseomeness testing in a calm, non-hysterical atmosphere.

Every method of processing and each food additive (or drug) involves some risk. The question we will have to face some day soon is the relative risk to the population of salmonellosis *v.* the radicidation of animal feeds. Is this question not worthy of examination and comprehensive evaluation?

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# Diffusion coefficients of water and organic volatiles in carbohydrate-water systems

L. C. MENTING*, B. HOOGSTAD AND H. A. C. THIJSSEN

## Summary

The diffusion coefficients of water, $D_w$, and acetone, $D_a$, in aqueous solutions of malto-dextrin have been determined over a range of moisture contents of the malto-dextrin above 10%. At a few selected moisture contents, the diffusion coefficients of ethyl acetate, benzene, carbon tetrachloride, camphor and methane have also been determined. Diffusion coefficients were derived from measurements of sorption and desorption by a malto-dextrin layer.

The diffusion coefficient was found to be dependent on both the moisture contents and the size of the diffusing molecule. Over the range of moisture contents investigated, log $D_w$ was found to be proportional to $C_w^{-1}$ and log $D_a$ proportional to $C_w^{-\frac{1}{2}}$, where $C_w$ is the concentration of water (kg/m$^3$) in the malto-dextrin. For the compounds studied, the logarithm of the diffusion coefficient measured at a moisture content of 20·1% was found to be approximately proportional to the molecular 'diameter' of the diffusant.

This knowledge helps to explain the phenomenon of flavour retention during the drying of liquid foods.

## Introduction

Diffusion in crystals and liquids has been studied extensively, while in the last decades a lot of research has been done on diffusion in synthetic polymers. Diffusion in foods, however, is still a relatively unexplored territory. Reliable measurements of the diffusion coefficients of water and flavour components in foods are scarce. Such data are prerequisite for a good insight into the drying of foods and the retention of flavour during drying and storage.

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Fish (1958) accurately measured the diffusion coefficient of water in starch gel and scalded potato at moisture contents ranging from 0·7 to 44% (by weight, wet basis*). Over this range, the diffusion coefficient was found to decrease by a factor of $10^3$ with decreasing moisture content. The decrease was very marked below a moisture content of 30%. Likewise, Duckworth (1962) found that the diffusion coefficient of glucose in carrot decreased with decreasing moisture content.

Between moisture contents of 40% and 100%, diffusion coefficients in foods vary by less than a factor of 10. This is apparent from results reported in the literature. For instance, the diffusion coefficient of water has been measured in aqueous solutions of honey and glucose by Fan & Tseng (1967) and in aqueous solutions of sucrose by Tuwiner (1962). Friedman & Kraemer (1930) measured the diffusion coefficients of urea, glycerine and sucrose in gels of up to 15% gelatin in water, while Friedman (1930) measured diffusion coefficients in gels of 1·5% and 3·0% agar-agar in water. The diffusion coefficients of oxygen and nitrogen in *albumen* (egg white) have been measured by Goldstick (1966).

In the present investigation, the diffusion coefficients of water and acetone, have been measured in malto-dextrin (partially hydrolysed starch) at moisture contents above 10%. Measurements were also made of the diffusion coefficients of ethyl acetate, benzene, carbon tetrachloride, camphor and methane in malto-dextrin. The object of the investigation was to provide data for quantitatively explaining the flavour retention observed when food liquids are dried (Thijssen & Rulkens, 1968; Saravacos & Moyer, 1968a, b; Mälkki & Veldstra, 1967; Pilnik, 1969) and, in particular, the retention of volatiles observed in model experiments on the drying of malto-dextrin solutions (Menting & Hoogstad, 1967a, b).

## Theory

The complex malto-dextrin solution is treated as a binary system. Thus, for the diffusion of water in the solution, the malto-dextrin, although a mixture of carbohydrates, is considered as one component, while for the diffusion of acetone in the solution, the water and the carbohydrates are together considered as one component. The diffusion coefficient can then be defined by Fick's first law:

$$\mathcal{N} = -D\frac{\partial C}{\partial x} \tag{1}$$

where $\mathcal{N}$ is the mass flux of the diffusing component relative to the volume–average velocity (kg/m$^2$sec), $C$ is the concentration (kg/m$^3$) and $x$ is distance (m). If the small volume change on mixing the components is neglected, the net volume flow with respect to stationary coordinates is zero everywhere within the solution. $D$ is then equal to the

* Percentages are invariably expressed as percentages by weight and, unless otherwise stated, on a wet basis.

mutual diffusion coefficient. For a non-stationary case and constant $D$, Eq. (1) leads to the differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

where $t$ is time (sec).

In this investigation the diffusion coefficients have been derived from measurements of the sorption and desorption of vapour by a layer of malto–dextrin solution, one side of which was in contact with the gas phase. The volume above the layer was stirred in order to ensure that the surface of the layer was in equilibrium with the gas phase.

One possible approach is to keep the concentration of diffusant in the gas phase constant and to determine the amount, $q$, taken up by the layer. Solutions of Eq. (2) for these boundary conditions are given by Crank. For short times, the amount sorbed by a layer of thickness $d$, can be approximated by:

$$\frac{q}{q_\infty} = \frac{2}{d}\sqrt{\frac{Dt}{\pi}} \tag{3}$$

where $q_\infty$ is the amount sorbed by the time equilibrium is reached. At $q/q_\infty = 0{\cdot}5$ the error incurred by using Eq. (3) is about 0·3%, which is less than the experimental error of our measurements.

An alternative possibility is to keep the total amount of diffusant in the system constant and to measure the change in concentration of diffusant in the gas phase. The concentration in the gas phase is kept uniform by stirring. The solution of Eq. (2) for this case of sorption is (Crank, 1967):

$$\frac{q}{q_\infty} = (1 + \alpha)\left\{1 - \exp(T/\alpha^2)\ \operatorname{erfc}\ (T/\alpha^2)^{\frac{1}{2}}\right\} \tag{4}$$

where $T = Dt/d^2$ and $\alpha = V_g/V_l K$, in which $V_g$ and $Vl$ are the volume of the vapour and of the layer respectively and $K$ is the distribution coefficient.

## Experimental

The malto-dextrin was from the same batch as that used for earlier experiments (Menting & Hoogstad, 1967a, b). In order to prevent microbiological spoilage, a small amount of benzoic acid (0·2% or less of dry malto-dextrin) was added to the malto-dextrin solution. As malto-dextrin with a moisture content higher than 18% is more or less liquid, some agar-agar (2·0% or less of dry malto-dextrin) was added to it in all

experiments for which its moisture content was above 18% and also in some cases when its moisture content was below this level. This addition of agar-agar prevented mass transfer by convection during the diffusion experiments and in some cases made it easier to prepare the layer. It was shown that, at a moisture content of 17·9%, the error in the measured diffusion coefficient of acetone due to the addition of agar-agar was smaller than the experimental error (Menting, 1969).

Moisture contents of the malto-dextrin layers below 30% were adjusted by equilibrating the layers with an atmosphere, which in turn was in equilibrium with a saturated salt solution. The equilibrium relative humidities of the salt solutions used were taken from O'Brien (1948). The equilibrium relative humidity curve of malto-dextrin is shown in Fig. 1. This figure also shows the density of malto-dextrin as a function of its moisture content, which enables the thickness of a malto-dextrin layer to be calculated from its weight. All the diffusion coefficients were measured at a temperature of 21·5°C.

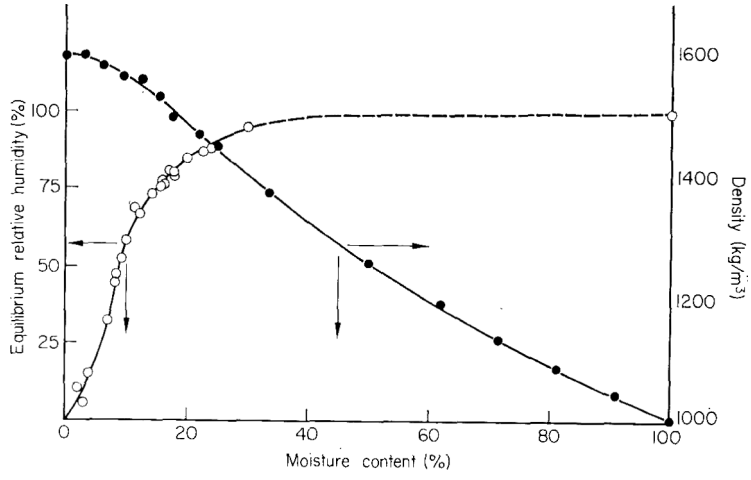


FIG. 1. Equilibrium relative humidity curve of malto-dextrin and its density as a function of moisture content (temperature: 20°C) after Menting (1969).

*Measurement of the diffusion coefficient of organic volatiles*

a. *Gas–chromatographic technique*

Experiments with a constant amount of diffusant in the system were performed by introducing an amount of vapour of that diffusant into a closed glass flask containing a malto-dextrin layer. The thickness of the layer and the surface area available for sorption were adapted respectively to the expected value of the diffusion coefficient and distribution coefficient of the diffusant. The concentration of the vapour in the gas phase was measured by gas-liquid chromatography.

Fig. 2(a) shows the experimental set up for measurement of the sorption of acetone and ethyl acetate by malto-dextrin layers with moisture contents of 30% and more. Small brass dishes were filled with a warm malto-dextrin solution of the desired moisture content. The thickness of the layers ranged from 0·8 to 3·1 mm. The solution contained some agar-agar (1·0% of the water) and some benzoic acid (0·1% of dry malto-dextrin). Before use they were placed for 15 hr or more in a closed vessel, which contained a large amount of malto-dextrin also with the desired moisture content. One or more of the dishes were put in the closed 200 ml glass flask, which was provided with a magnetic stirrer. The change in the moisture content of the malto-dextrin after it had been placed in the flask could be neglected on account of the relatively small volume of the latter. The flask was placed in thermostated water with a temperature of (21·5 ± 0·2°C). Liquid acetone and ethyl acetate, together with benzene as a reference, were mixed in such a proportion that the vapour in equilibrium with the solution gave equal peak heights for the three components when analysed on the gas chromatograph.

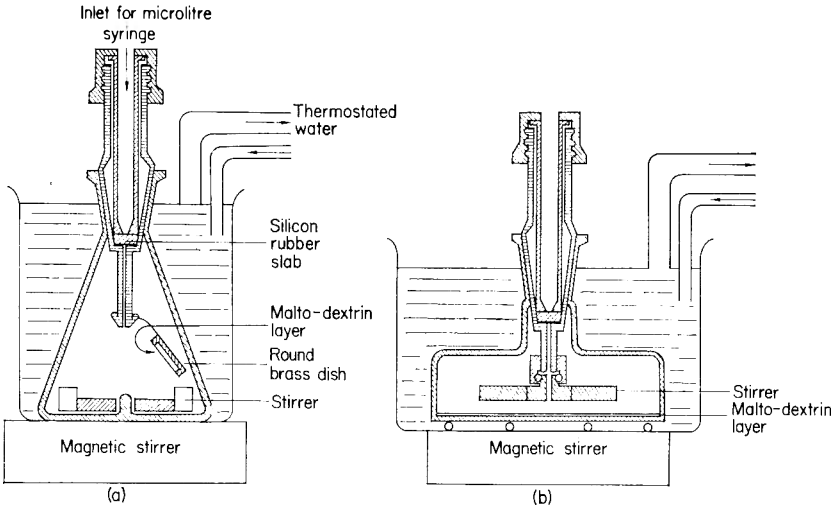


FIG. 2. Experimental set up for the measurement of (de)sorption by the gas-chromatographic technique. (a) Sorption of acetone and ethyl acetate, and (b) sorption of camphor and desorption of methane.

Then, 10 ml of this vapour was injected into the flask containing the malto-dextrin layer(s). The initial partial vapour pressure of acetone was about 12 mmHg. Gas samples of 25 or 30 μl were taken periodically by inserting the needle of a Hamilton gas-tight syringe through a silicone rubber slab into the capillary at the top of the flask. The proportion of benzene sorbed by the malto-dextrin layer was 2–3% of that for acetone and 10%, or less, of that for ethyl acetate. The sorption of benzene was, therefore, neglected and the peak height of benzene was used as a reference for the other

components. Fig. 3 shows a typical curve for the sorption of acetone with time. The diffusion coefficient can be calculated by substituting a measured value of $q/q_\infty$, the corresponding sorption time and $\alpha$ in Eq. (4). For this investigation, however, calculated values of $q/q_\infty$ for a certain value of $Dt/d^2$ were derived from a graph given by Crank. The diffusion coefficients were then deduced by comparing the calculated value with the measured sorption (Crank, 1967). The standard deviation of the diffusion coefficient of acetone, derived from the spread of the points of the sorption curves (and thus representing the error only for a single determination of $D$), varied from 7% (at a moisture content of 99%) to 30% (at a moisture content of 30·3%). For ethyl acetate this standard deviation varied from 22% to 54%. The true standard error in $D$, as it would be obtained by replicate determinations, was not determined in this investigation.

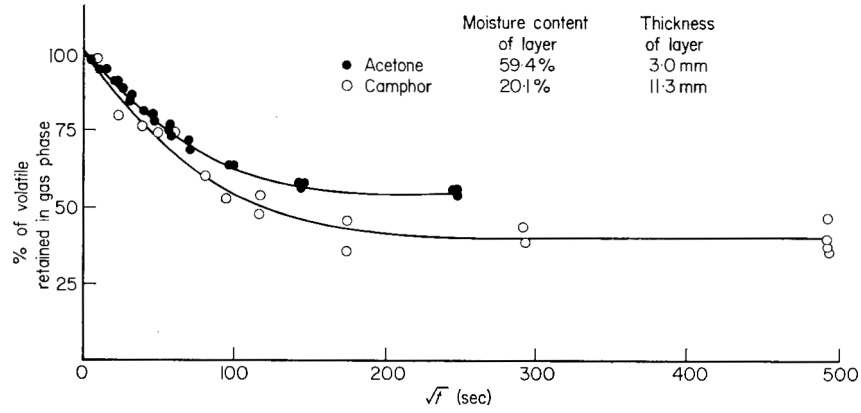


FIG. 3. Sorption of acetone and camphor by a malto-dextrin layer when the amount of diffusant in the system is kept constant.

As camphor and methane are only slightly soluble in aqueous malto-dextrin solution, a much larger area of sorption or desorption is necessary. The experimental set-up for these measurements is shown in Fig. 2(b). A thin malto-dextrin layer was obtained on the bottom of a glass flask by evaporating a solution of 3–10% malto-dextrin in water gelled by the addition of agar-agar. The moisture content was then adjusted to the required value by equilibrating the layer with one of the saturated salt solutions. The composition of the dry matter of the layers in these experiments was malto-dextrin 97·8%, agar-agar 2·0% and benzoic acid 0·2%. The concentration of the diffusant in the vapour phase at a given time was determined with reasonable accuracy by taking three successive samples with a Hamilton syringe and averaging the peak heights recorded on the gas chromatograph.

The diffusion coefficient of camphor was determined from sorption curves at moisture contents of the malto-dextrin of 20·1% and 22·8%. An example of a sorption curve is shown in Fig. 3. The thickness of the malto-dextrin layer varied between 10–170 μm

and the initial concentration of camphor vapour was between 10 and 40% of the saturation concentration over pure camphor. The diffusion coefficient of methane, which is much less soluble than even camphor, was determined from desorption curves. The moisture content of the malto-dextrin layer was 20·1%. The flask was filled with methane, the relative humidity of which was chosen so as to be in equilibrium with the layer. The partial vapour pressure of methane was between 0·8 and 1 atmosphere but was not further recorded. After equilibrium sorption of methane had been reached, the flask was opened and the methane in the vapour phase was removed by flushing with air. This took 40 sec. The flask was then closed and the desorption of methane was followed gas-chromatographically. Fig. 4 is an example of a desorption curve. Five such desorption experiments were performed in all, for thicknesses of the malto-dextrin layer between 0·3 and 0·7 mm.

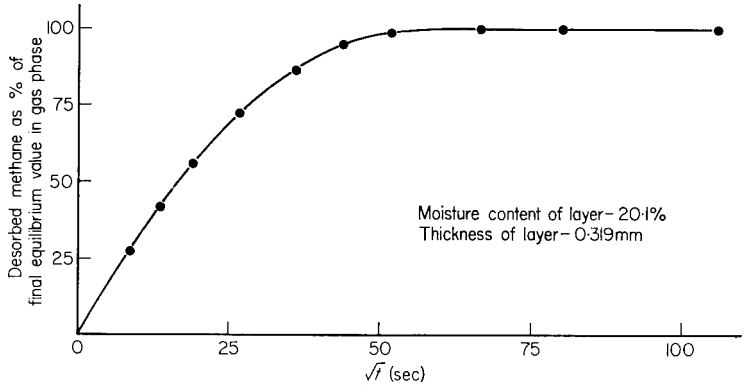


FIG. 4. Desorption of methane from a malto-dextrin layer when the amount of methane in the system is kept constant.

b. *Radioactive tracer technique*

At moisture contents of malto-dextrin below 30%, where the value of $D$ becomes very small, the diffusion coefficients of those volatiles, which were readily available in radioactively labelled form, were measured by the radioactive tracer technique. The concentration of labelled volatile in the gas phase was kept constant and the amount sorbed by thin malto-dextrin layers was followed as a function of time.

Small glass bars were coated with a thin layer of malto-dextrin by withdrawing them with a constant velocity from a 50% aqueous malto-dextrin solution containing 0·1% benzoic acid, and drying them in a current of hot air (80°C). For measurements of the diffusion coefficients at moisture contents above 18%, 1·0% agar-agar was added to the malto-dextrin solution from which the bars were drawn. A number of coated, dried bars were placed in a chamber containing a saturated salt solution with the desired equilibrium relative humidity. The chamber, shown in Fig. 5(a), was kept at a temperature of 21·5 ± 1°C, and the vapour phase was stirred continuously. After the

coatings had reached their equilibrium moisture content, the bars were put in another similar chamber containing the same saturated salt solution, to which 1%, or less, radioactively labelled acetone or other volatile had been added. For benzene and carbon tetrachloride, which are only slightly soluble in aqueous solutions, the vapour pressure of the volatile in the chamber was equal to the saturated vapour pressure. In order to keep the concentration in the gas phase constant for these two volatiles, the salt solution was saturated with the volatile in question and, in addition, a capillary filled with liquid benzene or carbon tetrachloride was placed in the chamber.

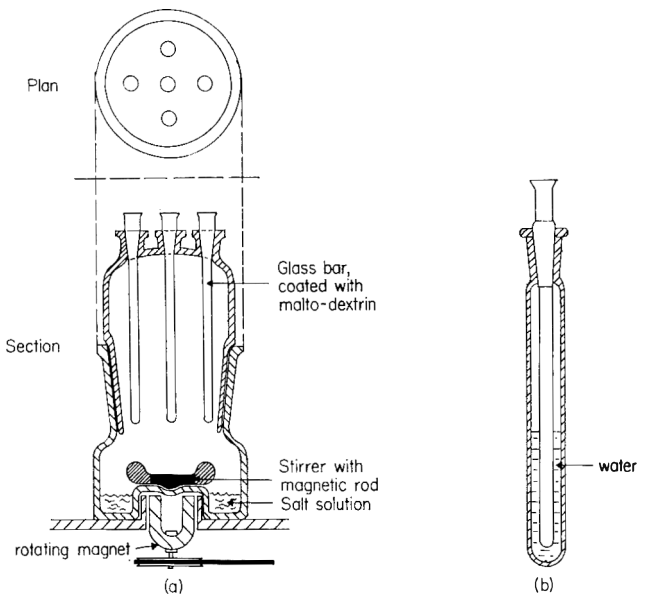


FIG. 5. Experimental set up for the measurement of sorption by the radioactive tracer technique. In (a) is shown the plan and section of the chamber with five bars and (b) shows tube containing water to dissolve the malto-dextrin coating on the bar.

After preselected times, a bar was taken from the chamber and put in a tube containing 1 ml water to dissolve the malto-dextrin layer (see Fig. 5b). The content of acetone (or other volatile) of the resulting solution was measured with a liquid scintillation counter. Figure 6 shows two curves for the sorption of acetone by malto-dextrin at moisture contents of 20·1% and 10·2%. The diffusion coefficient was calculated from the initial slope of these curves with the aid of Eq. (3). At moisture contents above 12%, the standard deviation of the diffusion coefficient, derived from the spread of the points of the sorption curve, was 30% or less.

The sorption of volatiles becomes very low at low moisture contents of the malto-dextrin layer, which must be very thin in order to reach equilibrium within a reasonable time. This makes the method unsuitable at moisture contents below 10%.

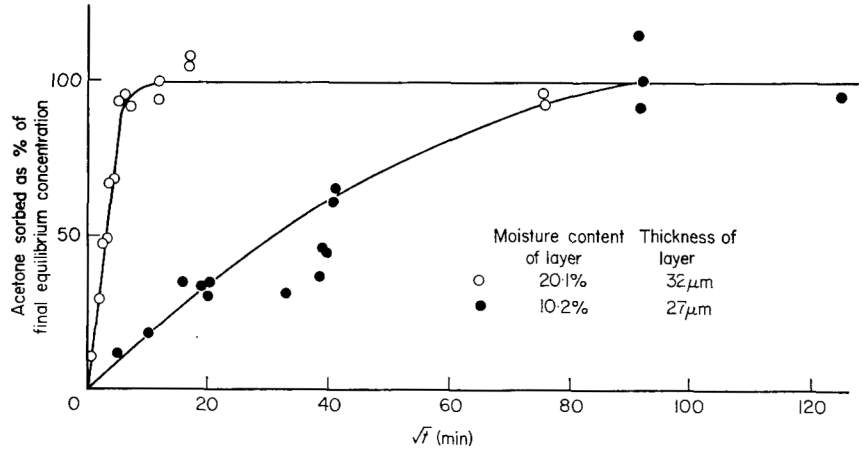


FIG. 6. Sorption of acetone by a malto-dextrin layer when the partial vapour pressure of acetone is kept constant.

*Measurement of the diffusion coefficient of water*

Eq. (3) applies only when $D$ is independent of $C$, $x$ or $t$. When $D$ is a function of $C$ only and the partial vapour pressure of the diffusant is kept constant, $q/q_\infty$ is still a linear function of $\sqrt{t}$ for the first stage of sorption (Crank & Park, 1968). Eq. (3) can be used to define two unequal diffusion coefficients $D_s$ and $D_d$, which are determined from the initial slopes of the sorption and desorption plot respectively. Provided $D_s$ and $D_a$ relate to the same small concentration range, a mean value for $D$ over this concentration range is given approximately by

$$D = \tfrac{1}{2}(D_s + D_d) \tag{5}$$

as is explained by Meares (1965). Therefore, in order to determine the diffusion coefficient of water in malto-dextrin of a particular moisture content, sorption and desorption were measured over a moisture content range around the required value. The width of this range varied from about 2% moisture for the lower moisture contents to 7·2% moisture for the highest moisture content used in the experiment. The diffusion coefficient defined by Eq. (3) corresponds to a moisture content somewhere in the chosen range. This was taken to be the average moisture content for the range, i.e. $\frac{1}{2}(C_1 + C_2)$. The value of $d$ was taken as the average thickness of the layer over the range in question.

A small brass dish (inner diameter 5·0 cm) was filled with a malto-dextrin solution, which contained 1% agar–agar and 0·1% benzoic acid on a dry matter basis. The desired moisture content of the layer was achieved by equilibrating it with a suitable saturated salt solution. The dish was then put on the scale of an analytical balance and its weight recorded. This balance was contained in a box in which both the temperature and the relative humidity were kept constant. Air was blown at a velocity of between

5·5 and 6·0 m/sec across the surface of the malto-dextrin. This velocity was sufficient to ensure that, at the highest moisture content of the layer used, the resistance to mass transfer in the gas phase was negligible with respect to the resistance to mass transfer in the layer, for sorption times longer than 1 min. At lower moisture contents, this time is shorter: it is only 2 sec, for example, for a moisture content of about 17% at which the sorption curves in Fig. 7 were recorded. For all experiments, the time during which the mass transfer resistance of the gas phase is not negligible, was very small compared with the sorption times used to calculate $D$. The weight of the dish was recorded at intervals. The thickness of the malto-dextrin layer (usually only slightly less than the depth of the dish) was adapted to the expected diffusion coefficient and varied from 0·09 to 0·6 mm. The diffusion coefficient of water was measured only at moisture contents below 30%.

Fig. 7 shows a typical sorption and desorption curve for water. The very first part of the plot of sorption against $\sqrt{t}$ is not linear. This non-linearity was observed in many experiments, and may be due to the disturbance of the relative humidity in the box when the door is opened to enable the dish to be placed on the balance.

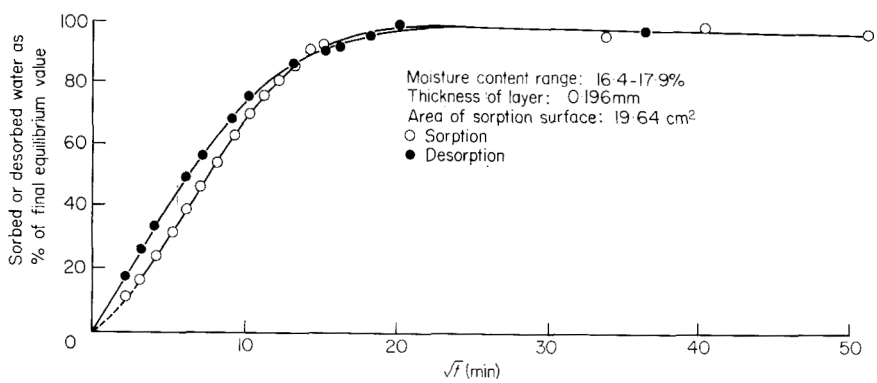


FIG. 7. Sorption and desorption of water by a malto-dextrin layer when the partial vapour pressure of water is kept constant.

## Results

Fig. 8 shows the diffusion coefficients of water ($D_w$) and acetone ($D_a$) in malto-dextrin as a function of its moisture content. The corresponding numerical data are given in Tables 1 and 2. Table 1 also includes the diffusion coefficients of methane, ethyl acetate, benzene, carbon tetrachloride and camphor. The variation of the diffusion coefficient of water with the water concentration ($C_w$) can be described over the range investigated by the relation:

$$\frac{D_w}{D_w^0} = 5{\cdot}0 \exp\left(-\frac{1{\cdot}6\ \rho_w}{C_w}\right) \qquad (6)$$

TABLE 1. Diffusion coefficients of organic volatiles in malto-dextrin at various moisture contents

| Moisture content of malto-dextrin (%) | Diffusion coefficient ($m^2$/sec) | | | | | |
|---|---|---|---|---|---|---|
| | Acetone | Ethyl acetate | Benzene | Carbon tetra-chloride | Camphor | Methane |
| a. Measured by the gas-chromatographic technique | | | | | | |
| 99·0 | $1·2 \times 10^{-9}$ | $1·3 \times 10^{-9}$ | | | | |
| 79·2 | $6·5 \times 10^{-10}$ | $4·4 \times 10^{-9}$ | | | | |
| 69·3 | $5·7 \times 10^{-10}$ | $7·3 \times 10^{-10}$ | | | | |
| 59·4 | $2·9 \times 10^{-10}$ | $3·6 \times 10^{-10}$ | | | | |
| 49·5 | $1·3 \times 10^{-10}$ | $1·7 \times 10^{-10}$ | | | | |
| 39·5 | $3·1 \times 10^{-11}$ | | | | | |
| 30·3 | $7·0 \times 10^{-12}$ | | | | | |
| 22·8 | | | | | $5·8 \times 10^{-14}$ | |
| 20·1 | | | | | $3·1 \times 10^{-15}$ | $2·5 \times 10^{-11}$ |
| b. Measured by the tracer technique | | | | | | |
| 30·0 | $4·4 \times 10^{-12}$ | | | $5·6 \times 10^{-14}$ | | |
| 24·1 | $1·8 \times 10^{-12}$ | | $1·1 \times 10^{-13}$ | | | |
| 20·1 | $3·0 \times 10^{-13}$ | | $5·8 \times 10^{-14}$ | $7·0 \times 10^{-15}$ | | |
| 17·9 | $1·1 \times 10^{-13}$ | $1·1 \times 10^{-13}$ | | | | |
| 16·3 | $4·6 \times 10^{-14}$ | | | | | |
| 14·2 | $2·3 \times 10^{-14}$ | | | | | |
| 12·1 | $4·0 \times 10^{-15}$ | | | | | |
| 10·2 | $1·5 \times 10^{-15}$ | | | | | |

TABLE 2. Diffusion coefficient of water in malto-dextrin at various moisture contents

| Moisture content of malto-dextrin (%) | Diffusion coefficient ($m^2$/sec) | | | Range of moisture content used (%) | Mean thickness of the layer (mm) |
|---|---|---|---|---|---|
| | $D_s$ | $D_d$ | $D_w = \frac{1}{2}(D_s + D_d)$ | | |
| 26·4 | $1·3 \times 10^{-11}$ | $2·5 \times 10^{-11}$ | $1·9 \times 10^{-11}$ | 22·8 — 30·0 | 0·601 |
| 21·5 | $1·2 \times 10^{-11}$ | $8·9 \times 10^{-12}$ | $1·0 \times 10^{-11}$ | 20·1 — 22·8 | 0·426 |
| 20·4 | $8·5 \times 10^{-12}$ | $7·2 \times 10^{-12}$ | $7·9 \times 10^{-12}$ | 17·9 — 22·8 | 0·537 |
| 17·2 | $3·4 \times 10^{-12}$ | $3·6 \times 10^{-12}$ | $3·5 \times 10^{-12}$ | 16·4 — 17·9 | 0·196 |
| 16·1 | $3·7 \times 10^{-12}$ | $2·6 \times 10^{-12}$ | $3·1 \times 10^{-12}$ | 14·3 — 17·9 | 0·497 |
| 15·4 | $1·8 \times 10^{-12}$ | $2·1 \times 10^{-12}$ | $1·9 \times 10^{-12}$ | 14·3 — 16·4 | 0·196 |
| 13·2 | $4·9 \times 10^{-13}$ | $4·6 \times 10^{-13}$ | $4·7 \times 10^{-13}$ | 12·1 — 14·3 | 0·189 |
| 11·1 | $7·3 \times 10^{-14}$ | $1·6 \times 10^{-13}$ | $1·2 \times 10^{-13}$ | 10·1 — 12·1 | 0·091 |

where $\rho_w$ is the density of water. The constant $D_w^0$ is the value of $D_w$ obtained by extrapolation (of a plot of log $D_w$ against $1/C_w$) to a water concentration of 100% ($D_w^0 = 3{\cdot}4 \times 10^{-10}$ m$^2$/s). According to the definition of mutual diffusion, $D_w$ in the aqueous malto-dextrin solution is equal to the diffusion coefficient of malto-dextrin in the same solution. Consequently at malto-dextrin concentrations approaching zero, the diffusion coefficient of water equals the diffusion coefficient of malto-dextrin in pure water. The value of $D_w^0$ is therefore much lower than that of the self-diffusion coefficient of water, which is $2{\cdot}2 \times 10^{-9}$ m$^2$/s (Wang, Robinson & Edelman, 1953). Over the range of moisture content studied, the dependence of the diffusion coefficient of acetone on the water concentration can be described by the relationship:

$$D_a = A \exp\left(-\frac{B}{\sqrt{C_w}}\right) \tag{7}$$

where:

$$A = 2{\cdot}1 \times 10^{-5} \text{ m}^2/\text{sec}$$
$$B = 308 \text{ (kg/m}^3)^{\frac{1}{2}}$$

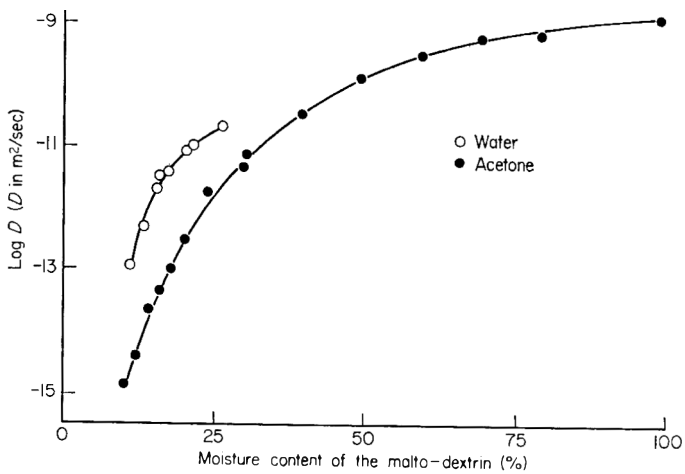


FIG. 8. Dependence of the logarithm of the diffusion of water and acetone in malto-dextrin on the moisture content of the latter.

## Discussion

The logarithm of the diffusion coefficient of acetone in malto-dextrin was found to be a linear function of moisture content when the latter was less than 25%. For very low moisture contents this proved to be a better approximation of the relationship between $D_a$ and $C_w$ than that given by Eq. (7). Similarly, there was a linear relation between

log $D_w$ and $C_w$ below a moisture content of 16%. This agrees with the measurements of Fish (1958), from which it can be derived that log $D_w$ in gelled starch and scalded potato is likewise a linear function of the moisture content in the range 0–16%. A similar relationship has been observed for most synthetic polymers studied, when the diffusant is readily soluble in the polymer and when its concentration is not too high (Meares, 1965).

In Fig. 9 the logarithm of the diffusion coefficients of water and organic volatiles measured in malto-dextrin with a moisture content of 20·1% has been plotted as a function of the molecular 'diameter' of the diffusant. The molecular 'diameter' was taken as the side of the smallest square opening through which a molecular model of the substance could just pass. Molecular models were obtained from Courtaulds' Maidenhead Laboratory and Griffin & George Ltd. The almost linear relationship between molecular 'diameter' and log $D$ is striking. No meaningful relationship could be found between $D$ and other molecular properties such as polarity, molecular weight, and molecular volume (i.e. the parachor of Sugden). Thus, of all molecular properties which might influence diffusion, the 'diameter' is predominant. A relationship similar to that shown in Fig. 9 is often found for the diffusion of gases in synthetic polymers (Michaels, 1966).

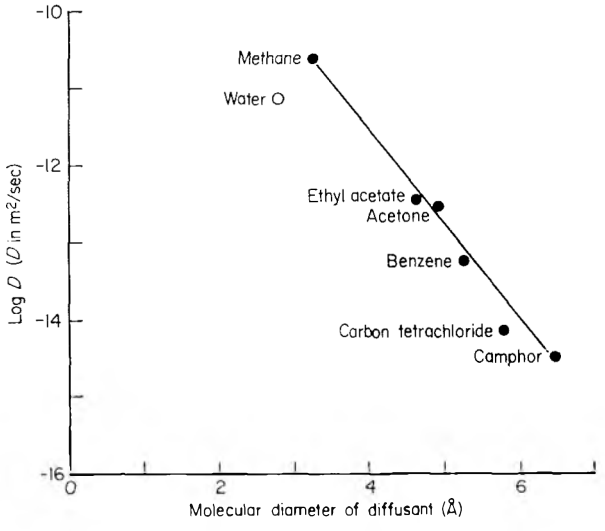


FIG. 9. Plot of the logarithm of the diffusion coefficient of water and organic volatiles in the malto-dextrin (moisture content: 20·1%) against the molecular 'diameter' of the diffusant.

The five corresponding values for the diffusion coefficient of methane were not in close agreement with one another. The two extreme values differed by a factor of 18, which is an order of magnitude greater than the experimental error. This spread, however, is relatively small compared with the factor of $10^4$ by which the values of the

measured diffusion coefficients of the different components vary. A higher value of the diffusion coefficient of methane was accompanied by a higher equilibrium sorption. Probably the diffusion coefficient of methane in malto-dextrin depends on the concentration of methane over the range used.

Attempts to describe the diffusion in an amorphous polymer matrix generally make use of the 'hole' theory. The holes are produced by movements of the polymer chain segments (Brandt, 1959). The energy necessary for the formation of a hole ($E_f$) depends on the cohesive energy of the polymer and the chain stiffness. For a diffusing molecule to jump from one hole into a neighbouring hole of sufficient size, it may have to overcome an energy barrier $E_m$. If the diffusing molecule is strongly bound to the polymer chain, then $E_m$ will be large. Thus the diffusion process is characterized by an energy $E$, which is equal to $E_f$, plus a possible additional term $E_m$. One can derive that $E$, equal to $E_f + E_m$, is related to the diffusion coefficient as follows (Van Bueren, 1961; Jost, 1960):

$$D = D_o \exp\left(-\frac{E}{RT}\right) \tag{8}$$

where $R$ is the gas constant and $T$ is the absolute temperature. In practice, $D_o$ is usually considered to be independent of temperature.

Values of $D_o$ and $E$ for diffusion in malto-dextrin are not known and a complete explanation of the diffusion characteristics in malto-dextrin is therefore far from possible. Only the two most notable aspects can be made plausible, namely the strong dependence of the diffusion coefficients of water and volatiles on the moisture content (Fig. 8) and the marked influence of the molecular 'diameter' of a component upon its diffusion coefficient (Fig. 9).

As the moisture content of the malto-dextrin increases, more of the bonds between the hydroxyl groups of neighbouring carbohydrate molecules will be disrupted. As a result these molecules will become more mobile, which makes it likely that the mobility of water and organic volatiles increase: when the malto-dextrin molecules move more freely, holes of sufficient size are formed more readily between them, thus decreasing $E_f$ and consequently $E$. A small decrease in $E$ causes, according to Eq. (8), a marked decrease in $D$. In agreement with this, Fish (1958) found that the increase of the diffusion coefficient of water in gelled starch with increasing water content was mainly caused by a decrease of $E$ from 9·8 kcal/mole at a water content of 0·74% to 4·5 kcal/mole at a water content of 44·5%. It is true that also $D_o$ changes with the water content, but the effect of the cause in $E$ on $D$ is considerably greater. There is no reason to expect that the diffusion behaviour of malto-dextrin (partially hydrolysed starch) differs appreciably from that of gelled starch.

If the extent of binding between a diffusing molecule and the carbohydrate is low (which is mostly the case for flavour components), then $E_m$ will be small with respect

to the energy necessary to form a sufficiently large hole. Thus the activation energy for diffusion will be primarily determined by $E_f$ for most flavour components. It seems reasonable to assume, that $E_f$ increases with increasing molecular diameter, since a larger hole is needed for a diffusion jump of a larger molecule. It may then be expected that $D$ will decrease sharply as the molecular diameter increases. For the very small water molecule, $E_f$ will also be very small. Since, however, the very polar water molecule can be bound to the hydroxyl groups of the malto-dextrin, $E_m$ will no longer be negligible. This might explain why the diffusion coefficient of water in malto-dextrin is somewhat lower than the diffusion coefficient of methane (see Fig. 9), although the 'diameters' of both molecules hardly differ. The fact that the diffusion coefficient of water in malto-dextrin with a low moisture content is higher than that of most of the organic volatiles must, according to the above explained model, be attributed primarily to the very small size of the water molecule and not to its high polarity. Its polar character is responsible for a strong interaction between it and the malto-dextrin which in fact has the effect of lowering the diffusion coefficient of the water. That this interaction between water and polymer does indeed act so as to lower $D_w$ has been demonstrated by Honeycutt (1966) for the system water/partially hydrolysed derivatives of poly (vinyl acetate).

The overwhelming influence of the molecular diameter on diffusion coefficients at low water content, explains why a thin, dry, carbohydrate layer is much more permeable to water molecules than to the much larger flavour molecules and why during the drying of foods, thin layers comprising mainly carbohydrate and protein can cause a surprisingly high retention of very volatile flavour components (Menting & Hoogstad, 1967a, b).

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# Aroma retention during the drying of liquid foods

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AND H. A. C. THIJSSEN

## Summary

Factors determining aroma retention during the drying of food liquids have been investigated with the aid of a model system. Slabs of an aqueous solution of partially hydrolysed starch, containing a small amount of acetone, were dried in air and the percentage of acetone retained was measured.

Acetone was lost almost exclusively during the 'constant-rate' period of drying and its rate of loss could be described in terms of a binary diffusion process. At high moisture contents, the rate of loss of a component from a drying solution is mainly dependent on its volatility, while at low moisture contents the diffusion coefficient of the component becomes the determining factor.

Loss of volatile components will be only very slight if, at the onset of drying, the value of the dimensionless group $Bi_{wo}K_{wo}$ is sufficiently large. Here $Bi_{wo}$ is the Biot number for water transport and $K_{wo}$ is the ratio of the equilibrium water concentration in the gas phase and the water concentration in the solution to be dried. The minimum value of the group necessary to ensure high aroma retention increases with increasing relative humidity of the drying air. This value is larger for a drop than for a slab and is equal to 22 for a droplet under normal spray-drying conditions.

## Introduction

Drying is one of the oldest and most important food preservation techniques. The quality of a rehydrated food, however, can rarely match that of the fresh product. One of the reasons for this is loss of flavour, due to both chemical reactions and the evaporation of volatile compounds during the drying operation.

When an aqueous food liquid with a low dry matter content is concentrated by

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evaporation, the loss of an aroma component is mainly determined by its volatility ($\alpha_{aw}$) relative to water:

$$\alpha_{aw} = \frac{K_a}{K_w} \tag{1}$$

in which $K_a$ and $K_w$ are defined by

$$K_a = \frac{C'_a}{C_a}, \quad K_w = \frac{C'_w}{C_w}$$

Here $C'_a$ and $C'_w$ are respectively the concentrations of an aroma component and water in the vapour in equilibrium with a liquid phase in which their concentrations are $C_a$ and $C_w$*. If the vapour removed is in equilibrium with the liquid and if there is no concentration gradient in the solution, the retention of an aroma component after partial evaporation of the water can be expressed by:

$$\frac{M_a}{M_{ao}} = \left(\frac{M_w}{M_{wo}}\right)^{\alpha_{aw}} \tag{2}$$

$M_{ao}$ and $M_{wo}$ are the amounts of the aroma component and water initially present in the liquid and $M_a$ and $M_w$ are the amounts left after partial evaporation. The value of $\alpha_{aw}$ for the aroma components of fruit juices varies from 0·1 to more than 100, although the majority have relative volatilities between 5 and 50. Even if the boiling point of an aroma component at atmospheric pressure is appreciably higher than 100°C, its relative volatility in dilute aqueous solutions can still be of the order of 10–100. Such high values of $\alpha_{aw}$ should, according to equation (2), result in extremely low aroma retentions in concentrated or dried juices. This is clearly illustrated by the following example. The boiling point of 2-heptanone is 150°C, yet its relative volatility at parts-per-million concentrations in pure water is about 200 at 54°C (Bruin, 1969). This means that if only 4% of the water were evaporated, hardly any 2-heptanone (0·01% of the initial amount) would remain in solution.

Eq. (2), however, only holds if the evaporation at the surface is not limited by the mass transport in the liquid phase. In the dehydration of juices and extracts this condition can only be fulfilled at high water concentrations. At low water concentrations the diffusion coefficients in the liquid phase are very low, and thus the resistance to mass transfer in the liquid phase becomes much greater than that in the gas phase. Moreover convection, which increases the effective diffusion coefficients, is more or less excluded at low moisture contents. The loss of an aroma component then no

*The prime always denotes the vapour phase.

longer depends primarily on its volatility but is determined by its diffusion coefficient in the liquid. In agreement with this, Saravacos & Moyer (1968a, b) found that the loss of a component during freeze drying and vacuum drying depends mainly on its volatility only in the initial drying phase. When the initial dry matter content of the liquid to be dried is about 50% or higher, the retention of very volatile compounds can be high both after freeze drying (Rey, 1962) and air drying (Menting & Hoogstad, 1967a).

Thijssen & Rulkens (1968) explained how the loss of a volatile component during drying depends on both its relative volatility and its diffusion coefficient. Their theory has been tested for the model system maltodextrin/water/acetone. Slabs of a solution of malto-dextrin (partially hydrolysed starch), with various moisture contents and an acetone content of less than 0·1%,* were dried in a current of air and the acetone retention was measured. The measured retention values were compared with those predicted from previous determinations of the diffusion coefficients and vapour pressure isotherms for water and acetone in the same system (Menting, 1969; Menting, Hoogstad & Thijssen, 1969). The conditions necessary for high aroma retention in drying food liquids are discussed.

## Experimental

The malto-dextrin (type T, ex Scholten, Foxhol, The Netherlands) was from the same batch as that used for earlier experiments (Menting & Hoogstad, 1967a, b; Menting *et al.*, 1970). Slabs of malto-dextrin solution were gelled with a little agar-agar in order to make them self-supporting and to prevent mass transport by convection. For initial moisture contents above 55%, the amount of agar-agar added was 1% of the water. At lower initial moisture contents the amount added was 2·5% of the malto-dextrin. The initial acetone concentration in the slabs was 1·00 kg/m$^3$ (0·096% for a 100 g/l solution), of which 0·15% was radioactively labelled. The acetone content of the slab was determined by measuring the radioactivity of small samples with a liquid scintillation counter.

A slab was made by pouring a warm solution into a Teflon frame held between two glass plates, which were removed after the slab had gelled. The slab, which measured 11·0 × 3·3 × 0·41 cm, was then placed in a horizontal tube through which drying air was blown with a velocity of 3 ($\pm$ 0·5) m/sec. The air was adjusted to the desired relative humidity by recirculation through a climate chamber, in which dishes containing a drying agent or a saturated salt solution were placed (Fig. 1). The relative humidity near the slab during drying varied by about $\pm$ 4% absolute. The air temperature was regulated so as to keep the slab at 21·5 ($\pm$ 1)°C during drying. This was done by connecting the electrical air heaters in the climate chamber via a Honeywell Servotronik regulator to a thermocouple in the slab. The thermocouple was positioned

*Unless otherwise stated, percentages are expressed as percentages by weight.

in the middle of a 4 cm long section at the extreme downwind end of the slab. Measurements were made in this section only. The slab was long enough to ensure that the partial mass transfer coefficient in the gas phase over the surface of this section was almost constant. During drying, samples were taken from the 4 cm long section with a cork borer (diameter 2·1 mm). The samples were put into weighed vials containing 1 ml of water. These vials were reweighed, 10 ml of scintillator solution was added, and the radioactivity was measured. The water and acetone contents of the drying slab could thus be determined as a function of time.

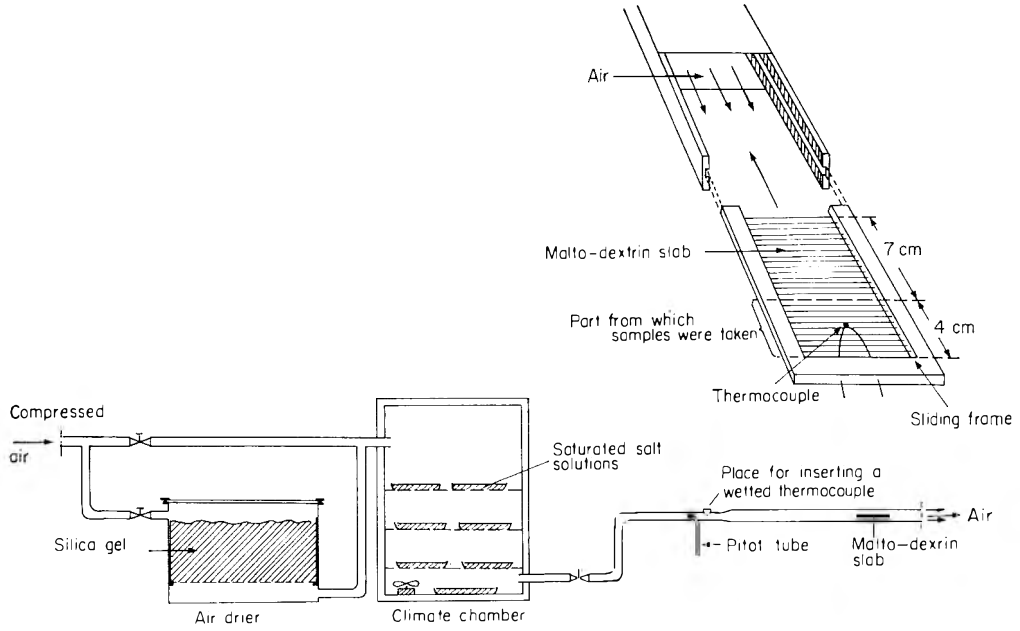


FIG. 1. Apparatus for the drying of slabs.

## Results

Fig. 2 illustrates the decrease of the moisture and acetone contents of the slab with dehydration time for a typical experiment. The variation of the temperature difference ($\Delta T$) between the slab and the drying air is also indicated. Fig. 3 shows how the acetone retention after drying increases steadily with increasing initial dry matter content of the slab (above 200 g/l). For a given initial dry matter content, the acetone retention after drying decreases strongly with increasing relative humidity ($H_r$) of the drying air (Fig. 4). The decrease of the acetone content of a slab with increasing dry matter content during drying is illustrated in Fig. 5 for two relative humidities of the drying air.

The variation of $\Delta T$ with time (Fig. 2) shows that the drying of the slab can be divided into a constant-rate period of evaporation and a falling-rate period. Fig. 6

compares the duration of this constant-rate period with the time during which the acetone escapes. The data are from the same experiment as those in Fig. 4. The time at which the constant-rate period ends coincides roughly with the time after which the acetone content becomes more or less constant.

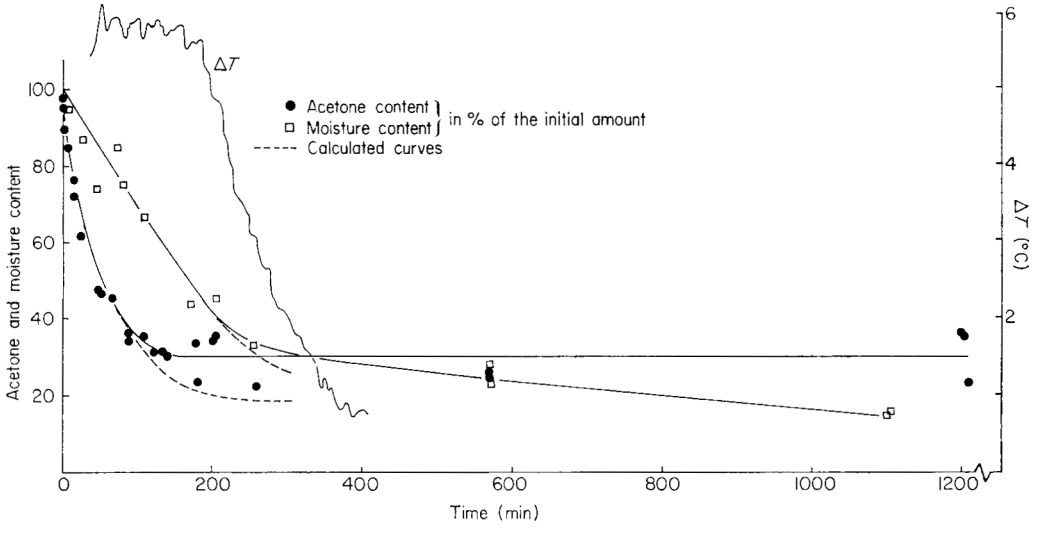


FIG. 2. Moisture content, acetone content and the temperature difference ($\Delta T$) between the slab and the drying air as functions of time. Initial dry matter content of slab, 400 g/l; relative humidity of drying air, 53%.

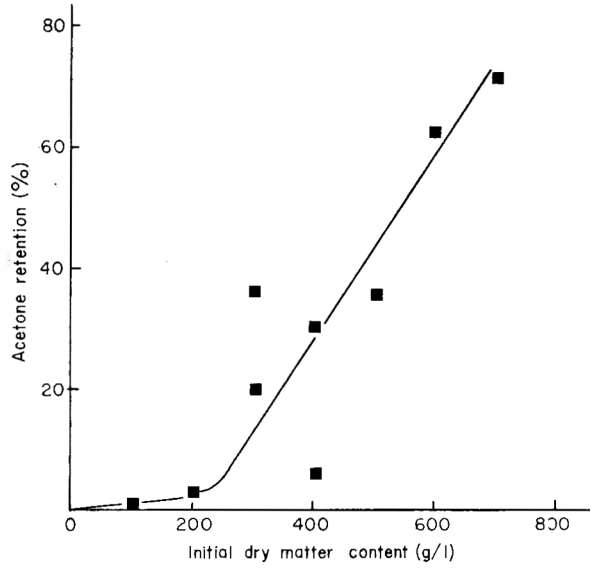


FIG. 3. Acetone retained by a dried slab as a function of its initial dry matter content. Relative humidity of drying air, 56%.

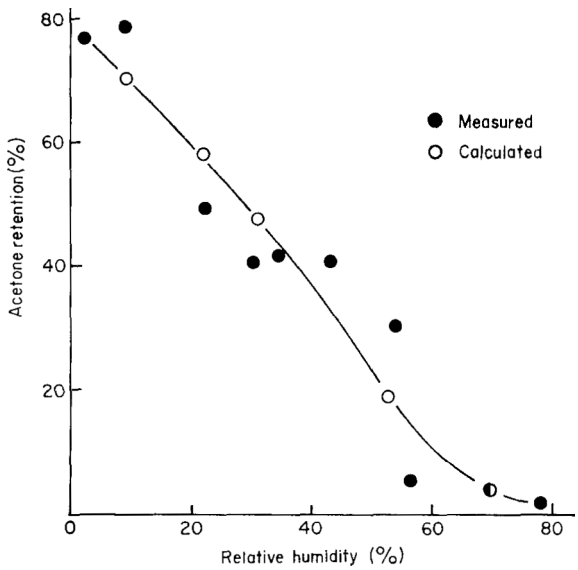


FIG. 4. Acetone retained by a dried slab as a function of the relative humidity of the drying air. Initial dry matter content of slab, 400 g/l.

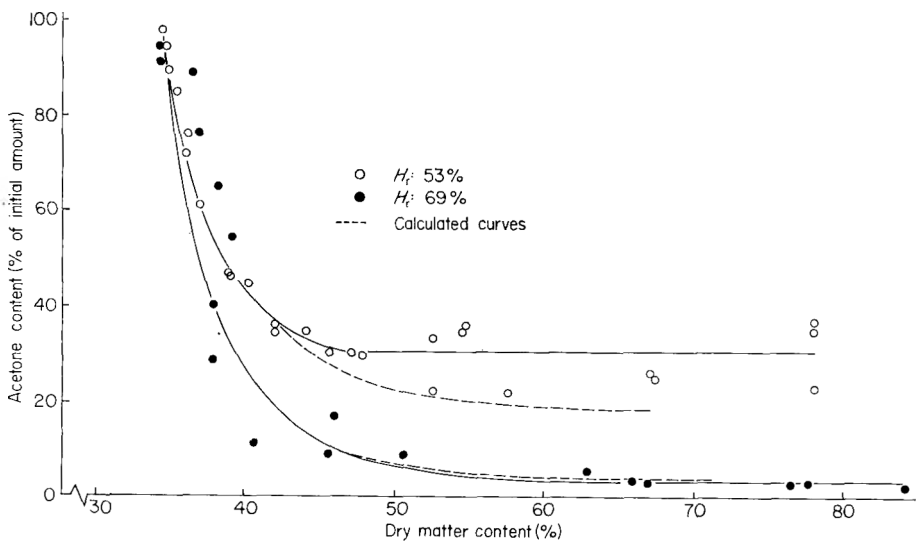


FIG. 5. Acetone content of the slab as a function of its dry matter content during drying, for two relative humidities (*Hr*) of the drying air. Initial dry matter content of the slab, 400 g/l.

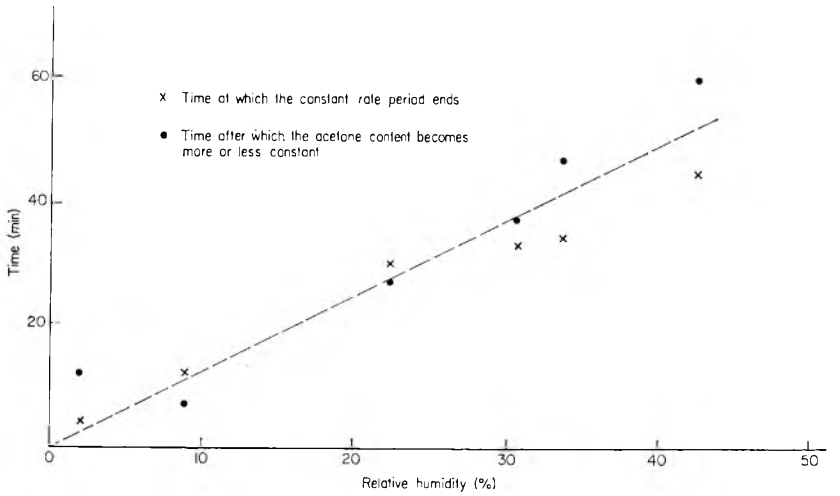


FIG. 6. The approximate coincidence of the end of the constant-rate period and the end of acetone loss.

With experimentally derived equations for the concentration-dependence of the diffusion coefficients of acetone and water (Menting *et al.*, 1970), Förch (1969) calculated numerically the acetone and water contents of the slab throughout the drying process. These calculated values are included in Figs. 2, 4 and 5. The calculations were based on Fick's equation, which is strictly valid only for diffusion in binary systems. From the close agreement between the calculated and the measured values in Fig. 4, it appears that the retention of acetone can be described in terms of a normal binary diffusion process. As soon as the surface of the evaporating liquid has become nearly dry, the loss of volatile aromas becomes negligible. This is because the evaporation rates of water and aroma components at low surface water concentrations are determined by their diffusion coefficients. Previous measurements (Menting *et al.*, 1970) showed that the values of these diffusion coefficients at low moisture contents of the malto-dextrin primarily depend on the molecular 'diameter' of the components concerned. The smaller the molecular 'diameter', the higher the diffusion coefficient. Since the water molecule is much smaller than the molecules of most aroma compounds, the diffusion coefficient of water is correspondingly higher.

## Discussion

*Influence of volatility*

For flavour components of low relative volatility, the rate of evaporation from a slab increases with increasing relative volatility. The evaporation rate continues to increase until, for components of high relative volatility, it becomes completely determined by the molecular transport to the surface. For, if a particular component is much more

volatile than water, the surface layer rapidly becomes depleted in this component. A further increase in relative humidity then no longer causes an increase in the loss of the component during drying. In this case, the flux ($\mathcal{N}_{ai}$) of the component across the surface does not depend any more on its volatility, and can be calculated with the aid of the differential equation of diffusion by assuming the interfacial concentration of the component to be zero. If the concentration, $C_{ao}$, of the flavour component in the slab is homogeneous for $t = 0$ and its surface concentration approaches zero immediately after the onset of drying, $\mathcal{N}_{ai}$ can be expressed by:

$$\mathcal{N}_{ai} = - C_{ao} \sqrt{\frac{D_a}{\pi t}} \quad \text{for } t \leqslant \tau_a \tag{3}$$

Here $t$ denotes time and $\tau_a$ is the time after which half of the volatile component has evaporated from the slab. The error involved in assuming Eq. (3) is negligible for $t \leqslant \tau_a$, provided both the diffusion coefficient ($D_a$) of the component in the slab and the slab thickness are constant.

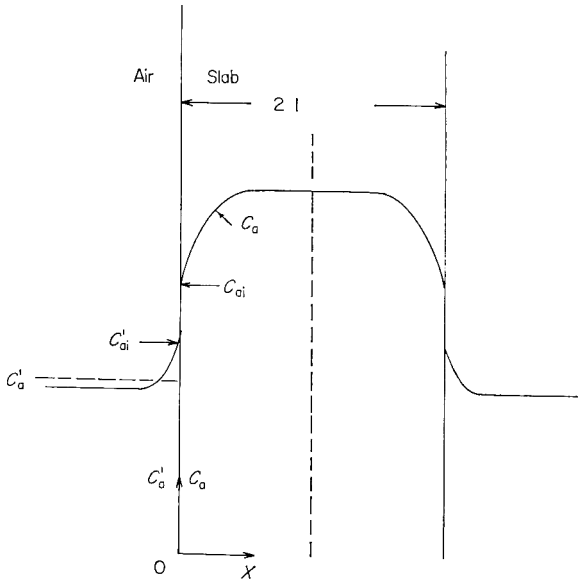


FIG. 7. Schematic representation of drying slab.

A slab is represented schematically in Fig. 7. The condition that the surface concentration ($C_{ai}$) of the component in the slab should be zero can be approximated by:

$$C_{ai} \ll C_{ao} \tag{4}$$

If the concentration of the component in the bulk of the drying air is zero, its flux, $\mathcal{N}_{ai}$, across the surface is given by:

$$\mathcal{N}_{ai} = - k'_a C'_{ai} \tag{5}$$

where $k'_a$ is its mass transfer coefficient in the gas phase and $C'_{ai}$ is its concentration in the gas phase at the surface of the slab. From Eqs. (3) and (5) it follows that:

$$k'_a K_{ai} C_{ai} = C_{ao} \sqrt{\frac{\overline{D_a}}{\pi t}} \tag{6}$$

where $K_{ai}$ ($= C'_{ai}/C_{ai}$) is a measure of the volatility of the component, as defined for Eq. (1). Combination of Eqs. (4) and (6) gives the following condition for a surface concentration almost equal to zero:

$$k'_a K_{ai} \gg \sqrt{\frac{\overline{D_a}}{\pi t}} \tag{7}$$

or

$$t \gg \frac{D_a}{\pi (k'_a K_{ai})^2} \tag{8}$$

If a factor of 10 is chosen for inequality (8), the error introduced is small compared with the error in the measurements.

The time ($t_{ao}$) after which $C_{ai} \approx 0$ is then given by:

$$t_{ao} = \frac{10}{\pi} \cdot \frac{D_a}{(k'_a K_{ai})^2} \tag{9}$$

In order that $C_{ai}$ may be taken to equal zero from the very onset of drying, $t_{ao}$ must be very small, i.e.:

$$t_{ao} \ll \tau_a \tag{10}$$

which at the same time satisfies the requirement $t \leqslant \tau_a$ in Eq. (3). For a slab drying at both sides it can be derived from Eq. (3) that:

$$\tau_a = \frac{\pi}{16} \cdot \frac{l^2}{D_a} \tag{11}$$

where l is the half-thickness of the slab. Combination of (9), (10), and (11) gives the

following condition to be satisfied if the interfacial concentration of the component is to be zero from the very beginning of drying:

$$Bi_a K_{ai} \gg \frac{4\sqrt{10}}{\pi} \approx 4 \tag{12}$$

where $Bi_a$ is the Biot number for mass transfer and equals $k'_a l/D_a$. The concentration of flavour components in juices and extracts is sufficiently low so as not to influence $D_a$ and $K_{ai}$. Condition (10) requires that $t_{ao}$ should be negligible with respect to $\tau_a$. If $\alpha_{aw} \gg 1$, the change in the concentration of water during $t_{ao}$ can be neglected, and the values of $D_a$ and $K_{ai}$ during $t_{ao}$ remain nearly equal to those at the onset of drying. Inequality (12) can then be written as:

$$Bi_{ao} K_{ao} \gg 4 \tag{13}$$

where $K_{ao}$ ($= C'_{ao}/C_{ao}$) is the distribution coefficient of the flavour component for the solution to be dried at the initial drying temperature.

For a sphere of radius $r$, Eq. (11) becomes: $\tau_a = 0{\cdot}03\ r^2/D_a$. The value of $\tau_a$ for a sphere is therefore less than that for a slab with $l = r$, and the right-hand side of inequalities (12) and (13) become 2·5 times larger, i.e. 10 instead of 4.

If condition (13) is satisfied, the loss of the component during drying is not influenced by its relative volatility. The loss then depends only on the value of the effective diffusion coefficient. With spray drying, for instance, condition (13) is readily satisfied for components with $\alpha_{aw} \geqslant 5$. This explains the finding of Thijssen & Rulkens (1968) that the loss of volatile components during the spray drying of coffee extract was not dependent on their relative volatility.

*Condition for almost no loss of volatile flavours during drying*

If we assume that the Biot number for water transport ($Bi_w$) and the distribution coefficient of water ($K_w$) are independent of water concentration over the relevant concentration range, inequality (13) can also be applied to the water. When the air in contact with the slab is nearly dry, satisfaction of the inequality means that the water concentration at the surface of the slab becomes almost zero nearly immediately after the onset of drying. Since $Bi_w$ is more strongly dependent on water concentration than $K_w$, the increase in $Bi_w$ during drying is greater than the decrease in $K_w$. Thus we can be sure that the surface concentration of water will be in equilibrium with the drying air almost immediately after the onset of drying if:

$$Bi_{wo} K_{wo} \gg 4 \tag{14}$$

If inequality (14) is satisfied, aroma retention after drying will be close to 100%, since

the dry surface layer is almost impermeable to aroma components. Thus the surface of the slab becomes covered almost immediately by a layer which is permeable to water only. The surface layer does not have to be totally dry to ensure high retentions. If the minimum value which $Bi_w K_w$ must have to guarantee almost no loss of volatile components is denoted by $G$, the condition for hardly any aroma loss becomes:

$$Bi_{wo} K_{wo} \geqslant G. \tag{15}$$

The value of $G$ increases with increasing humidity of the air. At relative humidities above about 80%, Eq. (15) cannot be applied any longer because, even after phase equilibrium, the diffusion coefficients of aroma components at the surface of the liquid phase are still appreciable. $G$ is also determined by the form in which the liquid is dried: its value for a droplet is greater than that for a slab. Moreover $G$ depends to some extent on the type of volatile component, on the nature of the solution to be dried, and on the liquid temperature.

One can assume that the Sherwood number for the small droplets in a spray-drying tower is approximately equal to 2. From this it follows that:

$$k'_w = \frac{D'_w}{r} \tag{16}$$

where $r$ is the radius of the droplet and $D'_w$ is the diffusion coefficient of water vapour in the gas phase at the so called film temperature, which can be approximated by the half-sum of the temperature of the surface of the droplet and the air temperature. Substitution of Eq. (16) in (15) gives the following condition for a high retention of volatiles after spray drying:

$$\frac{D'_w}{D_{wo}} K_{wo} \geqslant G \tag{17}$$

This condition is, in contrast with (15), independent of the droplet size. The left-hand side of the expression increases with increasing dry matter content, since $D_{wo}$ then decreases. It also increases with increasing droplet temperature, mainly because of the marked temperature dependence of $K_{wo}$.

The value of $G$ can be determined by either measuring or calculating the retention of a volatile component under various process conditions. During the spray drying of coffee extract or other aqueous food liquids the retention of volatile components generally increases with increasing initial dry matter content, up to a dry matter content of 50%, above which the retention becomes nearly constant. Evidently, $Bi_{wo} K_{wo}$ is then about equal to $G$. Thus the value of $G$ for spray drying can be calculated from the values of $D'_w$, $D_{wo}$ and $K_{wo}$ at that water concentration at which

retention reaches a constant, maximum level. The diffusion coefficient of water in solutions, for which the water concentration is 50% or more, is only slightly dependent on the nature of the dissolved solids, and its value in malto-dextrin (Menting *et al.*, 1970) can be taken as being representative for aqueous food liquids. Moreover, at high water concentrations, $C'_{wo}$ is about equal to the concentration of water vapour in equilibrium with pure water. If the initial droplet temperature in the spray tower is 50°C and the air inlet temperature 250°C, we find for an aqueous solution of 50% dry matter:

$$K_{wo}\,(50°C) = \frac{C'_{wo}}{C_{wo}} = 1{\cdot}3 \times 10^{-4}$$

$$D_{wo}\,(50°C) = 2{\cdot}6 \times 10^{-10}\ m^2/sec$$

$$D'_{w}\,(150°C) = 4{\cdot}3 \times 10^{-5}\ m^2/sec$$

Here $D_{wo}$ has been calculated from its value at 21·5°C, the activation energy for diffusion being taken as 4·6 kcal/mole. This value represents the activation energy for self-diffusion of water, but differs only slightly from the value for the diffusion of water found by Fish (1958) in a gelled aqueous solution of starch. $Bi_{wo}K_{wo}$ is then equal to 22, which represents the value of $G$ for spray drying of foods under conventional conditions.

When food liquids with a dissolved solids content of about 50% are spray dried, retention of volatiles is usually well below 100% and is generally somewhere between 50 and 80%. This is not in contradiction with the theory outlined above, but is due to the loss of volatiles during the formation of the droplets and the additional loss due to the puffing of the droplets.

## Acknowledgments

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# Effect on various spoilage values of the addition of sulphite and chlortetracycline to beef stored at 5°C

D. PEARSON

## Summary

Methods for determining various chemical spoilage values in meat, previously considered in some detail by the author, have been applied to various samples of beef to which sulphur dioxide and chlortetracycline had been added.

The incorporation into minced beef of these preservatives when compared with the effect on untreated meat, caused retardation of proteolytic breakdown as measured by the relative increases of the total volatile nitrogen during storage. There was also a corresponding delay in the fall of the extract-release volumes. Concurrently fat hydrolysis increased at a considerably faster rate than the controls.

## Introduction

The shelf life of minced meat is limited due to relatively rapid multiplication of bacteria which causes sourness and putridity within a day or so at room temperature. Although the properties are affected by the initial contamination of the meat, an important factor is the storage temperature. The rate of increase in bacterial numbers can be lessened by the addition of sulphur dioxide, which may be present up to a maximum of 450 ppm of mince from June to September in Scotland (The Preservatives in Food (Scotland) Regulations 1962 (SI 1962 No. 1926 (S.94)). In Australia Christian (1963) added metabisulphite ($\equiv$ 500 ppm $SO_2$) to minced meat and carried out storage experiments at 1°C and 5°C and also at 20°C after initial storage for 24 hr at 1°C. It was found that although an off-odour usually develops in untreated mince, by the time it contains about 100 million bacteria/g, objectionable odours were not readily detected in treated meat until the population reached about 500 million/g. Not only was the spoilage delayed, but the different group of organisms present gave rise to a weaker and less objectionable odour so that the addition of preservative tends to mask the number of bacteria present in spoiling mince. As the addition of sulphur dioxide apparently reduces the need for refrigeration there is a danger of minced meat being stored above 10°C, at which temperature growth of pathogens is possible.

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Some countries permit the presence of tetracyclines in poultry and fish. With meat, however, it would appear that their use is tolerated only in Israel and certain parts of South America.

The author (Pearson, 1968, 1968a, b, c, d) has previously drawn attention to the usefulness of various chemical values for assessing the spoilage of minced beef, viz. the total volatile nitrogen (TVN), free fatty acids of the extracted fat (FFA) and the extract-release volume (ERV). Work described in this paper was designed to assess the effect on such values of adding preservatives to minced beef.

The reasons for using chemical rather than microbiological techniques and the degree of replication found with the methods used has been previously stated (Pearson, 1968, 1968b, c, d).

## Experimental

*Sample preparation*

The general principles employed in preparing and storing minced beef samples have been described previously (Pearson, 1968a). For the purpose of the work covered in this paper a solution of sodium metabisulphite ($\equiv$ 400–450 ppm $SO_2$) or chlortetracycline (10–25 ppm aureomycin hydrochloride, Cyanamid) was intimately mixed with the meat using a pestle and mortar. For the controls the minced sample was mixed with the same volume of water. The concentration of added sulphur dioxide in the meat so treated was confirmed immediately by distillation and titration with iodine on 50 g as described in the Report of the Preservatives Determination Committee of the Chemists of the Manufacturing Confectioners' Alliance and of the FMF (1928).

Samples were stored at 5°C.

*Spoilage values*

The methods and scales used for the assessment of odour have been previously described (Pearson, 1968a). The TVN was determined by distillation from magnesium oxide based on the standardized procedure of Lucke & Geidel (Pearson, 1962).

The FFA of the extracted fat was determined by titration of a chloroform macerate after mixing with neutral alcohol (Pearson, 1965). The ERV was assessed after maceration of 15 g sample with 60 ml extraction reagent (pH 5·8) and the volume measured after filtration for 15 min (Pearson, 1967).

## Results and Discussion

*Colour.* During storage the meat treated with sulphur dioxide usually retained a satisfactory red colour until the amount of preservative present fell below about 250 ppm, which was usually reached after about 1 week's storage at 5°C. Amounts below this level were therefore apparently insufficient to prevent oxidation of the oxy-

form to brown metmyoglobin. The tetracyclines do not have reducing properties and samples so treated became brown at an earlier stage of the spoilage history.

*Spoilage values.* In each storage run the added preservative, whether sulphur dioxide or chlortetracycline (CTC), retarded the increase in TVN during storage when compared with the untreated controls. The effect is shown graphically in Fig. 1, which represents the mean of five storage runs using sulphur dioxide and seven storage runs using CTC, covering in all some 106 samples examined. Thus, on the average, after 7 days storage at 5°C the presence of both preservatives retarded protein breakdown such that the TVN showed a minimal increase (to 13·7 with sulphur dioxide and 18·0 with aureomycin treatment), whilst the control meat reached a figure of 81·2 mgN/100 g.

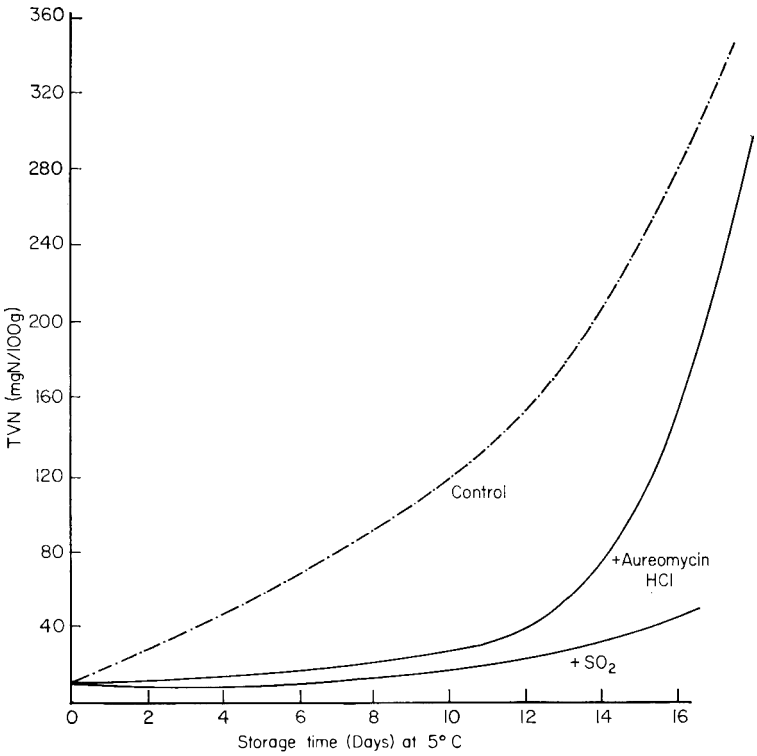


FIG. 1. The mean effect on TVN of addition of 450 ppm sulphur dioxide and 15 ppm aureomycin hydrochloride to samples of minced beef.

The effect of such additions on the extract-release volume is shown in Fig. 2, which represents the results obtained on a sample taken at a slaughterhouse. The rise during the first 2 days of storage at 5°C corresponded with a fall in the pH as would be expected to occur during the pre-rigor period. Subsequently the ERV fell steadily. Samples containing added preservative showed a slower reduction in the ERV during the storage

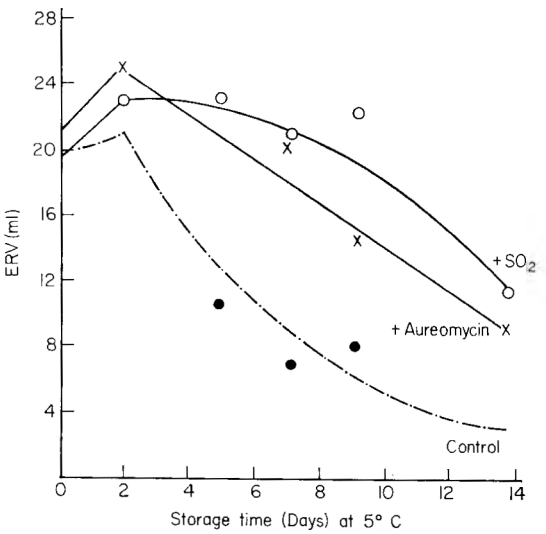


FIG. 2. Effect on ERV of addition of 450 ppm sulphur dioxide and 20 ppm aureomycin hydrochloride to beef obtained from slaughterhouse.

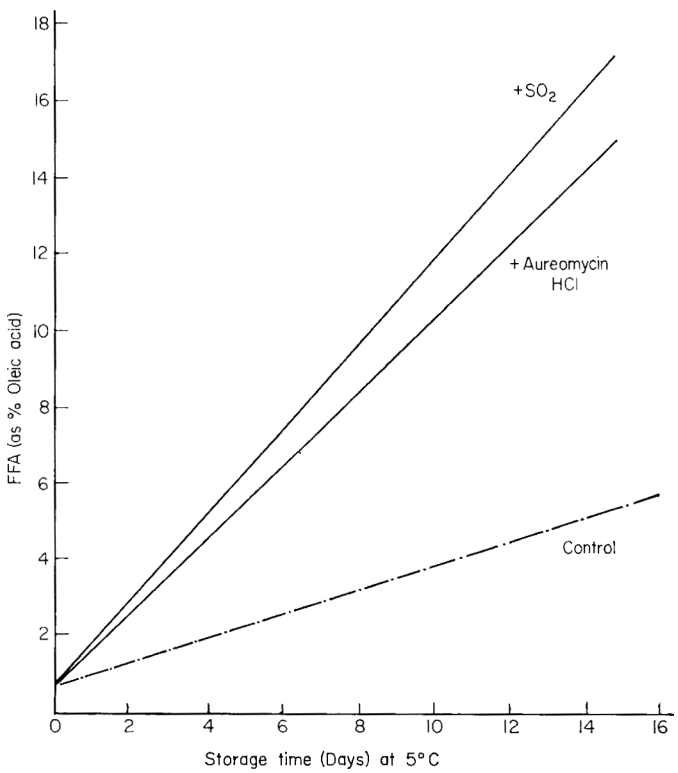


FIG. 3. The mean effect on FFA of extracted fat of addition of 450 ppm sulphur dioxide and 20 ppm aureomycin hydrochloride to samples of minced beef.

period. Such effects on the TVN and ERV correspond with the lower bacterial counts reported by Christian (1963) using metabisulphite and by Jay (1964, 1965) using CTC.

The results obtained from storage experiments indicated that twenty-three samples treated with sulphur dioxide and eighteen samples treated with CTC show higher FFA figures than the corresponding twenty-six control meats (Fig. 3). It is well known that the broad spectrum antibiotics are active against bacteria, but are ineffective against other groups of micro-organisms such as yeasts and moulds. The results obtained in this investigation appeared to confirm the original findings of the writer (Pearson, 1962, working in conjunction with Wight, who was responsible for the microbiological procedures used), which indicated that the yeasts which appear on CTC-treated meat resemble *Candida lipolytica* and therefore tend to enhance fat hydrolysis. Also in view of the close similarity of the lines in Fig. 4 (showing the increase of

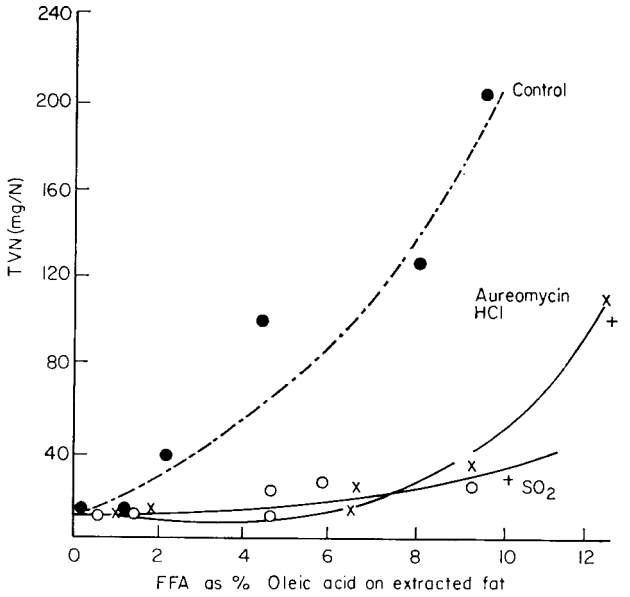


FIG. 4. Comparison of variation of TVN with FFA of stored beef containing added preservatives with the control sample.

TVN with rising FFA for treated and untreated meat) with those in Fig. 1 (TVN *vs* storage time) it is probable that the presence of sulphur dioxide causes similar effects. The variation of the FFA with the ERV in the treated and untreated samples is shown in Fig. 5.

The presence of preservatives in the minced meat had some effect on the organoleptic characteristics. The superiority of sulphur dioxide in retaining an attractive red colour has been referred to previously. Unacceptable odours were not reached in the treated samples until some days after this phase was attained in the controls. With CTC-

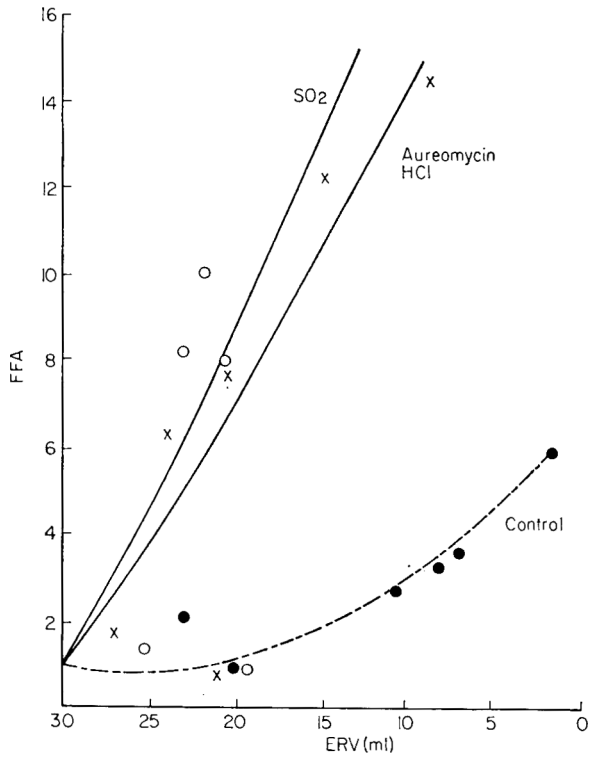


FIG. 5. Comparison of variation of FFA with ERV of stored beef containing added preservatives with the control sample.

treated samples however the odour altered before becoming unacceptable. Unfortunately Christian (1963) has pointed out that the odour of mince treated with sulphur dioxide does not reach an objectionable level until the bacterial population reaches 500 million/g. In view of this comparatively high level it would seem to be inadvisable to rely on odour as a reliable spoilage indicator in samples containing added preservative.

Similar comparative trends to the above were found in meat stored at 10°C, but with a correspondingly increased spoilage rate.

## Conclusions

Sulphur dioxide and chlortetracycline are equally efficient for the inhibition of protein breakdown, but the former is superior for colour retention during storage. Although treated beef shows enhanced free fatty acid formation (compared with control meat), the odour is not affected until the meat is beyond the commercially usable level. In general the incorporation of preservatives produces a marked and measurable increase in the keeping quality of refrigerated beef. Christian (1963), however, found that

sulphite-treated mince did not appear to have spoiled organoleptically until the bacterial count reached a high level. Therefore although minced beef is cooked for a considerable time before eating, sanction of the addition of sulphur dioxide to minced beef must be treated with considerable caution.

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# A method for reconstituting fat extracted flour

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R. N. GREENSHIELDS*

## Summary

A low temperature technique is described for the reconstitution of fat extracted wheat flour which allows the return of lipid material with the minimum alteration of flour properties. A study of the effect of moisture level on lipid binding in reconstituted flour is compared with a similar study of the original flour. Flours with augmented lipid contents were produced and confirmation that the method avoided the introduction of mechanical work obtained.

## Introduction

Investigations of the role of lipid in breadmaking using the technique of extracting flour with solvent and subsequently reconstituting have produced many contradictory results as reviews of the subject show (Cookson & Coppock, 1956; Fisher, 1962; Daniels, 1963). Apart from the choice of a suitable method of lipid extraction, reconstitution also presents problems if changes in flour properties are to be avoided. A successful method of reconstitution would have to satisfy the following requirements if subsequent study of lipid binding was intended. Firstly it is essential that the lipid be completely and evenly dispersed throughout the flour; secondly, the use of solvent (including water) must be avoided; thirdly, mechanical work must be excluded and finally adequate precautions must be taken against the risk of lipid oxidation. Such precautions are necessary since these factors have been reported to affect lipid binding or breadmaking properties of flour (Daniels *et al.*, 1966; Daniels *et al.*, 1969; Davies, Daniels & Greenshields, 1969; Pomeranz, Shogren & Finney, 1968; Ponte *et al.*, 1964). To try to fulfill these requirements, a technique for adding water to flour (Davies *et al.*, 1969) was adapted to return lipid to extracted flour. The essential features of the technique are the grinding of the material to be added to a fine powder in liquid nitrogen and the addition of this fine powder to flour suspended in liquid nitrogen. This allows the return of lipid material to flour without the introduction of mechanical work or other factors which might influence lipid binding.

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## Materials and methods

An unbleached, untreated flour of a commercial breadmaking grist was used which contained 14% moisture and, on a dry basis, 14·5% protein (nitrogen × 5·7), 0·58% ash and 1·65% total lipid, 1·13% of which was free and 0·52% bound. All solvents were of analytical reagent quality and used without further purification except for light petroleum (b.p. 40–60°C) which was redistilled. Fat extracted flour was obtained by percolation of light petroleum through flour (5 l/Kg) contained in a glass cylinder (130 × 8) cm for 24 hr, followed by air drying. This removed free lipid as efficiently as Soxhlet extraction yet without the use of heat. Free lipid was stored at −20°C under nitrogen after the solvent had been removed also under nitrogen on a rotary flash evaporator.

To reconstitute, the extracted flour was added to liquid nitrogen contained in a beaker and the level of boiling liquid nitrogen maintained to keep the suspension as a mobile slurry. The appropriate weight of flour lipid was then added to liquid nitrogen in a metal mortar. The lipid was sufficiently brittle at this temperature to be ground down to a fine powder with a pestle. This powder, suspended in liquid nitrogen, was then transferred to the beaker containing the suspension of flour in liquid nitrogen. The liquid nitrogen boiled off and produced an excellent dispersion of the lipid throughout the flour.

When required for studies on lipid binding, portions of the reconstituted flour were raised to required moisture levels by the technique previously described (Davies *et al.*, 1969), and the distribution of free, bound and unextractable lipids determined. Flour was extracted for 7 hr in a Soxhlet extractor using light petroleum (b.p. 40–60°C). The extracted lipid was called free lipid. The dried extracted flour was then re-extracted by the method of Tsen, Levi & Hlynka (1962) which used chloroform, methanol and water. The lipid thus extracted was called bound lipid. The remaining lipid, derived by difference, was called unextractable.

Flours with augmented lipid levels were obtained using the same liquid nitrogen technique but with greater proportions of added lipid. These flours (Series A) were wetted to 50% moisture by the liquid nitrogen technique, thawed, freeze-dried and then finely ground for lipid distribution determinations. Flours of series A.W. were flours of series A at the final stage, i.e. freeze-dried and ground (see diagram), which were remoistened to 14% by the liquid nitrogen technique. This minimized any effects due to the heat evolved during hydration of the freeze-dried material. This material was then wetted to 50% moisture in a mixer by the method described by Olcott & Mecham (1947).

## Results and discussion

*Reconstitution of flour*

Flour that had been fat extracted and reconstituted by the liquid nitrogen technique

was compared visually and physically with unextracted control flour and fat extracted flour. As graphically described by Cookson & Coppock (1956) fat extraction of a flour produces a whiter, fine or light material which has not the cakiness of the control flour but is easily dispersed in air when disturbed. It would seem that as well as bearing the fat soluble pigments the free lipid tends to hold the flour particles together. Furthermore, when a suspension of 20% fat extracted flour in water was beaten, a frothiness was obtained which was not found in the original flour. The reconstituted flour retained none of these differences and was indistinguishable from the original flour. Reconstitution by the liquid nitrogen technique had successfully restored the original appearance and handling properties to the fat extracted flour.

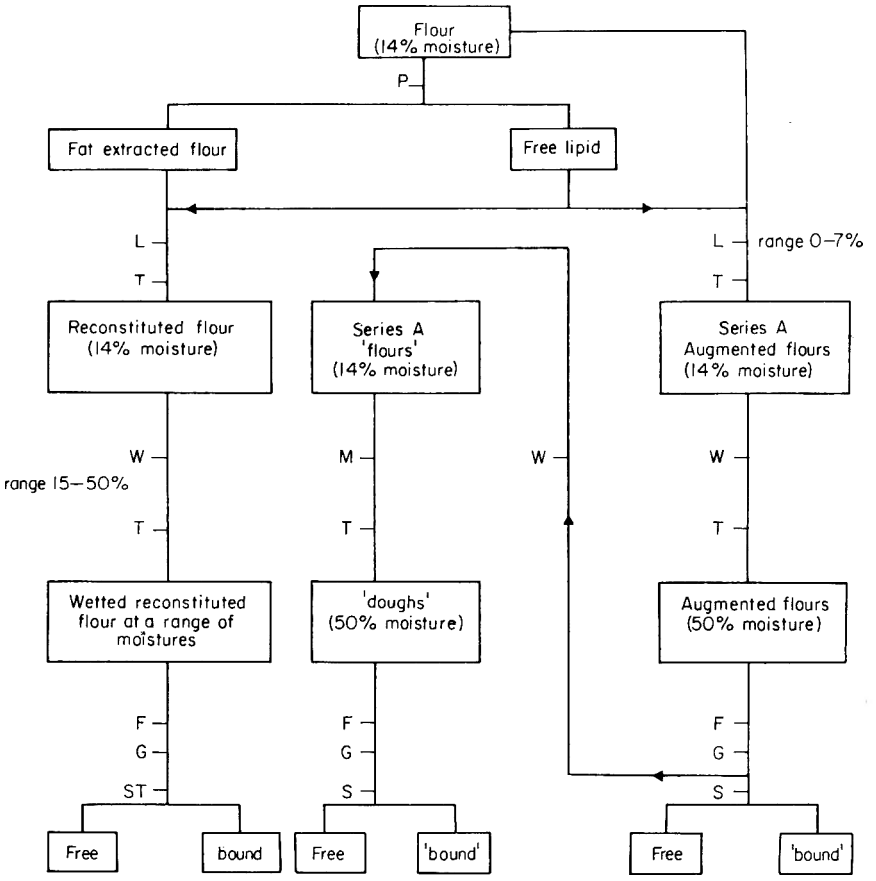
In order to assess the effect of reconstitution on lipid distribution, free and bound lipids were determined and the results compared with those obtained from the original flour (Davies *et al.*, 1969) and from the original flour after fat extraction. The results are presented in Table 1. Reconstitution by the liquid nitrogen technique restored the

TABLE 1. Lipid distribution of original fat extracted and reconstituted flours at 14% moisture: expressed as % of flour dry weight in each case (% of total lipid of original flour in parentheses).

| Flours | Free | Bound | Total | |
|---|---|---|---|---|
| Original | 1·130 (68·5) | 0·520 (31·5) | 1·650 (100·0) | 1·10 (66·7) removed by fat extraction |
| Fat extracted | 0·064 (3·9) | 0·422 (25·6) | 0·486 (29·5) | 1·095 (66·25) flour lipid returned |
| Reconstituted | 1·107 (67·0) | 0·424 (25·7) | 1·531 (92·8) | |

free lipid close to the original level without increasing lipid binding. The bound lipid found in the reconstituted flour was 0·424% compared with 0·422% in the extracted flour. It should be noted that percolation with light petroleum reduced the recoverable bound lipid from 0·520% to 0·422%; this loss will be discussed elsewhere. The new technique permits the restoration of free lipid without further effect on lipid binding.

Judged by the criteria of reproducing the appearance, handling and lipid distribution of the original flour it was thought that the liquid nitrogen technique was a satisfactory method of producing a reconstituted flour. A particular advantage of the method was that a flour was produced and not a dough. Furthermore factors such as heat, water, solvent and mechanical work, which influence lipid binding, were avoided during the production of the flour.




KEY

F Freeze-drying
G Grinding to a fine powder
L Addition of lipid using the liquid nitrogen technique
M Addition of water using the technique described by Olcott and Mecham (1947)
P Petrol extraction by percolation
S Petrol extraction in a Soxhlet for 7 hr
ST Petrol extraction in a Soxhlet for 7 hr followed by extraction with Tsen solvent
T Thawing
W Addition of water using the liquid nitrogen technique

*Effect of water on reconstituted flour*

When the moisture level of the original flour was increased, a distinct pattern of lipid binding occurred (Davies *et al.*, 1969). As a further test of reconstitution, the effect of moisture level on the lipid distribution of the reconstituted flour was investigated to see the effects of reconstitution on lipid binding properties. As with the original flour the moisture level was adjusted using the liquid nitrogen technique (Davies *et al.*, 1969). The distribution of free, bound and unextractable lipid was determined over the same moisture level range (14–50%) as the original flour. The effect of moisture level on the free lipid of the original and reconstituted flours is shown in Fig. 1. A similar loss of free lipid was found for both flours.

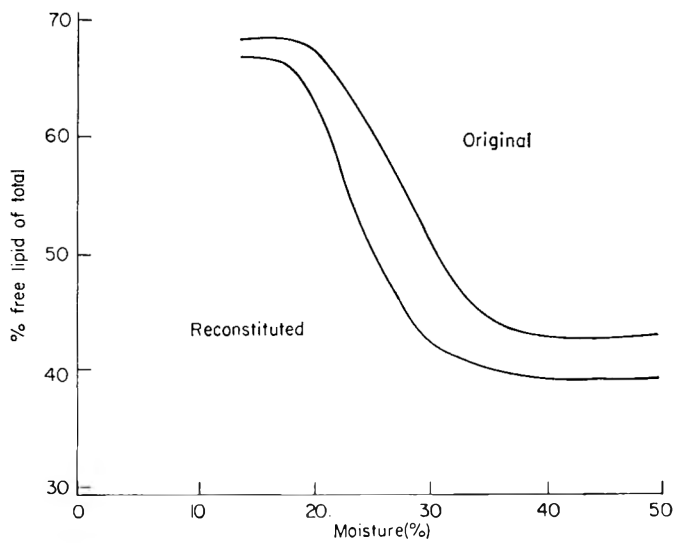



FIG. 1. Effect of moisture level on free lipid. Comparison of reconstituted with original flour. Total lipid 1·65% of flour dry weight in each case.

As shown in Fig. 2, although a small loss of extractable lipid followed reconstitution, increasing the moisture content led to a comparable increase of bound and unextractable lipid in both flours. Furthermore the same changes of physical form across the range of moistures were noted, e.g. when the flour had a moisture level greater than 28% a continuous structure was apparent and shrinkage occurred with time. It was concluded that reconstitution appeared to have little significant effect on the lipid binding properties of the flour.

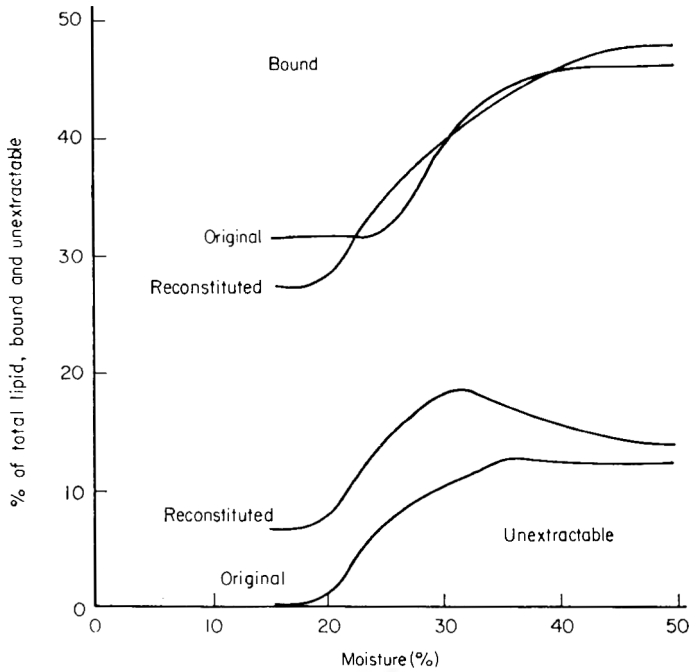



FIG. 2. Effect of moisture level on bound and unextractable lipid. Comparison of reconstituted with original flour. Total lipid 1·65% of flour dry weight in each case.

*Flours with augmented lipid levels*

The liquid nitrogen method of lipid addition proved to be an excellent means of producing flours with augmented lipid levels. The required lipid levels were predetermined and the only observable change in the flour was a stronger colour and an increase in 'cakiness'. The work of Olcott & Mecham (1947) suggested that if such flours were wetted to 50% moisture much of this excess free lipid would become bound. However, we have found (Davies *et al.*, 1969) that when a control flour was wetted without the introduction of mechanical work, only a proportion of the available free lipid became bound. It was possible therefore that either our results represented an equilibrium at 50% moisture which would be altered by the presence of excess lipid or that the method of water and excess lipid addition used by Olcott & Mecham (1947) introduced mechanical work or some other lipid binding factor. The flours with augmented lipid levels were wetted to 50% moisture by the liquid nitrogen technique to see whether any additional binding occurred above that found for the control flour. Fig. 3 shows that in the absence of work, only an insignificant amount of additional lipid binding occurred when the moisture was raised by the liquid nitrogen technique.

To investigate the possibility that the lipid binding reported by Olcott & Mecham

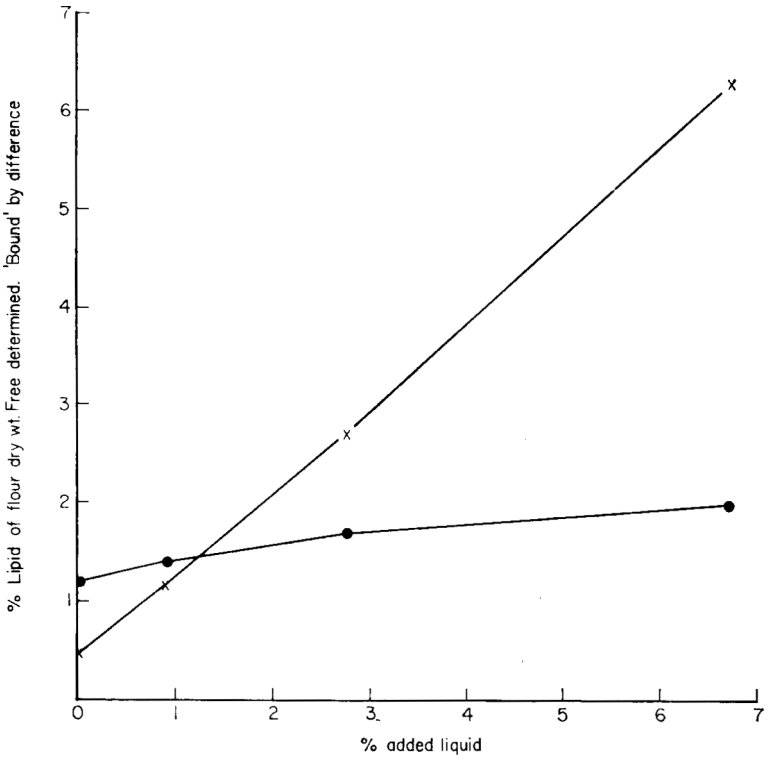



FIG. 3. Effect of wetting to 50% moisture by the liquid nitrogen technique of flours with augmented lipid levels: series A, × ; free lipid, ●; Lipid remaining after petrol extraction: (bound + unextractable).

(1947) was caused by their method, their wetting technique was imitated. The flours (series AW) were added to the amount of water required to raise the moisture to 50% in an Atomix mixer. The speed of the mixer was kept to a minimum using a Variac transformer and mixing stopped when the addition and blending was completed. The distribution of lipids in these 'doughs' was then determined. The results (Fig. 4) matched those of Olcott & Mecham (1947) very closely and indicated that the binding of much of the available free lipid was probably produced by the minimum mechanical work introduced by the mixer. Apart from confirming the value of the liquid nitrogen technique for avoiding the introduction of work, this experiment confirmed that the flour had a limited capacity for binding in the presence of excess free lipid under these experimental conditions. A comparison of the colour of the extracted free lipid of the two series showed that bleaching had occurred during the mixing of the AW series, probably by atmospheric oxygen in the open mixer (Hawthorn & Todd, 1955).

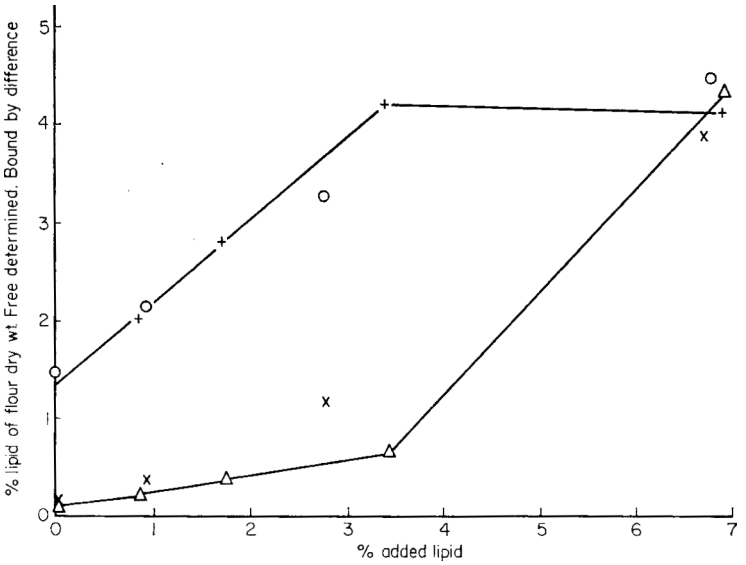



FIG. 4. Effect of wetting to 50% moisture in a mixer on flours with augmented lipid levels. Series AW, × ; free lipid, O; bound lipid (by difference). Results reported by Olcott & Meecham (1947) with a similar flour, △; free lipid, + ; bound lipid.

This method fulfills the requirements for producing a reconstituted flour suitable for lipid binding studies. A satisfactory flour was produced without the introduction of mechanical work which matched the appearance and lipid binding properties of the original flour. It is proposed to use this technique to prepare synthetic flours containing specific free lipids for further studies of lipid binding.

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# The equilibrium water vapour pressure of frozen cod

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## Summary

The equilibrium water vapour pressure of frozen cod has been measured and found to be equal to that of ice at the same temperature. The concentration of solutes in unfrozen cod, calculated from a plot of the fraction of unfrozen water remaining and the relative lowering of the vapour pressure of supercooled water to that of ice at the same temperature, is equivalent to a 1·34% solution of sodium chloride. This value is in good agreement with values obtained by other workers.

## Introduction

It is generally accepted that when fish and meat are frozen pure ice separates from the tissue fluids and that the equilibrium water vapour pressure is equal to that of pure ice at the same temperature. Recent work on frozen meat (Dyer, Carpenter & Sunderland, 1966; Hill & Sunderland, 1967) has thrown doubt on this assumption, although the validity of the observations of these workers has been questioned (Bralsford, 1968).

Current studies on the dehydration of frozen cod during cold storage (Storey, unpublished) have shown that there are two phases of drying, an initial constant rate period and a falling rate period, analogous to the drying of fish above its freezing point (Jason, 1958). During the initial constant rate period of dehydration the rate of sublimation of ice is dependent on the physical condition of the air in contact with the frozen fish, i.e. the rate of sublimation per unit area is a function of the velocity and the difference in water vapour pressure between that at the subliming surface and that in the air (Powell, 1939; Zaitsev, 1965; Rutov & Alekseyev, 1956; Khachaturov, 1956), whereas the rate of sublimation during the falling rate period is diffusion controlled and largely temperature dependent.

It is believed that dehydration of fish in commercial cold stores takes place under constant rate conditions where, for a given air velocity, the rate will be dependent on the difference in equilibrium water vapour pressure of the frozen fish and the partial pressure of the water vapour in the air. Thus the equilibrium water vapour pressure of frozen fish is an important parameter in the determination of the rate of sublimation

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of ice during cold storage and the onset of the opaque surface dehydration known as freezer burn.

## Experimental

The equilibrium water vapour pressure of cod (*Gadus morhua*) was determined by the direct method of Dyer *et al.* (1966), with slight modifications.

Pieces of fish and blocks of ice approximately 2 × 1 × 0·5 cm were frozen on to a 30 s.w.g. copper constantan thermocouple. The output from the thermocouple was measured by a Comark Type 169C Direct Reading Electronic Thermometer, the calibration of which was checked against a certified mercury-in-glass thermometer. A discrimination of ± 0·1°C is possible with this instrument. The thermocouple was threaded through a standard ground glass joint air leak tube and sealed in with epoxy resin. The frozen sample was inserted via a two-way adaptor into a 1 litre round-bottom flask, the second outlet of the adaptor being connected to a vacuum pump and a Wallace and Tiernan type FA 160 vacuum gauge. The latter is calibrated from 0·1 to 20·0 mmHg and it is possible to interpolate to ± 0·02 mmHg. All ground-glass joints were lubricated with high vacuum silicone grease.

The flask containing the sample was placed in a 40 × 40 × 25 cm refrigerated insulated tank containing 50% ethylene glycol and cooled by means of a condensing unit. The refrigerator was run continuously, the temperature of the tank being controlled to ± 0·1°C by means of a heater and adjustable thermostat. The flask was initially evacuated for about an hour to remove moisture and air from the system before being placed in the bath. Evacuation was continued until the sample temperature was slightly below that of the bath, the vacuum line was closed and the system allowed to come to equilibrium. When the sample temperature was within ± 0·1°C of that of the bath the pressure was noted. Observations were repeated at each bath temperature several times after first evacuating the flask for a few minutes to cool the sample slightly. Experiments on each sample were repeated over several days, after which time surface dehydration was obvious, although there was no change in the measured equilibrium vapour pressure.

No facility for checking the calibration of the pressure gauge was available and published values (Hodgman, 1951) for the equilibrium vapour pressure of ice were therefore used as a reference.

## Results

The combined results for all experiments are plotted in Fig. 1. The experimental values for ice agreed well with accepted values within the precision of the gauge (± 0·02 mmHg), as did the values for fish. Since no significant differences could be found between ice and fish, the equilibrium pressure of beef (purchased as 'best steak') was measured and these values were also close to those for ice. It was concluded that,

over the range of temperatures employed, there was no significant difference in the equilibrium water vapour pressure of ice, cod or the beef sample.

It was also found that when geometrically identical samples of ice and frozen cod are stored simultaneously by suspending them in a cold chamber from an analytical balance, the loss in weight of the ice and the fish is the same. Since, in this case, all the potential variables which determine the rate of sublimation are the same for both fish and ice, the equilibrium water vapour pressure of cod must be equal to that of ice.

## Discussion

It is well known that when meat and fish are frozen the proportion of muscle fluid removed as ice depends on the initial concentration of solutes and the temperature. For cod the initial concentration of solutes has been found to be equivalent to a 1·4% solution of sodium chloride (Dyer *et al.*, 1957). Jason & Long (1955) assumed a somewhat different value of 0·28 molar (1·64%) from data on the freezing point of cod. More recently Kelly & Dunnett (1969) have measured the osmolality of tissue fluid pressed from cod and their results support that of Dyer.

Riedel (1956) obtained precise values for the fraction of water frozen in cod, by an adiabatic calorimetric method, which are in general agreement with those values reviewed by Dyer *et al.* (1957). Riedel (1961) later found that there was no increase in the amount of water frozen out below about −65°C, some 8% of the total water remaining unfrozen. This has been confirmed by nuclear magnetic resonance studies on frozen cod (Sussman & Chin, 1966). More recently Hazlewood, Nichols & Chamberlain (1969) found that the liquid water signal of rat muscle at above zero temperatures was equivalent to only 72% of the signal for pure water, whereas the rat muscle contained 80% water, indicating that 10% of the total water does not behave as ordinary water. The latter authors' work is generally confirmed by Cope (1959).

The concentration of the solutes in the liquid phase of frozen fish will increase as the temperature is lowered, due to the removal of liquid water as ice. Therefore the vapour pressure of the liquid phase will become progressively lower than that of supercooled pure liquid water at the same temperature due to the presence of increasing concentrations of solute as the temperature is decreased.

The simplest assumption to make is that the relative lowering of the vapour pressure of the liquid phase is directly proportional to the molar concentration of solutes i.e.

$$\frac{p_0 - p}{p_0} = \frac{n_1}{n_1 + n_2} \qquad (1)$$

where $p_0$ = vapour pressure of supercooled water at temperature $T$,

$p$ = vapour pressure of the liquid phase of frozen fish at same temperature, $T$,

= vapour pressure of pure ice at the same temperature, $T$,

$n_1$ = number of moles of solute,

$n_2$ = number of moles of solvent.

Let $n_1 = w/m$, where $w$ is the weight of solute in 100 g of freezable water in the unfrozen fish, and $m$ the molecular weight of solute; let $n_2 = W/M$, where $W$ is the percentage of freezable water remaining at temperature $T$, and $M$ the molecular weight of water.

$$\text{Therefore} \quad \frac{p_0 - p}{p_0} = \frac{w/m}{(w/m) + (W/M)} \tag{2}$$

By inversion, equation (2) becomes

$$\frac{p_0}{p_0 - p} = 1 + \frac{W}{M(w/m)} \tag{3}$$

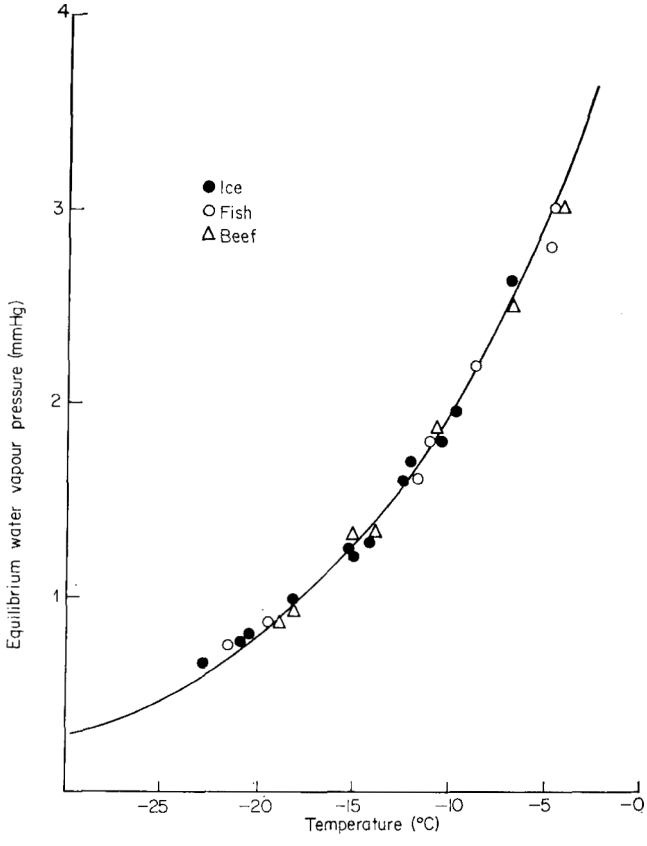


FIG. 1. Equilibrium vapour pressure of ice, cod and beef.

Thus, when only pure ice separates during freezing, the mass of unfrozen water remaining should be directly proportional to the reciprocal of the relative lowering of vapour pressure. In order to test this hypothesis values for $W$ and $p_0/(p_0 - p)$ are required. The latter values are readily obtained, $p$ from Fig. 1 and $p_0$ from published values (Hodgman, 1951). $W$ has been calculated from Riedel's experimental data, assuming that only 92% of the total water present can be frozen. Fig. 2 shows that the relationship in equation (3) is applicable, so that even though the liquid phase in frozen fish is ionic and not dilute, the relative lowering of its vapour pressure is directly proportional to the concentration of the solutes. This behaviour is very much simpler than that shown by dilute ionic solutions (Robinson & Stokes, 1968).

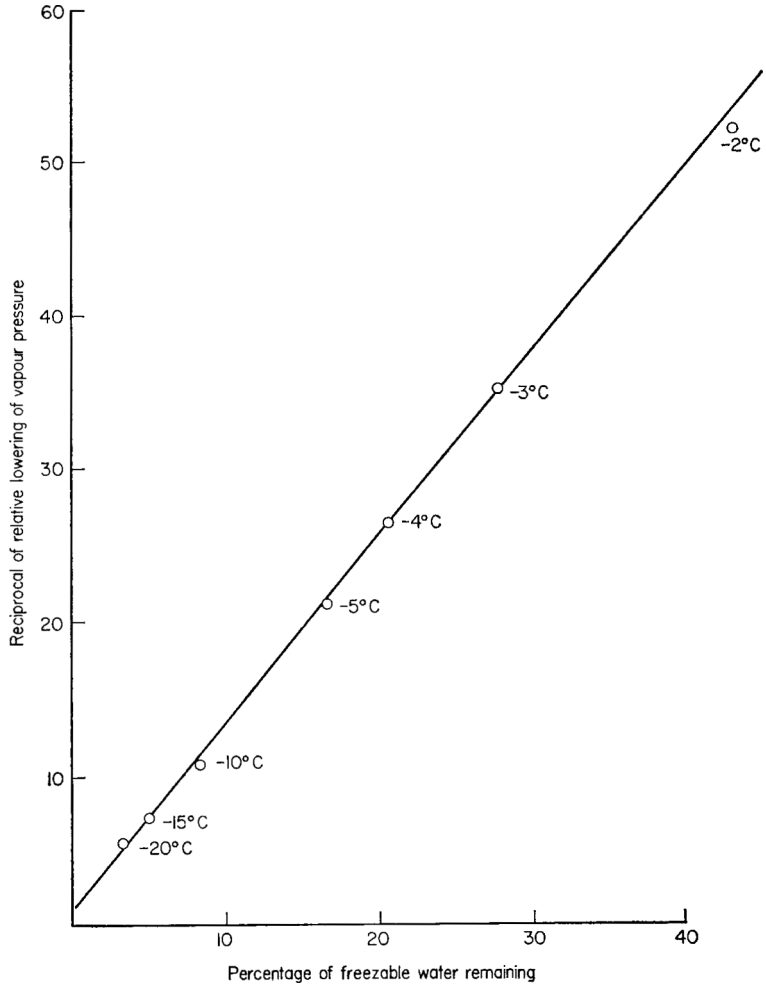


FIG. 2. Relative lowering of vapour pressure.

The initial concentration of solutes in unfrozen cod, $w$, may be calculated from the slope of Fig. 2. From equation (3) the slope is equal to $1/M(w/m)$. Since the mixture of solutes is complex the concentration is calculated as an equivalent concentration of sodium chloride, assuming ideal behaviour. The value of $w$ from the slope of Fig. 2, for $M = 18$ and $m = 58{\cdot}5/2$ (2 ions), is 1·34 g. Thus the initial solute concentration in the cod sample from which Riedel obtained his data was equivalent to 1·34% sodium chloride. This value is close to that obtained by Dyer *et al.* (1957). Assuming ideality Kelly & Dunnett's measured osmolalities are equivalent to a range of 1·27–1·43% sodium chloride.

The experimental results (Fig. 1) support the view that the activity of the water in the liquid phase is equal to the activity of the water in the ice phase at a given temperature. That this should be so was pointed out by Riedel (1961) who stated that at a given temperature ice will continue to form as the stable phase until the equilibrium vapour pressure is equal to that of the ice.

No explanation can be offered as to why Dyer *et al.* (1966) and Hill & Sunderland (1967) found up to 20% lower pressure for meat. Dyer *et al.* suggested that in frozen meat a solid solution exists with a lower vapour pressure than that of pure ice. However, Aitken (1966) found that the X-ray diffraction pattern of frozen cod showed the presence of only the common hexagonal form of ice. If a solid solution of sufficient concentration to reduce significantly the equilibrium vapour pressure of pure ice had been present, it is suggested that this would have been demonstrated in the X-ray diffraction pattern.

## Acknowledgment

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# Estimation of volatile onion aroma and flavour compounds

M. SAGUY, C. H. MANNHEIM AND Y. PELEG


## Summary

The Chemical Oxygen Demand (COD) method was used for the evaluation of onion aroma components. The method was found to be reliable and to correlate well with odour threshold values for raw onions and with taste scores for dehydrated onion products. Odour threshold values could not be used for the latter products due to the development of undesirable off-odour after exposure to high temperature or prolonged storage.


## Introduction

The development of the characteristic flavour and aroma in Allium edible species, such as onion, garlic and leek, is related to an enzymatic cleavage of Alliin and its derivatives, thus forming thiosulphinates, pyruvic acid and ammonia, as described below:

$$\underset{\text{(Alliin or derivatives)}}{2R - \overset{\overset{O}{|}}{S}CH_2CH(NH_2)COOH} \xrightarrow{\text{Alliinase}} \underset{\text{(Alliicin or derivatives)}}{R - \overset{\overset{O}{|}}{S}-S - R} + \underset{\text{(Pyruvic acid)}}{2CH_3COCOOH} + NH_3$$

where $R$ is an alkyl radical.

$$2R' - \overset{\overset{O}{|}}{S}CH_2CH(NH_2)COOH \longrightarrow \text{Lachrymatory Factor} + 2CH_3COCOOH + 2NH_3$$

where $R'$ is propenyl.

A survey of methods used for evaluation of aroma and flavour of onions reveals three categories—namely, overall indices, gas chromatographic evaluations and determination of enzymatic products.

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Among the overall indices Platenius (1935) estimated total sulphur in a distillate of onions after an acidified hydrolysis. Platenius & Knott (1941) also found a correlation between total solids of onions and pungency. Kohman (1952) showed the difficulties in the definition of pungency and he, as well as Foley (1955), suggested taking the total sulphur found in an onion distillate as a criterion for pungency. Farber (1957) suggested using total volatile reducing substances as an index of onion pungency. All these methods are laborious and some need expensive and complicated systems.

Gas chromatographic evaluations are characterized by the common approach to determine products of the enzymatic reaction rather than the thiosulphinates, or sulphenic acids. Saghir *et al.* (1964) estimated and identified onion sulphides taken from the headspace, while Bernhard (1968) estimated disulphides in fresh onions and dried onion products.

Schwimmer & Weston (1961) developed a method estimating the increase of pyruvic acid in onion tissues due to mechanical maceration. Schwimmer & Guadagni (1962) correlated the quantity of pyruvic acid developed enzymatically with olfactory threshold determinations and found a good correlation ($r = -0{\cdot}97$) between those parameters.

However, Saghir *et al.* (1964) could not find a correlation between the aliphatic mono and disulphides and pyruvate content. Schwimmer, Weston & Guadagni (1964) claimed that the pyruvic acid test could also be used for evaluation of pungency in dried onion powders as well as for raw onions.

Bernhard (1968) found that loss of measured volatiles in dried onion products averaged 98%, while loss of disulphides was greater than 89%. However, Peleg (1967) found that the pyruvic acid test—Method A, used by Schwimmer *et al.* (1961, 1962, 1964), did not correlate with the odour threshold values of dehydrated kibbled onions. This was explained by the formation of carbonyls, other than pyruvic acid, during storage which affect the results of the test.

Watanabe & Komoda (1966) modified the Schwimmer & Mazelis method (1963) for estimation of thiosulphinates. We found this method to be extremely sensitive to time, temperature and other conditions and therefore difficult to obtain reproducible results. Therefore, to date there is no reliable chemical method for flavour estimation in onion products. The object of this work was to develop a method for estimating volatile reducing water soluble substances from fresh and dehydrated onion products and correlate the results with sensory evaluations.

## Materials and methods

*Fresh onions:* The examinations were done on three varieties of fresh onions namely:

(1) Egyptian (yellow skinned) variety.
(2) Sweet Spanish Yellow Riverside variety.
(3) Early Sweet Spanish variety.

*Dehydrated onions.* The examinations were carried out on products made from the Egyptian variety, dried in a pilot plant through flow dehydrator. The dehydrated particles were of two sizes according to the American Onion and Garlic Dehydrators' Association, namely:

(1) Large sliced onions (through 58 in. on 8 mesh screen)

(2) Large chopped onions (through 13 in. on 12 mesh screen)

The onion products were packed (at about 4% moisture content) in A2 (307 × 408) plain tin cans. Each can contained 150 g dehydrated onions. The cans were divided, randomly, into two lots, and stored under controlled temperature conditions of 25 ± 1°C and 35 ± 1°C.

*Methods of analysis*

The quality of dehydrated onions was determined six times during 36 weeks storage. Each time, two cans of each treatment and storage temperature were taken out randomly from storage and their contents were mixed. All the tests were performed in duplicate on a powder obtained after milling and screening through a 20 mesh screen after determining the moisture content on a 10 g sample which was dried for 16 hr at 70°C (± 1°C) in a vacuum oven operating at 1 in. Hg absolute pressure.

A method for evaluating aroma compounds known as the COD method (Chemical Oxygen Demand) was suggested by McNary, Dougherty & Wolford (1957) and modified by Dougherty (1968). This procedure, consisting of oxidizing a distillate of the product with potassium bichromate and determining the volatile aroma compounds colorimetrically, was modified as described below.

To a sample of 10·0 g (moisture free basis) of onion product 100 ml of distilled water were added into a 500 ml distillation flask. The slurry was left for 15 min with occasional stirring at room temperature and then distilled slowly on an heating plate. The first 10 ml were collected. To the 10 ml distillate 5 ml of 0·25 N potassium bichromate were added in a 100 ml flask and stirred carefully. During stirring 15 ml conc. phosphoric acid were slowly added. After reflux for 10 min the mixture was brought to room temperature in a water bath. The percent transmittance was determined at 650 mμ in a Bausch and Lomb Spectronic 20 spectrophotometer. As a blank distilled water was used after adding the oxygenating mixture and refluxing as noted before. A standard calibration curve (Fig. 1) was prepared by oxidizing 10 ml sucrose solutions of known concentrations.

*Sensory evaluations*

The dehydrated onions were tasted after 36 weeks of storage in form of a soup. The soup was prepared by boiling water with 0·75% salt, 1·75% cornstarch and 0·75% wheat semolina. After cooling mixture to 50°C, 0·5% of dehydrated or fresh onion were added and the mixture was kept at 50°C for tasting. A panel of twelve to fifteen

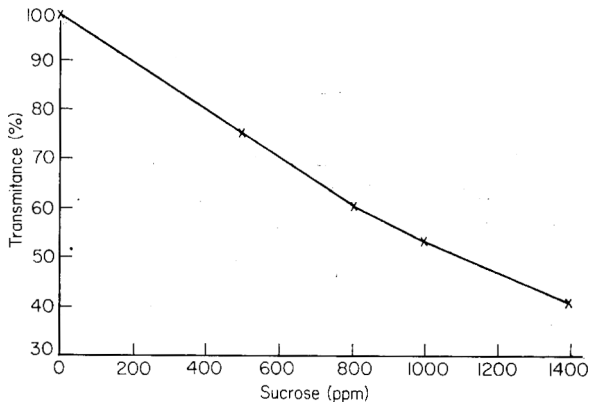


FIG. 1. Standard calibration curve for COD determination.

judges was asked to taste the onion soup and to rank it from 1 (worst) to 10 (best), 5—being still acceptable. The value is given as rank score.

For threshold concentration a suspension of macerated fresh onions in water, or of rehydrated onions in water, was filtered and diluted to the desired dilutions. The procedure for odour threshold determinations consisted of smelling four to six pairs of solutions, in which one sample in each pair is odour free water, and determining which sample in each pair contains aroma. The order of presentation and position of blanks was randomized. Twelve to fifteen judges evaluated each series of concentrations in at least two separate sessions. The average threshold was determined from the results of all judges and replications. All comparisons were conducted in individual booths in a well ventilated room. The threshold concentration was defined as the dilution corresponding to 70% correct judgments.

## Results and discussion

Fresh onions from three different locally grown varieties were examined after storage at room temperature. Several onions were taken at random and were tested after peeling and blending. The results are shown in Fig. 2. The correlation factor between odour threshold and COD was found to be $r = -0{\cdot}98$ which indicates a good correlation, independent of variety.

In order to determine if COD analyses can also be used for the evaluation of dehydrated onion products they were compared with sensory evaluations of such products. Results of analysis of different dehydrated onion samples during storage are given in Table 1. A good correlation was found between the rank score and the oxygen demand—namely $r = -0{\cdot}90$. However, no correlation was found between odour threshold values and rank score, nor between threshold values and COD. This indicates that the odour perceived from dehydrated onion juice was different from the odour

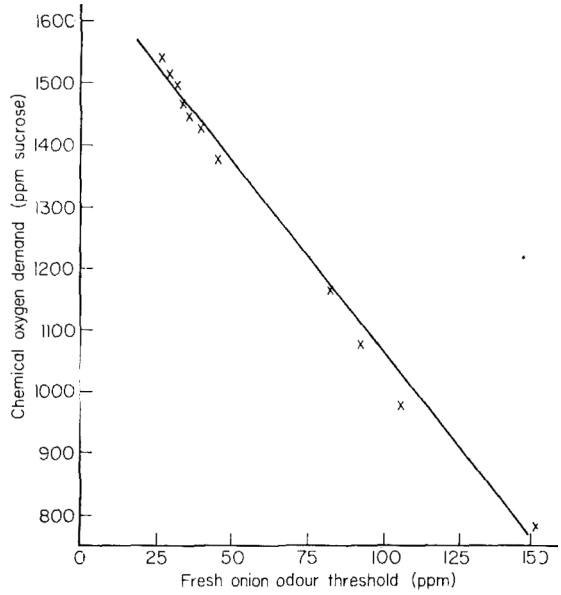


FIG. 2. Odour threshold value of fresh onion *vs.* COD.

TABLE 1. Oxygen demand, rank score and threshold values of dehydrated onions

| Sample No. | Organoleptic rank score | Oxygen demand (as ppm sucrose) | Threshold value (ppm) [8] |
|---|---|---|---|
| 1 | 9·80 | 1480 | 200 |
| 2 | 6·52 | 480 | 145 |
| 3 | 7·23 | 540 | 160 |
| 4 | 6·26 | 440 | 100 |
| 5 | 7·09 | 520 | 165 |
| 6 | 8·47 | 760 | 145 |
| 7 | 7·69 | 820 | 105 |
| 8 | 8·73 | 1060 | 158 |
| 9 | 8·02 | 940 | 185 |
| 10 | 4·92 | 440 | 115 |
| 11 | 6·53 | 530 | 168 |
| 12 | 5·71 | 400 | 92 |

of fresh onion juice. This could be due to the appearance of an off-odour produced during storage and thus changing the composition of volatiles.

The changes in the threshold values due to storage at 25°C and 35°C in the dehydrated products are given in Fig. 3. Results show a decrease of threshold values

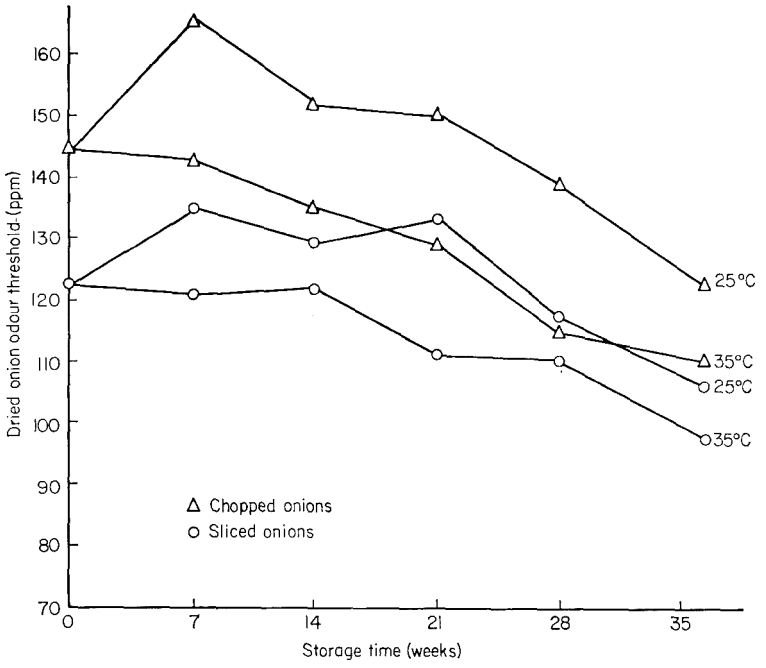


FIG. 3. Changes in odour threshold values of dehydrated onion products as affected by production and storage conditions.

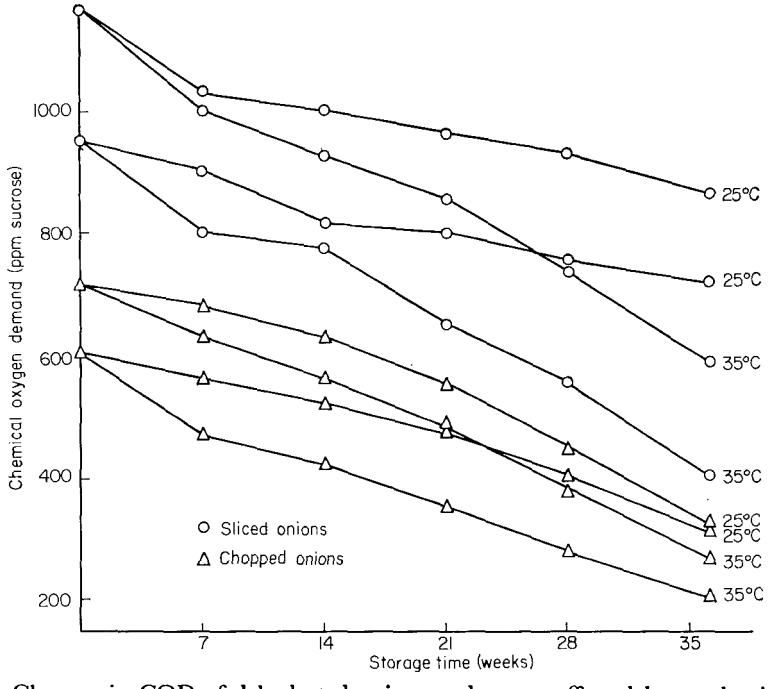


FIG. 4. Changes in COD of dehydrated onion products as affected by production and storage conditions.

(indicating intensification of odour) during storage in all samples. Furthermore, it was noted that at the higher storage temperature (35°C) the threshold values decreased more than at 25°C. This also bears out the assumption that an off-odour is produced during storage.

The changes in COD values during storage at 25°C and 35°C in dehydrated onion products were given in Fig. 4. Results show that COD values decreased with storage time as well as with storage temperature. This indicates a loss in volatile reducing substances which were attributed to the typical onion aroma.

In conclusion the above results indicate that the COD method for estimating volatile onion aroma does correlate well with sensory tests and thus can be used to evaluate onions and their products. Use of threshold values cannot be recommended since development of strong undesirable off-odours during storage tend to obstruct the results.

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# Chlorophyll, colour and pH changes in H.T.S.T. processed green pea puree

K. A. BUCKLE AND R. A. EDWARDS


## Summary

Pea puree of pH 6·95 and pH 8·45 was heat processed in thermal death-time tubes at temperatures between 115·6°C and 148·9°C to a process value of $F_0 = 6·0$. Chlorophyll pigments, Hunterlab colour indices and pH were determined before and after high temperature–short time (H.T.S.T.) processing and during storage for 18 months at 20°C, 2·8°C, and −23·3°C.

Highly significant correlations were found between per cent conversion of chlorophylls to pheophytins and objective colour indices derived from tristimulus measurements on stored pea puree. The degree of chlorophyll conversion, and hence puree colour, were both markedly affected by process temperature, product pH, storage time and storage temperature, but long-term storage stability was achieved only by combinations of two or more variables.

Changes in pH of processed and stored puree were directly related to changes in pigments and colour, and it appears that pH control during processing and storage offers the most likely means of colour and pigment retention in heat processed chlorophyll-containing foods.


## Introduction

Heat processing techniques have played a major role in the preservation of foods, one of its disadvantages being the modification of pigments which results in changes in the original colour of the food material. The effect of conventional heat processing methods on chlorophyll degradation in green vegetables has been reported by a number of workers (Siegele, 1955; Westcott *et al.*, 1955; Heintze, 1957; Gold & Weckel, 1959; Bowman & Remmenga, 1965; Kapsalis *et al.*, 1965). In most cases, a substantial conversion of chlorophylls to pheophytins and the appearance of unattractive colours was found.

In recent years advantage has been taken of the logarithmic order of thermal death of bacteria, as opposed to the first order kinetics of many chemical and biochemical

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reactions during heat processing, to develop high temperature–short time (H.T.S.T.) processes which have been claimed to produce food products of the same bacterial status but of a higher quality than those produced by conventional heat processing. H.T.S.T. processing methods have been shown to have a significant effect on chlorophyll and colour retention in heat processed foods (Livingston, 1957; Epstein, 1959; Brody, Bedrosian & Ball, 1960; Joffe *et al.*, 1961; Luh *et al.*, 1964).

The effects of process time and temperature on chlorophyll and colour retention in whole peas and pea puree were studied by Gold & Weckel (1959). They found a quantitative relationship ($r = 0{\cdot}922$) between the change in objectively measured colour of the peas, and the degree of chlorophyll degradation.

Several workers have reported the effects of H.T.S.T. processing on colour and pigment retention in spinach puree. Tan & Francis (1962) found that increasing the process temperature from 115·6°C to 137·8°C, while maintaining equivalent sterilizing values, resulted in greater retention of chlorophyll pigments and also green colour as measured by colorimeter. Later work from the same laboratory extended these investigations to include pH adjustment and H.T.S.T. processing at temperatures up to 148·9°C (Gupte & Francis, 1964; Resende, Francis & Stumbo, 1969) in conjunction with pre-process conversion of chlorophylls to chlorophyllides (Clydesdale & Francis, 1968). In all cases, H.T.S.T. processing resulted in better retention of chlorophyll pigments and colour than controls processed by conventional methods.

Many reports have attributed chlorophyll degradation during heat processing to reactions between pigments and acids liberated from ruptured cells, and accordingly, attempts have been made to inhibit such changes by neutralizing the acid (Blair & Ayres, 1943; Malecki, 1964). Gold & Weckel (1959) investigated the effect of pH adjustment on chlorophyll retention in processed pea puree and showed that raising the pH had a definite protective effect upon chlorophyll at low process temperatures, but the effect was negligible at high process temperatures.

Gupte & Francis (1964) showed that increasing the pH of spinach puree with magnesium carbonate, or processing by H.T.S.T. methods, gave greater pigment retention initially but resulted in considerable degradation during storage. A combination of the two methods gave more pigment retention than either method alone, but again gave a product which lacked storage stability at room temperature.

Clydesdale & Francis (1968) found no significant gain in stability when chlorophylls were converted to chlorophyllides prior to H.T.S.T. processing. Considerable retention of chlorophyll(ide) occurred when pH adjustment was used in combination with H.T.S.T. processing, but retained pigments again degraded rapidly during storage. The decrease in pH during H.T.S.T. processing was substantially less than in conventional retort processing. During storage at room temperature, H.T.S.T. samples decreased in pH at a faster rate than did samples processed by conventional methods, a result consistent with observations that H.T.S.T. processing produces an initial gain in pigment retention which is rapidly lost on storage.

The work described in this paper was part of an investigation into the effects of storage time and temperature, process temperature and product pH on the relationships between chlorophylls, colour and pH in heat processed pea puree.

## Experimental

*Materials*

Fresh green peas (*Pisum sativum*, var. Edgell Freezer) were hand shelled, blanched 1 min in boiling water, cooled, blended with distilled water, then comminuted under nitrogen to form a puree of pH 6·95 and moisture content 86·0–86·5% ( = normal pH puree). Pea puree of pH 8·45 was prepared by blending blanched peas and distilled water with magnesium carbonate powder followed by comminution.

De-aerated puree was filled into Pyrex thermal death-time tubes (25 cm × 0·7 cm i.d., walls 0·1 mm thick) which were sealed 3 cm above the level of puree, the temperature adjusted to 37°C, and processed in glycerol to a process value of $F_0 = 6{\cdot}0$ based on $Z = 18$ for *Clostridium botulinum* spores using extrapolated thermal death-time data (National Canners Association, 1954). The process times required were as follows:

| Temperature (°C) | Time (sec) |
|---|---|
| 115·6 | 1386 |
| 126·7 | 254 |
| 137·8 | 100 |
| 148·9 | 68 |

Heat penetration data were recorded with a direct reading potentiometer using 30 gauge copper-constantan thermocouples fixed into one end of the tubes with epoxy resin. The processed tubes were immediately cooled in ice water and stored at 20°, 2·8° and − 23·3°C for up to 18 months.

Anaesthetic grade (BP) diethyl ether was purified for spectrophotometry by repeated distillation, treatment with acidified ferrous sulphate solution and thorough drying (Vogel, 1961). Other solvents used were AR or spectroscopic grade. All chemicals were AR grade.

## Methods

*Pigments*

All pigment extractions were carried out in a darkened room, and pigment solutions in flasks were covered with black polythene.

The puree from ten randomly chosen thermal death-time tubes (75–80 g) was thoroughly mixed, and duplicate 20·0 g samples were blended with cold acetone and 80% acetone until all pigments were extracted. The filtered solution was adjusted to 80% acetone and made up to 250 ml ( = acetone solution 1). Pigment determinations by the method of Dietrich (1958) and Vernon (1960) were made on 80% acetone

solutions before and after conversion of chlorophylls to pheophytins by addition of saturated oxalic acid in 80% acetone.

Chlorophylls were also determined in diethyl ether by a modification of the method of White, Jones & Gibbs (1963). Acetone solution 1 (100 ml) was shaken with 50 ml purified diethyl ether, and 10% (w/v) sodium chloride (pH 5·5–6·0) slowly added to transfer the pigments into the ether layer. The aqueous acetone layer was run off and extracted with ether, and the combined ether extracts scrubbed free of acetone through five 250 ml portions of sodium chloride solution using apparatus similar to that described by Mackinney (1940). The ether solution was dried over granular anhydrous sodium sulphate and made to volume (100 ml) with dry diethyl ether (= ether solution 1). Aliquots of ether solution 1 were acidified with hydrochloric acid, or extracted several times with 0·01 N potassium hydroxide, and pigments analysed according to White *et al.* (1963).

Absorbances of pigment solutions were measured on a Unicam S.P. 600, or spectra recorded with a Unicam S.P. 800 spectrophotometer (Unicam Instruments Limited, Cambridge). Corrections were made for turbidity by subtracting absorbance values at 700 nm from values at wavelengths of maximum absorption.

*Subjective colour ranking*

Visual ranking of pea puree samples in order of 'desirable green pea colour' was performed by a panel of judges on coded samples under artificial illumination.

*Objective colour*

Objective colour measurements were made with a Hunterlab Colour and Colour Difference Meter Model D-25 (Hunter Associates Laboratory, McLean, Virginia, U.S.A.) standardized with a green ceramic tile with values $L = 59{\cdot}7$, $a = -16{\cdot}4$, $b = 7{\cdot}4$. Puree was contained in a cylindrical plastic cell (5·7 cm diameter, 1·2 cm deep) covered with a thin plate of optical glass, taking care to avoid inclusion of air bubbles.

*pH*

Ten g samples of puree were slurried with 20 ml distilled water and pH measured on a Pye Dynacap pH meter (W. G. Pye & Co. Ltd, Cambridge) standardized with buffers of pH 6·99 and 9·00 at 20°C.

*Statistical analyses*

Correlation coefficients relating pigment and colour determinations on stored puree were calculated by computer (IBM CDC 3600) at the CSIRO Division of Computing Research, Canberra. Relationships between visual ranking and pigment and colour determinations were calculated according to Brownlee (1949).

## Results

*Effects of process temperature and pH on pigments*

Chlorophylls *a* and *b*, pheophytins *a* and *b*, their phytol-free derivatives, total pigments and percent conversion of total and individual chlorophylls to pheophytins were determined. The presence of chlorophyllides or pheophorbides could not be established in any sample analysed. The effects of process temperature and pH on pigments are presented in Table 1.

TABLE 1. Chlorophyll pigments in normal and elevated pH pea puree after H.T.S.T. processing.

| Puree pH before processing | Process temperature (°C) | Total chlorophyll | | Chlorophyll a | | Chlorophyll b | |
|---|---|---|---|---|---|---|---|
| | | Pigment content (μg/g) | Conversion (%) | Pigment content (μg/g) | Conversion (%) | Pigment content (μg/g) | Conversion (%) |
| 6·95 | Unprocessed | 86·0 | 4·0 | 60·8 | 5·6 | 25·2 | 0·0 |
| 6·95 | 115·6 | 15·5 | 83·2 | 5·5 | 91·7 | 10·0 | 60·8 |
| 6·95 | 126·7 | 61·8 | 30·1 | 38·3 | 39·2 | 23·5 | 7·8 |
| 6·95 | 137·8 | 78·3 | 14·6 | 55·6 | 10·5 | 22·7 | 9·6 |
| 6·95 | 148·9 | 76·0 | 16·3 | 51·9 | 19·3 | 24·1 | 9·1 |
| 8·45 | Unprocessed | 77·2 | 4·0 | 54·6 | 5·5 | 22·6 | 0·0 |
| 8·45 | 115.6 | 51·4 | 34·9 | 35·0 | 39·5 | 16·4 | 25·5 |
| 8·45 | 126·7 | 67·3 | 15·8 | 48·0 | 17·5 | 19·3 | 11·1 |
| 8·45 | 137·8 | 76·4 | 8·1 | 53·6 | 10·1 | 22·8 | 3·0 |
| 8·45 | 148·9 | 73·0 | 10·7 | 51·8 | 11·9 | 21·2 | 7·4 |

*Effects of storage time and temperature on pigments*

Results as percent conversion of total chlorophyll in normal pH puree are presented in Table 2.

Analyses by spectrophotometry on samples of elevated pH puree stored 18 months at 20°C gave some unusual results. Values for total chlorophyll after 18 months storage were higher than values determined at 12 months. Similar results were found for chlorophylls *a* and *b*, while percent chlorophyll conversion decreased at 18 months compared to shorter storage periods.

Subsequent thin-layer chromatography of extracts from elevated pH puree stored 18 months at 20°C showed the presence of three chlorophyll degradation products with visible and infrared spectra and chemical properties different from chlorophyll-derived pigments normally found in heat processed vegetables (Buckle & Edwards, 1969). The absorbance values used for pigment determinations were found to be in error due to the presence of the degradation products.

TABLE 2. Conversion of chlorophylls to pheophytins in H.T.S.T. processed, normal pH pea puree stored for 18 months

| Storage temperature (°C) | Storage time (months) | % Chlorophyll conversion | | | |
|---|---|---|---|---|---|
| | | Process temperature (°C) | | | |
| | | 115·6 | 126·7 | 137·8 | 148·9 |
| Unprocessed | | 4·0 | 4·0 | 4·0 | 4·0 |
| Processed | | 83·2 | 30·1 | 14·6 | 16·3 |
| 20 | 2 | 98·6 | 91·3 | 89·2 | 86·9 |
| 20 | 3 | 100·0 | 94·1 | 95·3 | 90·1 |
| 20 | 6 | 100·0 | 100·0 | 98·2 | 90·8 |
| 20 | 12 | 100·0 | 100·0 | 95·1 | 100·0 |
| 20 | 18 | 100·0 | 100·0 | 100·0 | 100·0 |
| 2·8 | 3 | 90·1 | 73·3 | 54·6 | 57·2 |
| 2·8 | 6 | 96·2 | 85·6 | 71·8 | 70·2 |
| 2·8 | 12 | 100·0 | 90·3 | 84·9 | 87·1 |
| 2·8 | 18 | 100·0 | 98·1 | 91·8 | 93·4 |
| − 23·3 | 6 | 88·7 | 28·7 | 18·3 | 17·2 |
| − 23·3 | 12 | 86·6 | 31·4 | 15·9 | 15·2 |
| − 23·3 | 18 | 85·3 | 32·8 | 16·8 | 17·8 |

TABLE 3. Visual rank order, Hunterlab values and total chlorophyll content of processed pea puree

| Mean rank order* | Puree sample | | Hunterlab values | | | Hunterlab indices | | | Total chlorophyll content (μg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | pH | °C | *L* | a | b | $-a/b$ | $-a/L$ | $(a^2+b^2)^{\frac{1}{2}}$ | |
| 1 | 6·95, | unpro. | 45·1 | − 20·0 | 25·5 | 0·784 | 0·443 | 32·40 | 86·0 |
| 2 | 6·95, | 137·8 | 40·8 | − 16·5 | 23·0 | 0·717 | 0·404 | 28·30 | 78·3 |
| 3 | 6·95, | 148·9 | 41·7 | − 16·6 | 23·3 | 0·712 | 0·398 | 28·61 | 76·0 |
| 4 | 8·45, | unpro. | 52·8 | − 19·4 | 26·2 | 0·740 | 0·366 | 32·61 | 77·2 |
| 5 | 8·45, | 148·9 | 51·9 | − 18·5 | 25·7 | 0·720 | 0·356 | 31·65 | 73·0 |
| 6 | 8·45, | 137·8 | 52·1 | − 18·6 | 25·9 | 0·718 | 0·357 | 31·89 | 76·4 |
| 7 | 8·45, | 126·7 | 50·8 | − 17·3 | 24·9 | 0·695 | 0·341 | 30·32 | 67·3 |
| 8 | 6·95, | 126·7 | 39·5 | − 13·5 | 21·9 | ·616 | 0·342 | 25·73 | 61·8 |
| 9 | 8·45, | 115·6 | 46·6 | − 11·7 | 22·3 | 0·525 | 0·251 | 25·18 | 51·4 |
| 10 | 6·95, | 115·6 | 41·0 | − 5·7 | 22·5 | 0·253 | 0·139 | 23·21 | 15·5 |

*Number 1 indicates most desirable pea greenness,
Number 10 indicates least desirable pea greenness.
Numbers are mean values of rank scores by all panel members to nearest whole numbers. unpro.: unprocessed.

Similar compounds were not present, or found only in trace amounts, in all normal pH samples, and in elevated pH samples stored at lower temperatures.

*Colour ranking of unprocessed and processed pea puree before storage*

Visual ranks in terms of 'desirable green pea colour', and objective colour determinations using the Hunterlab colour difference meter on samples of unprocessed and processed pea puree are presented in Table 3. The total chlorophyll content of the samples is included for comparison.

For the samples analysed in Table 3, correlation coefficients were calculated relating visual rank, total chlorophyll content and Hunterlab colour indices (Table 4). Relationships were also determined separately for each pH group.

TABLE 4 Relation between visual rank order, total chlorophyll content and Hunterlab colour indices for unprocessed and processed pea puree

| Relationship | Correlation coefficient 'r' | | |
|---|---|---|---|
| | All samples | pH 6·95 | pH 8·45 |
| Visual rank *vs* total chlorophyll | − 0·854 | 0·905 | 0·814 |
| Visual rank *vs* % chlorophyll conversion | 0·741 | 0·877 | 0·876 |
| Visual rank *vs* index $^{-a}/b$ | − 0·789 | 0·869 | 0·820 |
| Visual rank *vs* index $^{-a}/L$ | − 0·880 | 0·877 | 0·825 |
| Visual rank *vs* index $(a^2 + b^2)^{\frac{1}{2}}$ | − 0·693 | — | — |

*Effects of processing and storage on colour*

Changes in the Hunterlab index $^{-a}/b$ for puree samples stored for 18 months are shown in Fig. 1. The relationship between percent chlorophyll conversion and the Hunterlab index $^{-a}/b$ for processed and stored puree samples at pH 6·95 and pH 8·45 is shown in Fig. 2. Correlations between pigment and colour indices are presented in Table 5. Results of analyses on elevated pH puree stored 12 and 18 months at 20°C were omitted from the calculations.

*pH*

Analyses on processed and stored puree are presented in Table 6.

TABLE 5. Relation between percent chlorophyll conversion and Hunterlab indices for stored, processed pea puree

| | Correlation coefficient 'r' | |
|---|---|---|
| | pH 6·95 | pH 8·45 |
| Per cent chlorophyll conversion *vs* index $^{-a}/b$ | − 0·997 | − 0·962 |
| Per cent chlorophyll conversion *vs* index $^{-a}/L$ | − 0·995 | − 0·950 |
| Per cent chlorophyll conversion *vs* index $(a^2 + b^2)^{\frac{1}{2}}$ | − 0·888 | − 0·951 |

TABLE 6. pH values of processed and stored pea puree

| Storage temperature (°C) | Storage time (months) | Normal pH puree | | | | Elevated pH puree | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Process temperature (°C) | | | | | | | |
| | | 115·6 | 126·7 | 137·8 | 148·9 | 115·6 | 126·7 | 137·8 | 148·9 |
| — | Unprocessed | 6·95 | 6·95 | 6·95 | 6·95 | 8·45 | 8·45 | 8·45 | 8·45 |
| — | Processed | 6·47 | 6·80 | 7·04 | 7·16 | 8·25 | 8·34 | 8·40 | 8·49 |
| 20 | 2 | 6·38 | 6·54 | 6·69 | 6·72 | 8·18 | 9·25 | 8·26 | 8·28 |
| 20 | 3 | 6·31 | 6·50 | 6·60 | 6·67 | 8·02 | 8·18 | 8·22 | 8·26 |
| 20 | 6 | 6·25 | 6·48 | 6·55 | 6·57 | 7·97 | 8·14 | 8·24 | 8·26 |
| 20 | 12 | 6·18 | 6·43 | 6·49 | 6·48 | 7·88 | 7·95 | 8·19 | 8·20 |
| 20 | 18 | 6·09 | 6·14 | 6·28 | 6·30 | 7·79 | 7·88 | 7·95 | 8·10 |
| 2·8 | 3 | 6·39 | 6·69 | 6·81 | 6·95 | 8·25 | 8·28 | 8·30 | 8·30 |
| 2·8 | 6 | 6·31 | 6·68 | 6·79 | 6·86 | 8·24 | 8·20 | 8·25 | 8·32 |
| 2·8 | 12 | 6·27 | 6·56 | 6·77 | 6·84 | 8·19 | 8·21 | 8·27 | 8·27 |
| 2·8 | 18 | 6·30 | 6·58 | 6·69 | 6·77 | 8·11 | 8·18 | 8·23 | 8·28 |
| − 23·3 | 6 | 6·52 | 6·61 | 6·92 | 7·05 | 8·21 | 8·33 | 8·35 | 8·36 |
| − 23·3 | 12 | 6·46 | 6·61 | 6·92 | 7·05 | 8·21 | 8·33 | 8·35 | 8·36 |
| − 23·3 | 18 | 6·39 | 6·52 | 6·70 | 6·95 | 8·16 | 8·22 | 8·30 | 8·34 |

## Discussion

*Pigment changes during processing and storage*

Considerable retention of chlorophyll pigments in pea puree was achieved by H.T.S.T. processing at temperatures up to 148·9°C, in agreement with the results of work on spinach puree (Tan & Francis, 1962; Gupte & Francis, 1964; Clydesdale & Francis, 1968). Significant reductions in chlorophyll conversion occurred by raising the process temperature from 115·6°C to 126·7°C and 137·8°C, but above this temperature no further improvement was noticed.

Higher process temperatures also reduced the extent of chlorophyll conversion in elevated pH puree, but the conversion at low process temperatures was markedly less than in the corresponding lower pH samples (Table 1). Initially, more chlorophyll was retained in normal pH puree processed at high temperatures than in elevated pH puree processed at lower temperatures, but raising the pH before processing at 115·6°C gave almost a four-fold increase in retained chlorophyll.

The different rates of conversion of chlorophylls *a* and *b* to their magnesium-free derivatives found in this study were also in agreement with data for the other food products containing chlorophylls (Sweeney & Martin, 1958, 1961; Tan & Francis, 1962; Gupte, El-Bisi & Francis, 1964; Eheart, 1967). The difference in conversion rate was not as large, however, as reported in *in vitro* systems containing pure chloro-

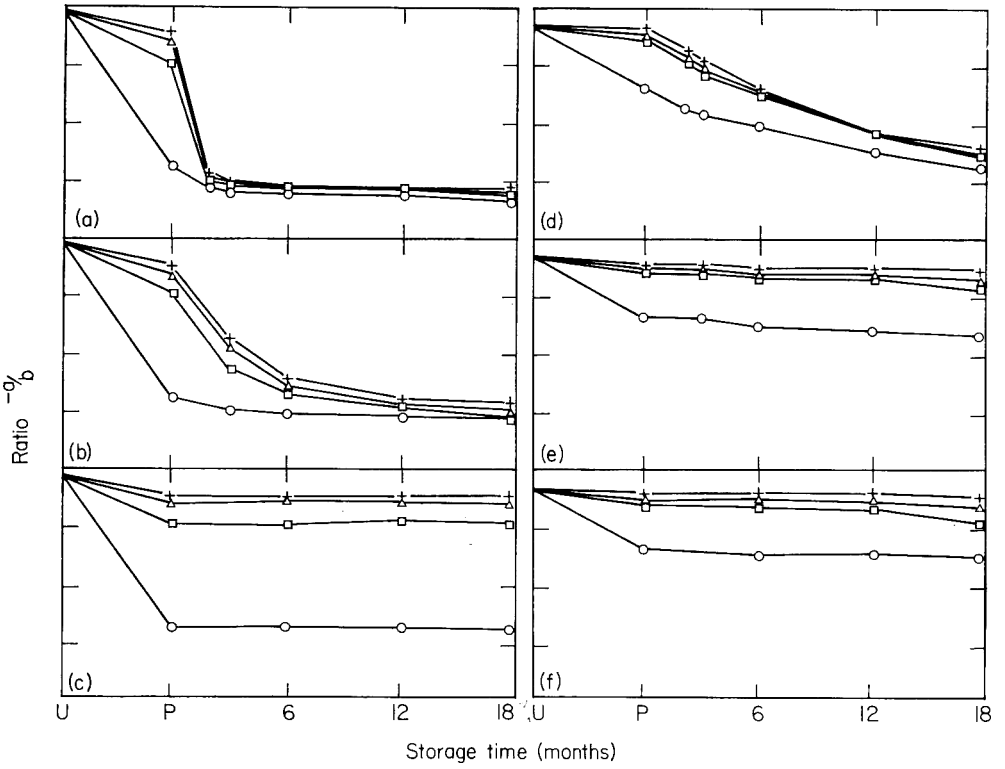


FIG. 1. Effect of processing and storage on the Hunterlab ratio $-\frac{a}{b}$ of pea puree.

(a) Normal pH, storage temperature 20°C; (b) normal pH, storage temperature 2·8°C; (c) normal pH, storage temperature — 23·3°C; (d) elevated pH, storage temperature 20°C; (e) elevated pH, storage temperature 2·8°C; (f) elevated pH, storage temperature — 23·3°C.

○, process temperature 115·6°C; □, process temperature 126·7°C; △, process temperature 137·8°C; +, process temperature 148·9°C; U, unprocessed; P, processed.

phylls (Schanderl, Chichester & Marsh, 1962). In all cases, chlorophyll *a* degraded faster than chlorophyll *b*.

The total chlorophyll content of normal pH puree (86·0 μg/g) was higher than that for elevated pH puree (77·2 μg/g). While some of this discrepancy can be attributed to the incorporation of powdered magnesium carbonate in the latter samples, it would appear that either pigment extraction was incomplete or some pigment degradation had occurred prior to extraction. The results were reproducible and were not due to experimental error. The visual colour of the elevated pH samples was also a lighter green than samples at the lower pH.

Complete conversion of chlorophylls to pheophytins occurred with all samples of normal pH puree after 18 months storage at 20°C (Table 2). All samples showed more than 85% conversion after only 2 months storage even though samples processed at

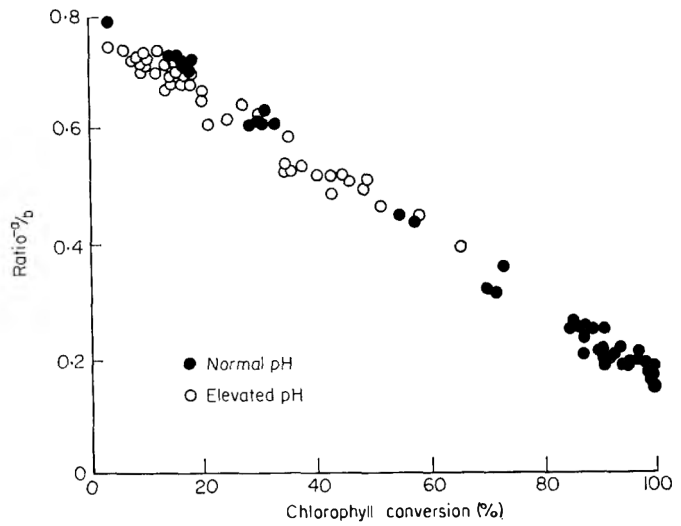


FIG. 2. Relationship between Hunterlab ratio $^{-a}/b$ and % chlorophyll conversion for processed and stored pea puree.

137·8°C and 148·9°C showed a greater initial retention of chlorophylls. All samples stored at 2·8°C showed at least 85% conversion after 12 months, but after 18 months only the sample processed at 115·6°C showed complete conversion.

For normal pH samples processed at 115·6°C, any chlorophyll retained was degraded rapidly during storage. Thus at 20°C, 91% of the retained chlorophyll was degraded in the first 2 months of storage while at 2·8°C, 41% was degraded in the first 3 months.

For samples processed at high temperatures and stored at 20°C, the largest proportion of the chlorophyll conversion due to storage also occurred during the first 2 months. Although more chlorophyll was retained by high process temperatures, the remaining chlorophyll was degraded at approximately the same rate during storage, i.e. the rate was independent of the residual chlorophyll concentration. Thus for normal pH puree stored at 20°C, the proportions degraded during the first 2 months storage after processing at 115·6°, 126·7°, 137·8° and 148·9°C, compared to the total degradation over 18 months, were 91·7, 87·6, 87·4 and 86·0% respectively, although five times as much chlorophyll was present in the 148·9°C sample (76·0 μg/g) than in the 115·6°C sample (15·5 μg/g) at the beginning of storage. At 2·8°C, the proportions degraded during the first 3 months were 41·1, 63·5, 51·8 and 53·0% respectively of the total storage changes. Since more chlorophyll was retained at higher process temperatures, there was more chlorophyll present to be degraded during storage and hence the colour changes were more noticeable, explaining the observations of other workers that the colour of H.T.S.T. processed vegetables was less stable than samples processed by conventional methods.

For elevated pH puree, high process temperatures and low storage temperatures

produced only minor pigment changes during storage. The influence of storage temperature on pigment degradation in elevated pH puree was not as marked as that in normal pH puree.

In agreement with the results of Gupte & Francis (1964), phytol-free chlorophyllides and pheophorbides were not found in any sample analysed.

*Colour ranking of pea puree*

Visual rankings and objective colour measurements on unprocessed and processed pea puree are presented in Table 3. It should be noted that visual rankings do not attempt to assign a colour score but only represent the average placement of the samples in order of desirability of green pea colour. With two exceptions, the samples were ranked in order of decreasing total chlorophyll content.

As mentioned previously, elevated pH puree was a lighter green colour than the normal pH puree due to the incorporation of magnesium carbonate. This was shown clearly in the Hunterlab values for the unprocessed purees, where the largest difference was in the '*L*' value (7·7 units), while the 'a' and 'b' values were similar. This difference was also evident in the Hunterlab ratio $^{-a}/L$ for the unprocessed purees, being higher for the normal pH samples.

The order of visual ranking showed that the judges considered the darker colours to be more typical of peas. The lighter colours of the elevated pH samples were considered more desirable (ranks 4–7) only when the total chlorophyll content of normal pH puree had decreased to such a level that the natural green colour was changed by the presence of grey and olive-green pheophytins.

The ratio $^{-a}/L$ was a more consistent indicator of desirable colour than $^{-a}/b$ or $(a^2 + b^2)^{\frac{1}{2}}$, since the samples were visually ranked in order of $^{-a}/L$ values with only two minor exceptions (ranks 5 and 6, and 7 and 8). For samples ranked 6 to 10, the rank order was in agreement with decreasing chlorophyll content and objective colour indices ($^{-a}/b$, $^{-a}/L$, $(a^2 + b^2)^{\frac{1}{2}}$) with only one minor exception. The relationship between rank order and objective measurements for the other five samples (ranks 1–5) was less clear. Allowing for the exceptions, however, there was still good agreement between visual ranks, pigment content and colour measurements (Table 4). Correlation coefficients relating determinations on normal pH samples were in each case higher than the corresponding results for elevated pH samples.

*Colour changes during storage*

Objectively measured colour changes during the storage of processed pea puree (Fig. 1) followed closely the changes in chlorophyll conversion. All objective colour indices gave good estimates of pigment changes under the conditions of these experiments. Correlation coefficients relating the indices $^{-a}/b$ and $^{-a}/L$ to percent chlorophyll conversion in normal pH puree were almost statistically perfect (Table 5).

Correlations between indices and pigments for elevated pH puree were lower with the exception of the index $(a^2 + b^2)^{\frac{1}{2}}$. Since this index approximates to the saturation of a colour, it is apparent that changes in saturation are of greater significance in lighter colours (elevated pH puree) than in darker colours, whereas changes in hue, e.g. green to yellow, as measured by $^{-a}/b$ or $^{-a}/L$, are satisfactory for light and dark colours, but especially for darker colours.

The regression equations relating the index $^{-a}/b$ to percent chlorophyll conversion for stored puree (Fig. 2) were calculated as:

*Normal pH:* $^{-a}/b = 0{\cdot}811–0{\cdot}0065$ (percent chlorophyll conversion), with standard error $S = 0{\cdot}0169$.

*Elevated pH:* $^{-a}/b = 0{\cdot}7816–0{\cdot}0066$ (% chlorophyll conversion), with $S = 0{\cdot}0321$.

*pH changes*

Irrespective of initial pH, lower process temperatures gave larger pH changes than higher temperatures (Table 6) because of the longer processing times required. The pH changes for normal pH puree, however, were larger than the changes for elevated puree processed at corresponding temperatures.

Within each pH group, changes in pigment content and colour for samples at each process temperature were directly related to the pH change during processing, e.g. normal pH samples processed at 115·6°C showed 79% chlorophyll conversion during processing and a pH change of 0·48 units, while elevated pH puree showed 31% conversion and a pH change of 0·20 units when processed at the same temperature. The pH changes at higher process temperatures varied with the process times for both pH levels.

Changes in pH during storage were affected by time and temperature and showed trends similar to those observed for chlorophylls and colour. Normal pH puree processed at 115·6°C decreased in pH by only 0·38 units during storage at 20°C for 18 months, while puree processed at 126·7°, 137·8° and 148·9°C decreased by 0·66, 0·76 and 0·86 pH units respectively. The pH changes during the first 2 months represented the largest single changes throughout the storage period of 18 months.

Changes in pH of elevated puree were in general smaller than those of normal pH samples, being 0·46, 0·46, 0·45 and 0·39 units for samples processed at increasing temperatures and stored 18 months at 20°C. From these results it would appear that in normal pH samples, the decrease in pH during processing is proportional to the heat treatment given, but the rate of pH change during storage at 20°C is dependent on the difference between the pH after processing, but before storage, and the ultimate or equilibrium pH of the product. The latter pH value would be typical of a particular food material processed and stored under given conditions, and dependent on the original constitution of the material with respect to organic acids and buffering capacity.

The pH change in elevated pH puree was also dependent on the severity of the heat process, but the changes during storage were similar for each process temperature and were presumably determined by the high initial pH and the buffering capacity of the alkaline puree.

While a H.T.S.T. process produced smaller pH changes during processing than a conventional process irrespective of initial pH, the pH of H.T.S.T. processed samples decreased more rapidly during storage than those processed at 115·6°C for normal pH puree, but less rapidly for elevated pH samples. The one exception was normal pH puree processed at 115·6°C which showed a smaller pH change during storage than any other sample due to the large decrease in pH that had occurred during processing.

Changes in pH during processing and storage of spinach puree (Clydesdale, 1966) were in agreement with the different rates of pH change between conventional and H.T.S.T. processes observed in the present investigation, but were largely different in other respects. Clydesdale found that (1) conventional processing of normal pH (pH 6·70) and elevated pH (pH 8·65) spinach puree resulted in a decrease in pH of 0·65 and 0·95 units respectively, and storage at 23·9°C for 6 months gave further decreases of 0·14 and 0·50 pH units respectively. The present work on pea puree showed a much greater pH decrease in the normal pH sample than in the elevated pH sample after a process at 115·6°C; (2) identical samples processed by a H.T.S.T method (148·9°C) showed very small pH changes due to processing to $F_0 = 4·9$ (zero and 0·20 pH units for normal and elevated pH puree), but storage for 6 months at 23·9°C gave decreases of 0·80 and 1·65 pH units respectively. This latter result, i.e. the greater pH change in the elevated pH sample processed by a H.T.S.T. method, is in direct contrast to the results of the present work, where the pH change during storage of elevated pH puree processed at 148·9°C (0·39 pH units) was smaller than the corresponding change in the normal pH sample during storage for 18 months (0·86 pH units). One explanation would be the greater buffering power of peas compared to spinach, which is substantiated by the fact that 0·35% magnesium carbonate was required to elevate the pH of spinach puree from 6·70 to 8·65 (Clydesdale, 1966), whereas more than 2% was required to raise the pH of pea puree from 6·95 to 8·45 in the present study. Other differences include the extent of heat processing and the containers, but these would hardly account for the results observed.

From these observations it is obvious that retention of green colour in processed vegetables is intimately connected with pH changes during processing and storage, and can be accomplished only if pH changes can be minimized or eliminated.

## Acknowledgments

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# The effect of delay between cooking and freezing on the flavour of pre-cooked frozen food

MARGARET A. HILL AND G. GLEW

## Summary

The effect of delay between cooking and freezing on the organoleptic properties of some foods after reconstitution has been examined. Difference tests were performed and it was shown that delays between cooking and freezing of as little as 15 min caused statistically significant differences between some samples subject to delay and those frozen immediately after completion of the cooking operation.

## Introduction

Platt, Eddy & Pellett (1963), after a survey of the quality of the food served in 152 hospitals in England and Wales, suggested that the use of pre-cooked frozen food might offer an alternative catering system which could have considerable advantages in terms of organoleptic properties and nutritional value. A system of catering based on the use of pre-cooked frozen food has been developed and installed at the Hospital for Women, Leeds (Armstrong, 1968).

It was found that the nutritional and organoleptic quality of the pre-cooked frozen food could be of equal or better standard than that prepared conventionally (Hill & Glew, 1969; Glew, 1968; Glew, *et al.*, 1969; Etim, 1967; Millross, 1967).

In order to assess whether delay between preparation and freezing was a factor which influenced organoleptic properties, difference tests using a taste panel were performed, using a number of foods after periods of delay between cooking and freezing.

## Materials and methods

### A. *Food preparation*

The standard methods of preparation for the foods tested were based on the recipes developed for the production of pre-cooked frozen food at the Hospital for Women, Leeds.

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A batch of food was prepared by a standard recipe. The ingredients were weighed and all the cooking processes were controlled. Each batch was portioned into the standard containers (240 mm × 240 mm × 40 mm 14 gauge aluminium with loose fitting lid). Half of the containers were frozen in the blast freezer immediately, the other half were frozen in the blast freezer after a controlled delay period of up to 60 min. The blast freezer had an air speed of 1000 ft/min and an air temperature of −25°C. The food was frozen solid to the centre within 90 min.

These foods, after freezing, were removed from the container, packaged in polythene (120 gauge), then stored between −18°C and −22°C for a few weeks until required. The samples were removed from storage, placed in the standard container, covered with a lid and reheated to 80°C in the Elektrohelios (Helimatic Ltd, London) hot air circulation oven at 180°C for 25 min, immediately before service to the taste panel.

1. *Omelettes*

The omelettes were prepared from a standard mixture and they were frozen individually.

2. *Minced beef with onions*

A sample of 850 g of the cooked product was weighed into the standard trays for freezing.

3. *Macaroni cheese*

The macaroni and the cheese sauce were cooked separately. A modified tapioca starch (Purity 69) was incorporated in the sauce to prevent separation of the reheated product.

A sample of 400 g of cooked macaroni was weighed into the standard tray and 500 g of cheese sauce were poured over it before freezing.

4. *Poached fish*

Weighed portions of fish were cooked in seasoned milk, four portions at one time. Six portions were placed in a standard tray and 200 ml of cooking liquid were added before freezing.

5. *Sole in white wine sauce*

The fillets of sole were cooked in fish stock and wine. This cooking liquor was then used to prepare the sauce. Five fillets of sole were placed in each standard tray and 400 ml of sauce were poured over the fish before freezing.

6. *Chicken in velouté*

The chickens were boiled, the meat was removed from the carcass and diced and 260 g of the diced chicken were placed into each standard tray.

The velouté was prepared from the stock and 500 ml of this sauce were poured over the diced chicken.

7. *Brown lamb stew*

The prepared meat and vegetables were fried in fat, and flour was then added and

cooked until it was brown in colour. Tomato purée, stock and seasoning were added and the mixture was simmered for 2 hr.

A sample of 330 g of the cooked meat was weighed into the standard tray and 300 ml of gravy were poured over the meat.

B. *Taste panel method*

A mouthwash was provided consisting of equal parts of tap water and carbonated water.

The hot food was served in disposable petri dishes which were placed on a polystyrene tray to prevent the food from cooling before tasting was completed.

Food science students were used throughout as tasters during two sessions each week. Thirty-seven students were screened during panel selection tests and fourteen selected as being sufficiently discriminating and consistent for use as permanent members of the panel.

The declared control difference test was used. The taster was presented with three samples, one sample was labelled 'Standard', the remaining two were labelled B and C respectively. The taster was asked to taste the 'Standard' first (scored 5 points), then B and C to score these two samples independently on a five point scale, assessing the degree of difference from the 'Standard'. The scale ranged from a score of 5 (same as 'Standard') to 0 (extremely different from 'Standard'). One of the samples B or C was always the same as the 'Standard' acting as a hidden control.

C. *Statistical analysis*

The correlated *t*-test was used to assess the significance of differences between samples. All the four possible combinations in which the samples could be presented to the tasters were used. The score of the hidden control was subtracted from the score of the test sample.

A frequency distribution chart was then constructed as in the following example:

| Difference between the hidden control and the test sample ($d$) | $-5$ | $-4$ | $-3$ | $-2$ | $-1$ | $0$ | $+1$ | $+2$ | $+3$ | $+4$ | $+5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Frequency of occurrence of ($d$) | 0 | 0 | 1 | 9 | 2 | 6 | 5 | 1 | 0 | 0 | 0 |

Total number of differences ($n$) $= 24$

Mean difference score $\bar{d} = \dfrac{\Sigma d}{n} = -0{\cdot}667$

$$t = \frac{\bar{d}}{\sqrt{\dfrac{\Sigma d^2 - (\Sigma d)^2/n}{n(n-1)}}} = \frac{-0{\cdot}667}{\sqrt{\dfrac{45{\cdot}33}{552}}}$$

Degrees of freedom $(n - 1) = 23$

$t = -2{\cdot}33$

which gives, $p = < 0{\cdot}05$

## Results

Table 1 shows the effect of delay between cooking and freezing on seven products. Delays of up to 1 hr did not result in significant differences from the control in the case of minced beef with onions, sole in wine sauce, chicken in velouté and brown lamb stew. In the case of the other three foodstuffs, delays of 1 hr or less between cooking and freezing caused significant differences between the control and the sample subjected to delay. Omelettes were very sensitive to delay and a highly significant difference was found between samples frozen immediately and those subjected to only

TABLE 1. The effect of time delays between cooking and freezing on the flavour of pre-cooked frozen food

| Product | Delay (min) between preparation and freezing | No. of tasters | No. of observations | Mean difference score | $t$ | $p$ |
|---|---|---|---|---|---|---|
| Omelettes | 15 | 5 | 30 | − 0·966 | − 4·58 | < 0·001 |
| | 30 | 6 | 18 | − 0·944 | − 8·84 | < 0·001 |
| | 60 | 7 | 14 | − 0·928 | − 3·04 | < 0·01 |
| Minced beef with onions | 60 | 6 | 24 | − 0·042 | − 0·014 | NS |
| Macaroni cheese | 20 | 7 | 28 | − 0·571 | − 2·57 | < 0·02 |
| | 40 | 7 | 28 | − 0·607 | − 2·53 | < 0·02 |
| | 80 | 6 | 24 | − 0·54 | − 2·30 | < 0·05 |
| | 120 | 6 | 24 | − 0·667 | − 2·33 | < 0·05 |
| Poached fish | 15 | 4 | 28 | + 0·049 | + 0·049 | NS |
| | 30 | 4 | 28 | − 0·178 | − 0·816 | NS |
| | 60 | 5 | 20 | − 0·80 | − 7·332 | < 0·001 |
| Sole in white wine sauce | 60 | 10 | 44 | + 0·045 | + 0·26 | NS |
| Chicken in velouté | 60 | 10 | 40 | − 0·025 | − 0·22 | NS |
| Brown lamb stew | 60 | 10 | 40 | − 0·025 | − 0·18 | NS |

($t$ = Student's $t$-test; $p$ = probability; NS = not significant at the 5% level of probability. Delayed samples compared with samples from the same cooked batch frozen immediately after completion of cooking)

15 min delay between cooking and freezing. Macaroni cheese was judged to be significantly different from the control after a delay of 20 min, whereas poached fish was rather less sensitive, exhibiting an organoleptic difference after 60 min delay between cooking and freezing.

## Discussion

The results show that delay between cooking and freezing can affect the organoleptic properties of some dishes. These experiments are concerned with the rate at which food is cooled immediately after completion of the cooking operation. Although there are statistically significant differences between some samples subjected to delay and those frozen immediately after cooking, this does not prove that the delayed samples are inferior in flavour, but it does indicate that definite differences in flavour exist. This phenomenon is particularly marked in those foods of blander flavour. Lowe (1961) and Gortner, Erdman & Masterman (1948) consider that delay between cooking and eating causes undesirable changes. If this is the case, then any form of large batch production is undesirable, because it may result in variable quality between the samples portioned earlier or later in the batch. In practice, therefore, to prevent flavour change, delay between cooking and freezing should be avoided.

## Acknowledgments

The authors would like to acknowledge the technical assistance of Miss S. Brock and Miss S. Newsome. They would also like to thank the members of the taste panel for their participation in this work, and the Ministry of Health and Social Security for financial support.

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*J. Fd Technol.* (1970) **5**, 193–195.

# A study of the natural disappearance of the limonin monolactone in the peel of Shamouti oranges

SOLANGE FLAVIAN AND A. LEVI

## Summary

A previously unknown process has been found to occur in the peel of Shamouti orange at the end of the season, which may be responsible for the disappearance of the limonic acid *A*-ring lactone, the non-bitter precursor of limonin. The nature of this process is not yet established, but there are indications that it is of an enzymic nature.

## Introduction

Shamouti juice is not produced commercially in Israel in the early part of the season because of the development in it of a bitter unacceptable flavour. It has been established (Levi *et al.*, 1970) that the bitter flavour is caused by limonin, which creates the same problem in Washington Navel and Australian Valencia (Chandler & Kefford, 1966). Maier & Beverly (1968) identified a non-bitter precursor of limonin, a limonin monolactone, which subsequently was shown to be limonoic acid *A*-ring lactone (Maier & Margileth, 1969). The same non-bitter compound is found in the tissue (membranes, peel and carpellary membranes) of Shamouti fruit; it is gradually converted into the bitter limonin when the fruit tissue comes in contact with the acidic juice, after juice extraction. The conversion of monolactone to limonin occurs (in the presence of the juice) at pH ~ 3 and is facilitated by heat. Maier & Margileth (1969) also found indications of an enzyme in tissue extract which converts the limonin monolactone into limonin.

No bitterness has been detected in the juice extracted from late-harvested Shamouti oranges; in such fruit, limonin and monolactone were not found in significant amounts (Levi *et al.*, 1970).

Attempts have been made to find the reason for the disappearance of the monolactone from the fruit tissue at the end of the season and evidence has been obtained for its being a process of presumably enzymic nature.

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## Experimental

Limonin (mp 292°C) was extracted from citrus seeds. The monolactone used was prepared from limonin by refluxing for 2 hr with a slight excess of 0·1 N NaOH (Maier & Beverly, 1968). The hydrolysis was complete, as proved by analysis for residual limonin.

Extraction of late-season peel was performed as follows: Approximately 20% albedo and membrane in water was blended at high speed. The slurry was rapidly filtered and one portion of the filtrate was boiled for 5 min. Equal amounts of monolactone (final concentration around 20 ppm) were added to both the boiled and non-boiled filtrates and the mixtures were brought back to the initial pH of the peel (~ 5·5) with citric acid. The mixtures were allowed to stand at various temperatures between 0° and + 50°C and for various periods of time between 1 and 4 hr.

The monolactone concentration in each sample was determined by converting the monolactone into limonin (heating at 95°C for 10 min at pH 3·3) and subsequent estimation of the limonin by the spectrophotometric method of Wilson & Crutchfield (1968).

## Results and Discussion

There was no change in the concentration of the monolactone in the boiled extract system on standing, except for very small fluctuations due to experimental errors or losses. On the other hand, there was a very marked decrease (over 50%) in the concentration of the monolactone which remained in contact with the non-boiled peel extract.

This process was found to be temperature dependent. As shown in Fig. 1, the monolactone disappears most rapidly in 30–40°C temperature range.

The final concentration of the monolactone at a given temperature was found to be independent of holding periods when the samples were kept for any period between

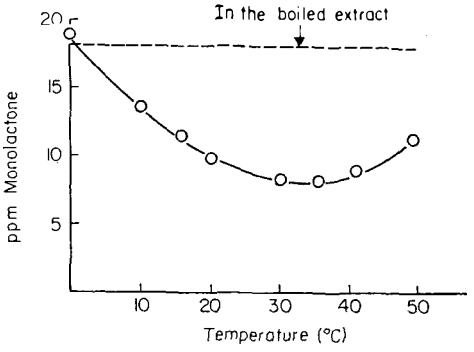


FIG. 1. Concentration of the monolactone after standing for 1 hr with the orange-tissue extracts at various temperatures. Initial concentration: 20 ppm monolactone.

1 and 4 hr. In this preliminary work the reaction was not studied for shorter periods of time.

These results indicate that the natural disappearance of the monolactone from the orange tissue towards the end of the season is caused by the presence of a catalytically active compound in the peel and membrane. This compound may be enzymic in nature. Enzymes causing the decomposition of limonin have been found in micro-organisms (Namura, 1966).

Work is in progress to study the influence of pH and of time, to identify the compound responsible for this process, and to identify the decomposition products of the monolactone. Applications to debittering of early-season Shamouti orange juice are envisaged.

## Acknowledgments

We wish to thank Mrs H. Weisselovitz for invaluable technical assistance.

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# The effect of heat treatment on the β-glucosidase activity in canned whole apricots

ESTHER HERSHKOVITZ AND J. KANNER


## Summary

Undesirable odour and flavour in canned whole apricots are caused by the products of the β-glucosidase activity in the apricot kernels. The hydrocyanic acid content in canned apricots heat treated for 38 min at 86°C was found to be approximately 1 ppm, with no changes occurring even after long storage; the figure reached a maximum of 16–17 ppm after 150 days of storage at room temperature in fruit heat treated at the same temperature but for only 20 min.


## Introduction

An enzyme system, 'emulsin', is found in the kernels of stone fruits such as prune, peach and apricot. This enzyme system is characterized by its ability to hydrolize the glucoside 'amygdalin', which is present in such kernels. Amygdalin is decomposed by emulsin to glucose, benzaldehyde and hydrocyanic acid (Cruess, 1938). Dickinson (1957) found β-glucosidase activity in canned plums and cherries, even after a heat treatment which provided adequate protection against microbiological spoilage. In a chromatographic study of the stages of amygdalin hydrolysis by emulsin β-glucosidase, Haisman & Knight (1967a) found that, according to the intermediate products, the so-called β-glucosidase includes at least three enzymes: amygdalin lyase, hydroxinitrile lyase and prunasin lyase, each responsible for one of the stages of hydrolysis. The optimal temperature for the β-glucosidase activity in canned whole prunes was found to be 50°C at a pH range of 5–6. The enzyme is most heat stable at the same pH range. Heat processing of the cans—blanching for 6 min at 85°C and pasteurization at 100°C for 12 min—was sufficient to prevent the enzyme activity; however, pasteurization for only 8 min did not destroy the enzyme, and after 12 months of storage 2 ppm hydrocyanic acid was found in the cans (Haisman & Knight, 1967b).

## Materials and Methods

Apricot fruits of the Canino variety, with a colour intensity of Pl.10–FG 5 (Maerz & Paul, 1950), were stored for 1, 15 and 28 days at 0°C before canning.

A commercial sample of amygdalin was obtained from the British Drug Houses.

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Citrate buffer (0·1 M) was prepared using analytical reagent grade chemicals.

Size A2 cans were filled with fruit, covered with 30 deg. Brix hot sugar syrup, exhausted for 8 min, closed, and heat treated for 12 and 30 min at 86°C. At each sampling (after 40, 90, 150 and 210 days), six cans from each treatment were opened and the hydrocyanic acid content was determined according to Russell & Wilkinson (1959).

Apricot kernel enzymes were extracted in an aqueous solution of blended kernels and water by homogenization in a Waring Blendor (1 g fresh kernels/100 ml water; 5 g kernels from canned fruits/100 ml water.) The enzyme activity of the apricot kernel extract was estimated by the rate of decomposition of pure amygdalin to hydrocyanic acid and, subsequently, the quantitative determination of the latter product. All measurements were performed in a shaking thermostat bath in glass stoppered conical flasks, before and after heating for various periods of time at 30°C in a citrate buffer (0·1 M, pH = 5).

Evaluation of the canned products was performed by a trained taste panel of ten members, sensitive to almond flavour. The members were selected in the following way: samples of canned apricots were prepared under varying conditions of heat treatment and four cans were chosen in which the HCN content was determined, i.e. 0·3; 1·5; 3·4; 6·7 ppm HCN. Those who were able to arrange these samples in order of increasing concentration of HCN were chosen for the taste panel.

The organoleptic analysis of the experimental cans was performed using the triangle test difference method of sampling in which the HCN concentration was already known.

The members of the taste panel were asked to judge the following:

1. To determine which of the three samples was different from the others.
2. To score the difference.
3. To indicate the preferred sample.

The two equal reference samples contained approximately 1 ppm HCN having been heat treated for a long time (38 min); the third sample was heat treated for a shorter time (20 min) and stored after processing for various periods of time, in conditions under which the quantity of HCN was increased.

## Results

*I. β-glucosidase activity in the kernels of fresh fruit*

The initial quantity of hydrocyanic acid in the extract solution of fresh apricot kernel 1 g/100 ml water was found to be 1·9 mg/g kernels (Fig. 1).

After activation of the extract of a 0·022 M amygdalin solution at pH 5, at 30°C up to 90 min reaction time, the amount increased to 25 mg/g kernel.

*II. β-glucosidase activity in the kernels of the canned apricots*

The hydrocyanic acid content in the water extracts (5 g/100 ml) of canned apricot kernels was nearly equal after heat treatment for 20 and 36 min at 86°C, and storage

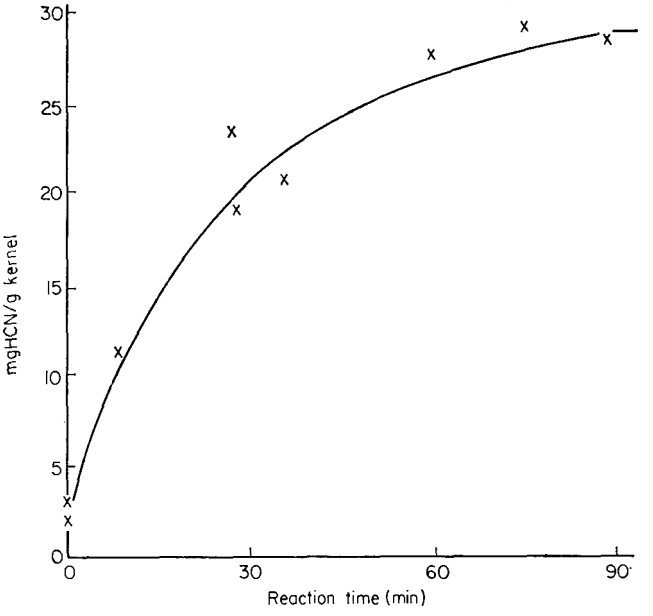


FIG. 1. β-glucosidase activity in fresh apricot kernels.

of 60 days (Fig. 2). Activating an amygdalin solution of 1% at pH 5 and 30°C for 60 min. with water extract from kernels of canned apricots, heat treated for 20 min, gave a rapid increase in the hydrocyanic acid content (developed from the amygdalin).

Water extract from kernels of canned apricots, heat treated for 38 min at 86°C did not show any β-glucosidase activity under the same conditions of enzymic reaction (Fig. 2).

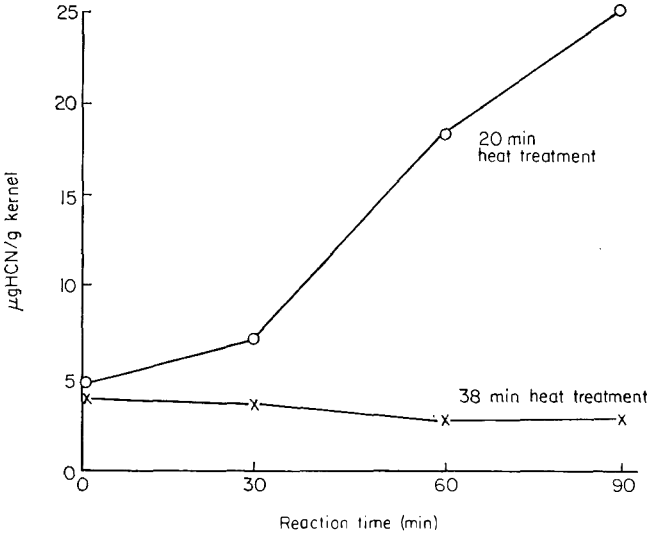


FIG. 2. β-glucosidase activity in canned apricot kernels.

*III. Hydrocyanic acid content of the canned apricots*

The hydrocyanic acid content of the syrup in the cans remained constant during storage up to 150 days after heat treatment of the cans for 38 min at 86°C. On the other hand, in the cans which were heat treated for 20 min at the same temperature more HCN was found, the increase being time dependent. After 40 days of storage 3 ppm was found, and after 150 days, 16 ppm (Fig. 3). A statistical evaluation of the results showed that there was no difference in hydrocyanic acid content between cans prepared from fresh fruit and from fruit stored up to 28 days at 0°C.

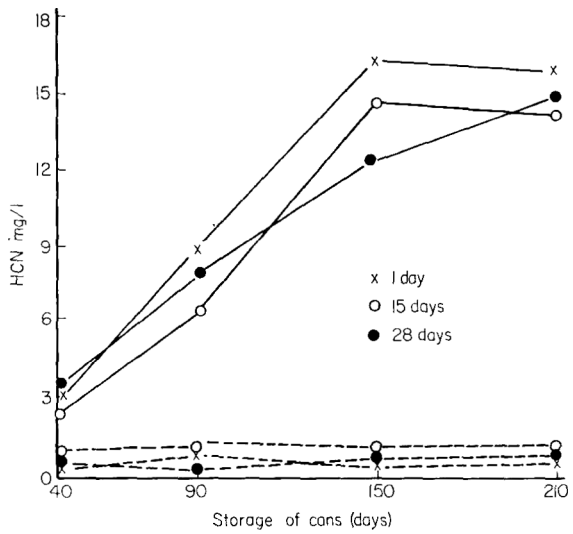


FIG. 3. HCN content in the syrup of canned whole apricots during storage. Solid line denotes 20 min heat treatment of fresh fruit prior to canning, broken line denotes 38 min heat treatment of fresh fruit prior to canning.

*IV. Evaluation of fruit flavour as compared to hydrocyanic acid content of the canned fruit*

The results of the organoleptic analysis, analysed statistically (Kramer & Twigg, 1962), showed that:

1. Samples containing 1–3 ppm HCN were preferred, and samples containing more than 6 ppm HCN were classified as having a too strong almond flavour.

2. The samples heat treated for only 20 min were of low acceptability after 90 days and unacceptable after a longer time. On the other hand, in the samples heat treated for 38 min, the quantity of HCN was small and constant during storage time and the taste remained stable.

## Conclusions

Storage of fresh apricot fruit at 0°C for up to 28 days prior to canning did not cause any significant changes in the β-glucosidase activity in the kernel, or increase the hydrocyanic acid content in the cans over syrup.

It seems that the enzyme system remains active in the kernels of canned apricots for long periods after processing, if the heat treatment is not sufficiently long to inactivate the enzyme.

The HCN content in canned apricots heat treated for an insufficient time (20 min at 86°C)—and in which an enzymic activity remained—increase with increasing storage time, reaching a level of 16 ppm up to 150 days in storage, after which it remained practically constant. In canned apricots heat treated for a longer time (38 min 86°C), explained by the lack of enzyme activity. Canned apricots containing more than 6 ppm HCN were classified as having a too strong almond flavour.

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# Book Reviews

**The Bacterial Spore.** Ed. by G. W. GOULD and A. HURST.
Academic Press, New York and London, 1969. Pp. xiv + 724. 180s ($27·50).

It is less than a century since bacteriology has been acknowledged as a distinct discipline, and the obstinate and refractory bacterial spore has played a major role in the controversy which was responsible for the delay and (ultimately) justification of this recognition.

In spite of this, real interest in the unique properties of this dormant structure exhibiting extraordinary resistance to heat, radiation, antibiotics and environmental factors is less than 15 years old. This volume is a worthy tribute to and an impressive record of the progress made in this short period and is the first attempt to bring together within a single volume, accounts of the fascinating physiological and morphological changes which bring about the formation of this structure, as well as the conditions which can effectively disturb its dormancy and induce a new cycle of development.

The opening chapter (Sussman) introduces and reviews the widely occurring phenomenon of dormancy, and thus in perspective clearly underlines some of the unique features of the bacterial spore. Chapters 2–9 give an excellent and critical account of the morphology, physiology, chemistry and enzymology of the spore, as well as the processes leading to its formation. The chapter by Lewis on dormancy is well worth singling out amongst a galaxy of outstanding contributions. Chapters 10–12 deal with the reactions concerned in spore activation, germination and outgrowth and again represent lucid presentations of a series of complex reactions. The remaining four chapters are devoted to applied aspects. The chapter on spore insecticides (Norris) is a model of clarity, readability and style.

To the food scientist the chapter on 'Sporeforms as food spoilage organisms' (Ingram) will prove particularly rewarding. Here for the first time will be found not only the presentation of the basic data on the kinetics of radiation and heat destruction but a critical evaluation and collation of data on spores, not found elsewhere.

Each of the chapters is dealt with by an authority and it is invidious to find fault with any of them. It may be worth recalling however that heat activation was first recognized not, as claimed (p. 362), by Weizmann but has been clearly described as early as 1881 by Brefeld. The stature of the late Dr Weizmann as scientist and statesman is in no way diminished by this correction.

JOSEPH WOLF

**Meat Production from Entire Male Animals: Proceedings of a Symposium held at the Meat Research Institute,** April 1969. Ed. D. N. RHODES.
J. and A. Churchill, London, 1970. Pp. 332. 60s.

Whether the rearing of uncastrated males for meat is or is not practicable in this country, the question has to be answered as to how the meat produced from such animals compares with that from the castrate. That this is not an easy question to answer is indicated by the fact that the Meat Research Institute regarded it as necessary to organize a symposium on the subject. There are twenty-five contributions under the headings of growth performance, management, meat quality, sex odour in boars, and legislative and economic aspects. Since the bulk of the meat from male animals marketed on the Continent is from entire animals, the contributions from France, Sweden, Denmark and Germany are especially useful. These contributions, and also a comprehensive survey of published work by J. B. Turton of the Commonwealth Bureau of Animal Breeding and Genetics, leave it in no doubt that the entire animal has an advantage over the castrate both in live weight gains and in current consumer preference for the meat produced. There are, however, well-known reservations with regard to the latter in respect of boar-taint, and in some respects also in respect of bull-taint, but it is indicated how these defects can be avoided. In the case of boar-taint, recent work identifying the cause of the taint as a derivative of male sex hormone has helped in providing methods of evaluation and control.

The difficulties of management of entire animals under conditions of mixed herding are not overlooked, but Turton (pp. 43 and 44) comments that since 'any difficulties are likely to be minimized in intense rearing units . . . the maintenance of outmoded standards of carcase excellence can only reflect adversely on the industry in terms of economic efficiency of production'.

The book includes vigorous discussion of these and other questions raised.

E. C. BATE-SMITH

**The Value of Food.** By P. FISHER and A. E. BENDER
Oxford University Press, London: Pp. 174, 0000, 60s.

This is an admirable little book well suited for the instruction of sixth-form pupils studying for their 'A-levels' in home economics or for those training to become caterers in hospitals, schools and industrial establishments and anxious to acquire a knowledge of nutrition. The arrangement of topics is slightly unusual. The chapter on energy metabolism, entitled 'Foods for muscular work', deals with the significance of carbohydrate and fat as sources of energy although the contribution made by protein is rather pointedly minimized to a mere mention. The B-vitamins, thiamine, riboflavine and niacin are also discussed in this chapter which, though unusual, is logical. 'Foods

for vitality' is a chapter about iron and ascorbic acid and the foods which contain them. 'Vitality foods', like the 'happiness vitamin' so popular with television advertisers is hardly a term with scientific precision but there is little to quarrel with in the accompanying text. Protein, calcium, vitamin D and vitamin A are dealt with together in another section followed by short chapters on digestion, and on the special requirements of infants, old people and other vulnerable groups. The composition of the main food groups, meat, fish, dairy produce, cereals, nuts, fruit and vegetables, and sugar is touched on, the main manufacturing processes briefly described and the book ends with a reference to some of the world's food problems.

Nutrition has always attracted devout adherents. On page 1 of their book as on page 152 at the end, Miss Fisher and Dr Bender assert that of all the factors upon which good health depends—genetical inheritance, freedom from plague and pestilence, facilities to deal with the burning desert or the freezing plains (they do not actually mention avoidance of war)—food is the most important. Nevertheless, within the compass they have set themselves, the authors have succeeded in that most difficult task of summarizing in simple terms what is in fact a complex and developing subject. The book will be useful both to the pupils who learn from it, and to their teachers who will find both the succinct text and the questions at the end of each chapter valuable starting points for wider instruction.

MAGNUS PYKE

**Materials and Methods in Fermentation.** By G. L. SOLOMONS
Academic Press, London, 1969. Pp. 331. 90s ($14·00).

This book will be of value not only to experimentalists in the fermentation industries but to technologists in the general food industries. Chemists and biologists in the brewing, milk-handling and numerous other food industries will find plenty to interest them in the chapters on instrumentation and control systems for gas and liquid flow, temperature, pressure, pH, oxidation-reduction potential and dissolved oxygen content of fluid systems. The chapters discussing properties of materials employed in fermentation processes and the design of auxiliary equipment (valves, valve activating equipment, pumps and pump design, flow inducers) are also recommended to a wider range of readers than those working only in fermentation.

The practical fermentologist can learn from this book which medium to use in his fermenter; how to design, sterilize and operate the fermenter and how to sterilize the vessel, its contents and its air supply. A chapter discusses anti-foaming agents and devices for mechanical administration of the antifoams. The end of the fermentation sequence is adequately catered for by the chapter describing methods for the recovery of the product from the medium.

The book contains a multiplicity of valuable hints to the unwary. The 'Commercial

References' are especially valuable in naming a variety of suppliers of a wide range of equipment and materials.

It is to be hoped that in his next edition the author will considerably extend the Subject Index which is too small for a reference work of this nature.

There are few food and fermentation technologists who will fail to add considerably to their fund of practical knowledge by using this excellent book.

JOHN WHITE

**The Chemical Biology of Fishes.** By R. MALCOLM LOVE.
Academic Press, London & New York, 1970. Pp. 547 + xv. £7.

The disproportionate output of literature in fish science makes a synoptic comparison particularly welcome. To quote from the Preface, 'this book is a biology of fish seen through chemical analysis'. 'Biochemistry' is avoided in the title because of its 'rather restricted meaning as a study of isolated systems, without much reference to the animal as a whole'. Of the 550 pp., the last 300 pp. are indexes.

The text proper treats firstly the problems of sampling, chemical and anatomical, and the effects of exercise and resting on the results of analysis. Then, the life cycle is scanned from germination to death, through eggs, fry, metamorphoses, growth, maturity, spawning and aging. Differences between and variations within species are considered next. The influence of the environment is discussed under such ecological factors as the motion of the sea, the nature of the fishing ground, oxygen, depth, light, salinity, diet and temperature. Finally, starvation is studied, chiefly for its effects on water, proteins, lipids, salts, carbohydrates and vitamins.

There is a most comprehensive 150 pp. index of fish names and 35 pp. of chemical constituents, with cross references to the text and a 90 pp. bibliography listing 1407 publications. Although the text includes 40 comparative tables and 100 figures, previous experience of exhaustive compilation of recorded values 'has shown that this is not a practical proposition'. A special feature is the critical use of the extensive Japanese literature. Another is the harvesting of the technological to supplement the biochemical literature for figures for 'controls' before processing. The book is written in a very personal style and is thoroughly entertaining. Trivial errors are only to be expected in such an encyclopedic work, and the reviewer struck a dozen.

C. L. CUTTING

**Man and Food,** by MAGNUS PYKE
World University Library, Weidenfeld & Nicolson, London, 1970. Pp. 256. 35s.

It is a little difficult to know for whom this book is intended as the publishers, World University Library, 'aim to provide authoritative introductory books for students which will be of interest also to the general reader.' It would be interesting to meet this gen-

eral reader, sometimes called the intelligent layman, who is presumably able to derive enjoyment from wading through scientific jargon and chemical formulae.

In this book, for example, the author has to say, for the benefit of the general reader, that fats are a so-called ester, and that glycerol is sometimes called glycerine in common speech. What will the reader who needs such descriptions make of phrases like 'terminated in a so-called carboxy-group which gives them their acid character,' 'chain lengths are fully saturated with hydrogen atoms,' and 'essential amino acids of known chemical configuration,' not to mention three full pages of chemical formulae? It is difficult to cater for both types of reader.

Another problem for the lay reader is created by the very virtues of the book so far as the scientist is concerned – its enormous concentration of topics and facts. Dr Pyke has brought together a fascinating collection of historical, technical and scientific detail on a great variety of food topics but their very concentration and diversity must make the subject matter somewhat beyond the comprehension of the lay reader while making it so very valuable to the food scientist. For example in the space of twenty pages meat is dealt with from the diverse aspects of gas chromatography of flavour volatiles, eating quality, the value of hill farming, growth, yield, amino acid composition, glycogen storage, nucleotides, nutritive value and food habits and taboos. This is an encyclopaedia in miniature.

The inevitably brief comments on all these aspects—and other topics are dealt with in the same way—will mean much to the food scientist, whether nutritionist or food technologist, who already has some knowledge of these subjects, but can hardly mean much to the beginner.

On the other hand for those with any interest in and knowledge of the sciences of food this is a first-rate book. Everyone will find much of value, whether it is historical, anecdotal or the other man's speciality, or even if only for the large number of useful tables. Many of the classical and fundamental findings and comments in the food field are brought together here, such as the cartoon of Boyd-Orr measuring the starvation gap, Hopkins' first vitamin experiment, the picture of the smiling schoolchildren of today compared with those of 50 years ago, the composition of thirty different fish, the milk composition of twenty species of animals, the discovery of the amino acids spanning 115 years, and the five bizarre brothers who all require vitamin C in their diets—man, ape, guinea pig, the fruit-eating bat and the red-vented bul-bul bird.

The book is divided into three sections, commodities, nutrition and food technology; it will serve as fascinating light reading to those well-versed in the food field, as a reference book to those who are not, and as a source book to many a lecturer.

A. E. Bender

**Sensory Evaluation of Food.** Annotated Bibliography by BIRGER DRAKE and BIRGIT JOHANNSON.
2 Volumes Goteborg: Swedish Institute for Food Preservation Research. Report No. 255, 1969, pp. xvii + 418. Price 40 Swedish Crowns ($8·00) per volume (inc. postage).

The Swedish Institute for Food Preservation Research is one of the major centres in Europe where modern Sensory Evaluation Techniques have been used and developed and was was the host of the International Symposium on 'Sensory Evaluation of Food—Principles and Methods' in 1968. This meeting was under the sponsorship and support of ICFOST and certain Swedish organizations functioning in this area. The present Bibliography was in the final stages of preparation at that time.

The authors are to be congratulated on their achievement in bringing together a wide selection of annotated references, numbering in all just over 2200, relating to the Principles and Methods of Sensory Evaluation of Food. These are drawn mostly from seventy-one major Journal sources including nine Abstract Journals. The subject matter is sub-divided as follows:

| | | | | | |
|---|---|---|---|---|---|
| *Volume* 1 | a. | Physiology (725) | b. | Psychology | (465) |
| *Volume* 2 | c. | Methods (670) | d. | Applications | (364) |

The figures in brackets refer to the number of items in each section. A list of journals used, a subject index and an author index are also provided. The subject index (eleven pages of foolscap) is particularly comprehensive and includes references to individual chemicals, technical products, special concepts and methods, clinical studies, and most specific varieties of foods and edible products.

Each volume begins with short introductory statements referring to each separate section. The authors observe that the boundary between certain sections (e.g. Physiology and Psychology) is not always easy to define, but this is really a trivial matter. A feature of special note is that twenty-nine of the seventy-one sources refer to psychological journals, thus clearly confirming the importance of the concepts and methods of contemporary psychology, particularly experimental psychology, to Sensory Evaluation, a point of view long held by the present reviewer. The introductory section on Psychology runs to some four pages in which the precise meaning of such terms as Perception, Psychophysics, Detection, Recognition and Scaling are amply discussed.

In fairness to the authors it is essential to keep matters in perspective and to note that articles which can be referred to as purely statistical, medical or psychological have *not* been included. Articles which appeared to provide only trivial results, without discussion of the problems involved, have also been omitted.

Each section includes its own coding system, which is set out below, in slightly abbreviated form.

The authors fully recognize that this is only one of many possible coding systems. These are aimed at a quick identification and appreciation of the contents of particular

*Physiology*
C = Classification
M = Medical (clinical)
P = Phenyl-thio-urea

*Psychology*
I = Interaction
S = Scales, relations
T = Threshold
P = Preference

*General*
a = Taste
b = Smell
ab = Flavour
c = Vision
d = Touch
e = Temperature
f = Other senses

*Methods*
*Upper line*
C = Consumer
I = Influence on Results
L = Laboratory question (olfactometer etc.)
P = Persons (panel selection performance, etc.)
S = Statistics

*Applications*
C = Consumer studies
X = Non-food applications

*Methods*
*Lower line*
d = Descriptive methods
p = Pairwise comparison
r = Ranking
s = Scaling and or schoring
t = Triangle and other difference methods
h = Hedonic
m = Multidimensional analysis

references and the present system has proved useful to the authors. Not only is this bibliography a valuable contribution to the literature in general, but it will greatly assist those who are entering this area systematically for the first time rapidly to collect their own reference material. The fact that only one side of the sheets are printed on would make it possible to cut out the individual entries and mount them on reference cards, again suitably coded for purposes of classification and recovery. There are, of course, a number of other extensive Bibliographies in existence (some even longer) but few, if any, are annotated like the present one. A rapid sampling of about 300 items from each section has indicated the following proportions of papers actually summarized at varying lengths.

| | | | |
|---|---|---|---|
| Physiology | (42%) | Psychology | (22%) |
| Methods | (72%) | Applications | (62%) |

There is some slight overlap between the entries in the different sections, but when this occurs the fact is noted in the author index. No attempt has been made here to estimate

the distribution of the entries according to topic or nationality of author. However, it is interesting to note the appreciable number of significant papers from Japanese sources, totalling thirty-six. This development is noted simply because some readers may not yet be aware of it. Without quoting relative figures the selection includes items from many different countries. To sum up, this Bibliography represents an essential source of information and should be available in every library concerned with food science and technology. Many readers of this Journal will wish to have their own individual copies.

ROLAND HARPER

## Books Received

**Technological Forecasting and Corporate Strategy.** Ed. by GORDON WILLS, DAVID ASHTON and BERNARD TAYLOR.
Bradford University Press and Crosby Lockwood, London, 1969. Pp. 273 + xviii 90s.

**Soluble Tea Production Processes.** By NICHOLAS PINTAURO.
U.S.A.: Noyes Development Data Corporation, 1970. Pp. 183. $35.

**Fresh Meat Processing.** By ENDEL KARMAS.
U.S.A.: Noyes Data Corporation, 1970. Pp. 236. $35.

**Proceedings of International Symposium on Sensory Evaluation of Food—Principles and Methods.** (Sept. 9–13, 1968)
S.I.K. Goteborg, 1969. Pp. 56.

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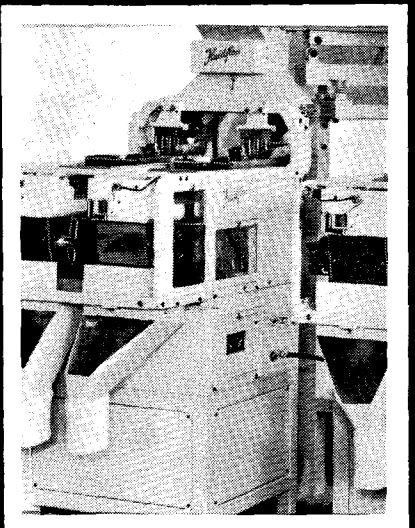

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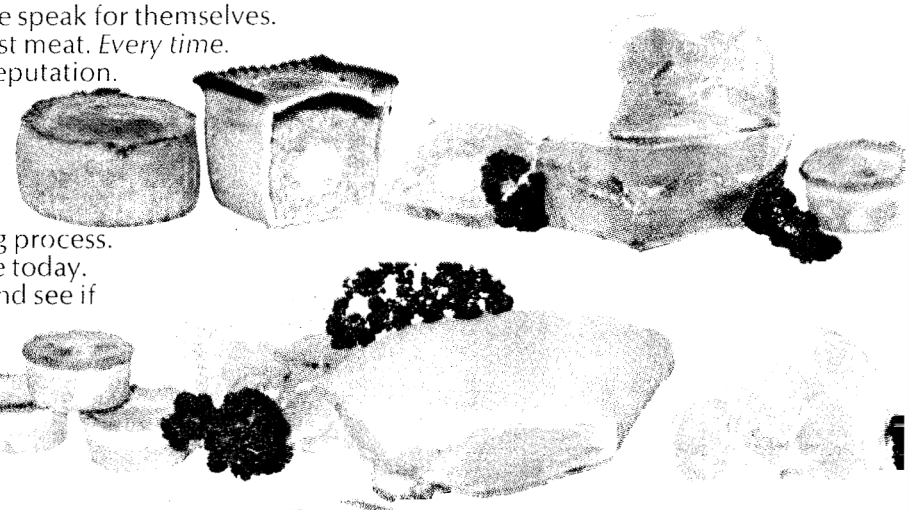

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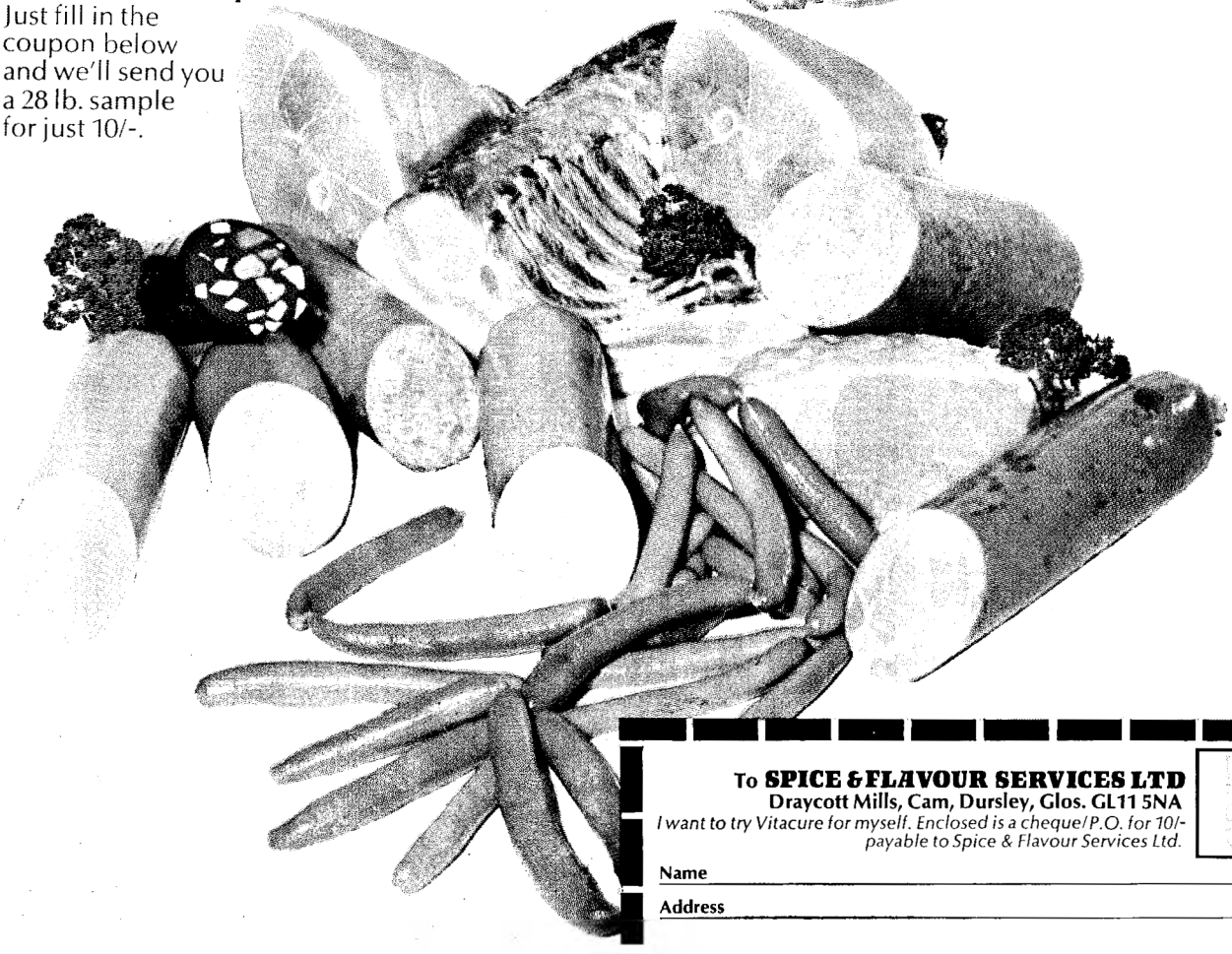

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Volume 24, Number 2, June 1970

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