VOLUME 5 NUMBER 1 MARCH 1970

JOURNAL OF FOOD TECHNOLOGY

PUBLISHED FOR

THE INSTITUTE OF FOOD SCIENCE AND TECHNOLOGY (U.K.)

BY

BLACKWELL SCIENTIFIC PUBLICATIONS

OXFORD AND EDINBURGH

JOURNAL OF FOOD TECHNOLOGY

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

Contributions and editorial correspondence should be sent to Mr W. B. Adam, George and Dragon Cottage, Chipping Campden, Glos.

General correspondence should be sent to Dr E. H. Steiner, British Food Manufacturing Industries Research Association, Randalls Road, Leatherhead, Surrey; and items for the Proceedings to Mrs J. V. Russo, 2 Hexham Gardens, Isleworth, Middlesex.

Objects of the Journal. The Journal covers a wide field ranging from pure research in the various sciences associated with food to practical experiments designed to improve technical processes. While the main object is to provide a forum for papers describing the results of original research, review articles are also included. The Editor welcomes papers from food scientists and technologists. These must be of a high standard of original research or comprehensive reviews of specialized sections of food science or technology.

Business matters, including correspondence and remittances relating to subscriptions, back numbers, advertising and offprints, should be sent to the publishers: Blackwell Scientific Publications Ltd, 5 Alfred Street, Oxford OX1 4HB.

The Journal of Food Technology is published quarterly, each issue consisting of 90–120 pages; four issues form one volume. The annual subscription is £7 ($24.00) post free; the price per issue is 40s ($6.50). Back volumes are still available at £6 ($20.00).

The Institute of Food Science and Technology of the United Kingdom was established in 1964. It is a professional qualifying organization having the following grades of membership: Fellows, Associates, Licentiates and Students. Application forms and information about the Institute can be obtained from the Honorary Secretary, Dr R. M. Johnson, Department of Food Science and Technology, Borough Polytechnic, Borough Road, London, S.E.1.

J. Fd Technol. (1970) 5, 1–32.

Rheology in food research

G. W. WHITE

Summary

A survey of rheology and its applications in the food industry is presented. The subject is considered under the headings of psycho-rheology, basic concepts in rheology, instrumentation for research, time-dependent materials and methods of interpretation (eighty-eight references).

Psycho-rheology

Food rheology can be defined as the study of the deformation and flow of the raw materials, the intermediate products and the final products of the food industry. Psycho-rheology is concerned with the relationship between consumer preferences and rheological properties. Szczesniak & Kleyn (1963) of the General Foods Corporation of America, have studied consumer awareness of texture and the terms used to describe texture. Word-association tests were conducted with seventy-four different foods, and a panel of 100 people. The percentage responses to the various attributes were: texture 32·1%, flavour 26·7%, colour 16·0%, form or temperature 12·5%, appearance 6·5%, aroma 2·1% and others 4·0%. These results suggest that the consumer is highly aware of texture. Of seventy-seven texture terms used by the panel, twenty-one of

TABLE 1. Rheological assessments made by consumers (from Szczesniak & Kleyn, 1963)

Term	No. of times used	Term	No. of times used	Term	No. of times used
Chewy	58	Greasy	30	Soft	78
Creamy	67	Hard	41	Sticky	32
Crisp	219	Juicy	104	Stringy	47
Crunchy	67	Light	37	Tender	31
Dry	117	Moist	34	Texture	58
Flaky	36	Mushy	33	Thick	29
Fluffy	30	Smooth	52	Wet	31

Authors' address: Lyons Central Laboratories, 149 Hammersmith Road, London, W.14.

them were used more than twenty-five times, and these are shown in Table 1, together with the number of times mentioned. Harper (1967) has also given a selection of words used to describe texture and consistency, as shown in Table 2.

TABLE 2. Subjective terms used to describe texture and consistency (from Harper, 1967)

Terms used subjectively			
Chalky	Juicy	Sandy	Thick
Crisp	Lean	Short	Thin
Doughy	Limp	Sleepy	Tough
Firm	Lumpy	Slimy	Treacly
Flabby	Mushy	Slushy	Viscous
Flaky	Oily	Soft	Watery
Fleshy	Powdery	Springy	Waxy
Floury	Ripe	Sticky	Woody
Greasy	Rotten	Syrupy	
Hard	Rubbery	Tender	

Food rheology is concerned basically with trying to measure objectively the qualities described in Tables 1 and 2. The practical reasons for undertaking such measurements are to remove product defects, to maintain product characteristics (quality control), to improve products above existing levels and as an aid in new product development.

Having discovered what texture characteristics the consumer was aware of, Szczesniak (1963) then made an analysis of the terms used and found that they could be classified into: (a) mechanical characteristics; (b) geometrical characteristics; and (c) other characteristics, referring mainly to moisture and fat content. The mechanical characteristics were divided into five primary parameters (hardness, cohesiveness, viscosity, elasticity and adhesiveness) and three secondary parameters (brittleness, chewiness and gumminess), as shown in Table 3, which also gives corresponding popular terms.

The next step in the investigation of Szczesniak was the objective measurement of the primary and secondary parameters of texture. This was done on an instrument known as the General Foods Texturometer (Friedman, Whitney & Szczesniak, 1963), which was developed from an earlier instrument, the M.I.T. denture tenderometer (Proctor, Davison & Brody, 1955, 1956a, b). The basic system of the G.F. texturometer is that of a plunger which compresses the sample at a standard rate of forty-two 'bites' per minute, the forces developed being measured by means of a strain gauge; for viscosity measurement a rotating paddle and cup are used. It is claimed that with the texturometer, all the primary parameters of hardness, cohesiveness, viscosity,

TABLE 3. Szczesniak's primary and secondary texture characteristics (from Szczesniak, 1963)

Primary parameters	Secondary parameters	Popular terms
Hardness		Soft, firm, hard
Cohesiveness	Brittleness	Crumbly, crunchy, brittle
	Chewiness	Tender, chewy, tough
	Gumminess	Short, mealy, pasty, gummy
Viscosity		Thin, viscous
Elasticity		Plastic, elastic
Adhesiveness		Sticky, tacky, gooey

elasticity and adhesiveness can be measured. The secondary parameters of brittleness, chewiness and gumminess are calculated from combinations of the primary parameters. A further refinement planned for the texturometer is the injection of enzymes to simulate salivary action during mastication.

Quantitative data have been obtained from taste panels for correlation with the objective parameters obtained from the texturometer. Szczesniak, Brandt & Friedman (1963) used a trained taste panel of nine members to choose and assign quantitative scores to several series of food products which would represent equal steps of hardness, brittleness, chewiness, gumminess, adhesiveness and viscosity. For example a standard rating scale for *hardness* was set up by assigning panel scores of 1–9 to cream cheese, hard-cooked egg white, uncooked frankfurters, yellow cheese, olives, peanuts, carrots, peanut brittle and rock candy. Good correlations were found between the panel scores and the texturometer readings for all six parameters studied. A description of panel techniques using these standard rating scales has been given by Brandt, Skinner & Coleman (1963).

It is very important to keep a clear distinction between what is perceived subjectively and what is measured objectively. It is often possible to represent the connection between the two by means of an equation:

$$\psi = k\varphi^n, \tag{1}$$

where ψ = the psychological magnitude (e.g. a panel score),
φ = the physical magnitude of the stimulus (instrumental measurement), and
k and n = constants.

The exponent n varies according to the stimulus and usually lies between 0·5 and 2 (Scott Blair, 1958; Wood, 1967). The naming fallacy occurs when an objective

measurement is given a subjective name, and it is then assumed that the objective test necessarily measures the subjective quantity (Harper, 1967). The great care needed in establishing and interpreting correlations between objective and sensory texture measurements has been emphasized in a recent publication by Szczesniak (1968). In the foreword to a survey by Gordon (1967), Steiner has suggested that further work on texture measurement should aim at developing the rheological aspects from the theoretical standpoint and relating them to the sensory assessment.

In addition to the publications already cited, a number of general reviews and symposia on food rheology are worth mention. These include publications by Scott Blair (1948, 1949, 1953, 1954, 1958), the Society of Chemical Industry Symposium on *Texture in Foods* (1958), a book by Matz on *Food Texture* (1962) and the recent Society of Chemical Industry/British Society of Rheology Symposium on *Rheology and Texture of Foodstuffs* (1967).

Basic concepts in rheology

Many books have been written on the fundamentals of rheology; particularly recommended are those by Scott Blair (1949, 1969), Eirich (1956–69), Reiner (1960), Fenner (1965) and Van Wazer *et al.* (1966).

Most readers will be familiar with Hooke's law of elasticity and Newton's law of viscosity. According to Hooke's law, if a stress (force per unit area) is applied to a body, the strain produced (fractional change in volume, length, etc.) is proportional to the stress, or:

$$P = cS, \tag{2}$$

where P is the stress (dynes/cm^2) and S is the strain (a pure number). The constant c may be the bulk modulus, K (when the specimen is subjected to a uniform pressure), Young's modulus, Y (when the specimen is stretched uniaxially) or the shear or rigidity modulus (when the material is sheared or twisted). Newton's law of viscosity states that the shear rate, $\dot{S}$ (sec^{-1}) in a liquid is directly proportional to the shear stress, P (force per unit area), or:

$$P = \frac{F}{A} = \eta \frac{dv}{dx} = \eta \dot{S}, \tag{3}$$

where dv/dx (sec^{-1}) is the velocity gradient or shear rate between two parallel planes in the liquid, each of area A, separated by a distance dx, and F is the force (dynes) acting on the area A, and responsible for the velocity gradient. The quantity dv/dx can also be regarded as the rate of change of shear strain with time, denoted by $\dot{S}$ ($=ds/dt$).

In practice, very few foodstuffs follow such ideal laws, but exhibit intermediate and other characteristics. The British Rheologists' Club has considered the various possible

types of rheological behaviour, and has drawn up a scheme of classification (British Rheologists' Club, 1942), a simplified version of which is given in Fig. 1. More recently,

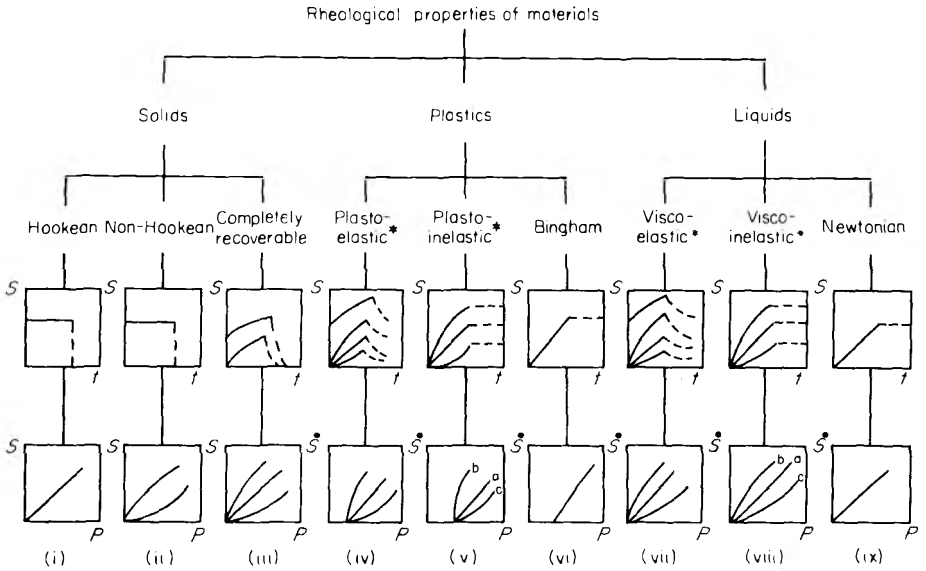


FIG. 1. Classification of rheological properties. P = stress (dynes/cm^2); $\dot{S}$ = shear rate (sec^{-1}); S = strain (a pure number; t = time (sec). *Upper and lower graphs cannot both be straight lines in these cases (see page 6).

some rheological definitions have been given by Reiner & Scott Blair (1967). In Fig. 1, two diagrams are given in each case. The upper graph shows how the shear strain varies with time when the material is subjected to a constant shear stress (solid curves), and how the strain decays on withdrawal of the stress (broken curves). The lower graph shows how the shear strain S or its rate of change with time, $\dot{S}$, varies with stress at a given time.

Some introductory notes on these different types of rheological behaviour are given below, followed by some examples of food products that fall in the various categories.

Hookean solids are those which obey equation (2). The deformation is recoverable immediately on removal of the stress.

Non-Hookean solids are those where the strain is not proportional to the stress, but the deformation is immediately recoverable as before.

Non-ideal elastic solids with completely recoverable deformation sometimes occur. Here the deformation and recovery show a time lag, and the strain–stress curve may have various shapes. The upper curve shows, firstly, an elastic strain, followed by a slow deformation.

Plasto-elastic materials show a yield value (critical stress) above which flow begins, and also partial recovery of the deformation when the stress is removed. The upper curve shows that an initial elastic strain can occur in this case.

Plasto-inelastic materials also show a yield value, but here there is no recovery after stress removal, and no possibility of initial elastic strain.

Bingham materials are those for which the shear rate is zero if the shear stress is less than or equal to a yield stress, and for which the shear rate is directly proportional to the increase in shear stress above this point. There is no recovery on removal of the stress.

Visco-elastic materials show no yield stress, and incomplete recovery when the stress is removed. Initial elastic strain may occur here as shown in the upper curve.

Visco-inelastic materials also show no yield value, but here there is no recovery on removal of the stress. If the curve is as shown in (b) the material is called a dilatant or shear-thickening fluid, and if as in (c) it is called a pseudoplastic or shear-thinning fluid.

Newtonian materials obey equation (3). There is no yield value, stress is directly proportional to shear rate, and no recovery occurs.

In Fig. 1 for the cases marked with an asterisk (*), the S–t and $\dot{S}$–P curves cannot both be straight lines, as this is a feature of Bingham and Newtonian materials. A 72-page report by Burgers & Scott Blair (1949) discusses in great detail the various cases given above.

Food products that show solid-like rheological behaviour include bread and some confectionery (e.g. boiled sweets), fruit, meat products (e.g. luncheon meat) and vegetables; it is probable that many solid food products show Hookean behaviour at low deformations. Plastic-like rheological behaviour is shown by concentrated emulsions, suspensions and foams including molten chocolate, fats, marzipan, mayonnaise and whipped creams. Liquid-like rheological behaviour of the Newtonian type is shown by water, solutions of inorganic compounds, sugar solutions, some beverages, organic solvents and some oils. Viscoelastic-type behaviour is shown by emulsions, gels, suspensions and foams including ice cream, melts and wheat flour dough, although strictly the last should be described as plasto-visco-elastic.

Instrumentation for research

Many different instruments for making rheological measurements have been described in the literature. Reviews on instrumentation for the measurement of food texture have recently been made by Gordon (1967, 1969).

Various authors have classified the available instruments in different ways. Scott Blair (1958) classified objective methods of texture measurement into: (a) fundamental, (b) empirical, and (c) imitative methods. Fundamental tests measure well-defined properties such as elastic modulus or viscosity, and complex systems can be explained by various combinations of these. Empirical tests measure parameters that are poorly defined, but which experience shows to be related to texture. Imitative tests measure various properties under test conditions similar to those to which the food is subjected in practice. In Table 4 are listed some examples of each type of

TABLE 4. Types of rheological instrument

Fundamental	Empirical	Imitative
Viscometers		
Orifice	Bloom gelometer	Butter spreaders
Falling ball	Cone penetrometer	Brabender farinograph
Capillary	Brinell hardness test	Chopin alveograph
Rotational	Consistometers	Brabender amylograph
Oscillatory	Warner–Bratzler shear apparatus	Volodkevich bite tenderometer
	Kramer shear press	Denture tenderometer
		G.F. texturometer
Mechanical testing apparatus		
Instron UTM		

instrument. Five other methods of classifying rheological instruments have been discussed by Bourne (1966).

The tendency now, in research, is to move away from empirical and purely imitative instruments to more fundamental and more versatile instruments, such as the Instron Universal Testing Machine (UTM) and the Ferranti–Shirley cone-plate viscometer, Haake Rotovisko or Weissenberg Rheogoniometer. The Instron UTM is particularly valuable for the more solid-like systems and the latter three, which are rotational viscometers, are of great use with liquid-like systems.

It is proposed to give a brief review of some of the apparatus used for routine rheological tests on solid, plastic and liquid-like systems, but a fuller description of two research-type instruments – the Instron UTM and the Ferranti–Shirley viscometer.

Solid-like systems

One of the most versatile instruments available for the rheological testing of solid-like systems is the Instron UTM (Hindman & Burr, 1949), available as either a floor or table model (Plate 1). It consists of two units – the crosshead loading assembly and the control console.

In the loading assembly, twin-drive screws move the crosshead upwards or downwards at a linear rate. Screw action and other types of grips can be fixed to the moving crosshead and to a tension cell (electrical strain gauge) in the upper fixed crosshead; this allows specimens to be stretched and measurements to be made of the elastic modulus, yield point, ultimate stress and ultimate elongation. Similarly, specimens can be placed on a compression table, which is in contact with a compression cell and the specimens compressed with flat circular plates and other types of plunger; this allows measurement of the modulus of axial compression, crushing strength, etc. An

advantage of the Instron UTM is that it can be fitted by the user with a wide variety of test probes and fixtures, such as compression discs, compression rods (flat or round ended), cones, needles, bending jigs; in addition, the working parts from any texture-measuring device that uses a linear movement can be fitted. One example of the many accessories used with the Instron UTM in our Laboratories is the device, adapted from the extensograph, for measuring the breaking strength of Swiss Rolls (Anon, 1968).

The chart gives a trace of load along the x-axis and distance (extension or compression) or time along the y-axis. The magnification is defined by the ratio:

$$M = \frac{\text{Chart speed}}{\text{Crosshead speed}}. \tag{4}$$

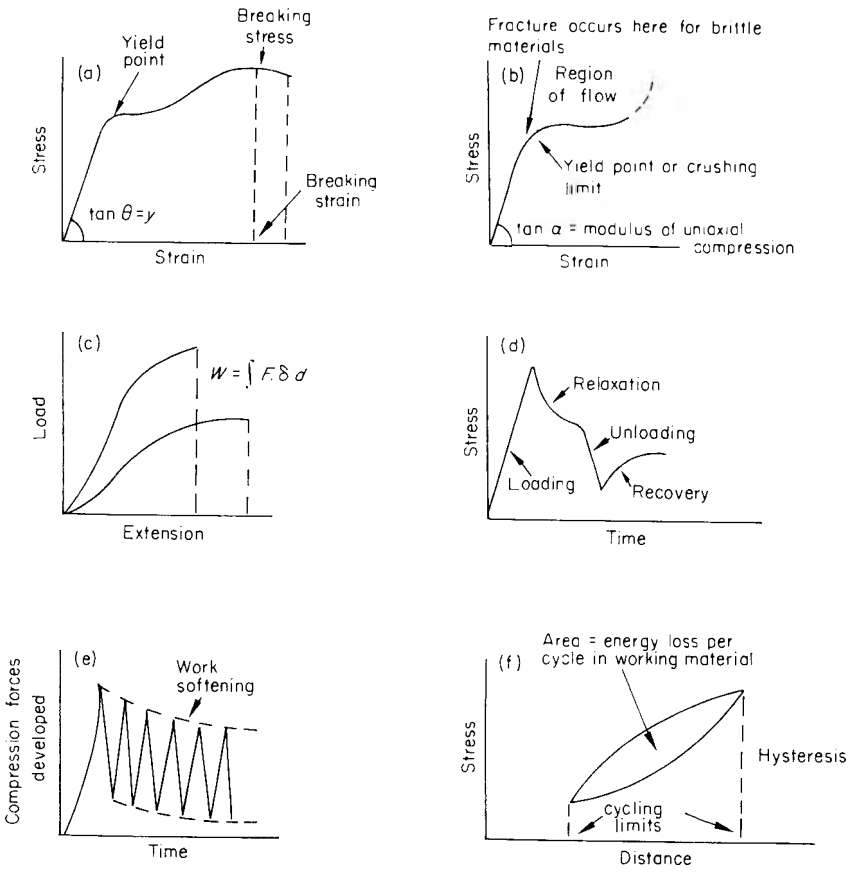


FIG. 2. Typical stress-strain curves obtainable on the Instron Universal Testing Machine. (a) Extension; (b) compression; (c) energy of rupture (area under curve); (d) stress relaxation and recovery; (e) strain cycling—normal chart run; (f) strain cycling—chart reversal.

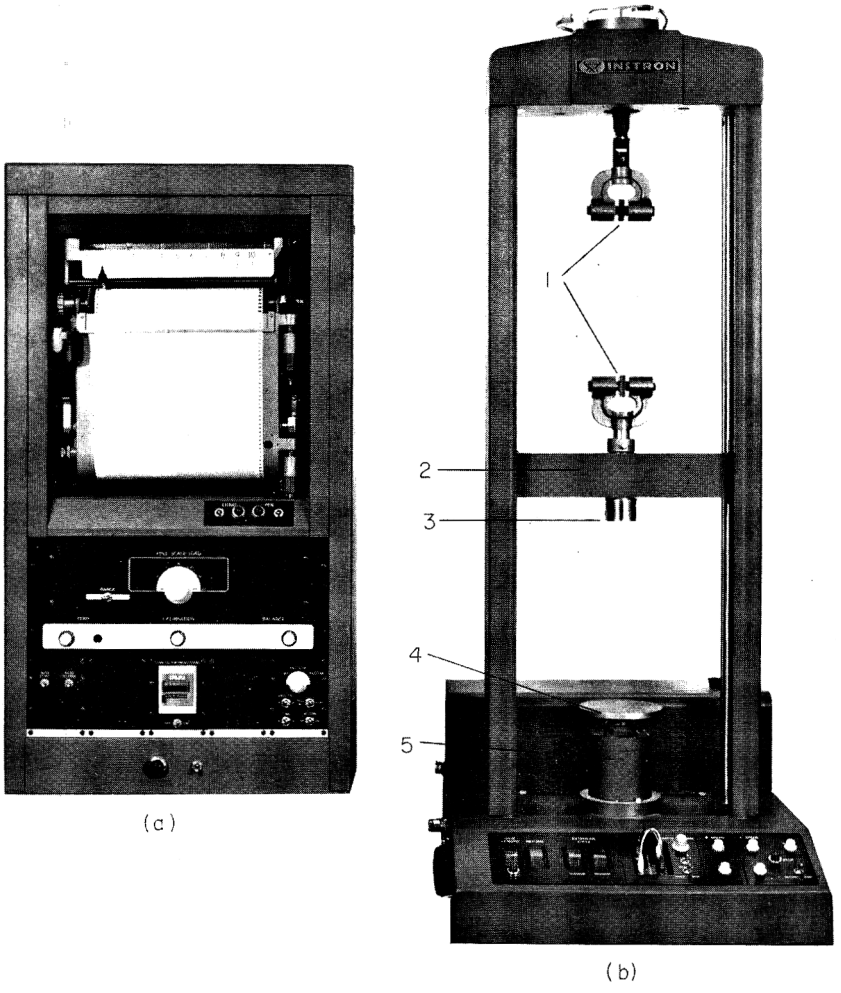


PLATE 1. Instron Universal Testing Machine (table model). (a) control console. (b) crosshead loading assembly: 1, screw action grips; 2, crosshead; 3, compression disc; 4, compression table; 5, compression cell.

(*Facing p.* 8.)

If the chart and crosshead speeds are identical, chart distance is a direct measure of extension or compression. Crosshead speeds are variable from 0·05 to 100 cm/min and chart speeds from 0·5 to 100 cm/min, so that the extension or compression distance can be magnified or reduced on the chart according to the speed of the phenomena. Accuracy of weighing is $\pm$ 0·25% and the pen response time is 1 sec for full scale deflection. The tension and compression cells on the table model allow forces up to 100 kg to be measured. According to Oldfield (1958) the forces developed by the molars in eating may reach about 45 kg, but Drake (1967) gives figures of 50–80 kg for the molars.

Many different types of curve can be obtained on the Instron UTM machine; a few examples are given in Fig. 2.

Fig. 2 (a) shows a typical stress–strain curve for elongation. The initial slope of the line gives *Young's modulus of elasticity*, Y, which for a cylindrical rod or a strip is given by:

$$Y = \frac{F/A_0}{\Delta l/l_0}, \tag{5}$$

where F is the applied force (dynes), A_0 the original cross-sectional area (cm^2), Δl the extension (cm) and l_0 the initial length of the sample. At the *yield point*, a rapid increase in extension occurs and the material begins to flow. The maximum stress and corresponding strain occur just before the breaking point, and are called the *breaking stress* and *breaking strain*, respectively. The breaking or ultimate stress is defined as the maximum load (dynes) divided by the original cross-sectional area. This is a measure of the cohesion of the material and, in food products, this is probably related to shortness, as judged subjectively.

Fig. 2(b) shows a stress–strain curve for compression. The initial slope defines the *modulus of axial compression*, E, which for a uniform cylinder of material compressed along the axis is given by equation (5) where Δl is now the compression. The yield point under compression is also known as the *crushing limit*. After this a region of flow is obtained which may be considerable for ductile materials, but very short for brittle materials, which tend to fracture at the yield point. The ultimate compressive strength or crushing strength may be defined as the load (dynes) at failure divided by the original cross-sectional area. It is, however, more advisable in compression testing to correct the stresses and strains to take account of changes in cross-sectional area. True stress is given by the load divided by the instantaneous area of the end faces, and true strain by $\log l/l_0$ (Fenner, 1965).

Fig. 2(c) shows elongation curves taken to the point of rupture. The energy of rupture is given by the work done in extension $\int F.\,\delta d$, which is also the area under the curve.

Fig. 2(d) shows the effect of straining a visco-elastic material, and then stopping the crosshead at a certain point. The material relaxes and the stress slowly falls. Similarly

if the strain is decreased so that the stress falls just to zero or a low value, and the crosshead is again stopped, the material will show stress recovery. Analysis of these *stress* relaxation and *stress* recovery curves is useful with materials such as doughs. The Instron UTM, however, is not suitable for studying *strain* relaxation and *strain* recovery.

Fig. 2(e) shows the effect of cycling between certain compression limits for a material that shows the phenomenon of *work-softening*; certain cakes show this type of phenomenon, and the general height of the curve is a measure of firmness.

Fig. 2(f) shows the effect of strain cycling again, between two extension or compression limits, but this time the chart is made to cycle backwards and forwards in synchronization with the crosshead. The resulting curve is called a *hysteresis loop*, and the area of the loop is a measure of the energy loss per cycle in working the material (the lost energy reappears as heat). This type of measurement may be of interest as an indication of the work expended during the mixing of liquids and solids.

Another type of test is the bending test. Here the specimen rests on two supports and a concentrated load is applied at the centre (three-point loading) or two concentrated loads are arranged symmetrically about the centre (four-point loading). The deflection at the centre for three-point loading is given by:

$$\delta = \frac{PL^3}{48IY} = \frac{MgL^3}{48IY}, \tag{6}$$

where P ($= Mg$) is the load (dynes), L is the length of the beam (cm), I is the moment of inertia of the cross-section about the neutral axis (for a circular section $I = Ar^2/4$ and for a rectangular section $I = Ab^2/12$, where A = cross-sectional area, r = radius and b = height of beam) and Y is Young's modulus, which can, therefore, be calculated. If the test proceeds to the point of fracture, the ultimate bending strength or modulus of rupture in bending, for a rectangular-section beam of area A and height b, is given (British Standard, 1322, 1956) by:

$$P = \frac{1{\cdot}5\,MgL}{Ab}. \tag{7}$$

Hardness in food products is a subjective term used to describe a conglomeration of various physical properties. It has been found, however, that it can be related to the peak force developed in compression (Friedman *et al.*, 1963).

The adhesion between food products and solid surfaces is often of interest, and the rheology of this phenomenon can also be studied on the Instron UTM.

Many interesting applications of the Instron UTM to food have been reported in the literature. Bourne, Moyer & Hand (1966) have published a comprehensive paper on the measurement of food texture with the Instron UTM. These workers have fitted

many parts to the instrument, including flat compression plates, a cylindrical compression box, assorted needles and punches with different diameters and shapes, single-needle and thirty-needle cherry pitters, the L.E.E.–Kramer shear-press cell, the Maturometer and a tube cutter. With these devices, texture tests were carried out on cherries, potato crisps, raw peas, canned snap beans, canned sliced apples, raw sweet corn and apples. The modulus of elasticity of individual wheat grains has been measured by Shelef & Mohsenin (1967) in connection with milling studies. A capillary rheometer for the Instron UTM has been designed by Sherr & Witnauer (1967), and used to obtain information on the flow behaviour of lard. Compression and puncture tests on apples have been carried out by Bourne (1965), who also studied the ripening of pears by measuring their texture profile on the Instron UTM, with a technique similar to that used in the G.F. Texturometer (Bourne, 1968). Cubes cut from apples and pears have been subjected to cyclic compression and stress relaxation studies, and the cytological significance of the results discussed (Somers, 1965). The tenderness of slices of roast pork has been evaluated on the Instron UTM by Kulwich, Decker & Alsmeyer (1963), and a test procedure for measurement of the textural properties of frankfurters has been established by Simon *et al.* (1965). The Maturometer test unit has been used in conjunction with the Instron UTM to study vining procedures and their influence on the quality of peas (Casimir *et al.*, 1967), and an extrusion type of test cell has been employed to evaluate the texture of fresh peas (Bourne & Moyer, 1968). The firmness of whole potatoes has been investigated by Bourne & Mondy (1967), while slices of raw potatoes have been subjected to cyclic elongation, stress relaxation and breaking, and cubes to cyclic compression and stress relaxation (Somers, 1965); the results were discussed in relation to cytology.

The rheology of finely-divided solids (i.e. powders), although of great interest in the food industry, is outside the scope of the present review, but it is noted that a vast literature exists on the flow properties of powders (Stairmand, 1967).

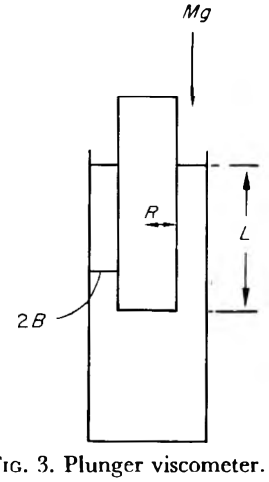


FIG. 3. Plunger viscometer.

Plastic-like systems

One of the simplest methods of studying plastic-like systems is with a plunger viscometer as shown in Fig. 3. This has been used by Bramhall & Hutton (1960) to predict the pumpability of lubricating greases through pipes, where low shear rates of 0·1–100 sec^{-1} usually apply. In the plunger viscometer the shear stress at the wall is:

$$P = \frac{Mg.2B}{2\pi LR(R + 2B)}, \tag{8}$$

while the shear rate at the wall is:

$$\dot{S} = \frac{3R\left(\frac{dL}{dt}\right)}{(2B)^2}. \tag{9}$$

A plot of $\dot{S}$ *versus* P gives for Bingham-type materials, at low shear stresses, a straight line whose intercept on the P axis gives the yield stress P_y, and whose slope is given by $(6d/2B\eta_p)$ where d is the thickness of the slip layer and η_p is the plastic viscosity.

Penetrometers have been widely used for the assessment of the rheological properties of fats and other materials. Usually a 150-g conical plunger is used, and the penetration after 5 sec is measured, starting from surface contact. The yield stress P_y can be calculated from the equation:

$$P_y = \frac{Kmg}{(h)^n}, \tag{10}$$

where K = $(1/\pi)\cos^2\alpha\cot\alpha$,
2α = apex angle of cone,
mg = force exerted by cone (dynes),
h = depth of penetration (cm), and
n = exponent, which has the value 1·6 for fats, but varies from one material to another.

Mottram (1961) has shown that the cone yield value and the yield stress derived from flow curves are closely related, while Haighton & Mijnders (1959) have used the yield value with considerable success to classify fats in respect of their spreading properties.

The FIRA/NIRD extruder (Prentice, 1954) is one of a number of extrusion-type instruments used for measuring the rheological properties of plastic-like materials. The instrument measures continuously the force required to extrude a cylinder of

material of $\frac{1}{2}$ in. diameter, $1\frac{1}{2}$ in. long through an orifice (normally $\frac{1}{8}$ in. diameter), by means of a plunger moving at uniform speed. Speeds of 0·017–0·066 cm/sec are available and forces up to 12 kg can be recorded.

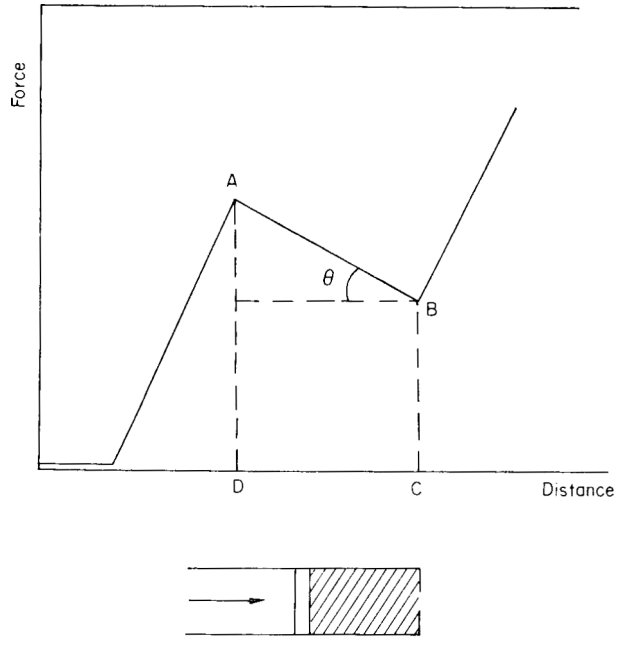


FIG. 4. FIRA/NIRD apparatus and extrusion diagram.

A typical trace from this machine might appear as in Fig. 4. When the thrust is sufficient the material begins to extrude (point A). The force at this point is the sum of the force required to overcome friction between the material and the wall of the sample cylinder and the force required to extrude the material though the orifice. As the material is extruded, the frictional resistance decreases, and the force falls to a minimum, at B, where the rod hits a stop. Measurements made from the trace are of

$$\text{Extruder friction} = \tan\theta \text{ (g/cm)}, \tag{11}$$

and

$$\text{Extruder thrust} = \text{CB (g)}. \tag{12}$$

The yield force is indicated by the height of the initial peak AD. The extruder friction is a measure of the stickiness of the sample, and for slippery materials such as jellies the friction is practically zero. The log (extruder thrust) for edible fats is linearly related to spreadability scores measured subjectively, and inversely related to subjective estimates of firmness. The area under the curve is a direct measure of the work

done during extrusion. Irregularities in the trace are an indication of inhomogeneity of the material. The extruder has been used to study the plastic properties of butter and margarine, compound fats, fondant, jelly, marzipan, pastry dough, etc.

More recently, Vasic & deMan (1967) have described an extrusion modification of the shear press, which can be used with lard, margarine and shortening; this could be fitted to the Instron UTM. Extrusion speeds of 0·04–0·06 cm/sec were used with the recorder set at about 25 kg FSD, and orifice diameters were 2, 4 and 6 mm. The extrusion diagram obtained had the form shown in Fig. 5.

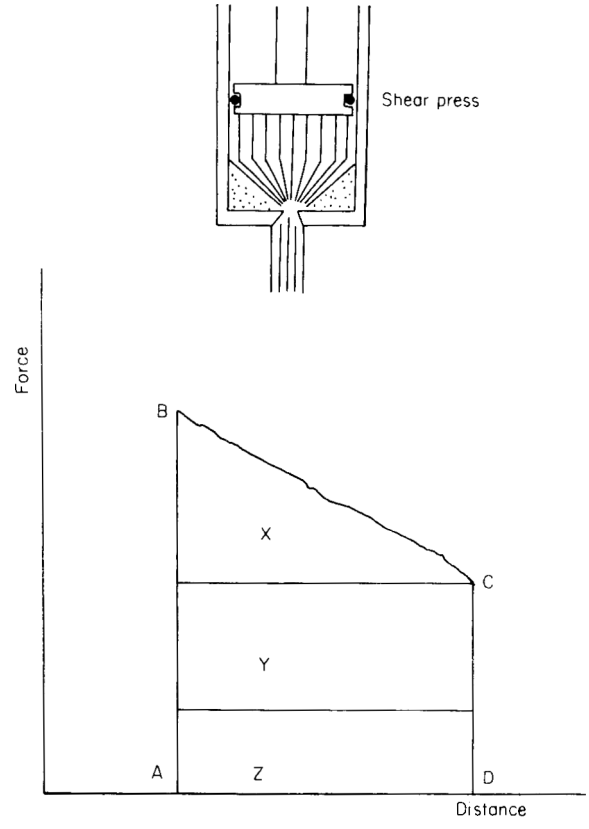


FIG. 5. Shear press and extrusion diagram.

Area X gives the work done in overcoming friction between the sample and the die (barrel). Area Z represents the work done overcoming friction between the plunger and the die, and is measured by repeating the stroke with an empty die. The remaining area Y represents the work done in actually extruding the material.

The extrusion pressure may be taken as the average force during the extrusion divided by the cross-sectional area of the extrusion die. Vasic & deMan (1967) have shown that the rate of deformation at the orifice for fats may be calculated from:

$$\dot{S} = \frac{2V_p(D_0 + d_0)}{(d_0)^2}, \tag{13}$$

where V_p = velocity of plunger,
D_0 = diameter of die, and
d_0 = diameter of orifice.

These workers also calculated the specific work of extrusion per gram, which they found to be linearly related to the rate of deformation, and determined the work softening by measuring the penetrometer yield value before extrusion (p_0) and after extrusion (p_w) and by use of the expression:

$$\text{Work softening } (\%) = \frac{(p_0 - p_w) \times 100}{p_0}. \tag{14}$$

Similar work has been described by Scherr & Witnauer (1967) who used a capillary extrusion rheometer on the Instron UTM to determine the flow characteristics of lard.

There are many other designs of plastometer (Scott Blair, 1949; Eirich, 1956–67; Van Wazer *et al.*, 1966) which cannot be described here, but mention must be made of rotational viscometers, which are often used with the more liquid-like plastic systems. Rotational viscometers used in research include several well-known types, such as the Ferranti portable viscometer, Haake Rotovisko, Ferranti–Shirley cone-plate viscometer and the Weissenberg Rheogoniometer. The first of these is a concentric-cylinder viscometer, the Haake instrument may be obtained with a wide variety of cups and rotors including coaxial cylinder and plate-and-cone combinations, and the last two are essentially cone-plate instruments.

Co-axial cylinder viscometers are well suited to the study of Newtonian liquids, but with plastic fluids considerable manipulation of the experimental data is necessary to obtain correct shear rates, yield values and plastic viscosities, especially in those cases where partial plug flow occurs in the viscometer. For this reason research investigators are turning more to the cone-plate type viscometer for the study of plastic and other non-Newtonian fluids (Van Wazer *et al.*, 1966).

The Ferranti–Shirley cone-plate viscometer (McKennell, 1954, 1956) consists of a stationary, flat, circular plate and a slightly conical rotating disc driven by a variable speed motor (Fig. 6). The included angle between cone and plate is $(\frac{1}{3})°$ and the apex of the cone (upper element) just touches the surface of the plate (lower element). When the sample fluid ($< 0{\cdot}5$ ml) is sheared in the cone-plate gap, the torque due to the viscous drag on the cone is measured by a dynamometer, and converted either to a pointer reading on an electrical meter or fed to an X–Y recorder, which gives a plot of the flow curve [rev/min (Y) *versus* torque (X)]. The plate is provided underneath

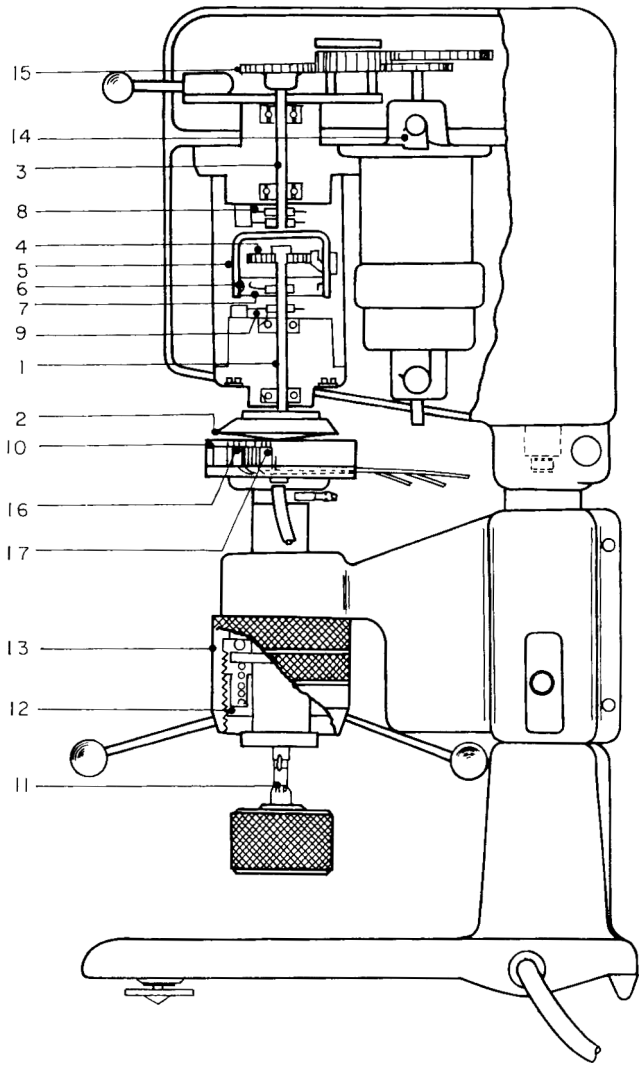


FIG. 6. Sectional diagram of the Ferranti–Shirley cone-plate viscometer. 1, Cone spindle; 2, cone; 3, driving spindle; 4, torque spring (torque dynamometer); 5, bridge housing; 6, potentiometer (torque dynamometer); 7, wiper for potentiometer; 8, slip rings; 9, slip ring; 10, plate; 11, micrometer; 12, nut (for raising plate); 13, screw (for raising plate); 14, driving motor; 15, gearing; 16, thermocouple; 17, water jacket.

with a jacket through which water at constant temperature may be circulated; thermocouples embedded in the plate are in direct contact with the sample fluid whose temperature may therefore be measured. The d.c. motor-generator supplies a voltage directly proportional to the rotational velocity; this voltage is compared with a reference voltage in an amplifier unit, and the potential difference after amplification is fed to the motor, so that the cone speed is independent of the viscous drag. Precise

adjustment of the cone with respect to the plate is obtained by means of a micrometer screw, and the gap can be accurately and reproducibly set to within 0·0001 in. Normally three cones are supplied with the instrument.

The complete range of speeds available is 0·1–1000 rev/min, corresponding to shear rates of approximately 1–20,000 sec^{-1}. The maximum shear stress measurable is of the order of 568,000 $dyne/cm^2$, and maximum viscosity approximately 32,000 poises. The speeds may be manually selected or programmed in various ways. Tufnol insulated cones are available for use in the temperature range 30–100°C, and a special measuring unit and ceramic insulated cones for use up to 200°C.

The principal advantages of the Ferranti–Shirley cone-plate viscometer are that it is well suited to the study of non-Newtonian fluids, the shear rate is uniform throughout the sample, only a small sample is needed, filling, cleaning and operation are easy, and the sample temperature is stable. The outstanding advantage is that of uniform shear rate, so that with plastic systems no complicated manipulation of data is needed to obtain the true shear rate.

The main disadvantage is that the normal cone-plate system is not suitable for coarse suspensions where the particle size exceeds 36 μm. However, flat-apex cones in stainless steel, Tufnol-insulated or ceramic-insulated are available for coarser suspensions.

It can be shown (Dinsdale & Moore, 1962) for the cone-plate system that the shear rate in the gap, at a distance r from the axis, is given by:

$$\dot{S} = \frac{\Omega}{\alpha}, \tag{15}$$

where Ω = angular velocity (radians/sec), and
α = cone-plate angle (radians),
and this is independent of r.

The shear stress, therefore, is also independent of r, and is given by:

$$P = \frac{3T}{2\pi R^3}, \tag{16}$$

where T = total torque (dyne cm), and
R = radius of cone-plate system (cm).

For Newtonian fluids the viscosity:

$$\eta = \frac{P}{\dot{S}} = \frac{3T\alpha}{2\pi R^3 \Omega}. \tag{17}$$

The shear stress or viscosity is directly proportional to the scale reading on the instrument. A recent paper by Cheng & Davis (1968) has examined the accuracy of the cone-plate system, and pointed to the need for careful calibration of each system.

For non-Newtonian materials, including plastic systems, it is better to plot flow curves (i.e. shear rate *versus* shear stress, viscosity *versus* shear stress or viscosity *versus* shear rate). Measurements can be made of yield value, plastic viscosity, shear-rate thinning and other anomalous flow properties. In the case of plastic systems, various types of flow curve are possible.

Fig. 1(v) shows shear rate–shear stress curves for: (a) a Bingham plastic, (b) a dilatant material with a yield value, and (c) a pseudo-plastic material with a yield value. Only when the shear stress exceeds the yield stress does the material begin to flow. A Bingham plastic is one that follows the linear law:

$$\dot{S} = \frac{1}{\eta_p}(P - P_y), \tag{18}$$

where $\dot{S}$ = shear rate ($\sec^{-1}$),
η_p = plastic viscosity (poise),
P = applied shear stress (dynes/cm^2), and
P_y = yield stress (dynes/cm^2).

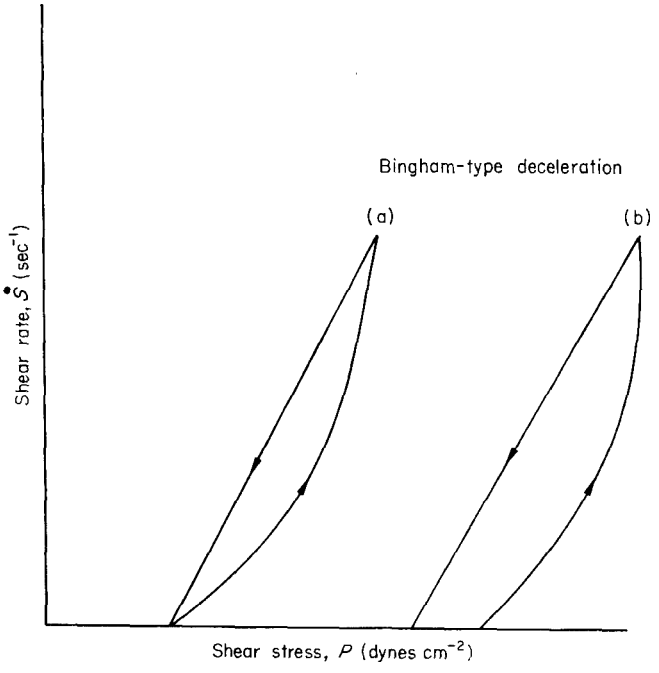


FIG. 7. Hysteresis curves in plastic systems.

Many plastic systems show time-dependent flow properties, and simple reversible curves of the above type are insufficient to characterize the material. Thixotropic materials become gradually thinner when sheared and thicken again when allowed to rest. Rheopectic materials show the opposite effect, becoming thicker when sheared, and thinner when allowed to rest. In general, shear-thickening and shear-thinning phenomena may be completely reversible, partially reversible or irreversible.

One method of investigating such materials is to determine the hysteresis curve (Fig. 7) by increasing the shear rate, in definite steps and at definite time intervals, to a maximum, and then in steps down to zero again.

Various types of hysteresis curves are possible and, in principle, the 'down curve' may be of the Newtonian, Bingham, pseudo-plastic or dilatant type. In practice, the Bingham case is often met with, and the down curve may form: (a) a closed loop (fast structure recovery), or (b) an open loop (slow structure recovery); shortenings give the latter type of curve. With these hysteresis curves, the area of the loop can be taken as a measure of thixotropy (see next section) provided that the shear rate *versus* time history is standardized. McKennell (1960) has described several other mathematical methods of characterizing these curves, and a paper by Hediger (1968) also discusses the treatment of non-Newtonian flow data including hysteresis curves.

Liquid-like systems

One of the simplest methods of measuring viscosity is with an orifice or efflux viscometer, in which the time required for a given volume of liquid to flow out is measured. The kinematic viscosity (υ) in stokes is given by the equation:

$$\upsilon = \frac{\eta}{\rho} = At - \frac{B}{t}, \tag{19}$$

where η is the viscosity (poises), ρ the density (g/ml), A and B are constants and t is the efflux time (sec). The constant B is often ignored in this expression. Data on the constants of these viscometers have been summarized by Gardner & Sward (1962) and van Wazer *et al.* (1966). This type of viscometer is widely used in industry, but is not very suitable for complex, non-Newtonian fluids because the flow conditions are ill-defined.

Capillary viscometers are more accurate, and recommendations for their use have been laid down in British Standard 188 (1957). Equation (19) is also applicable to capillary-type viscometers. When the kinematic viscosity is greater than 10 cS (centistokes) or a very long flow time is obtained, the kinetic energy correction (B/t) can be neglected. Capillary viscometers are calibrated either by means of standard fluids (Newtonian oils or solutions) or by a step-up procedure, as described in British Standard 188 (1957). With standard fluids, calibration is effected by measuring the flowtimes of two liquids, one liquid having a flow time two or three times greater than

the other. The constants A and B are then obtained by solving two simultaneous equations of type (19). Capillary viscometry has been discussed by Oka (1960), McKennell (1960), Dinsdale & Moore (1962) and van Wazer *et al.* (1966). The effects on flow time of tilting an Ostwald viscometer have been treated by Langton & Vaughan (1965), while the use of photoheads for capillary viscometers has been described by Lawrence (1966). Capillary viscometers are mainly used with Newtonian liquids, although the theory can be extended to materials following a Bingham law or even a power law.

The viscosity of Newtonian liquids can also be determined by means of falling or rolling sphere, rising bubble, falling cylinder, parallel plate compression, parallel plate sliding and vibrating reed viscometers. For non-Newtonian liquids it is better to use a rotational viscometer. In general, rotational viscometers may be of the rotating disc type, single cylinder type, co-axial cylinder type, conicylindrical type, cone and plate type or of the types with other-shaped rotors (e.g. paddle rotors as in the Stormer viscometer). The cone-plate type is best for non-Newtonian liquids, because the shear rate is uniform throughout the sample and easily obtained from the rotational frequency (rev/min). The shear rate and shear stress for this type of viscometer are given by equations (15) and (16), respectively.

The flow curves or rheograms for liquid systems may have various forms as in Fig. 1. Newtonian systems are characterized by the equation:

$$\dot{S} = \left(\frac{1}{\eta}\right) P = \varphi P, \tag{20}$$

where $\varphi = 1/\eta$ = fluidity (in rhe),
$\dot{S}$ = shear rate (in $\sec^{-1}$), and
P = shear stress (in dynes/cm^2).

The flow curve ($\dot{S}$ *versus* P) may be a straight line through the origin, as in equation (20), or may show curvature as in Fig. 1(vii) and (viii). If the curvature is as in (b)

TABLE 5. Sub-classification of anomalous fluid flow curves

		Time-dependent	
	Time-independent	Reversible	Irreversible
Shear thinning	Pseudo-plastic	Thixotropic	Permanent work softening
Shear thickening	Dilatant	Rheopectic	Permanent work hardening

the system is called dilatant (shear thickening) and if as in (c) the system is called pseudoplastic (shear thinning).

Visco-elastic and visco-inelastic materials differ from each other in that the former show recovery when the stress is removed (Fig. 1 vii).

A further sub-classification of fluid behaviour is shown in Table 5. Time-independent and time-dependent fluids are those for which, at a given shear rate, the shear stress is independent and dependent respectively on the time of shearing. Time-independent fluid behaviour includes pseudo-plastic and dilatant flow curves, either with a yield stress (i.e. plastic systems) or without a yield stress (liquid systems). Time-dependent fluids may show reversible or irreversible behaviour. Reversible shear-thinning behaviour is known as thixotropy, and reversible shear-thickening behaviour, which is rare, as rheopexy (Fig. 8). Thixotropy and dilatancy have been discussed by Bauer & Collins (1967).

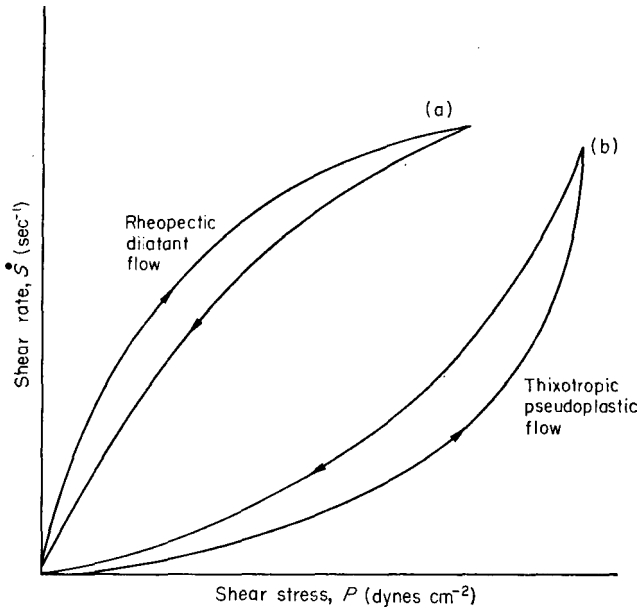


FIG. 8. Rheopectic (a) and thixotropic (b) flow curves.

When irreversible changes (rheodestruction) take place on shearing, we have the phenomena of permanent work softening or hardening. All these types of behaviour can be found in plastic systems.

There are a number of special viscosity terms that are widely used with dilute solutions, as follows:

The viscosity ratio or relative viscosity:

$$\eta_r = \frac{\eta}{\eta_0}, \tag{21}$$

where η, η_0 are the viscosities of solution and solvent, respectively.

The specific viscosity:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1. \tag{22}$$

The limiting viscosity number or intrinsic viscosity:

$$[\eta] = \lim_{c \to 0} \left(\frac{d\eta_{sp}}{dc} \right) \tag{23}$$

where c is the volume concentration (g/ml). That is, the intrinsic viscosity is the slope of the η_{sp} *versus* c curve at zero concentration.

An equation much used for determination of the viscosity-average molecular weight of polymers is the Houwink law:

$$[\eta] = aM^b. \tag{24}$$

The constant a usually lies between 10^4 and 10^7, and b between 0·5 and 1·0. When $b = 1$, the equation is known as the Staudinger law.

Many workers have investigated the dependence of viscosity on temperature and concentration. In many cases the temperature dependence can be represented by the equation suggested by Andrade:

$$\eta = Ae^{E/RT}, \tag{25}$$

where E is the activation energy of flow, and T the absolute temperature.

For many systems, over a limited temperature range a plot of log η *versus* I/T is linear. The temperature coefficient of viscosity for liquids is of the order of 1–30% per °C, so that temperature control to 0·1°C or better is often necessary.

The dependence of viscosity on concentration (c) in the case of solutions, emulsions and suspensions is usually represented by an equation of the form:

$$\eta_{sp} = \sum_{n = 1, 2, 3, \text{ etc.}} \alpha_n c^n. \tag{26}$$

A large number of such equations, and also equations of other types, have been developed by various workers for relating viscosity to concentration and these have been discussed by Scott Blair (1949), Frisch & Simha (1956), Sherman (1968) and others.

Time-dependent materials

Time-dependent materials are those which show creep under constant load, or stress relaxation at constant extension or compression; such materials exhibit some combination of elastic, plastic and viscous behaviour (Fig. 1 iii, iv, and vii). Examples include biscuit and bread doughs, cheese, corn and wheat grain, fruits, gels, ice cream and potatoes. Special methods have been developed for the experimental analysis of these systems; these methods include: (a) creep and recovery experiments, (b) stress relaxation and recovery experiments, and (c) oscillatory tests. In a creep experiment, a constant stress is applied and the extension, compression, shear or torsion is measured as a function of time (Fig. 1). In stress relaxation experiments, a constant strain (e.g. extension or compression) is applied and the stress is measured as a function of time (Fig. 2d). Recovery curves may be measured by removal of the stress or strain. The

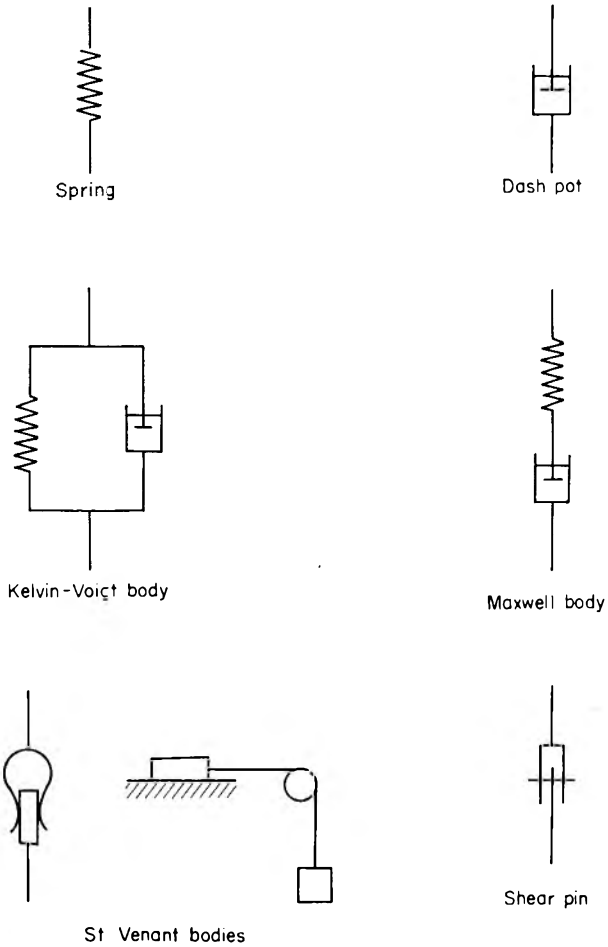


FIG. 9. Idealized rheological elements.

case of constant rate of deformation, as used in the Instron UTM machine, has been considered by Alfrey (1948).

Mechanical models are sometimes used to represent creep and relaxation curves. For visco-elastic materials two basic elements are used—the spring, representing elasticity, and the dashpot, representing viscosity (Fig. 9). These idealized bodies have rigorously defined rheological properties (Reiner, 1960). For the spring, the stress (P) and strain (S) are given by $P = ES$, where E is the effective rigidity or shear modulus, and for the dashpot the stress (P) and rate of strain ($\dot{S}$) are given by $P = \eta\dot{S}$, where η is the effective viscosity. These elements can be combined in parallel to give a Kelvin–Voigt body, and in series to give a Maxwell body (Fig. 9). In the parallel combination, the strain in each element is the same, but the stresses are additive, while in the series combination, the stress in each element is the same, but the strains are additive.

For the Kelvin–Voigt body. Total stress:

$$P = \eta\dot{S} + ES. \tag{27}$$

If a constant stress is applied (as in a creep experiment) the solution of equation (27) is:

$$S = S_\infty(1 - e^{-t/\tau}), \tag{28}$$

where S_∞ is the terminal strain and $\tau(= \eta/E)$ is the retardation time of the material.

For the Maxwell body. Total rate of strain:

$$\dot{S} = \frac{P}{\eta} + \frac{\dot{P}}{E}. \tag{29}$$

If a constant strain is applied, $\dot{S} = 0$ (as in a stress relaxation experiment), and the solution of equation (29) is:

$$P = P_0 e^{-t/\tau}, \tag{30}$$

where P_0 is the initial stress and $\tau(= \eta/E)$ is the relaxation time of the material.

In practice many such elements are needed to represent practical creep and relaxation curves, and additional elements are often necessary, such as a St Venant body depicting plastic yield stress, and shear pins, representing rupture above a specific stress.

The mathematical analysis of experiments on time-dependent materials normally assumes linear visco-elastic behaviour, so that the Boltzmann superposition principle

applies (Eirich, 1956, 1958). This assumption is only valid under strictly limited test conditions which usually imply very small strains.

Creep tests

Descriptions of experimental apparatus for creep studies have been given by various workers (Van Holde & Williams, 1953; Ferry, 1958; Shaw, 1963; Shama & Sherman, 1966; Sherman, 1966; Morrow & Mohsenin, 1966; Lerchenthal & Muller, 1967). The mathematical procedure for the analysis of creep curves has been set out in some detail by Alfrey (1948), Leaderman (1958), Shama & Sherman (1966) and Sherman (1966). The creep compliance ($\mathcal{J}$) is defined as the ratio of strain to stress at any time t, and can often be approximated by a Maxwell body, in series with several Kelvin–Voigt bodies, so that:

$$\mathcal{J} = \mathcal{J}_0 + \sum_{i=1}^{n} \mathcal{J}_i(1 - e^{-t/\tau_i}) + \mathcal{J}_N \qquad (31)$$

where $\mathcal{J}_0 (= 1/E_0)$ is the instantaneous elastic compliance and $\mathcal{J}_N (= t/\eta_N)$ the viscous compliance associated with the Maxwell body, and $\mathcal{J}_i (= 1/E_i)$ and $\tau_i (= \eta_i/E_i)$ are the time-dependent elastic compliance and retardation time, respectively, of the ith Kelvin–Voigt body.

This equation is fitted to the creep curve by a series of graphical approximations or by computer techniques, and in this way the various elastic moduli E_1, E_2, E_3, etc., and viscosities η_1, η_2, η_3, etc., needed to account for the creep curve are derived. These can then be displayed in a mechanical model representing the behaviour of the structure (Fig. 10).

Shama & Sherman (1966) have drawn some conclusions on the connection between the components of their model for ice cream and the actual structural elements shown to be present; in the case of wheat flour dough it is necessary to introduce dashpots (D), springs (S), sliders (SL) and shear pins (SP) to account for the behaviour of the material, and at the present stage of research it is not possible to relate the elements of the rheological model to the chemical structure (Lerchenthal & Muller, 1967). Shama & Sherman (1967) have also carried out creep studies on cakes, fish, margarine, meat and cooked potatoes.

Stress relaxation tests

Stress relaxation and recovery in solid-like materials may be studied by extension, uniaxial compression, etc., and the stress determined as a function of time after sudden imposition or removal of strain, or after cessation of steady state flow. Normally stress relaxation is studied under the latter conditions on the Instron, but instant extension can also be obtained if a lever to stretch the sample is built for attachment to the

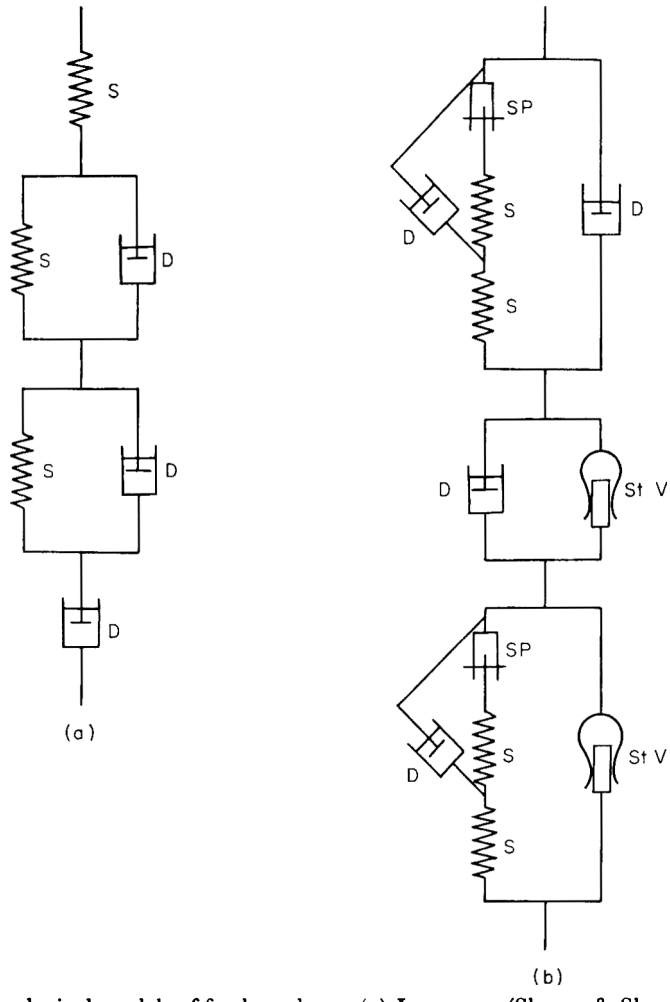


FIG. 10. Rheological models of food products. (a) Ice cream (Shama & Sherman, 1966); (b) wheat flour dough (Lerchenthal & Muller, 1967).

crosshead (Barney, Pollock & Bolze, 1965; Van Wazer *et al.*, 1966). Apparatus for stress relaxation studies on solids has been reviewed by Ferry (1958) and Morrow & Mohsenin (1966).

Stress relaxation in liquids may be studied by shear in a rotational viscometer. Stress–time curves are generally determined at zero shear rate (constant strain) or finite shear rates and the measurement may be conducted with a co-axial cylinder viscometer (Stainsby & Ward, 1949) or preferably a cone-plate viscometer (McKennell, 1960).

In practice, stress relaxation curves, at constant strain, can often be represented by a generalized Maxwell model consisting of a number of Maxwell bodies in parallel, so that:

$$E = \sum_{i=1}^{n} E_i e^{-t/\tau_i}, \tag{32}$$

where E_i and τ_i ($= \eta_i/E_i$) are the elastic modulus and relaxation time respectively of the i^{th} Maxwell body. More complicated mathematical functions have been used by Barney *et al.* (1965) in their study of stress relaxation in wheat gluten.

Morrow & Mohsenin (Morrow & Mohsenin, 1966; Mohsenin & Morrow, 1967) have reviewed work on creep and stress relaxation in selected agricultural products including cereal grains, fruit, and vegetables, and have reported creep and relaxation results for apple fruits.

Oscillatory tests

There is a growing interest in dynamic methods of rheological testing for visco-elastic materials. In these methods (Leaderman, 1958; Ferry, 1958), the body is subjected to a shear (or stress) varying sinusoidally with time, and the resulting stress (or strain) is measured. The complex modulus $E = |E| e^{i\varphi}$ where $|E|$ is the absolute modulus or ratio of peak stress to peak strain, φ is the phase angle between stress and strain, and $i = \sqrt{-1}$. This modulus can also be written as:

$$E = E' + iE'', \tag{33}$$

where E' (storage modulus) is the in-phase stress component divided by the strain, and E'' (loss modulus) is the out-of-phase stress component divided by the strain.

Alternatively, the stress may be separated into two components, one in phase with, and the other $\pi/2$ out of phase with the rate of strain. These components divided by the rate of strain give the real and imaginary parts of a complex viscosity:

$$\eta = \eta' - i\eta''. \tag{34}$$

An important relationship is $E'' = \omega\eta'$ so that:

$$E = E' + i\omega\eta', \tag{35}$$

E' and η' are two independent characteristics of the material, sometimes known, respectively, as the dynamic elasticity and dynamic viscosity. It is usual to express the results as response curves of E' and E'' or E' and η' against log ω where ω is the angular frequency ($2\pi f$).

Ferry (1958) and Mohsenin & Morrow (1967) have reviewed many of the experimental techniques for the dynamic (sinusoidal) testing of visco-elastic bodies. These methods include oscillating cylinder viscometers (Oka, 1960) and also oscillatory

cone-plate viscometers such as the Weissenberg rheogoniometer (Walters, 1968). The latter can now be used in conjunction with a Solartron transfer function analyser to give E' and η' directly in digital read-out form.

These dynamic methods have the advantage of giving two parameters only, representing the elastic and viscous characteristics of the material. The method has already been applied to doughs by several workers (Shimizu & Ichiba, 1958; Tschoegl, 1961; Hibberd & Wallace, 1966; Hibberd, Wallace & Wyatt, 1966; Hibberd, 1968) to study the short-time response characteristics, and to other products such as apples, corn and potato tissues (Mohsenin & Morrow, 1967).

Methods of interpretation

Scott Blair (1949) has drawn a useful distinction between two schools of rheological interpretation: (a) the analytical school, concerned with drawing conclusions about the structure of materials from rheological measurements; and (b) the integrative school, concerned with empirical mathematical description of the behaviour of materials as a whole.

In the analytical method, the rheological measurements made on complex bodies are explained by adding together idealized elastic, plastic, viscous and other elements, in such a way and in such numbers so as to account mathematically for the observed measurements. The idealized elements used are springs, sliders or spring clips, dashpots and shear pins (Fig. 9). These elements can be combined in series and parallel in a large number of different ways, and the rheological behaviour of each combination can be expressed mathematically. This approach has been discussed in some detail by Reiner (1960).

An advantage of the analytical approach is that complex rheological behaviour can be explained in terms of the interaction of a number of simple prototypes (Reiner & Scott Blair, 1967). A disadvantage is that in order to explain creep and relaxation in real materials, a large number of springs, dashpots, etc., must be postulated. Furthermore, having arrived at a many element model, it is difficult to relate the various elasticities, viscosities, etc., to the molecular elements of structure without a costly programme of work. Alfrey & Gurnee (1956) remark that 'it should be kept in mind that these models give a description only of the phenomenological behaviour of a sample and, in general, tell nothing of the detailed mechanisms that underlie this behaviour'.

Apart from model building, Reiner (1960) uses the term rheological analysis in a wider sense to mean the derivation of information about molecular structure from rheological measurements.

In the integrative method, data are plotted in the most convenient way using, where necessary, empirical power laws of various degrees of complexity. The stress–strain relationship for some solids is not linear, but becomes so with a log–log plot, and this implies that stress and strain are related by a power law:

$$P = AS^n, \tag{36}$$

where A and n are constants.

Similarly, some fluid flow curves can be represented by the Ostwald–de Waele law:

$$P = B(\dot{S})^n. \tag{37}$$

A Newtonian system has $n = 1$, a pseudoplastic system $n < 1$ and a dilatant system $n > 1$. In this case log P *versus* log $\dot{S}$ and log η *versus* log $\dot{S}$ are both linear.

Plasto-elastic and plasto-inelastic substances where a power law and a yield value apply can often be represented by:

$$P - P_y = C(\dot{S})^n, \tag{38}$$

where P_y is the yield stress and C, n are constants.

In this case log $(P - P_y)$ *versus* log $\dot{S}$ will be linear.

An important equation, which is a synthesis of simple power laws is the Nutting–Scott Blair equation, which is:

$$\psi = P^{\beta}S^{-1}t^{k}, \tag{39}$$

which relates ψ (a material constant) to stress (P), strain (S) and time (t). The meaning of ψ in this empirical equation can be illustrated by considering *Elastic solids*, for which $\psi = PS^{-1}t^0 = E$, where E = modulus of elasticity, *Viscous fluids*, for which $\psi = PS^{-1}t^1 = \eta$, where η = coefficient of viscosity.

ψ is a measure of intensity of firmness (Scott Blair, 1949), and can be regarded as a quasi-property characteristic of complex materials whose behaviour is intermediate between that of the Hookean solid and the Newtonian liquid. The constant β can be $>$ or $<$ 1, but k is usually < 1.

There are various ways of using the equation. If one of the three variables, P, S or t is constant, log–log plots of the other two should be linear. Thus in creep experiments, linear relationships have been obtained between log S and log t for such products as apple, bread, butter, cake, cheese, meat, potato, etc. (Scott Blair & Coppen, 1941).

The Nutting–Scott Blair equation undoubtedly applies in certain cases, but it must be admitted that for many materials it is inadequate.

Apart from the simple power law, many other equations have been proposed for the relationship between shear stress and shear rate in fluid flow. Discussions of many of these more complex relationships may be found in Skelland (1967), Sherman (1968) and Hediger (1968).

In conclusion we might say that the ultimate ideal in rheological interpretation is to

develop theories, based on molecular structure and chemical interaction, that will fully account for the observed data.

Acknowledgments

The author is indebted to Instron Ltd for Plate 1 and to Ferranti Ltd for Fig. 6, and also wishes to thank Mr K. G. Berger for helpful discussion in the preparation of this paper for publication.

References

ALFREY, T. (1948) *Mechanical Behaviour of High Polymers.* Interscience, New York.
ALFREY, T. & GURNEE, E. F. (1956) In EIRICH, F. R. (1956) Volume 1.
ANON (1968) *New Scient.*, **40,** 375.
BARNEY, J.E., POLLOCK, H.B. & BOLZE, C.C. (1965) *Cereal Chem.* **42,** 215.
BAUER, W.H. & COLLINS, E.A. (1967) In EIRICH, F.R. (1967) Volume 4.
BOURNE, M.C. (1965) *Fd Technol., Chicago,* **19,** 113.
BOURNE, M.C. (1966) *J. Fd Sci.* **31,** 1011.
BOURNE, M.C. (1968) *J. Fd Sci.* **33,** 223.
BOURNE, M.C. & MONDY, N. (1967) *Fd Technol., Chicago,* **21,** 97.
BOURNE, M.C. & MOYER, J.C. (1968) *Fd Technol., Chicago,* **22,** 1013.
BOURNE, M.C., MOYER, J.C. & HAND, D.B. (1966) *Fd Technol., Chicago,* **20,** 170.
BRAMHALL, A.D. & HUTTON, J.F. (1960) *Br. J. appl. Phys.* **11,** 363.
BRANDT, M.A., SKINNER, E.Z. & COLEMAN, J.A. (1963) *J. Fd Sci.* **28,** 404.
BRITISH RHEOLOGISTS' CLUB (1942) *Nature, Lond.* **149,** 197 and 702.
BRITISH STANDARD 188 (1957) *Determination of the Viscosity of Liquids in c.g.s. Units.* London.
BRITISH STANDARD 1322 (1956) *Aminoplastic Moulding Materials.* London.
BURGERS, J.M. & SCOTT BLAIR, G.W. (1949) *Proc. 1st Int. Congr. Rheology, Holland,* 1948. North-Holland, Amsterdam.
CASIMIR, D.J., MITCHELL, R.S., LYNCH, L.J. & MOYER, J.C. (1967) *Fd Technol., Chicago,* **21,** 109A.
CHENG, D.C.H. & DAVIS, J.B. (1968) *Rheol. Acta,* **7,** 85.
DINSDALE, A. & MOORE, F. (1962) *Viscosity and its Measurement.* Chapman & Hall, London.
DRAKE, B. (1967) S.C.I./B.S.R. *Symposium on 'Rheology and Texture of Foodstuffs'.* London.
EIRICH, F.R. (1956, 1958, 1960, 1967, 1969) *Rheology. Theory and Applications,* 5 volumes. Academic Press, New York.
FENNER, A.J. (1965) *Mechanical Testing of Materials.* Newnes, London.
FERRY, J.D. (1958) In EIRICH, F.R. (1958) Volume 2.
FRIEDMAN, H.H., WHITNEY, J.E. & SZCZESNIAK, A.S. (1963) *J. Fd Sci.* **29,** 390.
FRISCH, H.L. & SIMHA, R. (1956) In EIRICH, F.R. (1956) Volume 1.
GARDNER, H.A. & SWARD, G.G. (1962) *Paint Testing Manual.* Gardner Laboratory, Bethesda.
GORDON, A. (1967) *BFMIRA Sci. Tech. Survey* No. 50.
GORDON, A. (1969) *Fd Process. Mktg,* **38,** 54.
HAIGHTON, A.J. & MIJNDERS, A. (1959) *J. Am. Oil Chem. Soc.* **36,** 345.
HARPER, R. (1967) S.C.I./B.S.R. *Symposium on 'Rheology and Texture of Foodstuffs'.* London.
HEDIGER, M. (1968) *Measurement of Rheological Properties.* Contraves, Ruislip.
HIBBERD, G.E. (1968) *Cer. Sci. Today,* **13,** 138.
HIBBERD, G.E. & WALLACE, W.J. (1966) *Rheol. Acta,* **5,** 193.

HIBBERD, G.E., WALLACE, W.J. & WYATT, K.A. (1966) *J. Sci. Instrum.* **43,** 84.
HINDMAN, H. & BURR, G.S. (1949) *Trans. Am. Soc. mech. Engrs,* **71,** 789.
KULWICH, R., DECKER, R.W. & ALSMEYER, R.H. (1963) *Fd Technol., Chicago,* **17,** 83.
LANGTON, N.H. & VAUGHAN, P. (1965) *J. Sci. Instrum.* **43,** 317.
LAWRENCE, K. G. (1966) *Chemy Ind.* **No. 31,** 1338.
LEADERMAN, H. (1958) In EIRICH, F.R. (1958) Volume 2.
LERCHENTHAL, C.H. & MULLER, H.G. (1967) *Cer. Sci. Today,* **12,** 185.
MATZ, S.A. (1962) *Food Texture.* Avi, Westport.
MCKENNELL, R. (1954) Proc. 2nd. Int. Congr. Rheol. P. 350. Butterworth, London.
MCKENNELL, R. (1956) Anal. Chem., **28,** 1710.
MCKENNELL, R. (1960) *Instrument Manual,* Section XI. Ferranti, Manchester.
MOHSENIN, N.N. & MORROW, C.T. (1967) S.C.I./B.S.R. *Symposium on 'Rheology and Texture of Foodstuffs'.* London.
MORROW, C.T. & MOHSENIN, N.N. (1966) *J. Fd Sci.* **31,** 686.
MOTTRAM, F.J. (1961) *Lab. Pract.* **10,** 767.
OKA, S. (1960) In EIRICH, F.R. (1960) Volume 3.
OLDFIELD, R.C. (1958) *S.C.I. Symposium on Texture in Foods.* London.
PRENTICE, J.H. (1954) *Lab. Pract.* **3,** 186.
PROCTOR, B.E., DAVISON, S. & BRODY, A.L. (1955) *Fd Technol., Chicago,* **9,** 471.
PROCTOR, B.E., DAVISON, S. & BRODY, A.L. (1956a) *Fd. Technol., Chicago,* **10,** 327.
PROCTOR, B.E., DAVISON, S. & BRODY, A.L. (1956b) *Fd Technol., Chicago,* **10,** 344.
REINER, M. (1960) *Deformation, Strain and Flow.* H. K. Lewis, London.
REINER, M. & SCOTT BLAIR, G.W. (1967) In EIRICH, F.R. (1967) Volume 4.
SCOTT BLAIR, G.W. (1948) *Research,* **1,** 453.
SCOTT BLAIR, G.W. (1949) *A Survey of General and Applied Rheology.* Pitman, London.
SCOTT BLAIR, G.W. (1953) *Foodstuffs. Their Plasticity, Fluidity and Consistency.* North-Holland, Amsterdam.
SCOTT BLAIR, G.W. (1954) *J. Dairy Res.* **21,** 160.
SCOTT BLAIR, G.W. (1958) *Advanc. Fd Res.* **8,** 1.
SCOTT BLAIR, G.W. (1969) *Elementary Rheology.* Academic Press, New York.
SCOTT BLAIR, G.W. & COPPEN, F.M.V. (1941) *J. Soc. Chemy Ind.* **60,** 190.
SOCIETY OF CHEMICAL INDUSTRY (1958) *Symposium on 'Texture in Foods'.* SCI Monograph No. 7. London.
SOCIETY OF CHEMICAL INDUSTRY/BRITISH SOCIETY OF RHEOLOGISTS (1967) *Symposium on 'Rheology and Texture of Foodstuffs'.* SCI Monograph No. 27. London.
SHAMA, F. & SHERMAN, P. (1966) *J. Fd Sci.* **31,** 699.
SHAMA, F. & SHERMAN, P. (1967) S.C.I./B.S.R. *Symposium on 'Rheology and Texture of Foodstuffs'.* London.
SHAW, D.J. (1963) *Rheology of Emulsions* (Ed. by P. Sherman). Pergamon, Oxford.
SHELEF, L. & MOHSENIN, N.N. (1967) *Cereal Chem.* **44,** 392.
SHERMAN, P. (1966) *J. Fd Sci.* **31,** 707.
SHERMAN, P. (1968) *Emulsion Science.* Academic Press, New York.
SHERR, H.J. & WITNAUER, L.P. (1967) *J. Am. Oil Chem. Soc.* **44,** 275.
SHIMIZU, T. & ICHIBA, A. (1958) *Bull agric. Chem. Soc. Japan,* **22,** 294.
SIMON, S., FIELD, J.C., KRAMLICH, W.E. & TAUBER, F.W. (1965) *Fd Technol., Chicago,* **19,** 410.
SKELLAND, A.H.P. (1967) *Non-Newtonian Flow and Heat Transfer.* Wiley, New York.
SOMERS, G.F. (1965) *J. Fd Sci.* **30,** 922.
STAINSBY, G. & WARD, A.G. (1949) *Proc. 1st Int. Congr on Rheology, Holland,* 1948. North-Holland, Amsterdam.
STAIRMAND, C.J. (1967) *Characterisation and Manipulation of Powders,* pp. 163a and b. Pharmaceutical Press, London.

Szczesniak, A.S. (1963) *J. Fd Sci.* **28,** 385.
Szczesniak, A.S. (1968) *Fd Technol., Chicago,* **22,** 981.
Szczesniak, A.S., Brandt, M.A. & Friedman, H.H. (1963) *J. Fd Sci.* **28,** 397.
Szczesniak, A.S. & Kleyn, D.H. (1963) *Fd. Technol., Chicago,* **17,** 74.
Tschoegl, N.W. (1961) *Kolloid. Z.* **174,** 113.
Van Holde, K.E. & Williams, J.W. (1953) *J. polym. Sci.* **11,** 243.
Van Wazer, J.R., Lyons, J.W., Kim, K.Y. & Colwell, R.E. (1966) *Viscosity and Flow Measurement.* Interscience, New York.
Vasic, I. & deMan, J.M. (1967) *J. Am. Oil. Chem. Soc.* **44,** 225.
Walters, K. (1968) *Basic Concepts and Formulae for the Rheogoniometer.* Sangamo, Bognor.
Wood, F.W. (1967) S.C.I./B.S.R. *Symposium on 'Rheology and Texture of Foodstuffs'.* London.

J. Fd Technol. (1970) **5**, 33–39.

Effect of chilling shrinkage of pig carcasses on yield of Wiltshire bacon

T. J. R. COOPER

Summary

Twenty pig carcasses were taken fresh from the slaughterline and split into two sides. One-half of each pig was quick-chilled and the other rapidly chilled. Trimming, brine injection and curing were closely controlled and weights at various stages of processing were accurately measured.

Overall, there was no difference in the final weight of bacon produced by the two chilling systems. There was some variation in the curing weight loss of different pigs, pH appearing to be a factor.

Introduction

It is well known that the weight loss of freshly slaughtered animals during chilling is dependent on the time at which chilling commences and on the chilling rate. The shrinkage of pig carcasses which are chilled in 14 hr may vary from 1 to 2% according to the chilling conditions. The saving in weight loss achieved by rapid chilling is of considerable economic advantage, where carcasses are to be sold as fresh pork (Cooper, 1967, 1968).

Jul, Nielsen & Petersen (1959) found that a reduction in chilling shrinkage was offset by greater losses during trimming and tank curing, and that the overall yield of Wiltshire bacon at shipment was independent of the chilling loss. Their results are summarized in Table 1.

Some designers and operators of pig chilling equipment, while accepting that rapidly chilled carcasses incur greater curing losses, believe that in practice there is still some improvement in yield. The extent of the difference in yield is, however, extremely vague and there are more predominant factors such as butchery standard, pumping gain, and ratio of fat to lean. This paper gives the results of tests designed to investigate further the effect of chilling shrinkage on Wiltshire bacon yield, by eliminating any inherent differences in carcasses and with butchering and pumping strictly controlled.

Authors' address: Ulster Curers' Association, 2 Greenwood Avenue, Belfast 4, Northern Ireland.

TABLE 1. Chilling shrinkage and bacon yield—derived from data of Jul *et al.* (1959)

Test No.	Chilling shrinkage (%)	Bacon yield (%)*
1	1·74	82·13
	2·58	82·14
2	2·07	82·03
	3·46	81·86
3	1·32	87·31
	1·90	87·31
4	1·54	86·74
	2·11	86·81

* $\frac{\text{Bacon weight}}{\text{Weight hot dressed carcass}} \times 100.$

Experimental

Chilling conditions

Two Grade A carcasses (i.e. with maximum back-fat thicknesses of 26, 26 and 46 mm at the loin, mid-back and shoulder, respectively) were selected for each test. The weight range of the carcasses was 120–145 lb. The heads were removed, the sides wrapped in polythene and transported to the laboratory. The time interval from slaughter to the beginning of the test was about 1½ hr. Each side of the carcass was weighed to the nearest 5 g (about 0·02%) before chilling. The sides were allocated and chilled as shown in Table 2.

TABLE 2. Arrangement of carcasses and chilling conditions

	Rapid chill	Quick chill
Carcass No. 1	Right side (1R)	Left side (1L)
Carcass No. 2	Left side (2L)	Right side (2R)
Air temperature (°C)	−7° (chill) 4° (equalize)	4
Airspeed (m/sec)	2 (chill) ¼ (equalize)	¼
Chilling time (hr)	1½ (chill) 22½ (equalize)	24

A total of ten tests (twenty pigs) was carried out.

Butchering

The carcasses were removed from the chillrooms and weighed. They were trimmed in accordance with standard practice for Wiltshire bacon production and re-weighed.

Pumping

The sides were pumped with injection brine of the following analysis: (% w/v) NaCl 27·0; $NaNO_3$ 1·5; $NaNO_2$ 0·05.

Twenty-five 'stitches' were used to give as near as possible to 7·5% weight gain taken as a percentage of the trimmed side. Surplus brine was carefully drained off and the sides weighed again. One hundred and seventy grams of dry salt was stuffed into the 'pocket' of each side.

Tanking

Five hundred grams of dry salt was rubbed into each of the four sides which were stacked on top of each other, meat side up, in a small curing tank. The average chemical composition of the curing brine was as follows: (% w/v) NaCl 26·5; $NaNO_3$ 1·5; $NaNO_2$ 0·05.

The sides were immersed for 4 days.

Maturation

The bacon was removed from the curing tank, surplus brine drained from the rib cage and belly folds, and weighed. The sides were stacked on top of one another, skin side up, for 7 days at 4°C and 80–85% relative humidity. Weighing of each side was carried out every day and the relative position of the sides rearranged in the stack, to minimize the effect of stack pressure on drainage.

The pH of each bacon side (except test No. 1) was recorded after tanking out. Salt readings were taken after 7 days maturation, using a Radiometer salt meter.

Results

The percentage chilling shrinkage, trimmed weight, pumping gain, curing loss and bacon weight for the two chilling methods are given in Table 3. The chilling shrinkage and bacon weight percentages are based on the weight of the sides before chilling. The percentage trimmed weight is related to the weight of the chilled untrimmed side. The pumping gain and curing loss are calculated as a percentage of the trimmed weight.

It is seen from Table 3 that although there were some variations in the butchering (% trimmed weight) and in the pumping gains, the average percentages for both chilling methods were the same. The rapidly chilled sides had a lower chilling shrinkage, but a greater curing loss. The differences in curing loss at different stages of maturation are shown in Fig. 1. The difference remained constant after the first few days out of tank.

The salt distribution figures are given in Table 4, showing that there was no difference in the final 'cure' with both chilling systems.

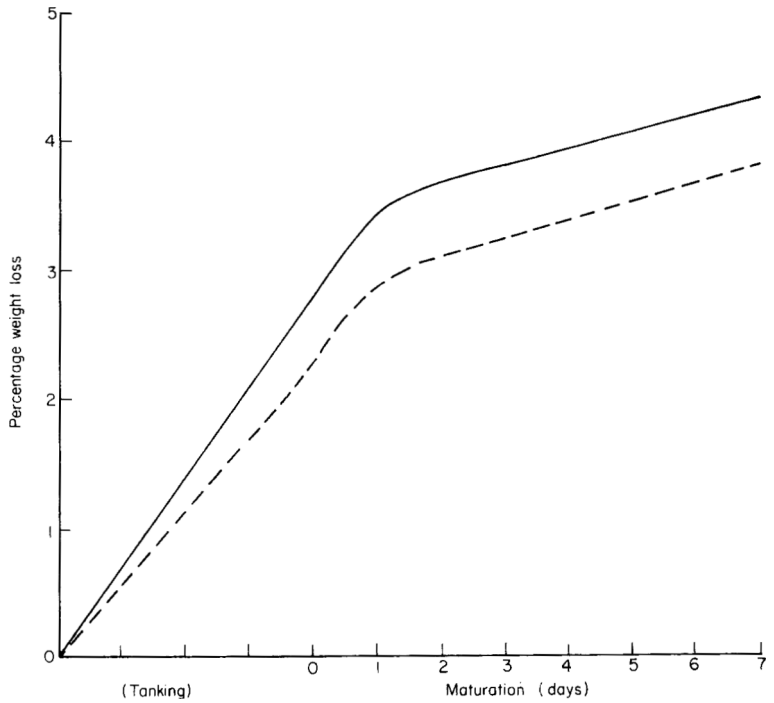


FIG. 1. Weight losses at various stages during maturation for rapidly chilled (———) and quick chilled (- - -) sides.

TABLE 3. Percentage chilling shrinkage, trimmed weight, pumping gain, curing loss and bacon weight for rapidly chilled (R) and quick chilled (Q) carcasses

Test No.	Chilling shrinkage		Trimmed weight		Pumping gain		Curing loss		Bacon weight (after 4 days maturation)	
	R	Q	R	Q	R	Q	R	Q	R	Q
1	1·28	2·01	89·39	89·84	7·35	7·25	4·70	3·97	90·61	90·95
2	0·95	1·77	98·31	89·73	7·57	7·26	3·66	2·88	91·99	92·02
3	1·28	2·28	90·06	89·62	6·95	7·57	3·64	2·79	91·28	91·72
4	1·05	1·96	89·89	90·10	7·64	7·79	4·55	4·11	91·71	91·59
5	1·11	1·66	90·58	90·56	6·94	6·93	3·32	2·34	92·51	93·47
6	1·26	1·53	89·99	89·86	7·73	7·99	4·37	3·22	91·83	92·71
7	0·99	1·55	90·49	90·02	7·97	7·39	3·50	3·26	93·47	92·31
8	1·16	1·55	89·09	89·51	7·69	7·44	3·59	3·22	91·69	91·68
9	1·00	1·51	91·82	91·47	7·59	7·38	4·09	4·09	94·02	93·21
10	0·94	1·47	90·87	91·21	7·51	7·54	4·46	4·33	92·84	92·69
Average	1·10	1·73	90·15	90·19	7·49	7·46	3·99	3·42	92·20	92·23

TABLE 4. Salt distribution

Sampling point	Percentage salt (average of ten tests)	
	Rapid chill	Quick chill
Gammon cushion	3·9	4·1
Gammon area around bone	4·2	4·2
Below oysterbone	4·0	3·9
Mirror	4·6	4·5
Under sixth rib	4·3	4·6
Under third rib	4·2	3·8
Above shoulder pocket	4·5	4·7
Hock joint	3·8	4·0
Neck	4·6	4·4
Average	4·2	4·2

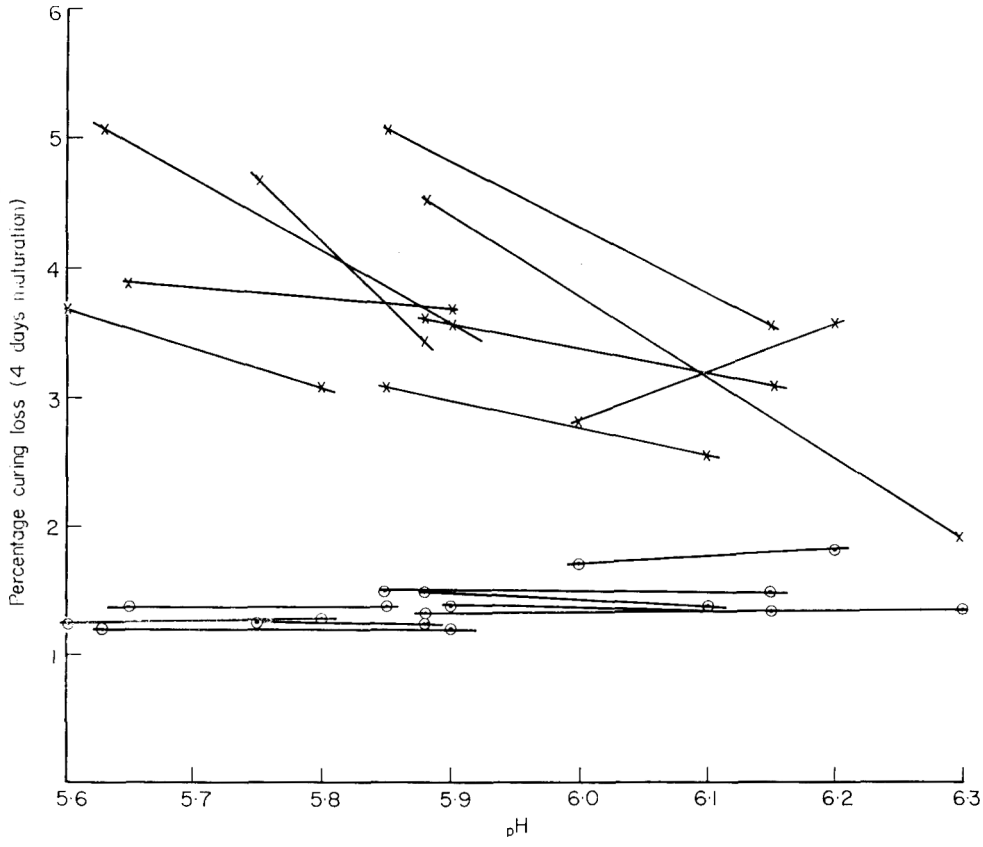


FIG. 2. Relationship between curing (×) and chilling (O) weight losses, and bacon pH.

The average pH of the bacon, the chilling shrinkage and curing loss after 4 days maturation are plotted in Fig. 2. Each point refers to the average loss of right- and left-hand sides of the same pig. The two points for each test, i.e. for sides 1L, 1R and 2L, 2R are joined. The chilling losses of different pigs were of the same order for each test, but there were large differences in curing loss between individual pigs.

Discussion

There are two possible interpretations of the results for chilling and curing weight loss and overall yield.

Firstly, the chilling shrinkage and curing loss can be compared directly. After 4 days maturation for a saving in chilling shrinkage of 0·63% there was an additional curing loss of 0·57% (see Table 3). Therefore, neglecting the effect of slight differences in pumping gain and trimming loss of sides treated by the two chilling systems, the

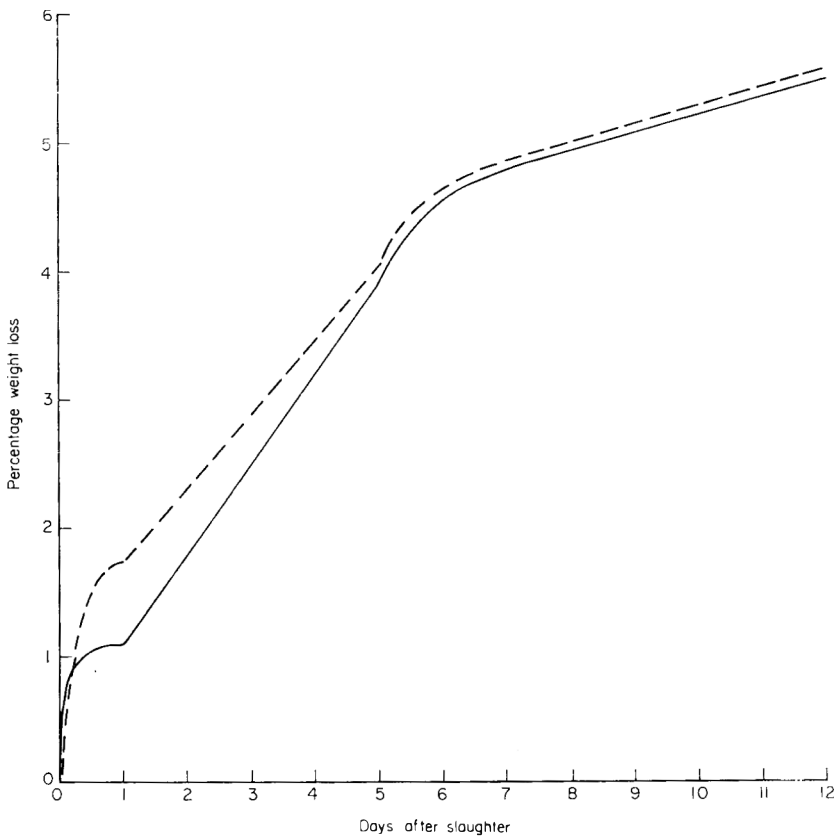


FIG. 3. Total chilling and curing losses at various stages of processing rapidly chilled (———) and quickly chilled (- - -) sides.

overall gain in yield achieved by rapid chilling could be calculated as 0·06%. The overall differences are illustrated in Fig. 3, where the total chilling and curing losses for both chilling methods are compared for the whole process.

There is a second method of comparing yields. It is standard practice to estimate bacon yield on a production basis by the following formula:

$$\% \text{ yield} = 100 \left\{ \frac{\text{Weight of bacon at shipment}}{\text{Weight hot carcasses including head and backbone} - \text{Shrinkage allowance}} \right\}.$$

The technique used for this experiment makes it impossible to arrive at an absolute bacon yield, since right- and left-hand sides of each pig were separated and chilled under different conditions. One can compare the percentage bacon weights for the two chilling treatments using the original hot weight of the sides. Therefore, for the overall percentage weight of bacon, taking into account actual differences in pumping gain and trimming losses, the sides with the higher chilling shrinkage also showed a higher yield of about 0·03%.

From the two methods of comparing yields, the differences between rapid and quick chilling on bacon yield are + 0·06 and − 0·03%. These are of so little significance that it may be concluded that on average the tests showed no improvement in bacon yield with rapid chilling.

It has been well established that pH markedly affects the water holding capacity of meats. Data published by Wismer-Pedersen (1959) suggested a relationship between pH and curing loss. From the results shown in Fig. 2 pH has a considerable influence on bacon yield. This was found in eight out of nine tests, where lower weight losses were recorded for the higher pH bacon, and this merits further investigation

References

Cooper, T.J.R. (1967) *J. Refrig.* **10,** 310.

Cooper, T.J.R. (1968) *ASHRAE Jl,* **12,** 79.

Jul, M., Nielsen, H. & Petersen, H. (1959) *Recent Danish Experiences in Chilling Hog Carcasses.* Danish Meat Research Institute Publication No. 11.

Wismer-Pedersen, J. (1959) *Acta agric. scand.* **9,** 91.

J. Fd Technol. (1970) 5, 41–46.

Quantitative identification of meat species after heating

MARY MATTEY,* A. L. PARSONS† AND R. A. LAWRIE†

Summary

A method, based on laser densitometry of starch gel electrophoretograms of proteins extractable in 8 M urea, is described for the quantitative identification of ox and rabbit in mixtures of meat from these species heated at 120°C for 3–6 min. It is suggested that the method could be developed for the analysis of unknown mixtures of proteins heated for as long as 20–25 min at such temperatures.

Introduction

The technique of serology can quantitatively assess specific proteins present in a mixture—provided the material has not been heated. Many meat products, however, are subjected to varying degrees of heat to make them safe microbiologically during storage. Such heat treatment is generally sufficiently severe to make impossible serological detection of the proteins present. Nevertheless, the heated proteins may still retain a measure of their original species characteristics. This can be measured by indirect haemagglutination (Kotter, Hermann & Corsico, 1966). Because the latter technique is time-consuming, requires skilled veterinary personnel and is not satisfactorily quantitative, an attempt has been made to devise an alternative method based on starch gel electrophoresis (Smithies, 1959).

Mueller & Perry (1962) showed that the water-insoluble proteins of muscle could be separated by electrophoresis on starch gel in the presence of 8 M urea. Neelin & Rose (1964) used this technique to follow changes in the myofibrillar proteins of chicken during conditioning; and Carmichael & Lawrie (1967) employed it to study age changes in the connective tissue proteins of muscle. It seemed feasible that meat proteins, which had become insoluble because of heat applied during processing, might respond to this reagent (Steele, 1967). We have subsequently noted that a similar approach has recently been applied to the *qualitative* detection of non-meat proteins in

Authors' address: Food Science Laboratories, Department of Applied Biochemistry and Nutrition, University of Nottingham, Sutton Bonington, Loughborough, Leicestershire.

* Present address: c/o Schweppes Limited, Histon, Cambridge.

† Present address: Food Science Laboratories, Department of Applied Biochemistry and Nutrition, University of Nottingham, Sutton Bonington, Loughborough, Leicestershire.

the presence of meat (Olsman, 1967), and to distinguish fish species (Anon., 1968), after heating.

It also appeared that the application of laser densitometry to protein components which separated during electrophoresis under these conditions would permit their quantitative assessment (Parsons *et al.*, 1969). Such a technique could be usefully applied to unknown mixtures of heated meats to determine the nature and amounts of the component species.

Materials and methods

General procedure

Fresh samples of the l. dorsi muscles of ox, sheep and pig, and of horsemeat were obtained from a local slaughterhouse. Rabbits were killed in the laboratory by decapitation, after injection of sufficient myanesin to cause relaxation. The l. dorsi muscles were dissected out immediately post-mortem and stored for 4 days at 2°C. Samples of equal weight from each species were cut into small pieces and spread thinly in evaporating dishes to permit effective heat exchange. These were then placed in a hot-air incubator and removed after exposure to 120°C for varying times. (The temperature of the meat was checked by a thermocouple located approximately in the centre of the sample.) Mixtures of l. dorsi muscles of rabbit and ox were made in varying proportions, but all of equal weight, and treated as above for 6 min.

Extraction of muscle proteins

After heating, all samples were homogenized for 2 min in 3 volumes of ice-cold 8 M urea (buffered at pH 7·5 in 0·01 M sodium barbitone). Homogenates were left for 24 hr at 0°C with occasional shaking and then centrifuged at 35,000 *g* for 45 min. The supernatants were decanted into small specimen tubes and retained for electrophoresis, no sample being stored for longer than 24 hr at 0°C.

Starch gel electrophoresis

Suitable conditions for starch gel electrophoresis of sparingly soluble proteins have been previously described (Parsons *et al.*, 1969). A vertical apparatus (Smithies, 1959) was employed, with the following non-discontinuous buffer system: inner and outer gel buffer, 0·01 M sodium barbitone–5 mM HCl, pH 7·5, at 0°C; upper and lower tray buffer, 0·1 M sodium borate, pH 7·5, at 0°C. Gels contained 16% starch (from Connaught Medical Research Laboratories, Toronto, Ontario, Canada) and urea at a molarity of 8, the latter being necessary to prevent polymerization of the proteins under study (Mueller & Perry, 1962). Electrophoresis was carried out at 220 V for 4 hr, 25–30 mA, in a coldroom maintained at 0°C. After being carefully sliced, the gels were stained with a solution comprising 1% Naphthalene Black 10B and 2% Nigrosine for 2 min. The upper halves of the gels were cleared of background stain with a solution of

methanol–acetic acid–water (5 : 1 : 4 by volume) and photographed; the complementary lower halves were cleared with 10% acetic acid to provide a translucent background, suitable for subsequent laser densitometry.

Densitometry

This was carried out in a similar manner to that already reported (Parsons *et al.*, 1969) using a transmission-type densitometer with a G3 helium gas laser as a light source. The gel being scanned was contained between two glass slides on a mechanically driven transverse, moving at 15 mm/min. Light transmitted through the gel was received by an Eel selenium photocell connected to a Servoscribe potentiometric recorder. The laser densitometry was confined to the anodic components which were more clearly defined than the cathodic components. The latter were poorly resolved; moreover their separation depended on electro-osmosis rather than mainly on charge effects (Neelin, 1963).

Results

Electrophoretograms obtained from extracts of l. dorsi muscles of ox, sheep, pig, rabbit and from horsemeat, after heating at 120°C for 3 or 6 min, are shown in Plate 1A. It will be clear that, even after 6 min at 120°C, species differences were still detectable. After periods beyond about 24 min heating at 120°C there were more or less severe changes in the electrophoretic pattern of the muscle extracts.

In Plate 1B the electrophoretic patterns obtained from extracts of l.dorsi muscles of rabbit and ox, after heating to 120°C for 3 min, are shown. Plate 1B(a), (b), (c), (d) and (e) represents the respective patterns for 100% rabbit, 50% rabbit/50% ox, 25% rabbit/75% ox, 90% rabbit/10% ox and 100% ox. It will be observed from Plate 1B, that the electrophoretograms show four major components migrating towards the anode. These are referred to, in order of increasing mobility, as 'A', 'B', 'C' and 'D'. It is clear that the relative quantity of component 'B' in the extract from 100% rabbit is very small; and that there are minor components on either side of 'A'. The major differences between ox and rabbit involve components 'B' and 'C'. As one proceeds from extracts prepared from 100% rabbit to those from 100% ox: (a) the relative concentrate of 'B' increases considerably and its mean distance from the origin decreases; and (b) the relative concentration of 'C' decreases, becomes less diffuse and its mean distance from the origin decreases slightly. In order to exploit the differences represented by these trends with a view to establishing a quantitative method for detecting the composition of unknown mixtures of meat species, the electrophoretograms were clarified and scanned by laser. Facsimiles of the laser densitometer traces obtained from the electrophoretograms in Plate 1B are shown in Fig. 1(a), (b), (c), (d) and (e). The relative band areas of 'B' and 'C' were determined from their maximum

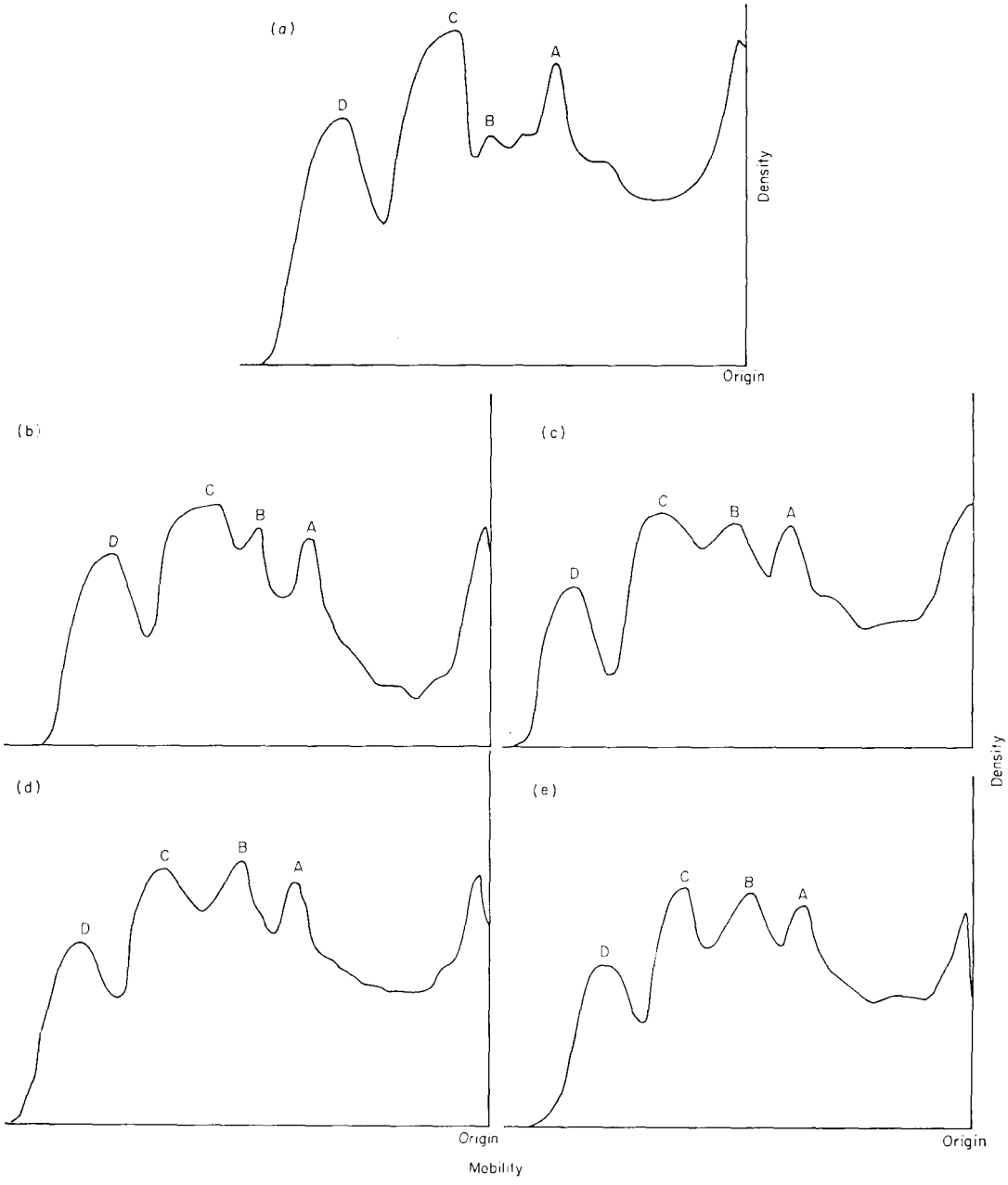


FIG. 1. Densitometer tracings (by laser beam) of starch gel electrophoretograms in 8 M urea of proteins extractable from mixtures of rabbit and ox l. dorsi muscles after heating at 120°C for 3 min. (a) 100% rabbit, (b) 50% rabbit/50% ox, (c) 25% rabbit/75% ox, (d) 10% rabbit/90% ox, and (e) 100% ox.

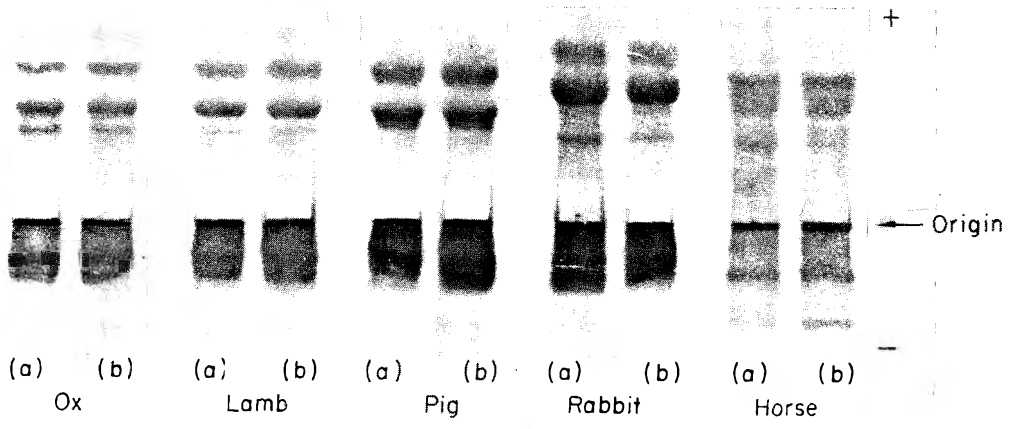


PLATE 1A. Starch gel electrophoretograms of proteins extractable by 8 M urea from l. dorsi muscles of various species after heating at 120°C for: (a) 3 min and (b) 6 min.

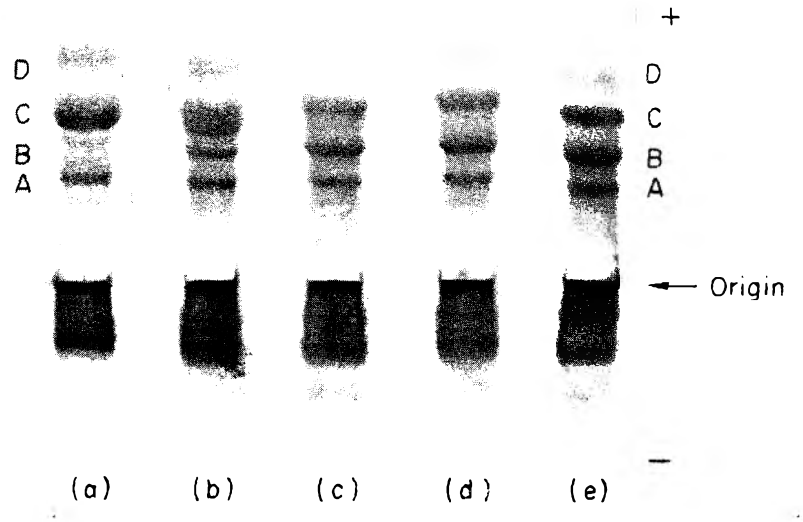


PLATE 1B. Starch gel electrophoretograms of proteins extractable by 8 M urea from mixtures of l. dorsi muscles of rabbit and ox after heating at 120°C for 3 min. (a) 100% rabbit, (b) 50% rabbit/50% ox, (c) 25% rabbit/75% ox, (d) 10% rabbit/90% ox, and (e) 100% ox.

(*Facing p.* 44)

TABLE 1. Data on bands 'B' and 'C' from densitometer tracings of starch gel electrophoretograms of mixtures of rabbit and ox heated at 120°C for 3 min

Composition of heated mixture	Band 'B'			Band 'C'			S*
	Maximum height (cm)	Maximum width (cm)	Mean distance from origin (cm)	Maximum height (cm)	Maximum width (cm)	Mean distance from origin (cm)	
100% rabbit	9·8	1·2	10·9	14·4	4·1	13·6	61·5
50% rabbit/ 50% ox	9·4	2·0	10·0	10·4	4·0	13·0	25·5
25% rabbit/ 75% ox	9·5	2·8	10·3	9·8	3·9	13·6	17·2
10% rabbit/ 90% ox	11·3	3·0	10·8	10·9	3·3	14·0	13·1
100% ox	10·0	3·1	9·8	10·3	2·7	11·9	9·7

$$*S = \left\{\frac{\text{Area C}}{\text{Area B}} \times \frac{(\text{distance B}+\text{C})}{2}\right\}.$$

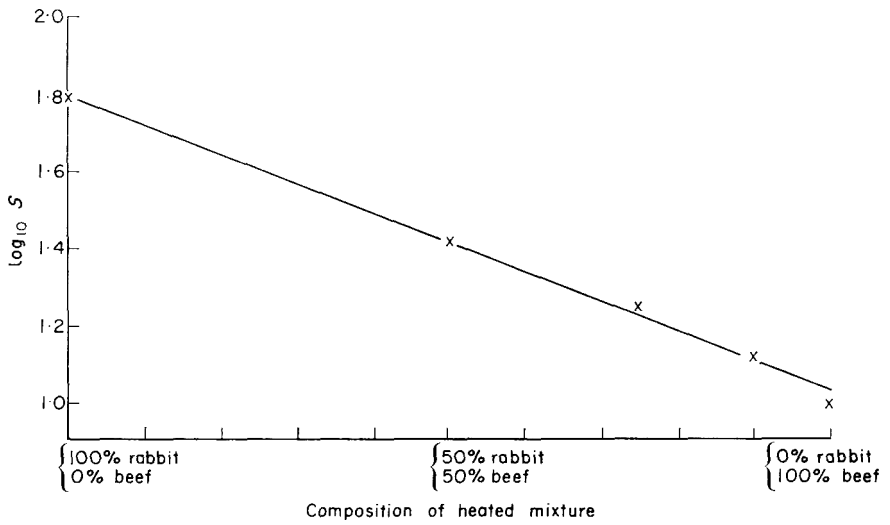


FIG. 2. The relationship between the percentage composition of mixtures of rabbit and ox heated at 120°C for 3 min and the logarithm of the S value derived from laser densitometry of corresponding electrophoretograms.

width and height, and from their relative mobility (Table 1). A so-called species index (S) was calculated as follows:

$$S = \frac{\text{Area 'C'}}{\text{Area 'B'}} \times \frac{(\text{Mean distance 'B' from origin} + \text{mean distance 'C' from origin})}{2}.$$

These values are also given in Table 1. When the logarithm of S was plotted against the composition (Fig. 2) a linear relationship was obtained.

Discussion

It was somewhat surprising to observe that the electrophoretic patterns of proteins characteristic of ox, sheep, pork and horse muscles retained their distinctive features after exposure of the samples to 120°C for 3–6 min. It would appear that while 8 M urea is sufficiently powerful to dissolve proteins which have lost their native solubility on heating, it does not break the covalent links in the polypeptide chains by which the species specificity is determined. That some measure of specificity is retained up to 20–25 min heating at 120°C provides a useful working margin when dealing with meats which have been heated for an unknown period at temperatures of this order.

It was also unexpected to find that the electrophoretic patterns of mixtures of ox and rabbit muscles heated to 120°C for 3 min were qualitatively identifiable; and that when these patterns were scanned by laser, a relationship could be devised between them and the *quantitative* composition of the corresponding mixtures. There is no reason to suppose that the present approach would not be equally successful when applied to other muscles of meat proteins after the appropriate electrophoretic characteristics had been established with known mixtures.

Acknowledgments

The assistance of Mr P. Glover and Mr P. Yorston is gratefully acknowledged. This work was supported, in part, by the Meat & Livestock Commission.

References

Anon. (1968) *Annual Report, Torry Research Station*, 1967, p. 35. Her Majesty's Stationery Office, London.
Carmichael, D.J. & Lawrie, R.A. (1967) *J. Fd Technol.* **2,** 313.
Kotter, L., Hermann, C. & Corsico, G. (1966) *Z. Lebensm.-Untersuch. Forsch.* **133,** 15.
Mueller, H. & Perry, S.V. (1962) *Biochem. J.* **85,** 431.
Neelin, J.M. (1963) *Can. J. Biochem. Physiol.* **41,** 369.
Neelin, J.M. & Rose, D. (1964) *J. Fd Sci.* **29,** 544.
Olsman, W.J. (1967) *Proceedings 13th Meeting European Meat Research Institutes*, Rotterdam.
Parsons, A.L., Parsons, J.L., Blanshard, J.M. & Lawrie, R.A. (1969) *Biochem. J.* **112,** 673.
Smithies, O. (1959) *Biochem. J.* **71,** 585.
Steele, W.J.C. (1967) M.Sc. Dissertation, University of Nottingham.

J. Fd Technol. (1970) 5, 47–63.

Spontaneous heating in meat

H. F. T. JARVIS

Summary

The heat released in biochemical reactions immediately after slaughter apparently raises the carcass temperature initially by a degree or two Centigrade. No further significant heat is produced in small samples, kept under near-adiabatic conditions at various ambient temperatures, until bacterial numbers reach 10^9/g. Treatment of samples with antibiotics and restriction of oxygen supply reduce heat production. The release of heat by a putrid carcass is unlikely to affect the temperature of adjacent meat significantly, and in no circumstances could frozen meat that is not putrid produce sufficient heat to thaw itself.

Introduction

The primary reason for this investigation was the allegation that, occasionally, frozen meat cargoes arriving at British ports were found to be damaged to some extent, possibly due to spontaneous heating in one or more carcasses (*The Times*, 1939). In common with other organic materials, it is well known that such heating will take place under suitable conditions due to both bacterial and chemical action. Data are available for such substances as wool (Rothbaum, 1961; Walker & Harrison, 1960), fish (Kidd, 1952; Reay, 1955) and straw (Dodd, 1933) but little information appears to have been published for meat (Brooks & Smith, 1933). The present investigation considers the heat developed, under controlled conditions, when meat is allowed to putrefy at various ambient temperatures within the range $-1°$ to 30°C.

Preliminary experiments showed that when a sample of 100–150 g of fresh beef, locally purchased, was confined under near-adiabatic conditions at an ambient temperature of about 20°C, a rise in temperature of 3–4°C occurred during the first 24 hr. During the next 24 hr the temperature commenced to fall—only slightly at first but more rapidly towards the end of the period and this fall continued until ambient temperature was reached after 7–10 days. On examination at the end of the experiment the sample was completely putrid.

For the purpose of this investigation the heat evolved per hour per unit mass is defined as the heat of putrefaction, Q.

Author's address: Agricultural Research Council, Meat Research Institute, Langford, Bristol BS18 7DY.

Raw materials

Initial experiments were on meat of unauthenticated history. The later experiments used freshly slaughtered meat which would have been in full rigor by the time it was used. No attempt was made to control biochemical variability.

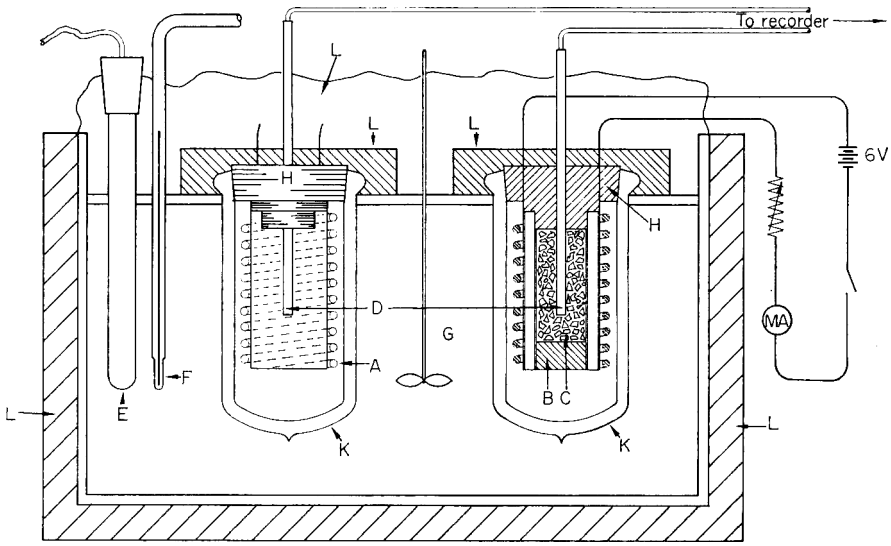


FIG. 1. Sectional diagram of the differential calorimeter. A, Heater coils; B, sample holder; C, sample; D, thermistors; E, bath heater; F, control thermometer; G, stirrer; H, ebonite plugs; K, thermos flasks; L, lagging.

Apparatus

Fig. 1 represents the differential calorimeter consisting of two thermos flasks of about 1500 cm^3 capacity, immersed to within $\frac{1}{2}$ in. of their open ends in a well insulated water bath whose temperature was thermostatically controlled to $\pm$ 0·1°C. The flasks were fitted with large ebonite plugs to which were attached copper heating coils of approximately 10 ohm resistance each. The sample holder, which could be fitted to either flask, inside the coil, consisted of a stainless steel gauze cylinder, 15 cm long and 5 cm diameter, and closed at its lower end by a stainless steel plug.

The samples investigated were taken from fresh lean beef, diced so as to present a large surface area, and weighing about 100 g. In the initial experiments no special arrangements were made to prevent entry of air into the flasks although in later work the flasks were sealed, as far as possible, with plasticine. The temperatures of the two flasks were continuously monitored by thermistors connected to a two channel instrument recording hourly temperatures to 0·1°C and, by estimation to 0·025°C.

The apparatus was erected in a small room whose temperature could be thermostatically controlled to $\pm$ 0·5°C and the bath thermostat was set at a temperature just in

excess of that of the room. Heat losses from the flasks were reduced to a minimum by suitable insulation and evaluated by a preliminary calibration.

Theory

Let θ_1 = temperature of flask A containing the sample at any time.
θ_2 = temperature of control flask B at the same time.
θ = temperature of surroundings,

$$\theta_1 > \theta_2 > \theta.$$

H = Heat lost per degree Centigrade excess temperature above surroundings per hour of either flask. Assume that H is the same for both.
W_1, W_2 = the effective heat capacities of A and B, respectively.
M = mass of sample.
Q_1, Q_2 = the gain of heat per hour by A and B, respectively.
Q = heat of putrefaction per unit mass per hour.

Then
$$Q_1 = W_1\frac{d\theta_1}{dt} = MQ - H(\theta_1 - \theta),$$

$$Q_2 = W_2\frac{d\theta_2}{dt} = -H(\theta_2 - \theta),$$

and
$$W_1\frac{d\theta_1}{dt} - W_2\frac{d\theta_2}{dt} = MQ - H(\theta_1 - \theta_2),$$

or
$$Q = \left[W_1\frac{d\theta_1}{dt} - W_2\frac{d\theta_2}{dt} + H(\theta_1 - \theta_2)\right]/M.$$

which is the working equation.

In most cases the temperature of flask B remained constant and the second term in the numerator could be neglected $[(d\theta_2/dt) \to 0]$.

Calibration and determination of constants

(a) *Heat capacities W_1 and W_2*

With the apparatus empty, a current of 300 mA was passed through the heating coils of A for approximately 1 hr giving a temperature rise of 5–6°C. The current was then cut off and the flask allowed to cool for a further 3 hr. The temperatures of both flasks were taken every 5 min and a large scale heating and cooling curve for the flask A was plotted, the temperature of B remaining constant throughout.

From the cooling curve an auxiliary plot was drawn giving the rate of fall of temperature due to heat losses at any temperature. The classical corrections were then applied to the heating curve and the linear plot so obtained gave the corrected rate of heating, $W_1(d\theta/dt)$, due to the current.

Then if I = current and R_1 = resistance of heating coil:

$$W_1\frac{d\theta}{dt} = \frac{I^2R_1}{J},$$

from which, knowing I, R_1 and $d\theta/dt$, W_1 is found.

The experiment was repeated for the flask B giving the value of W_2.

The resistances of the coils were accurately determined by a Universal Bridge. The mean of a number of experiments gave W_1 = 135 cal/°C and W_2 = 112 cal/°C

Later, owing to modifications to the apparatus, a larger value of W_1 = 190 cal/°C was used.

(b) *Determination of H*

From the cooling curve values of the rate of temperature fall, $d\theta/dt$, were obtained graphically for a series of points corresponding to excess temperature θ^1.

The linear plot of $d\theta/dt$ against θ^1 gave the value of H from:

$$H = \frac{\frac{d\theta}{dt}W_1}{\theta^1}$$

H was found to be the same for both flasks, within $\pm 2\%$, and the value H = 62 cal/hr/°C excess was used in all experiments.

(c) *Specific heat of beef muscle*

To test the accuracy of the method an auxiliary experiment was performed with flask A loaded with 100 g of lean diced beef. The effective heat capacity W'_1 was determined as in (a) under the same conditions and from the difference in heat capacities, loaded and empty, the specific heat of lean beef was calculated. The result, 0·85 cal/g, agreed with the published data (Awberry & Griffiths, 1933).

Determination of heat of putrefaction, Q

In order to obtain comparable results, lean beef from rump purchased locally, was used throughout the initial investigation. The beef was diced into pieces of approximate volume 1 cm³ and, after weighing, was allowed to come to room temperature. It was then loaded into the sample holder in flask A.

In the course of three to four hours the whole apparatus had reached ambient

temperature. Readings of the temperatures of both flasks were recorded every hour and room temperature at less frequent intervals. Graphs of temperature against time were plotted for the whole period of the experiment from which $(d\theta_1/dt)$ and $(d\theta_2/dt)$ expressed in °C/hr were obtained. The values of $\theta_1 - \theta_2$ at 5-hourly intervals were obtained from the recorder chart and Q evaluated from the working equation. Table 1 gives an abbreviated specimen set of results for an initial temperature of 25°C.

TABLE 1. Evaluation of heat of putrefaction for lean beef at 25°C

Time from start (hr)	$d\theta_1/dt$ (°C/hr)	$d\theta_2/dt$ (°C/hr)	θ_1 (°C)	θ_2 (°C)	$\theta_1 - \theta_2$ (°C)	$W_1 \frac{d\theta_1}{dt}$ (cal/hr)	$W_2 \frac{d\theta_2}{dt}$ (cal/hr)	$H \times (\theta_1 - \theta_2)$ (cal/hr)	Total heat (cal/hr)	Q (cal/g/hr)
15*	+ 0·10	− 0·04	25·75	25·6	0·15	+ 21	− 4	9	26	0·28
25	+ 0·36	− 0·02	28·10	25·25	2·85	+ 77	− 2	176	251	2·70
35	+ 0·09	− 0·03	29·95	25·1	4·85	+ 19	− 2	300	317	3·41
45	− 0·09	− 0·04	29·77	24·9	4·87	− 19	− 4	302	279	2·98
55	− 0·05	+ 0·02	29·20	25·20	4·00	− 11	− 2	248	235	2·53
65	− 0·08	0	28·60	25·25	3·35	− 17	0	208	191	2·06
75	− 0·08	0	27·75	25·25	2·50	− 17	0	152	135	1·45
85	− 0·04	0	27·10	25·3	1·80	− 8	0	112	104	1·10
95	− 0·03	0	26·75	25·3	1·45	− 6	0	90	84	0·90
105	− 0·02	0	26·52	25·3	1·22	− 4	0	76	72	0·77
115	− 0·02	0	26·25	25·25	1·00	− 4	0	62	58	0·62
125	0	0	26·15	25·3	0·85	0	0	53	53	0·57
135	− 0·02	0	25·95	25·3	0·65	− 4	0	40	36	0·38

Mass of sample = 93 g.
Specific heat = 0·85 cal/g/°C.
W_1 = 135 + 93 × 0·85 = 214 cal/°C.
W_2 = 112 cal/°C.
H = 62 cal/hr/°C excess temperature.
* Results prior to 15 hr are insignificant.

Similar experiments were carried out at 0°, 10° and 20°C and the results are illustrated graphically in Fig. 2. The scales at 0°C are different from those at other temperatures.

In all of the foregoing experiments the samples examined were from meat purchased locally and, although normal laboratory cleanliness was observed, no attempt was made at aseptic manipulation. Further, in the earlier experiments the flask containing the sample was not specially sealed to prevent access of air from the surroundings. Fig. 2 shows that the maximum rate of heat evolution occurs at times varying from 30 hr in the case of ambient temperature 25°C to 13 days at ambient temperature

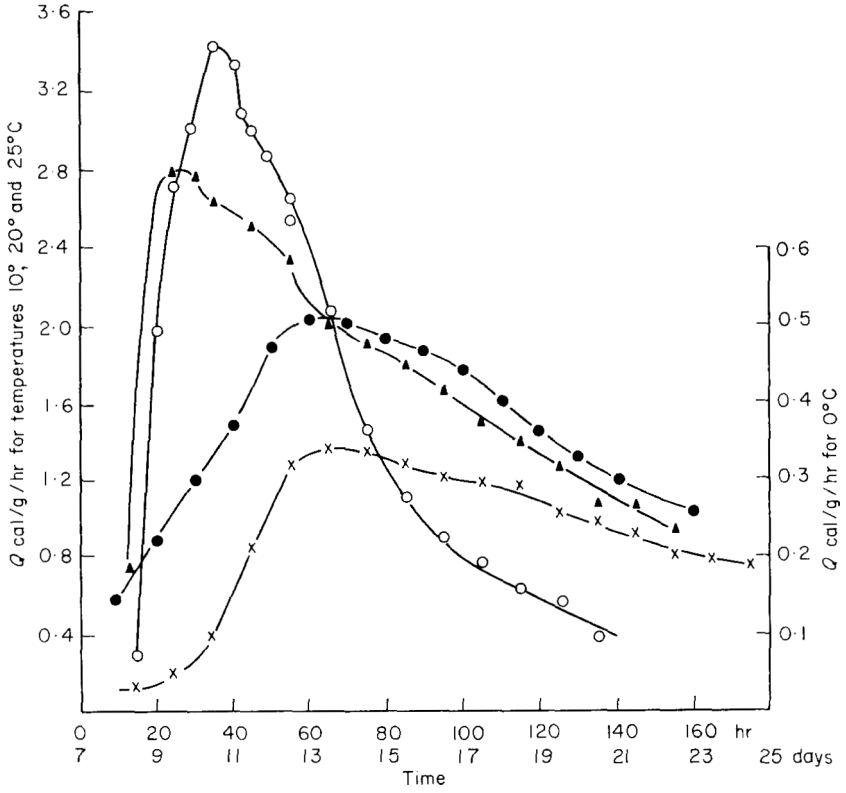


FIG. 2. Heat of putrefaction at ambient temperatures, 0°C (●), 10°C (×), 20°C (▲) and 25°C (○). Time measured in days for 0°C and hours for 10°, 20° and 25°C.

0°C. It is also noticeable that, after this maximum has been reached, some kind of discontinuity or 'hump' occurs where the value of Q falls only slightly before the general decrease with time takes place. After this discontinuity the value of Q falls rapidly in the case of 25° and 20° C but only slowly at 10° and 0°C.

Effects of bacteria and access of oxygen

In order to attempt an explanation for the hump observed in the heat evolution curves, a series of experiments was undertaken at the same ambient temperature, 25°C.

Initially a sample from the rump of a freshly slaughtered animal was removed aseptically and injected with an antibiotic, chlortetracycline, to give a final concentration of 2 ppm. This was minced and loaded into the gauze cylinder under aseptic conditions at 25°C. No heating was observed during the 1st week; and only a very little after 3 weeks, the maximum rate of heating being less than 0·2 cal/g/hr, as compared with 3·4 cal/g/hr with normal microbial contamination (see Table 1 and Fig. 1). On examination after 3 weeks it was found that although yeasts and moulds

had grown upon the outer surface of the meat in contact with the walls of the cylinder, the interior had remained in fresh condition, no micro-organisms being detected in a direct smear.

Since it appeared likely that the spontaneous heating observed in the first experiments was mainly the result of bacterial activity, further experiments were carried out at 25°C varying the microbiological conditions and also the access of oxygen.

The apparatus was modified so that the flask containing the sample could be sealed and a valve provided to enable a few ml of the air inside to be withdrawn for gas analysis. Bacterial counts were made at the end of these experiments and later a further modification was made so that small specimens (1–2 g) could be removed from the bulk at regular intervals for bacterial examination.

The results of six experiments are summarised in Table 2 but the following observations seem worthy of note.

(a) *Experiments A, B and C* were made using 100-g samples from the same animal, prepared under aseptic conditions and kept in refrigeration until required. The sample flask was sealed in all three experiments and gas samples extracted as indicated. Experiment A was allowed to run for the full 7 days while B and C were stopped after 3 and 4 days, respectively, bacterial counts being made at the end of each. It was anticipated that B and C would behave in much the same way as A and that the bacterial counts after 3, 4 and 7 days might throw light on the shape of the Q curves. However, Q_{max} in B and C was less than in A, whilst bacterial counts showed that the population after 4–7 days was a decimal order of magnitude greater than after 3 days. At the same time gas sampling revealed variations in the rate of increase in carbon dioxide and corresponding decrease in oxygen. It was, therefore, concluded that the discrepancies may have been due to variability in air leakage into the flask consequent upon incomplete sealing.

(b) *Experiment D* was undertaken to obtain gas samples at more frequent intervals (12-hourly). The results of the gas analysis showed an increase in the CO_2 content to 14% after 24 hr and to 20% after 36 hr, remaining more or less constant at this value to the end of the experiment. These figures correspond roughly to 0·4 and 0·5 g CO_2/100 g meat. If it be assumed that the heat of combustion for CO_2 production is roughly 130 k-cal/M CO_2 provided that oxygen is present (Rothbaum & Stone, 1961) the above data would correspond to a calculated heat production of $1{\cdot}2 \times 10^{-4}$ cal/g/sec which agrees reasonably well with the value of Q obtained 24 hr from the start. It is also interesting to note that although the maximum rate of heat production occurred after 25 hr the CO_2 content did not reach a maximum until 48 hr.

(c) *Experiment E* was a repeat of the original experiment under non-sterile and unsealed conditions and gave approximately the same value of Q_{max} as before.

(d) *Experiment F* was devised with a view to taking bacterial counts at more frequent intervals. The sample was prepared from fresh beef under aseptic conditions. During the heating process small samples of 1–2 g were extracted by sterile forceps at daily

TABLE 2. Effect of aseptic handling and air-tightness on heat production of meat

	Experiment					
	A	B	C	D	E	F
Mass of sample (g)	100	100	100	99·3	94·6	100
Age pm and origin	4 days; M.R.I.*	15 days; M.R.I.*	22 days; M.R.I.*	1 day; M.R.I.*	Unknown	4 days; M.R.I.*
Refrigeration (R or NR)	R	R	R	NR	Unknown (R)	R
Manipulation (aseptic, A, or not NA)	A	A	A	NA	NA	A
Sealing (S or NS)	S	S	S	S	NS	NS
Duration of experiment (days)	7	3	4	7	4	7
Gas sampling (%)	CO_2 N_2 O_2	CO_2 N_2 O_2	CO_2 N_2 O_2	CO_2 N_2 O_2		
Initial	0 78 22	—	—	—		
After 24 hr	—	0·8 81·4 17·8	6·1 8·3 10·9	14·1 81·8 5·1		
After 36 hr	—	—	—	17·3 78·3 3·4		
After 48 hr	—	16·3 76· 7·7	23·7 75·9 0·4	20·9 75·4 3·7	None taken	None taken
After 72 hr	15 77 8	17·0 77·9 5·1	25·1 73·1 1·8	19·3 76·7 4·0		
After 96 hr	12 78 10	—	—	20·2 74·5 5·3		
Maximum temperature difference (°C)	2·6	1·84	2·0	2·82	4·80	2·90
Time to maximum (*hrs*)	55	48	30	27	33	90
Maximum value of Q (cal/g/hr)	1·7	1·2	1·5	1·98	4·80	2·90
Time to Q_{max} (hr)	40	45	25	25	30	90
Bacterial count at end (per g)						
25°C	$1·2 \times 10^9$	$2·15 \times 10^8$	$3·4 \times 10^9$	None	None	See
37°C	—	$7·0 \times 10^8$	$3·0 \times 10^9$	taken	taken	Table 3

* Slaughtered in Meat Research Institute licensed abattoir.

intervals. It was observed that the value of Q_{max}, although eventually the same as in previous experiments under aseptic conditions, did not occur until 90 hr from the start. It is probable that the extraction of small samples interfered with the general temperature rise usually observed.

The results of the bacterial counts in conjunction with the rate of heat development are shown in Table 3 and Fig. 3.

TABLE 3. Bacterial growth and heat output at 25°C

Time from start (hr)	Q (cal/g/sec $\times 10^4$)	Bacterial count (/g)	Heat output (cal/sec/cell $\times 10^{14}$)
0	—	$4{\cdot}36 \times 10^3$	—
26	1·2	$2{\cdot}42 \times 10^8$	50·0
47	3·5	$8{\cdot}72 \times 10^9$	4·0
71	4·4	$2{\cdot}08 \times 10^{10}$	2·1
90	5·0	$2{\cdot}0 \times 10^{10}$	2·5
95	4·2	$1{\cdot}93 \times 10^{10}$	2·1
120	2·5	$2{\cdot}82 \times 10^{10}$	0·9
140	1·3	$3{\cdot}98 \times 10^{10}$	0·4
160	0·7	$9{\cdot}33 \times 10^{10}$	0·07

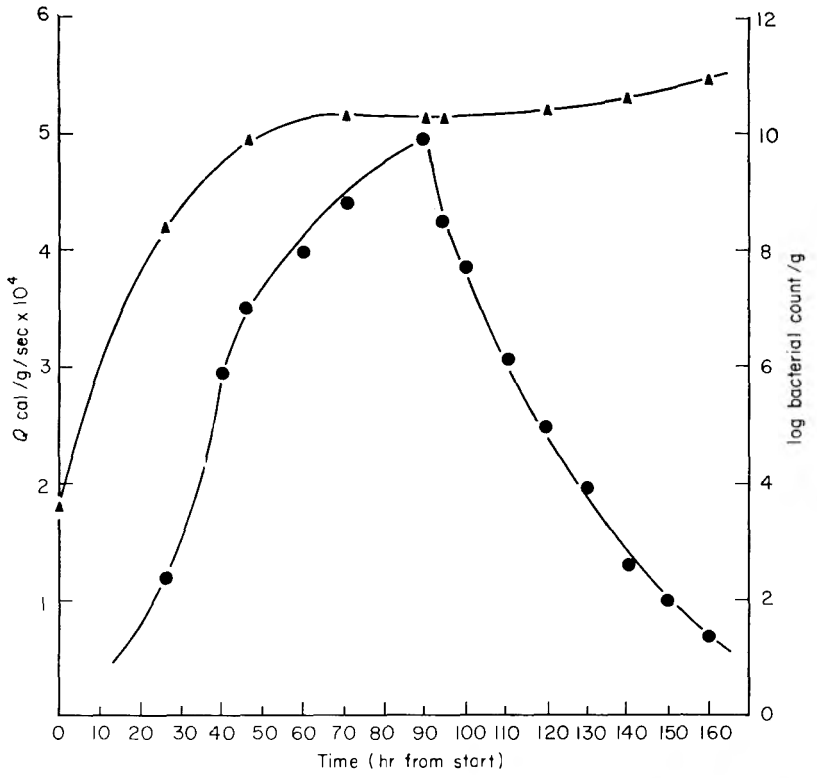


FIG. 3. Bacterial growth and heat output at 25°C. ▲, log bacterial count; ●, heat output.

The identity of the main groups of bacteria present at the various stages was established. During the first 4 days one organism *Flavobacter* spp. predominated almost to the exclusion of other species. This period corresponds to that of maximum heat production. At the end of the experiment the flora consisted mainly of *Proteus* spp. which had overgrown the *Flavobacter*, together with some aerobic sporing rods, *Bacillus* spp. The growth of the *Proteus* during the last 3 days would appear to be simultaneous with the decrease in the value of Q.

Discussion

Considering the results as a whole it is evident that spontaneous heating in meat is almost wholly bacterial in origin and that the maximum rate of heat production varies between 1·3 and 9·5 $\times$ 10^{-4} cal/g/sec according to the origin of the meat and the physical conditions under which it is kept.

The principal factors which affect heat production are:

(a) *Ambient temperature*

In general Q_{max} increases and the time to this maximum decreases as the ambient temperature rises.

(b) *Time from initial conditions*

The value of Q for all ambient temperatures above about 10°C increases fairly rapidly to its maximum value and then, after a slight fall, there appears to be a short period when it tends to remain fairly constant before the general fall to practically zero with advanced putrefaction.

(c) *Degree of contamination*

If all reasonable precautions are taken to avoid contamination, the value of Q_{max} may be reduced to about one-half of the value obtained when such precautions are not taken.

(d) *Oxygen availability*

Although the method did not permit observation under varying conditions of aeration, gas sampling showed that the limitation of oxygen supply decreases the value of Q_{max} and that the CO_2 content in the closed flask rises to about 20% in a time equal to or greater than that in which Q attains its maximum value.

(e) *Age of sample*

Although in the earlier experiments there was no means of estimating the time after slaughter, in all cases rigor and pH fall were certainly completed by the time the experiments were set up. It, therefore, follows that any heat production arising from the breakdown of glycogen to lactic acid and other biochemical reactions, calculated

to amount to 2–3 cal/g during the first few hours after death, had ceased (Bendall, private communication 1969). Although variations in the initial pH might affect the rate of putrefaction, no significant variability in pattern of heat production was observed with meat handled as described.

There appear to be few data with which the present results may be compared. Referring to Table 3 and Fig. 3 the heat output per cell, at 25°C, of the *Flavobacter* appears to be greatest after 24 hr having a value 50×10^{-14} cal/cell/sec falling to 2×10^{-14} cal/cell/sec after 4 days. There is then a rapid fall as the *Proteus* population increases, to $0{\cdot}9 \times 10^{-14}$ cal/cell/sec after 7 days. These results may be compared with those of Bayne-Jones & Rhees (1929) for *Escherichia coli* suspensions at 37°C which give a maximal heat output of 200×10^{-14} cal/cell/sec for the log phase of growth falling to about 20×10^{-14} cal/sec/cell during the stationary phase.

Carbon dioxide determinations of Walker & Winslow (1932) for *E. coli* at 37°C give values of about $1{\cdot}4 \times 10^{-16}$ g/cell/sec falling to $0{\cdot}04 \times 10^{-16}$ g/cell/sec. Using a value of 130 k-cal/M CO_2 for the heat of combustion of CO_2 these figures correspond to 41×10^{-14} cal/cell/sec for the log phase and $1{\cdot}2 \times 10^{-14}$ for the stationary phase which give close agreement with the present results.

It is recorded that haddock muscle kept at 0°C without being allowed to putrefy produces up to 3 cal/g/24 hr (Kidd, 1952; Reay, 1955) as against 12 cal/g/24 hr for beef muscle at the same temperature in the present report. Brooks & Smith (1933) state that the uptake of oxygen in ox muscle at 0°C is 12 μl/g/hr falling to 4 μl/g/hr after 1 month. While no figures are available in this report for oxygen uptake at 0°C it is interesting to note that the oxygen content of the sealed flask fell by 15% in 24 hr corresponding to about 100 μl/g/hr at 25°C. These results would appear consistent with the figures obtained in the determination of oxygen consumption by beef muscle by Taylor (unpublished results 1967), but little is known about oxygen consumption, and what is being oxidised in post-rigor meat, such as was used in these experiments.

Rothbaum & Stone (1961) report that heat output and carbon dioxide production in wet slipe wool after 24 hr at 26°C were as follows:

CO_2, $18{\cdot}5 \times 10^{-8}$ g/sec/g; heat output, 11×10^{-4} cal/g/sec; heat output/cell, 140×10^{-14} cal/cell/sec.

The corresponding figures for beef muscle would appear to be about one-third of the above: 6×10^{-8} g/sec/g, $1{\cdot}2 \times 10^{-4}$ cal/g/sec and 50×10^{-14} cal/cell/sec.

Possible effects of spontaneous heating in meat

Preliminary consideration has been given to the conditions under which heat generated by a contaminated carcass in a frozen cargo can accumulate so that the temperature remains sufficiently high long enough for local putrefaction to occur.

For the purposes of this argument it is assumed that the cargo is close packed and that there are no interior air spaces.

The temperature θ at any given distance from the contaminated carcass must depend upon the value of Q, the surface area of the carcass, its specific heat and thermal conductivity.

If an ideal spherical carcass of radius r_1 and temperature θ_1 be introduced inadvertently into a bulk cargo at a temperature $\theta_2(\theta_1 > \theta_2)$ then, using the conductivity equation for spherical symmetry, the temperature at any given distance r from the centre of the carcass at time t is given by the differential equation:

$$\frac{\partial_2 \theta}{\partial r^2} + \frac{2}{r}\frac{\partial \theta}{\partial r} = \frac{\rho s}{K}\frac{\partial \theta}{\partial t}$$

where ρ = density,
s = specific heat,
K = thermal conductivity, and
$\frac{\partial \theta}{\partial t}$ = rate of change of temperature due to the heat generated by putrefaction Q.

The solution of this equation is almost certainly possible by analogue computation but it is doubtful whether sufficient data have been obtained to fix boundary conditions. The additional complications of the variation in specific heat and thermal conductivity would also have to be included in any computer solution.

It seemed worthwhile, however, to consider a steady state equation which might, at least, give some idea as to how the temperature of the bulk would be affected assuming a constant value of the specific heat (s = 0·85 cal/g) and of thermal conductivity (K = 1·0 × 10^{-3} cal/cm² °C/cm) (Lentz, 1961). It is reasonable to argue that the temperatures obtained by considering the effects of changes in Q by a series of steady state 'steps' should not be greatly different from those given by the continuous change in Q as found experimentally, especially as temperature changes are small and times comparatively large.

In any case it is probable that the temperatures given by steady state conditions will be in excess of those which actually occur. In Fig. 4, let the contaminated carcass radius r_1, temperature θ_1 be generating heat at a rate Q cal/g/sec which is transmitted by thermal conductivity to the bulk at a temperature θ_0.

Then, under steady state conditions, the heat H, transmitted across a spherical shell of radius r and thickness dr is given by;

$$H = -4\pi r^2 K \frac{d\theta}{dr} \text{ cal/sec}, \qquad (1)$$

where K = thermal conductivity.

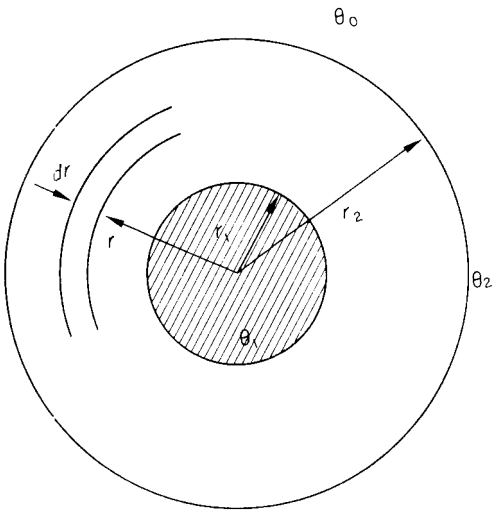


FIG. 4.

Writing this as $dr/r^2 = -(4\pi K/H)d\theta$ and integrating between the limits r_1 and r_2, θ_1 and θ_2:

$$\left[-\frac{1}{r}\right]_{r_1}^{r_2} = \frac{-4\pi K}{H}\left[\theta\right]_{\theta_1}^{\theta_2},$$

or
$$H = \frac{4\pi K(\theta_2 - \theta_1)r_1 r_2}{r_2 - r_1}. \tag{2}$$

But this must be equal to the heat of putrefaction developed by the carcass:

$$= Q\frac{4}{3}\pi r_1^3 \rho \tag{3}$$

where ρ = density
And if Q be assumed constant, from equations (2) and (3) we have:

$$\theta_1 - \theta_2 = \frac{Qr^2\rho(r_2 - r_1)}{3Kr_2} \tag{4}$$

giving the temperature θ_2 at a distance of $(r_2 - r_1)$ from the surface of the carcass under steady state conditions.

The temperature usually associated with the thawing point of frozen meat is -1°C. It may be assumed, therefore, that all the heat arriving at the surface whose temperature is -1°C will be used in thawing (Riedel, 1957).

Assuming that the carcass, of radius 20 cm, is initially at 20°C and that the maximum value of Q at this temperature is 2·8 cal/g/hr then the distance of the -1°C

surface is given by:

$$21 = \frac{2{\cdot}8 \times 20^2 \times 1}{3600 \times 3 \times 10^{-3}}\left(1 - \frac{r_1}{r_2}\right),$$

giving:

$$\frac{r_1}{r_2} = 0{\cdot}8 \text{ and } r_2 = 25 \text{ cm},$$

i.e. thawing would extend to 5 cm from the surface of the carcass. Some idea may now be obtained as to the rate at which thawing takes place.

If the carcass continued to emit heat at Q cal/g/sec then the heat arriving at the r_2 surface/sec $= \frac{4}{3}\pi r_1^3 \rho Q$ and if all this heat is used in thawing a thin layer of thickness d then latent heat absorbed $= 4\pi r_2 d\rho L$ where L = effective latent heat ~ 50 cal/g

Hence: $4\pi r_2^2 d\rho L = \frac{4}{3}\pi r_1^3 \rho Q$

or $d = \frac{r_1^3 Q}{3r_2^2 L}$,

and substituting gives $d = 6{\cdot}7 \times 10^{-5}$ cm/sec $= 0{\cdot}24$ cm/hr. or perhaps 1 cm in approximately 4 hr if Q were maintained at 2·8 cal/g/hr.

In practice this will be considerably less as the maximum rate of heat development is only maintained for a short time.

The experimental graphs of Fig. 2 show that the value of Q rises to a maximum of 2·8 cal/g/hr after 30 hr. It then decreases progressively with time falling to about 0·4 cal/g/hr after 210 hr. This steady decrease in the value of Q must affect the distance at which thawing takes place $(r_2 - r_1)$, the surface temperature of the carcass (θ_1) and the rate of thawing.

The only simple equation between Q and the temperatures and distances involved is the steady rate equation (4) already quoted.

This equation involves three variables:

Q = a function of time,

θ_1 = surface temperature of the contaminated carcass, and

r_2 = radius of -1°C surface.

Rewriting equation (4)

$$Q = \frac{3K}{r_1^2 \rho}\left(\frac{\theta_1 - \theta_2}{r_2 - r_1}\right) r_2 \qquad (5)$$

the first term on right-hand side $3K/r_1^2\rho$ may be considered constant as neither K nor ρ will vary greatly.

Hence as Q decreases with time the value of the product:

$$\left(\frac{\theta_1 - \theta_2}{r_2 - r_1}\right) r_2,$$

must also decrease. It seems reasonable to suppose that after a considerable time the value of Q will be too small to give rise to any thawing at all, in which case $(r_2 - r_1)$ and $(\theta_1 - \theta_2)$ will tend towards zero and r_2 will be equal to r_1 (20 cm).

Since in the steady state the heat conducted per unit time is directly as the temperature gradient $(\theta_1 - \theta_2)/(r_2 - r_1)$, an approximate idea of the way in which the surface temperature of the contaminated carcass will fall may be obtained by associating mean values of Q over steps of 20 hr with a linear decrease in the thawing limit as given by r_2. Table 4 shows how the surface temperature may be expected to fall making the above assumptions. Fig. 5 shows the relation between Q, r_2 the thawing limit and θ_1 the surface temperature of the carcass, all with respect to time.

TABLE 4. Temperature of surface of contaminated carcass (θ) for values of Q every 20 hr

Time from start (hr)	Q (cal/g/hr) from Fig. 2	$\left(\frac{\theta_1 - \theta_2}{r_2 - r_1}\right) r_2$	r_2 (cm)	$\theta_1 - \theta_2$ (°C)	θ_1 (°C)
30	2·8	104	25	21	20
50	2·4	89	24·5	16·3	15·3
70	2·0	74	24	12·4	11·4
90	1·8	63	23·5	9·4	8·4
110	1·5	56	23	7·35	6·35
130	1·2	45	22·5	5·0	4·0
150	1·0	37	22	3·35	2·35
170	0·8	30	21·5	2·1	1·1
190	0·6	22	21	1·05	0·05
210	0·4	15	20·5	0·37	−0·6

Using equation (5) the value of the constant term: $3K/r_1^2\rho = 37$.

While no great accuracy is claimed for the figures in Table 4, they do suggest that, even in the relatively exaggerated case considered, spontaneous heating due to an isolated contaminated carcass is unlikely to affect the bulk as a whole and that any thawing due to this heating will be confined to a small volume in the immediate vicinity of the carcass.

Further, it would seem that, after a period of 2 weeks the contaminated carcass itself must begin to freeze as the transfer of heat gradually brings it to the temperature of its surroundings.

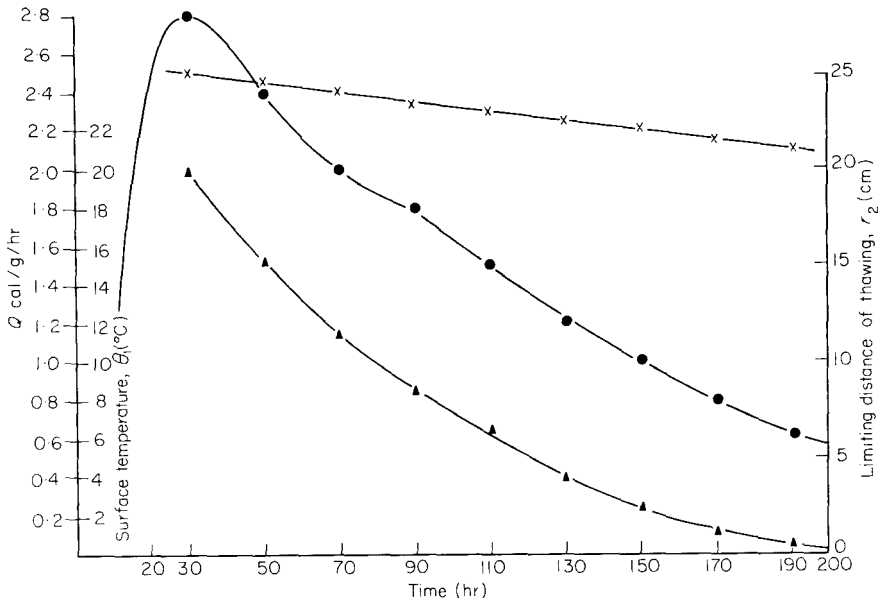


FIG. 5. Graph showing relation between Q, the heat of putrefaction for an ideal carcass at 20°C, the limiting thawing radius and the surface temperature of carcass, the temperature of the bulk being −8°C. ●, Q (cal/g/hr); ▲, θ_1, surface temperature; ×, limiting thawing distance.

Conclusions

(1) The spontaneous heat production of meat, although measurable, is negligible for practical purposes.

(2) Heat production in meat at 25–30°C is six times as great as at 0°C, the corresponding temperature rise in small samples reaching about 5° and 1°C, respectively.

(3) Significant heat production only occurs when the meat has reached an advanced state of putrefaction (10^9 bacteria/g) and is largely accounted for by bacterial respiration. The values obtained are in general agreement with previous determinations of bacterial respiration and heat production.

(4) The characteristic shape of the heat production curve can be associated with changes in bacterial flora as putrefaction proceeds. However, heat production can be almost entirely suppressed over a period of 6 weeks by treatment with chlortetracycline. It is also reduced if the supply of oxygen is restricted.

(5) It is difficult to envisage circumstances in which, even in an advanced state of putrefaction, such heat from a limited number of carcases could affect the bulk of a cargo to any significant extent, provided that normal refrigeration conditions are maintained.

(6) Meat which has been correctly frozen will not, of itself, evolve heat and give rise to putrefaction. Any such spoilage which is observed when a cargo is unloaded

must have been due to the presence of a carcass contaminated initially or to some fault in the refrigeration.

Acknowledgments

The author wishes to thank Dr C. L. Cutting, head of the Bioengineering Section, Meat Research Institute, for his help and interest, Mr A. A. Taylor of the same section for organizing the gas sampling, Dr A. G. Kitchell, head of Microbiology Section for his suggestions and Mr G. Ingram for undertaking the bacterial counting and identification.

References

AWBERRY, J.H. & GRIFFITHS, E. (1933) *J. Soc. chem. Ind.* **52,** 326.
BAYNE-JONES, S. & RHEES, H.S. (1929) *J. Bact.* **17,** 123.
BROOKS, J. & SMITH, E.C. (1933) *Rep. Fd Invest. Bd Lond.*, p. 44.
DODD, F.R. (1933) *Analyst, Lond.* **58,** 77.
KIDD, F. (1952) *Rep. Fd Invest. Bd, Lond.*, p. 49.
LENTZ, C.P. (1961) *Fd. Technol., Chicago,* **15,** 243.
REAY, G.A. (1955) *Rep. Fd Invest. Bd, Lond.*, p. 13.
RIEDEL, L. (1957) *Kaltechnik,* **9,** 38.
ROTHBAUM, H.P. & STONE, H.M. (1961) *J. Bact.* **81,** 172.
ROTHBAUM, H.P. (1961) *J. Bact.* **81,** 155.
The Times (1939) 4 February, p. 6, column 9, 3rd and 4th edns.
WALKER, H.H. & WINSLOW, C.E.A. (1932) *J. Bact.* **24,** 209.
WALKER, I.K. & HARRISON, W.J. (1960) *N.Z. J. agric. Res.* **3,** 6.

J. Fd Technol. (1970) 5, 65–76

A rheological investigation of the role of water in wheat flour doughs

T. WEBB, P. W. HEAPS, P. W. RUSSELL EGGITT
AND J. B. M. COPPOCK

Summary

Doughs of wheat flour, salt and water have been mixed to various levels of work input and water content. Rheological tests have shown that above a particular water content the dough system is unaffected by further addition of water. It is proposed that the water in dough is held with various degrees of strength and that the distribution of water is dependent upon the mechanical work input.

Introduction

For centuries bakers have appreciated that the level of water required to produce a dough with a consistency suitable for bread making varied from flour to flour. However, it is unlikely that the early bakers precisely recognized the connection which exists between this level of water and the baking quality of the flour. In 1821, Accum recognized that a flour was made into a dough 'with the requisite quantity of water which varies according to the quality of the flour' (Accum, 1821). The first simple mechanical apparatus for testing washed-out gluten or kneaded dough to indicate the baking strength of a flour was not described until 1886 (Jago, 1886). Brabender (1965) has given a lucid review of the evolution of such types of apparatus to the present time.

The dough testing instruments in common use today require either doughs of constant consistency or doughs whose total water content is constant. This is acceptable for the routine determination of flour quality in which comparative results are sufficient for the guidance of the baker. However, in using these instruments for research purposes an understanding of the fundamental role of water in dough would facilitate a decision between using constant water content or constant consistency as the basis for experimental procedure.

Since water constitutes about 42% of the total weight of a commercial dough it is unlikely that it is present simply as a diluent. A considerable amount of evidence has appeared in the literature to support this view. For example, Olcott & Mecham (1947) showed that the wetting of flour causes binding of a proportion of the flour lipid, subsequent kneading into a dough causing additional lipid to be bound. Bloksma & Hlynka (1964) have pointed out that water is unique in that it forms a dough with wheat flour and have suggested that a possible structural role of water in dough might

Authors, address: Spillers Limited, Technological Research Station, Station Road, Cambridge.

be its involvement in the cross-linkages between protein molecules. Such a system implies the participation of hydrogen bonds in the gluten structure. The more recent studies of Tkachuk & Hlynka (1968) involving heavy water have shown that hydrogen bonds are involved in the strength and, therefore, the structure of dough. Both Hlynka (1959) and Larsen (1964) have introduced the concept of free and bound water in considering the relationships between water and the individual components of flour: bound water being concerned with the structure of dough by hydration of the protein and absorption by the starch; free water being responsible for the mobility of the system.

Recently, Zentner (1968) has attempted to account for the effect of ascorbic acid upon the consistency of dough in terms of the displacement of bound water. Tracey (1966), in considering the basis of improver action in flour doughs, has suggested that the effect of additives on the physical properties of dough might be due to their effect upon the liquid phase (including soluble components) and not upon the insoluble dough proteins as such.

Since water appears to be an important structural factor in the formation of dough it is to be expected that the structural changes associated with dough development might involve changes in water relationships also. However, Bushuk & Hlynka (1964), in a study of water as a constituent of dough, have concluded that 'there is no evidence to suggest that the flour components change in their hydration properties' during dough development. More recently in a similar study Bushuk (1966) has stated that further work is required to relate changes which occur in water binding capacity, as indicated by farinograph consistency, with structural changes in the gluten during dough development.

Several different methods for the determination of free and bound water in doughs are to be found in the literature: these include methods based on cryoscopic (Vail & Bailey, 1940) and refractometric (Kuhlmann & Golossowa, 1936) methods, measurements of the alkaline water retention capacity (Yamazaki, 1953) and dough mobility (Hlynka, 1959).

The approach made in the present study was to define dough arbitrarily, though realistically, as any mixture of flour, salt and water having a finite extensibility. It was then possible to determine, by extrapolation, the level of water just required to permit the formation of a dough of zero extensibility. This level of water is termed the hydration capacity of the flour. Water in excess of the hydration capacity, referred to as free water, is then closely related to the subsequent extensibility of the dough.

Materials and methods

A strong bread flour was used which had been milled from 80% Manitoban and 20% Hard winters wheats without bleaching, treatment or the addition of solid improving agents. Its protein content was 12·8%, moisture 13·7% and starch damage (by the Stewart method) 5·4%.

Doughs containing 2% salt and a range of added water from 48 to 66%, based on the weight of flour, were mixed at 30° ± 1°C in a stainless steel-clad farinograph bowl attached to a modified Brabender do-corder. A dough consistency which permitted: (a) ease and reproducibility of handling, and (b) the desired rate of work input to be maintained was the factor governing the level of work introduced during mixing.

Doughs were mixed on a constant dough weight basis (470 g) at a constant rate of work input of either 0·2 or 0·4 HP min/lb/min (0·33 or 0·67 kW/kg) and the levels of work introduced were varied up to 3·6 HP min/lb (100 W-hr/kg). After mixing, the doughs were divided into three 150-g pieces, moulded and allowed to rest for 45 min in the humidified cabinets of the Brabender extensograph at 30°C. Each test-piece was then stretched to a predetermined extension on the extensograph and the weight of dough participating in the test determined as described previously (Heaps, Russell Eggitt & Coppock, 1965). The load-extension curves were integrated after correction for instrument constants, to give a number of total stress work values which in turn were divided by the weight of dough sample taking part in the test.

Baking tests were carried out on selected doughs in order to investigate the relative significance of the extensibilities and stress work values determined as described in the preceding paragraph. An addition of 2·14% yeast (6 lb/sk) was made to the above dough formulae to give doughs suitable for the baking tests.

Results

Rheological tests

The total stress work values ($W_{TOT,10}$) considered here are those obtaining at 10 cm extension and the values of maximum extensibility (E_{max}) are taken to be those which correspond to the maximum force observed on the extensograph. Table 1 summarizes the results of the rheological tests.

Figs. 1 and 2 are typical of the dependence upon mechanical work input of total stress work and maximum extensibility, respectively.

Baking tests

Experimental details of the baking tests are contained in Table 2 together with the loaf specific volumes obtained.

The loaves fell into three categories as follows when judged with respect to crumb structure:

Category	Dough Nos.
Good	1, 2, 4, 7 and 9
Fair	5, 10, 11 and 12
Poor	3, 6 and 8

Fig. 3 shows a typical member of each class.

TABLE 1. The variation of total stress work and maximum extensibility with percentage added water and level of mechanical work input at two constant rates of work input

Added water (%)	Level of work input (HP min/lb)	Rate of work input (HP min/lb/min)			
		0·2		0·4	
		$W_{TOT,10} \times 10^{-3}$ (erg/g)	E_{max} (cm)	$W_{TOT,10} \times 10^{-3}$ (erg/g)	E_{max} (cm)
48	0·1	145	17·9	141	19·3
	0·6	150	16·5	177	15·2
	1·1	168	14·6	179	11·3
	1·6	180	10·6	185	9·8
	2·1	178	10·4	195	8·9
	2·6	190	9·9	214	8·0
	3·1	192	9·1	200	7·9
	3·6	184	8·3	199	7·7
52	0·1	88	22·8	93	24·4
	0·6	101	19·7	106	19.2
	1·1	118	18·2	116	15·1
	1·6	131	13·1	133	11·4
	2·1	140	11·0	141	10·0
	2·6	146	8·6	150	9·0
	3·1	142	9·5	146	8·4
	3·6	139	8·5	145	8·0
56	0·1	58	28·5	59	27·0
	0·6	71	21·5	75	20·6
	1·1	80	19·0	89	17·6
	1·6	92	16·0	97	15·7
	2·1	98	12·3	104	11·6
	2·6	98	11·3	105	10·2
	3·1	97	10·3	104	10·3
	3·6	86	9·7	103	8·8
58	0·1	54	28·7	50	31·1
	0·6	63	24·8	62	21·8
	1·1	68	20·3	75	18·7
	1·6	86	16·3	86	14·0
	2·1	90	13·8	96	12·3
	2·6	91	12·0	98	11·9
	3·1	81	9·3	88	9·4
	3·6	78	7·2	89	10·0
62	0·1	36	35·1	31	33·6
	0·6	47	27·0	41	26·6
	1·1	51	23·6	53	21·3
	1·6	64	17·6	66	16·0
	2·1	67	14·3	—	—

Added water (%)	Level of work input (HP min/lb)	Rate of work input (HP min/lb/min)			
		0·2		0·4	
		$W_{TOT,10} \times 10^{-3}$ (erg/g)	E_{max} (cm)	$W_{TOT,10} \times 10^{-3}$ (erg/g)	E_{max} (cm)
66	0·1	23	40·1	—	—
	0·6	30	31·1	—	—
	1·1	41	22·5	—	—
	1·6	45	18·3	—	—
	2·1	48	16·1	—	—

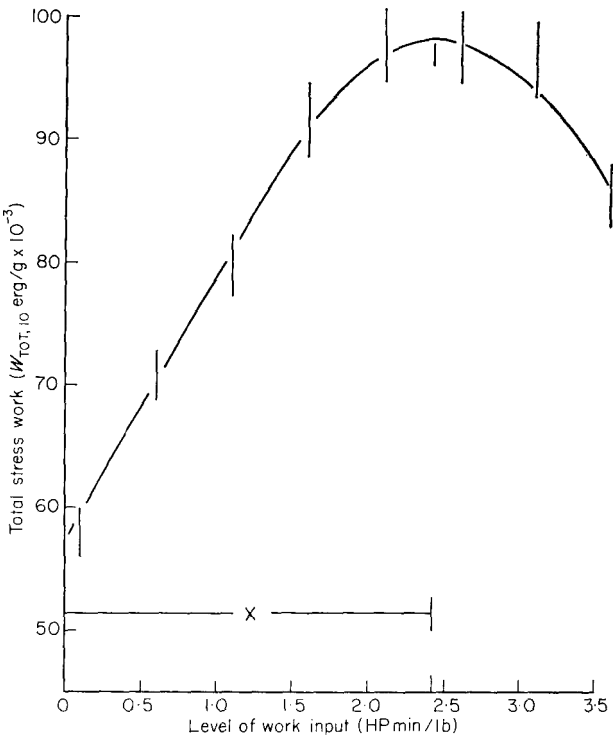


FIG. 1. The development of dough with mechanical work input (56% added water; rate of work input = 0·2 HP min/lb/min). The vertical lines represent the estimated deviations in the values of total stress work.

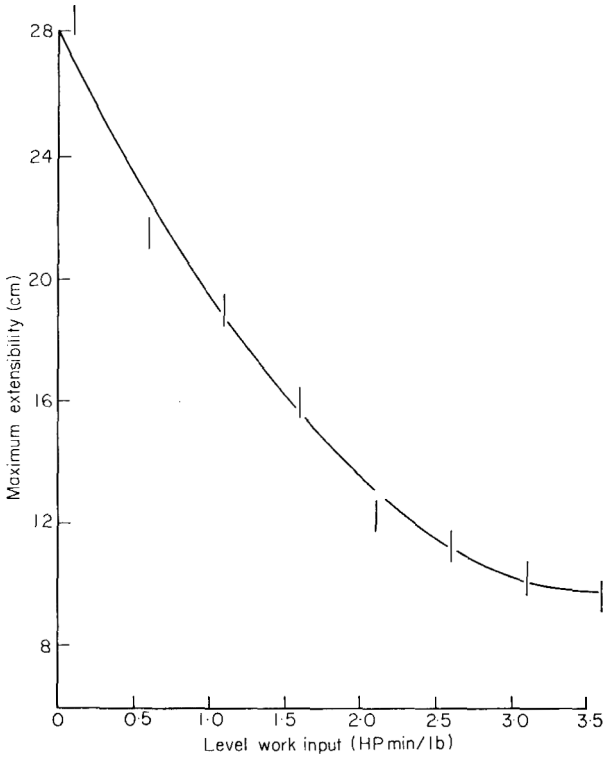


FIG. 2. The dependence of maximum extensibility upon level of work input (56% added water; rate of work input = 0·2 HP min/lb/min). The vertical lines represent the estimated deviations in the values of maximum extensibility.

TABLE 2. The physical properties of selected doughs together with the specific volumes of the corresponding loaves

Dough No.	Added water (%)	Level of work input (HP min/lb)	Rate of work input (HP min/lb/min)	$W_{TOT,10}$ $\times 10^{-3}$* (erg/g)	E_{max} (cm)	Specific volume (ml/g)
1	66·0	1·4	0·2	44	20·8	3·80 ± 0·00
2	58·3	1·0	0·2	70	20·8	3·69 ± 0·04
3	50·4	0·2	0·2	110	20·8	2·48 ± 0·03
4	61·5	1·0	0·4	55	22·0	3·66 ± 0·13
5	56·8	0·6	0·4	70	22·0	3·20 ± 0·13
6	51·5	0·2	0·4	100	22·0	2·42 ± 0·04
7	64·0	1·0	0·2	45	24·0	3·72 ± 0·20
8	53·3	0·2	0·2	80	24·0	2·67 ± 0·03
9	62·0	0·6	0·4	42	26·8	3·56 ± 0·03
10	56·5	0·2	0·4	60	26·8	2·92 ± 0·08
11	57·0	0·2	0·2	55	28·0	2·85 ± 0·03
12	54·1	0·6	0·4	90	20·0	2·85 ± 0·10

* The values of total stress work were obtained, where necessary, by interpolation between adjacent levels of added water.

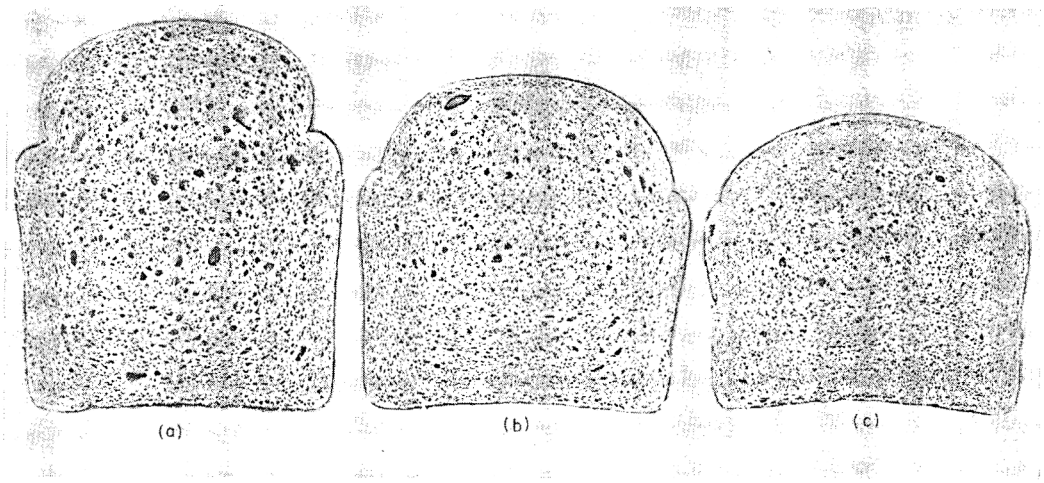


FIG. 3. The crumb structure of a typical member of each category of loaf produced in the baking test. (a) Dough No. 2, (b) dough No. 5, and (c) dough No. 8.

Discussion

Rheological tests

Reference to Table 1 shows that the dependence of $W_{TOT,10}$ and E_{max} upon the level of work input is qualitatively unaffected by changes in the amount of added water, over the wide range of water additions studied. This is true at both rates of work input used. For example, the level of work input required to produce maximum dough development (X in Fig. 1) does not vary with the level of added water. However, Figs. 4 and 6* show that the absolute values of $W_{TOT,10}$ and E_{max} at any given level of work input are observed to vary with the level of added water: the changes being consistent with the concept of water acting as a diluent or lubricant. The exponential dependence of $W_{TOT,10}$ upon total water content of the dough is illustrated in Fig. 5.

In Fig. 6(a), for the sake of clarity, only the pair of intersecting lines representing work input levels of zero and 0·2 HP min/lb are studied. This pair is typical of the changes taking place over a wider range of work levels. In the upper region of total water content, it is clear that as dough water content decreases, the values of E_{max} at the two levels of work input converge. It is thought that this effect might be explained in terms of two opposing characteristics of dough development which result from the introduction of mechanical work. First, as stated in an earlier paper (Heaps *et al.*, 1967), dough development involves a tightening of the structure with a consequent *decrease* in extensibility. Secondly, also resulting from the tightening effect there occurs a release of water from the dough structure (i.e. a net increase in free water) which tends to

* The total water content of the dough used in the graphs is the sum of the added water and the moisture content of the flour.

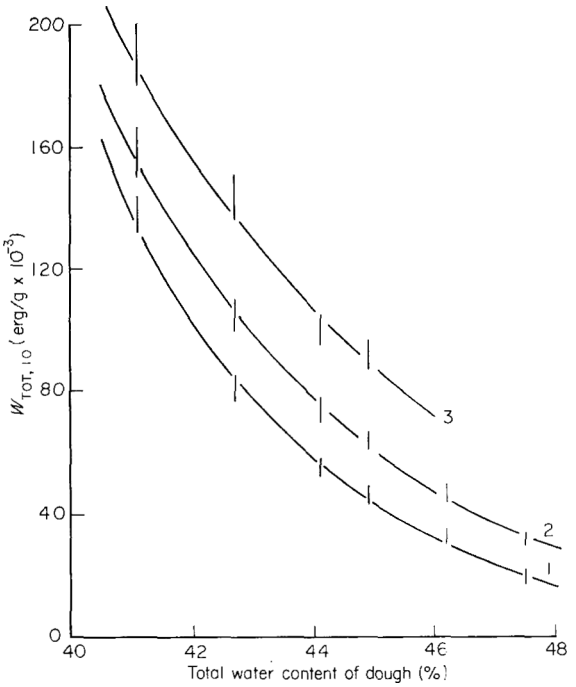


FIG. 4. The dependence of $W_{TOT,10}$ upon total water content for doughs of various levels of work input. 1, 0·0 HP min/lb; 2, 0·7 HP min/lb; and 3, 2·3 HP min/lb. Rate of work input = 0·2 HP min/lb/min. The vertical lines represent the estimated deviations in the values of $W_{TOT,10}$.

increase the extensibility. Above the point of intersection of the two lines it appears that the resultant of these two effects is a tightening of the dough structure, although with smaller total water contents the resulting effect becomes less.

At the point of intersection therefore it is thought that a balance of the opposing effects exists, i.e. that the decrease in E_{max} brought about by the various types of cross-linking is exactly counteracted by the lubrication of the system by the water freed in the development process.

Below the point of intersection it appears that the effect of the release of water outweighs the tightening of the structure and to an increasing degree as the total water content is reduced. Thus, for a given total water content, doughs of higher levels of work input contain more free water which leads, in the present case, to the observed spread of intercepts on the abscissa.

At levels of work input above maximum dough development, where dough breakdown probably occurs (Heaps *et al.*, 1967), it is considered that due to the difficulty in reproducible dough handling, the extrapolated lines are not sufficiently reliable for inclusion here.

At the higher rate of work input (Fig. 6b) the above arguments are applicable but to

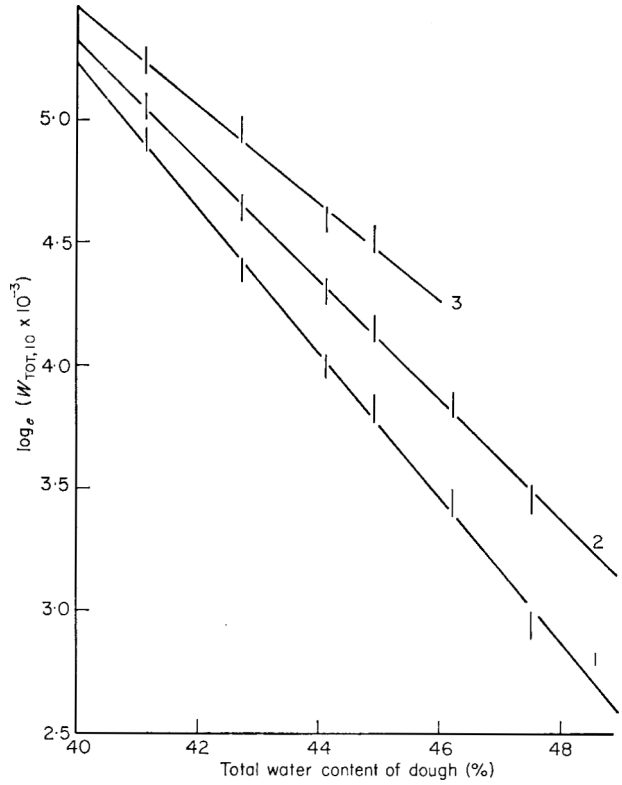


FIG. 5. Showing the exponential dependence of $W_{TOT,10}$ upon total water content for doughs of various levels of work input. 1, 0·0 HP min/lb; 2, 0·7 HP min/lb; and 3, 2·3 HP min/lb. Rate of work input = 0·2 HP min/lb/min. The vertical lines represent the estimated deviations in the values of $\log_e (W_{TOT,10} \times 10^{-3})$.

a greater extent owing to the increased net tightening reported in detail earlier (Heaps & Webb, unpublished work 1968). This leads to an alteration in the position of the point of intersection of any pair of lines compared with the corresponding lines at the lower rate and thus in the spread of intercepts on the abscissa.

Thus the observed dependence of hydration capacity upon the level *and* rate of work input necessitates qualification of the definition given earlier, as follows: the *absolute* hydration capacity of a flour is that level of water at which the dough, having had no mechanical work introduced into it, just attains zero extensibility.

The difference between the intercepts of the zero work input lines on the abscissa of Fig. 6(a) and (b) (36 and 34%, respectively) is considered to be no more than experimental error magnified by the relatively large extrapolations. Thus for the flour under consideration the absolute hydration capacity is about 35%. For a similar flour Davies (1968), has observed that this water content marked the conclusion of gradual changes in the binding of lipids with increasing total water content from an initial value of 20%.

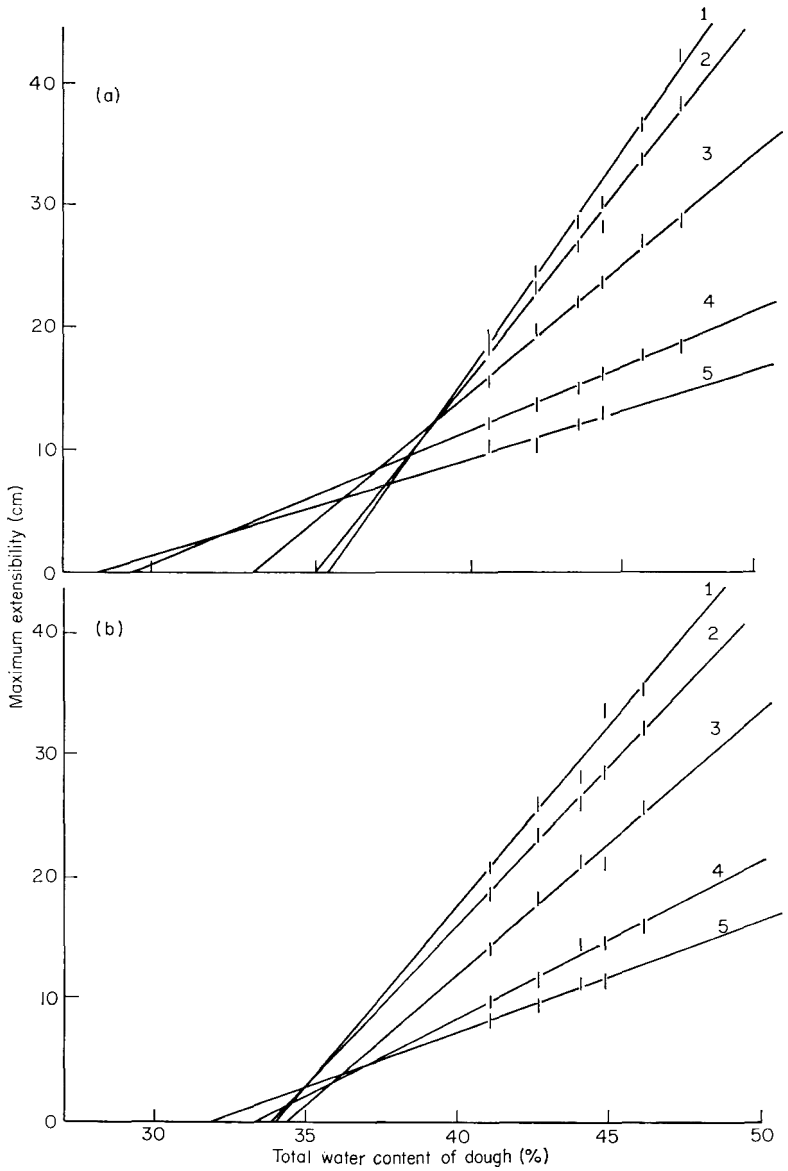


FIG. 6. Regression of maximum extensibility on total water content for doughs of various levels of work input. 1, 0·0 HP min/lb; 2, 0·2 HP min/lb; 3, 0·7 HP min/lb; 4, 1·6 HP min/lb; and 5, 2·3 HP min/lb. (a) Rate of work input = 0·2 HP min/lb/min; and (b) rate of work input = 0·4 HP min/lb/min. The vertical lines represent the estimated deviations in the values of maximum extensibility.

That the spread of intercepts resulting from mechanical development is real has been demonstrated by the introduction of mechanical work, at a rate of 0·2 HP min/lb/min,

into a mixture of flour, 30% added water and 2% salt (both based on the weight of flour). The total water content of the mixture was 33% which, as can be seen from Fig. 6(a), was somewhat below the hydration capacity of the flour. During the early stages of mixing the contents of the farinograph bowl were observed to ride on the blades as small, crumbly pieces of moist flour. After about 7 min the mixture appeared to take on the form of a dough and manual examination indicated a slight, finite extensibility. Thus the introduction of mechanical work increased the amount of free water and permitted the formation of a dough.

From these observations it is postulated that there exist in dough three forms of water: (a) free water, (b) lightly bound water, and (c) firmly bound water. It is possible that water of type (b) includes that which is physically held in the interstices of the structure and which may form the major part of the water released during mechanical dough development.

Baking tests

In an earlier paper (Heaps *et al.*, 1965), it was suggested that for the production of an optimum loaf a dough should possess a maximum extensibility within the range 20–28 cm. For a particular E_{max} within this range the present baking tests indicate that $W_{TOT,10}$ and loaf specific volume are inversely related and that in respect of the crumb structure loaves of good specific volume were the most acceptable.

In conclusion the present work shows that above the hydration capacity the level of water used in doughs for rheological investigation is not critical providing that it permits reproducible handling of the dough. However, in the case of baking tests the permissible levels of water fall within a relatively narrow range which is determined by the optimum range of maximum extensibilities.

References

Accum, F. (1821) *A Treatise on the Art of Making Good and Wholesome Bread*, p. 94. Thomas Boys, London.

Bloksma, A.H. & Hlynka, I. (1964) *Wheat Chemistry and Technology*, Monograph Series Volume III, p. 497. American Association of Cereal Chemists, Incorporated, St Paul, Minnesota.

Brabender, C.W. (1965) *Cereal Sci. Today*, **10,** 291.

Bushuk, W. (1966) *Bakers Digest*, **40,** (5), 38.

Bushuk, W. & Hlynka, I. (1964) *Bakers Digest*, **38,** (6), 43.

Davies, R.J. (1968) *J. Fd Technol.* **4,** 117.

Heaps, P.W., Russell Eggitt, P.W. & Coppock, J.B.M. (1965) *Brot und Geback*, **19,** 165.

Heaps, P.W., Webb, T., Russell Eggitt, P.W. & Coppock, J.B.M. (1967), *J. Fd Technol.* **2,** 37.

Hlynka, I. (1959) *Cereal Chem.* **36,** 378.

Jago, W. (1886) *The Chemistry of Wheat, Flour and Bread.* Jago, Brighton.

Kuhlmann, A.G. & Golossowa, O.N. (1936) *Cereal Chem.* **13,** 202.

Larsen, R.A. (1964) *Cereal Chem.* **41,** 181.

Olcott, H.S. & Mecham, D.K. (1947) *Cereal Chem.* **24,** 407.

TKACHUK, R. & HLYNKA, I. (1968) *Cereal Chem.* **45,** 80.
TRACEY, M.V. (1966) *Chemy Ind.* p. 68.
VAIL, G.E. & BAILEY, C.H. (1940) *Cereal Chem.* **17,** 397.
YAMAZAKI, W.T. (1953) *Cereal Chem.* **30,** 242.
ZENTNER, H. (1968) *Jl. Sci. Fd Agric.* **19,** 464.

J. Fd Technol. (1970) **5**, 77–87.

Interaction of monoglycerides in different physical states with amylose and their anti-firming effects in bread

N. KROG AND B. NYBO JENSEN

Summary

Saturated monoglycerides were prepared in six different physical states: aqueous gels, at pH 6·8 and pH 7·3; a hydrate, aqueous and freeze-dried; a spray-crystallized powder; and a mono-/diglyceride emulsion. Their anti-firming effects in Danish white bread differed greatly, and were found to be related to their ability to form insoluble complex with amylose. The results show the need for hydration of monoglycerides prior to their use. The alpha-crystalline gel (pH 6·8) gave the highest complexing index with amylose and also the best anti-firming effect in bread.

Introduction

Reports concerning staling or firmness of bread have mainly been published in the U.S.A. or the United Kingdom, and few have been published from the Continent. This is probably due to the fact that the consumption of white bread is still small on the Continent compared with that in the U.S.A. and the United Kingdom. Another factor is that on the Continent most white bread continues to be manufactured and consumed within 24 hr. This situation is slowly changing and, therefore, the whole staling problem is becoming more critical for producers and consumers. An up-to-date knowledge of the various factors that promote or inhibit the staling process in the Continental types of bread is, therefore, of great importance.

For many years it has been known (Schoch & French, 1947) that monoglycerides (GMS) have anti-firming effects in wheat bread, and several papers on this subject have been published (e.g. Strandine *et al.*, 1951; Ofelt *et al.*, 1958a, b; Jongh, 1961). According to Schoch (1965) the effect of GMS in bread is due to its ability to form insoluble inclusion compounds with the amylose part of the starch. Thus GMS prevents the formation of an amylose gel and subsequent retrogradation, with the result that the bread has a softer crumb.

Some years ago Kovats & Lasztity (1961) described the effects of some surface-active agents on the elastic and plastic properties of bread crumb. Recently, Seibel *et al.* (1968) have described the influence of saturated and unsaturated mono-/diglycerides on the rheological properties of dough and on the texture, flavour and firmness of a typical

Authors' address: Grindstedvaerket, The Laboratories, 38 Edwin Rahrs Vej, DK–8220 Brabrand, Denmark.

German type of white bread. In this paper effects of saturated monoglycerides on the firmness of Danish white bread are described. Special attention is focused on methods for incorporating the monoglycerides into the dough.

Wren (1968) has recently reviewed the importance of the physical state of the fat-derived emulsifiers and has found that in most cases α-crystallinity in the monoglycerides gives the best antifirming effect in bread. α-Crystallinity is also found to be important in securing the best effect of emulsifier mixtures in cakes (Wootton *et al.*, 1967). Since it is generally accepted that the main function of monoglycerides in products containing starch is the formation of water-insoluble complexes between amylose and monoglycerides, it is of interest to study what influence the physical state of the monoglycerides has on the reaction with starch components. This is also studied in the present work, and the results are discussed in relation to the anti-firming effects of the monoglyceride preparations in white bread.

Materials and methods

Distilled monoglycerides

The distilled monoglycerides (DGMS) used in these experiments were in the form of a commercial product (Dimodan P, produced by Aktieselskabet Grindstedvaerket, Denmark) made from fully hydrogenated lard.

Total monoglyceride content	95·0%
Free fatty acid content	0·4%
Free glycerol content	0·5%
Melting point	69°C
Iodine value (Wijs' method)	0·5

Mono-/diglycerides

This was a commercial product (Homodan HM, produced by Aktieselskabet Grindstedvaerket, Denmark) made from fully hydrogenated lard. The product was soap-free.

Total monoglyceride content	45·0%
Free fatty acid content	1·0%
Free glycerol content	1·5%
Melting point	60°C
Iodine value	0·8

Monoglyceride preparations

Preparation 1. *DGMS-gel, pH* 6·8. A dispersion of 15% DGMS in water was made by mixing 15 parts of DGMS with 85 parts of water and heating to 60°C until a translucent homogeneous, liquid dispersion was formed. The pH was 6·8. Before use, the DGMS dispersion was cooled to room temperature, when it formed a gel.

Preparation 2. *DGMS-gel, pH* 7·3. A 15% dispersion was made as described above but with the addition of 0·3% potassium stearate. The pH of this dispersion was 7·3. Before use, it was cooled to room temperature, when it formed a semi-translucent gel. Because of its higher pH this gel retained its α-crystallinity during storage for at least one week.

Preparation 3. *DGMS-hydrate.* Twenty-five parts of DGMS were mixed with 74 parts of water and heated to 60°C until the DGMS was dispersed, then 1 part of propionic acid was added and the mixture was cooled under agitation to room temperature. The pH of the hydrate was 3·0.

Preparation 4. *DGMS freeze-dried hydrate powder.* A portion of the DGMS-hydrate was freeze dried, yielding a white free-flowing powder.

Preparation 5. *DGMS powder, spray crystallized.* Melted DGMS was spray crystallized to give a particle size of less than 75 μ.

Preparation 6. *Mono-/diglyceride emulsion.* Twenty-five parts of mono-/diglycerides in powder form were mixed with 75 parts of boiling water and then cooled to room temperature under continuous agitation.

X-ray diffraction

A Philips model PW 1080 Generator, with a Cu X-ray tube, was used in conjunction with a Nonius Guinier–de Wolff Camera, model 1.

Determination of monoglyceride–starch complex

The 'amylose' used for these experiments was 'Starch soluble G.R.' obtained from E. Merck AG, Darmstadt, Germany. Pure amylopectin was obtained from Avebe, Veendam, Holland.

Clear solutions of these starch components were made by the procedure described by Schoch (1964) and mixed with a chosen amount of monoglyceride preparation corresponding to 0·1–1% monoglycerides, calculated on the starch content. After reaction at the chosen temperature and time, the mixture was centrifuged (35 000 *g*) and filtered. Five millilitres of the clear filtrate were diluted to 25 ml with distilled water and 1 ml of this solution was used for the determination of residual amylose content using a method described by Gilbert & Spragg (1964). This method measures the blue colour of the iodine–amylose complex in a spectrophotometer at 680 nm. The degree of complex formation is defined as follows:

$$\text{'Complexing index'} = \frac{\text{Absorbance of control} - \text{Absorbance of sample}}{\text{Absorbance of control}} \times 100.$$

The correlation between 'complexing index' and the weight of dried precipitated complex is shown in Fig. 1. The dried complex was examined by X-ray diffraction, and the following spacings were found: 12·0 Å (weak), 6·80 Å (medium) and 4·41 Å

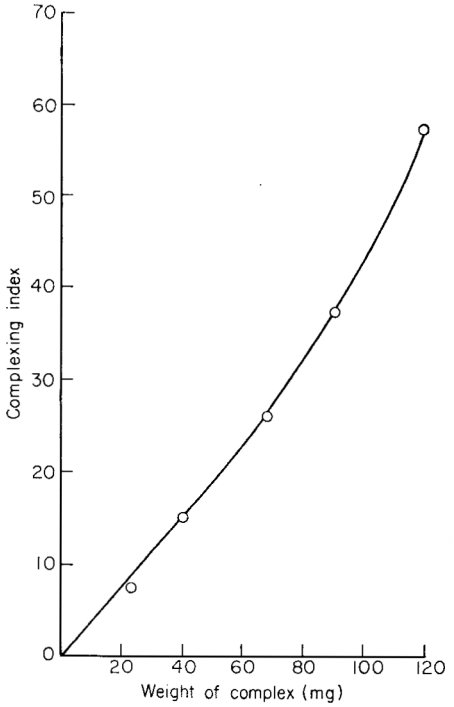


FIG. 1. Relationship between complexing index and weight of dried amylose–monoglyceride complex.

(strong intensity). These are in agreement with the values reported by Zobel (1964) for the V-pattern given by amylose precipitated with linear alcohols or higher fatty acids.

Bread

The following recipe for Continental white bread was used:

Wheat flour (Danish, 10·6% protein)	2000 g
Sugar	30 g
Yeast	90 g
Lard	21 g
Salt	30 g
Water	1140 g
Ascorbic acid (present at 60 ppm in the flour)	0·12 g

Each monoglyceride preparation was used at a rate corresponding to 0·5% monoglyceride, calculated on the flour weight; the water content was adjusted to be equal in all experiments.

The baking procedure was as follows:

Mixing: 15 min in first gear on an 'Artofex' mixer
Proving times: 2 × 10 min at 25°C
Fermentation: 40 min at 31°C
Scaling weight: 700 g
Oven temperature: 220°C
Baking: 36 min (in open-top tins)
Moulding: by hand

After baking, the loaves were kept at 22°C for 1, 2, 4 and 6 days sealed in polythene bags.

Measurement of bread firmness

A Panimeter constructed by the Institute for Cereals, Flour and Bread T.N.O., Wageningen, Holland was used. This instrument is constructed as a lever with a movable weight opposite the compression unit, which compresses a cylindrical bread sample of diameter 50 mm and height 28 mm. The sample stands between a stationary plate and a plate connected to the lever. The weight moves at a rate of about 0·6 cm/sec, and is stopped at a chosen value between 50 and 1000 g. Compression is registered automatically in the form of a curve by a recording system. The total compressibility of the bread is read in Panimeter Units (PU), and 1000 PU correspond to 18 mm compression. When comparing PU-values obtained with different weights it is necessary to convert them into the same basic weights, and in this case 600 g was chosen.

Results and discussion

Crystal forms of the monoglyceride preparations

X-ray data for the monoglyceride preparations are shown in Table 1. Both of the DGMS-gels gave a strong diffraction line at approximately 4·1 Å, which proves the α-crystalline state of the DGMS molecules; neither gave long spacings (only spacings up to approximately 30 Å could be detected with the camera used). It is known (Larsson, 1967) that the gel is a liquid crystalline mesomorphic phase of the lamellar type. A phase diagram for DGMS has also been published (Krog & Larsson, 1968).

The DGMS-hydrate gave a diffraction pattern which, according to the nomenclature for the polymorphic forms of glycerides (Larsson, 1966), indicates a β-crystalline form. The hydrate is a coagel, i.e. a suspension of β-crystals (Larsson, 1967) which probably have a polar surface structure (Larsson, 1968).

The freeze-dried DGMS-hydrate powder and the spray-crystallized DGMS powder were both in the stable β-crystalline form. When being used, the mono-/diglyceride emulsion was predominantly in α-form, but it was transformed to β-form during storage for 1–2 weeks.

TABLE 1. X-ray data for the monoglyceride preparations

Material	Spacings (Å)	Crystal form
1. DGMS-gel, pH 6·8	14·8 w–*4·13s*	α– (liquid crystalline)
2. DGMS-gel, pH 7·3	*4·11s*	α– (liquid crystalline)
3. DGMS-hydrate	24·8 w–16·1 m–11·9 m– *4·50s*–4·29w–4·06w–3·91w– 3·86w– 3·81w–3·70w	β–
4. DGMS-hydrate powder, freeze-dried	23·9 w–15·8 m–12·0 w–7·86w–*4·51s*–4·41w–4·29m–4·06w 3·95w– 3·86w– 3·74w–3·68w–2·43w	β–
5. DGMS powder spray-crystallized	24·6 w–16·4 m–12·3 w–8·20w–*4·55s*–4·32w–4·11w–3·97w– 3·86w– 3·76w–2·43w	β–
6. Mono-/diglyceride emulsion	23·5 w–15·4 m– 4·55w–*4·09s*–3·85w	α–

Intensity: s = strong, m = medium, w = weak.

Amylose-complexing effect of monoglycerides

The formation of amylose complexes was studied at temperatures of 31° and 60°C, and with reaction times of 40 and 60 min, respectively. The temperatures were chosen because of their relevance to dough fermentation and baking. The reaction time of 60 min at 60°C was chosen because preliminary experiments had shown that this allowed equilibrium to be obtained.

From the values of complexing index shown in Fig. 2(a), it can be seen that the DGMS-gels gave much stronger reaction with amylose than any of the other preparations. This is attributable to the high degree of translational freedom of monoglyceride molecules within gels. The different behaviours of the DGMS-gel, pH 6·8, and the DGMS-gel, pH 7·3, is surprising and not immediately explicable.

Both DGMS-hydrate and spray-crystallized powder, both of which were β-crystalline, showed only inferior effects at 31°C. The mono-/diglyceride emulsion was also rather ineffective at 31°C, even though it was in α-crystalline state. However, it should be remembered that the monoglycerides, which are the most hydrophilic glycerides in this mixture, will be bound on the surfaces between the water and the other glycerides and also might be unavailable for amylose-complexing. In this connection it can be mentioned that the complexing effect of the DGMS-hydrate was greatly reduced when lard was added in a ratio of 1 : 1.

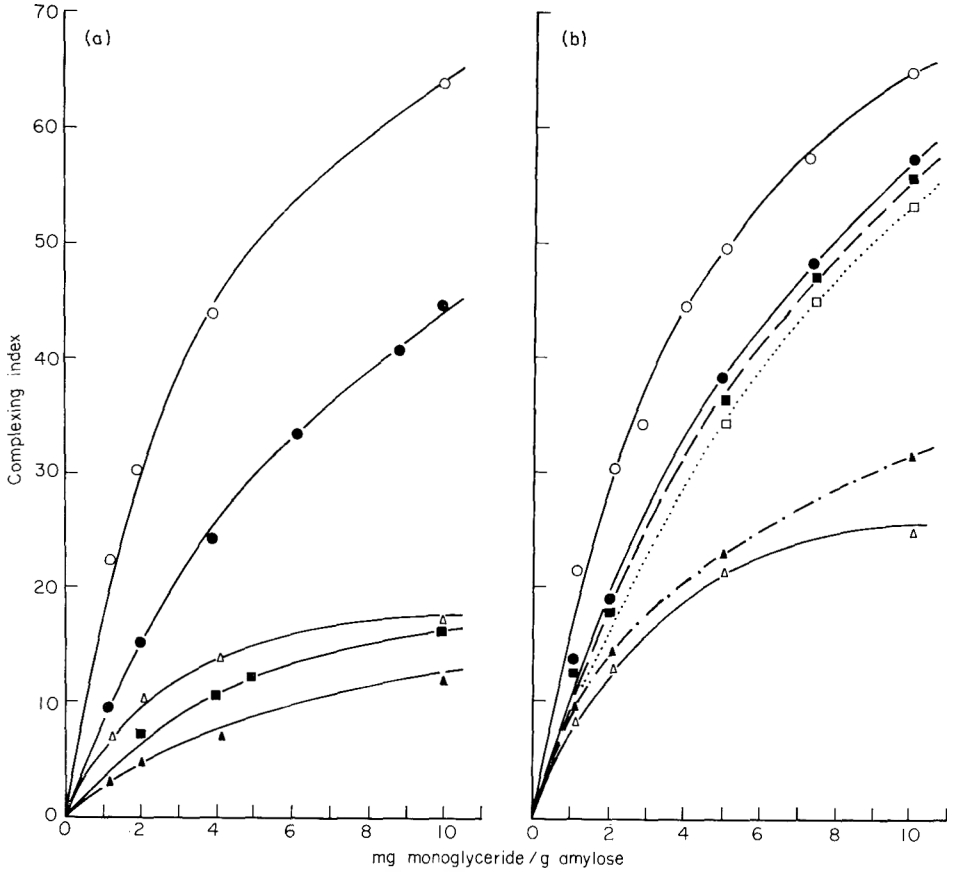


FIG. 2. The ability of the various monoglyceride preparations to form complex with amylose at 31°C (a) and at 60°C (b) ○, DGMS-gel, pH 6·8; ●, DGMS-gel, pH 7·3; ■, DGMS-hydrate; □, DGMS-hydrate powder; ▲, DGMS powder; △, mono-/diglyceride emulsion.

Fig. 2(b) shows the amylose complexing effects at 60°C. It can at once be seen that at 60°C the DGMS-hydrate is about as effective as the gels. Furthermore, the difference between the two gel types is much smaller at 60°C than at 31°C. The effects of the DGMS powder and the mono-/diglyceride emulsion have also been increased somewhat in comparison with the results at 31°C.

The reason why the DGMS-hydrate shows the same effect as the DGMS-gel at 60°C is quite clear; at this temperature it is transformed from the β-crystalline hydrate to a dispersion with the same liquid crystalline state as the gel. Actually, it could be expected that the spray-crystallized powder would give an effect corresponding to those of the gel hydrate form if a complete dispersion were obtained under the experimental conditions. However, particularly at higher concentrations, the effect was relatively low. This might be owing to the fact that the reaction time was not long enough to ensure a state of equilibrium. Reaction times of more than 1 hr were not

examined as it was assumed that materials requiring more than 1 hr reaction time have no practical interest.

It is very interesting that the freeze-dried hydrate powder, which was included among the samples examined at 60°C, gave approximately the same effect as the hydrates. From this it may be concluded that the structure of the freeze-dried hydrate powder and that of the spray-crystallized DGMS powder are entirely different. The reason for this may be that the specific hydrophilic surface of the β-crystals in a hydrate is maintained after the freeze-drying process. During the experiments it was also found that the freeze-dried product, when heated to 60°C in water, did form a liquid crystalline gel much faster than the spray crystallized DGMS powder.

Rate of monoglyceride–amylose complex formation

Some experiments were made to study the rates at which monoglyceride preparations formed complexes with amylose at 60°C. The concentration of DGMS was kept

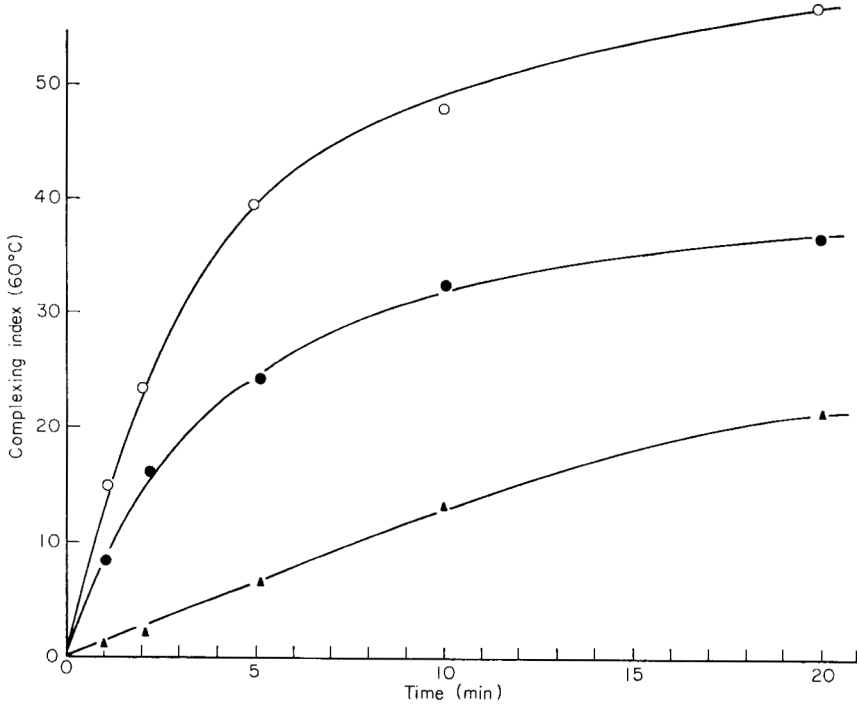


FIG. 3. The rate of complex formation at 60°C. O, DGMS- gel, pH 6·8; ●, DGMS-hydrate; ▲, DGMS powder.

constant (5 mg/g amylose). After cooling to 20°C the complexing index was determined. It can be seen (Fig. 3) that the α-crystalline gel forms complexes at a greater rate than the β-crystalline hydrate, which again reacts at a much greater rate than the non-hydrated powder.

Studies on Amylopectin

Addition of the various preparations to amylopectin solutions gave no visible precipitation, and no decrease in the colour (measured at 455 nm) of the iodine–amylopectin complex. Thus no evidence of interaction between monoglycerides and amylopectin was obtained.

Anti-firming effect in bread

Fig. 4 shows the effects of the various preparations in bread kept at about 22°C.

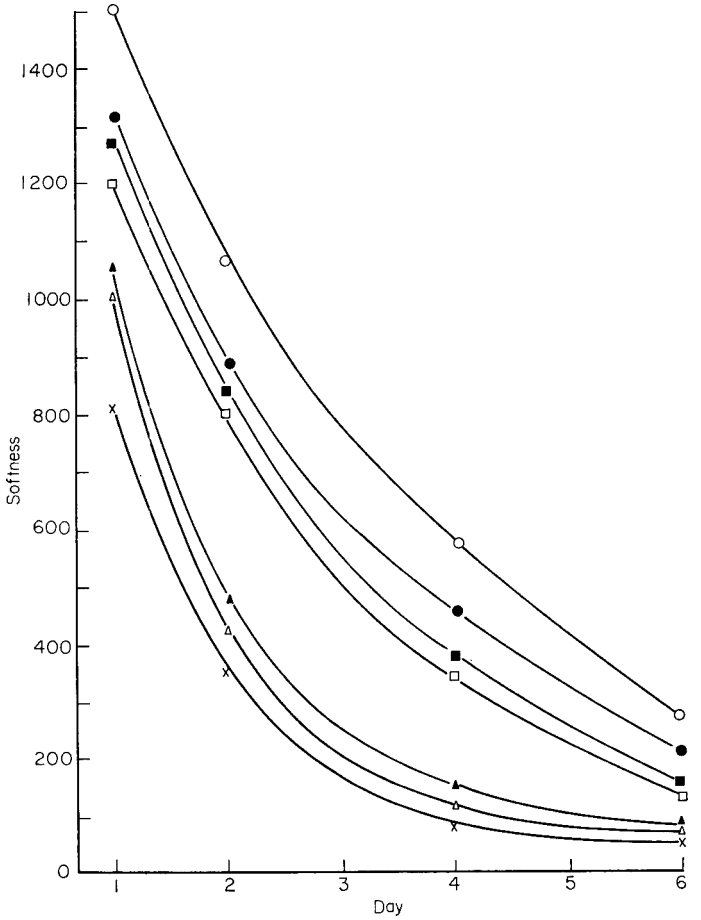


FIG. 4. Anti-firming effect of the monoglyceride preparations in white bread. ○, DGMS-gel, pH 6·8; ●, DGMS-gel, pH 7·3; ■, DGMS-hydrate; □, DGMS-hydrate powder; ▲, DGMS powder; △, mono-/diglyceride emulsion; ×, control.

The experiments lasted for about 1 year, for which reason the curves represent average values of results obtained at different times. In a number of experiments the bread was kept at 5°C for 1–3 days. As would be expected these experiments gave results similar to those shown in Fig. 4, except that all the values measured were lower, because the staling process takes place more quickly at this low temperature.

The greatest anti-firming effect was obtained with DGMS-gel, pH 6·8; DGMS-gel, pH 7·3, gave a slightly lower effect. Both the DGMS-hydrate and the freeze-dried DGMS-hydrate gave good effects, whereas the spray-crystallized DGMS powder and the mono-/diglyceride emulsion gave very poor effects.

It can be seen that the monoglyceride preparations that gave the highest complexing index with amylose also gave the best anti-firming effect, whereas the preparations (spray-crystallized DGMS powder and mono-/diglyceride emulsion) that gave a low amylose complexing index also gave a poor anti-firming effect in bread. This supports Schoch's (1965) theory.

The results confirm those given by Wren (1968) that the physical state of the monoglycerides, before they are added to the dough, is of the greatest importance for obtaining the optimum effect in bread. The best results were obtained when the monoglycerides were added in the form of an aqueous, liquid–crystalline gel. The reason for this is probably that monoglycerides in this form can complex with amylose at an earlier state during the bread-making process. According to the values for complexing index, shown in Fig. 2(a), the DGMS-gel, pH 6·8, can complex amylose as early as the dough mixing and fermentation stages; this is not possible to the same degree for the other preparations.

Although the β-crystalline DGMS-hydrate cannot complex amylose at temperatures below about 56°C, it gave a good anti-firming effect. Presumably this is due to its high amylose complexing ability at temperatures above 56°C (cf. Fig. 2b), which are reached during baking.

The same is presumably true of the freeze-dried DGMS-hydrate powder, but not of the non-hydrated spray-crystallized DGMS powder.

Acknowledgments

The authors wish to thank Dr J. J. Wren for many helpful discussions during the period in which this work was done. Thanks are also due to Avebe G.A., Veendam, Holland for the free sample of amylopectin.

References

Gilbert, G.A. & Spragg, S.P. (1964) *Methods in Carbohydrate Chemistry*, Vol. 4: *Starch*. (Ed. by R. L. Whistler), p. 168. Academic Press, New York and London.

Jongh, G. (1961) *Cereal Chem.* **38**, 140.

Kováts, L.T. & Lasztity, R. (1961) *Periodica Polytechnica*, Chapter VI/1, p. 1. Budapest, Hungary.

Krog, N. & Larsson, K. (1968) *Chem. Phys. Lipids*, **2**, 129.

LARSSON, K. (1966) *Acta chem. Scand.* **20,** 2255.

LARSSON, K. (1967) *Z. phys. Chem, Frankfurt,* **56,** 173.

LARSSON, K. (1968) *Surface-Active Lipids in Foods,* Monograph No. 32, p. 8. Society of Chemical Industry, London.

OFELT, C.W., MACMASTERS, M.M., LANCASTER, E.B. & SENTI, F.R. (1958a) *Cereal Chem.* **35,** 137.

OFELT, C.W., MEHLTRETTER, C.L., MACMASTERS, M.M., OTEY, F.H. & SENTI, F.R. (1958b) *Cereal Chem.* **35,** 142.

SCHOCH, T.J. (1965) *Bakers' Digest,* **39,** 48.

SCHOCH, T.J. & FRENCH, D. (1947) *Bakers' Digest,* **21,** 102.

SCHOCH, T.J. (1964) *Methods in Carbohydrate Chemistry,* Vol. 4; *Starch.* (Ed. by R. L. Whistler), p.157. Academic Press, New York.

SEIBEL, W., MENGER, A., HAMPEL, G. & STEPHAN, H. (1968) *Brot. u. Gebäck* **22,** 193.

STRANDINE, E.J., CARLIN, G.T., WERNER, G.A. & HOPPER, R.P. (1951) *Cereal Chem.* **28,** 449.

WOOTTON, J.C., HOWARD, N.B., MARTIN, J.B., MCOSKER, D.E. & HOLME, J. (1967) *Cereal Chem.* **44,** 333.

WREN, J.J. (1968) *Surface-Active Lipids in Foods,* Monograph No. 32, p. 158. Society of Chemical Industry, London.

ZOBEL, H.F. (1964) *Methods in Carbohydrate Chemistry,* Vol. 4: *Starch.* (Ed. by R. L. Whistler), p. 109. Academic Press, New York.

J. Fd Technol. (1970) 5, 89–99.

The use of Thiabendazole for the post-harvest treatment of bananas

DIANA M. BAILEY,* D. F. CUTTS,† L. DONEGAN,*
C. A. PHILLIPS‡ AND R. POPE*

Summary

Studies were carried out to assess the efficacy of thiabendazole (TBZ or [2-(4-thiazolyl)benzimidazole]) in controlling fungal rot damage of bananas in the Windward Islands. A dipping treatment proved to be more effective, especially in the reduction of rot in the banana cushions, than application of the fungicide by spraying, but both methods of application resulted in a very satisfactory control of fungal rots. Chemical analysis of the treated bananas showed that regardless of mode of application and location on the hand the residue levels were well below the limits permitted by American standards.

Introduction

The condition of bananas known as stem rot, stem-end rot, collar rot, finger-dropping or stalk rot arises from infection of the fruit by one or more of a large group of micro-organisms. Serious problems have arisen through high incidence of these rots in bananas shipped from the Windward Islands to the United Kingdom, especially in fruit packed in cartons (Phillips & Spector, 1969). The damage is manifest in decay of the stalk joining the individual banana finger to the cushion, which may be sufficiently severe to cause the individual fingers to become detached: even when this does not occur, extensive brown to black discoloration of the skin, spreading down the fruit from the cushion, takes place. These effects, together with visible fungal growth on the cushion and sometimes on the skin, detract from the appearance of the fruit to such an extent that it becomes completely unsaleable, even though the edible pulp may remain virtually undamaged.

Lesions of this type are associated with a wide variety of fungal species: some of the principal species involved are *Gloeosporium musarum* (Cooke et Massee), *Botryodiplodia theobromae* (Pat.) and *Thielaviopsis paradoxa* (de Seynes) von Hohn, but many others are involved, especially as secondary infections (Wardlaw, 1961; Simmons, 1966).

* Tropical Products Institute, Ministry of Overseas Development, 56–62 Gray's Inn Road, London, W.C.1.

† Geest Industries Limited, Spalding, Lincolnshire.

‡ Windward Islands Banana Research Scheme, P.O. Box 115, Castries, St Lucia, West Indies.

The recent discovery of the fungicidal properties of [2-(4-thiazolyl)benzimidazole] TBZ coupled with its low mammalian toxicity (Staron & Allard, 1964; Robinson, Phares & Graessle, 1964) prompted a series of investigations into the use of TBZ in the control of fungal rots on fruit. Several reports exist of its successful use in the fungicidal treatment of citrus fruits (Crivelli, 1966; Primo Yufera & Hernandez Gimenez, 1966; Harding & Schade, 1967; Eldon Brown, McCornack and Smoot, 1967; Eldon Brown & Wilson, 1967; McCornack & Eldon Brown, 1967; Harding, 1967, 1968; Eldon Brown, 1968); reduction of *Penicillium* and *Gloeosporium* spp. infections on stored apples (Pierson, 1966, Edney, 1968) and control of *T. paradoxa* infections in pineapple (Frossard, 1968).

Burden (1967) reduced *Colletotrichum musae* infections causing 'crown rot' in bananas in Queensland by using dips containing up to 800 ppm of TBZ. Similarly Scott & Roberts (1967) showed that dips containing 140 ppm of TBZ were effective in controlling damage caused by *G. musarum* in bananas in New South Wales. Detailed experiments in which bananas were artificially inoculated with *G. musarum* are reported by Cuillé & Bur-Ravault (1968). They showed that dipping or spraying of the infected fruit, prior to storage, with TBZ at levels up to 3000 ppm (using lactic acid as a solubilizing agent) substantially reduced the development of the inocula. Higher levels of application delayed ripening of the fruit. Conditions for practical application of TBZ are described in detail by Beaudoin, Champion & Mallesard (1969). Collar rot was effectively controlled using a dip containing 140 ppm of TBZ in trials in South Africa (Swarts, Jacobs & Nel, 1969).

The use of TBZ as a fungicidal treatment for bananas has recently been approved in the United States (Anon, 1968). The American regulations permit maximum residue levels of 3 ppm on the peel and 0·4 ppm on the edible pulp. It should be noted that TBZ is used primarily in medicine as an anthelmintic.

It was therefore considered that a large scale investigation into fungicidal control on bananas by TBZ would be worth while in order to establish possible codes of practice for its use in the Windward Islands. The experiment includes chemical analysis of residues as well as quality assessment on fruit either dipped or sprayed with TBZ.

Experimental

Six shipments of bananas were involved: each shipment comprised 600 cartons of fruit arising from the treatments listed below.

Treatment

Hands of freshly harvested bananas in St Lucia were washed in running water to remove latex exuding from the cut cushion. The wet hands were then treated with the fungicide either by dipping or spraying.

Dipping. Two hands of the wet fruit were dipped simultaneously for about 3 sec in 8 gal of the TBZ suspension, drained and packed into cartons while still wet. The suspension contained 400 ppm of TBZ prepared by diluting a 40% TBZ wettable powder formulation with water. The dip liquor was discarded after fruits for 100 cartons had been treated. Two hundred cartons (approximately 1200 hands or 20,000 fingers) were treated in this manner on the same day.

Spraying. A similar quantity of wet fruit was sprayed with 200 ppm TBZ suspension using a garden hand sprayer. The hands were laid on a padded dripping stand with their concave sides upwards exposing fully the cushion and pedicel. As with dipping, the fruit was boxed after spraying while still wet.

Controls. Approximately 1200 hands of washed bananas were redipped in water and drained.

Packaging and ripening

All the treated and control hands were packed in cartons (3 × 200/shipment). Each carton consisted of two sections each accommodating three or four hands weighing about 13 lb. The cartons were then shipped and the temperature of the hold lowered to 12·5°C (55°F) as quickly as possible. The voyage lasted approximately 12 days and the bananas reached the ripening rooms in the United Kingdom 2 days later.

By varying the temperature of the ripening rooms the bananas may be made to ripen in as little as 4 days or held back for as long as 8 days. All the experimental bananas were ripened for 8 days, this being the longest time that bananas are ever normally held in a ripening room: significant stem rot infections if present are very obvious by the 8th day. Identical treatments were applied to five further weekly shipments.

Quality assessment

On the 8th day all the cartons were removed from the ripening rooms and representative samples of the three treatments were selected at random. Bananas from these cartons were first examined visually for fungal damage etc. They were re-examined a second time 4 days later to simulate their condition on reaching the consumer within 1–5 days after removal from the ripening rooms. The degree of the stem rot occurring on each 'hand' of bananas in the experimental cartons was rated either as zero (indicating perfect condition) or from 1 to 4 indicating progressively increasing degrees of fungal attack, the highest score indicating that disintegration of the hand occurred when it was lifted, the individual fingers breaking off under their own weight. These assessments were made on the cushion, the finger stalks and the skins of each hand, respectively.

Chemical analysis

The method employed to estimate the TBZ residues was supplied privately by Merck, Sharp & Dohme Ltd and is specifically detailed for the analysis of bananas.

It involves extraction of the TBZ from the macerated fruit with ethyl acetate and examination of the extract in a spectrofluorimeter after purification via a series of consecutive partitions of the compound between the ethyl acetate and acid or buffered aqueous phases. TBZ contents are calculated by comparison of the readings with those obtained from known standards subjected to identical procedures. The method has the great advantage of being highly sensitive; a solution containing 0·1 μg/ml TBZ gives a transmission reading of about eight transmission units at the maximum sensitivity setting which corresponds in the method to about 0·1 ppm TBZ in the fruit.

Banana fingers were sampled from both inner and outer layers of a hand. Also to obtain a wider spread of results mixed half bananas were analysed, i.e. two bananas from the same bulk sample were cut transversely into halves, one half from each was peeled, the peels combined, macerated and an aliquot (10 g) analysed and the pulps treated similarly.

This method has the disadvantage that repeatability in spectrofluorimetry is poorer than that in ultraviolet or visible region spectrophotometry. Samples of untreated banana pulp and peel dosed with known amounts of TBZ in the laboratory (0·100 and 1·00 ppm respectively) gave recoveries by this method ranging from 88 to 110%.

Other methods for estimating TBZ are a colorimetric procedure which involves reduction with zinc (Szalkowski & Kanora, 1965) or measurement of the ultraviolet absorption. These procedures are less sensitive than the spectrofluorimetric method.

Results

Quality assessment

For the statistical analysis, the unit was the sum of the scores on all the hands in the carton section expressed as a percentage of the highest possible score if all the hands were scored as 4. Considerable differences were found between assessments at the first inspection of the various shipments, due to seasonal and other uncontrolled factors which are not the subject of study.

The variability was greater within a consignment if the mean percentage score was near 50% than if it was smaller or greater. This is analogous to a binomial distribution, and the empirical result $s = 39{\cdot}7 \sqrt{PQ} - 1{\cdot}53$ was obtained, and used in all *t*-tests.

Cushions

On average the improvement due to TBZ treatment is about 30% (Table 1), and is greater at the second inspection than at the first. Between spray and dip treatments there is an average difference of about 6% at the first inspection and about 11% at the second inspection in favour of dipping (Table 2).

TABLE 1. Percentage fungal rot score

Shipments	No. of carton sections inspected	Cushions		Finger-stalks		Skins	
		Mean of first inspection	Mean of second inspection	Mean of first inspection	Mean of second inspection	Mean of first inspection	Mean of second inspection
Control							
1	30	43	65	25	50	19	24
2	32	38	61	21	41	15	29
3	32	46	75	22	55	7	17
5	32	35	62	18	39	7	15
6	32	47	66	15	44	8	22
Spray							
1	20	10	29	15	22	14	21
2	32	18	43	17	34	12	22
3	32	27	49	14	29	7	15
5	32	14	26	6	17	5	9
6	32	18	29	9	15	3	7
Dip							
1	30	8	19	13	17	14	16
2	30	11	28	13	26	9	21
3	32	22	40	14	24	12	18
5	32	3	12	2	6	1	1
6	32	13	21	5	7	3	3
Averages of five shipments							
Control	158	42	66	20	46	11	21
Spray	148	17	35	12	24	8	15
Dip	156	11	24	9	16	8	12

Shipment 4 was not examined.

Finger stalks

The average improvement is nearly 18% and greater at the second inspection than the first. Between the two treatments the differences are much smaller (Table 3). Dipping has an average advantage of 3% over spraying, at the first inspection, rising to 8% at the second inspection. The incidence of fungal rot in both treated categories is considerably lower in the last two consignments, while chemical analyses show that the TBZ residues in the dipped fruit in these shipments are higher than in earlier consignments.

TABLE 2. Percentage fungal rot *t*-tests of differences in means between untreated, sprayed and dipped bananas

Comparison	Shipments	Cushions					
		First inspection			Second inspection 4 days later		
		Difference	*t*	Significance	Difference	*t*	Significance
Control–spray	1	33	7·2	***	36	6·9	***
	2	20	4·9	***	18	3·9	***
	3	20	4·5	***	26	5·8	***
	5	22	5·6	***	36	7·9	***
	6	29	6·8	***	37	8·2	***
Control–dip	1	35	8·6	***	46	9·9	***
	2	27	6·8	***	33	7·1	***
	3	24	5·7	***	35	7·8	***
	5	32	9·0	***	50	11·3	***
	6	34	8·1	***	45	10·0	***
Spray–dip	1	2	0·7		10	2·2	*
	2	7	2·2	*	15	3·4	**
	3	5	1·3		9	2·0	*
	5	10	4·3	***	14	3·9	***
	6	5	1·5		8	2·0	*
Averages							
Control–spray		25	13·0	***	31	14·7	***
Control-dip		30	16·8	***	42	20·4	***
Spray–dip		6	4·0	***	11	5·8	***

Shipment 4 was not examined.
* Over 95% significance point.
** Over 99% significance point.
*** Over 99·9% significance point.

Skins

Treatment by spraying with TBZ on the average makes an improvement of about 4%, and by dipping about 6%, again considerably better at the second assessment than at the first (Table 4).

It is noticeable that the TBZ treatments have a continuing effect, so that the average improvement observed at the second inspection is significantly greater than at the first (Table 5).

Chemical analysis

The residues found are listed in Table 6 correct to the nearest significant digit; the

TABLE 3. Percentage fungal rot *t*-tests of difference in means between untreated sprayed and dipped bananas

Comparison	Shipments	Finger stalks					
		First inspection			Second inspection 4 days later		
		Difference	*t*	Significance	Difference	*t*	Significance
Control–spray	1	10	2·4	*	28	5·6	***
	2	4	1·3		6	1·5	
	3	9	2·5	*	26	5·8	***
	5	12	4·3	***	23	5·6	***
	6	7	2·4	*	29	6·9	***
Control–dip	1	12	3·4	**	33	7·5	***
	2	8	2·3	*	15	3·4	**
	3	8	2·4	*	31	7·0	***
	5	16	6·0	***	33	8·7	***
	6	11	4·1	***	37	9·3	***
Spray–dip	1	2	1·0		5	1·3	
	2	3	1·1		8	2·0	
	3	0	0·1		5	1·3	
	5	4	2·2	*	10	3·7	***
	6	4	1·9		8	3·0	**
Averages							
Control–spray		8	5·6	***	22	11·3	***
Control–dip		11	7·7	***	30	15·7	***
Spray–dip		3	2·1	*	8	4·6	***

Shipment 4 was not examined.
* Over 95% significance point.
** Over 99% significance point.
*** Over 99·9% significance point.

table is subdivided according to the variables concerned, e.g. treatment, outer or inner location on the hand and part of the fruit analysed. For ease of comparison the results for treated bananas only are summarized in Table 7 as averages for the different series involved, together with overall averages for the two treatments.

Analysis of inner and outer bananas were made as there could be a possibility that the inner layer of bananas on a hand received a larger dose of TBZ than the outer layer during spraying, since it shielded the latter to some extent, and the inner layer on dipped hands could also have accumulated some 'run off' from the outer layer.

TABLE 4. Percentage fungal rot *t*-tests of differences in means between untreated, sprayed and dipped bananas

Comparison	Shipments	Skins					
		First inspection			Second inspection 4 days later		
		Difference	*t*	Significance	Difference	*t*	Significance
Control–spray	1	5	1·4		3	0·7	
	2	2	0·8		7	1·7	
	3	0	0·1		2	0·6	
	5	2	1·1		6	2·1	*
	6	5	2·5	*	14	4·6	***
Control–dip	1	5	1·6		8	2·2	*
	2	7	2·0		8	2·0	*
	3	−5	2·0	*	0	0·1	
	5	6	4·1	***	13	5·8	***
	6	5	2·7	**	19	6·5	***
Spray–dip	1	0	0·0		5	1·2	
	2	3	1·2		2	0·4	
	3	−5	2·1	*	−2	0·7	
	5	4	3·3	**	8	4·1	***
	6	0	0·2		4	2·3	
Averages							
Control–spray		3	2·5	*	6	4·1	***
Control–dip		3	3·0	**	10	6·4	***
Spray–dip		0	0·4		3	2·3	*

Shipment 4 was not examined.
* Over 95% significance point.
** Over 99% significance point.
*** Over 99·9% significance point.

TABLE 5. Average percentage rates of development of fungal rot in the 4 days between inspections

	Cushions	Stalks	Skins
Control	24	26	10
Spray	18	12	7
Dip	13	7	4

TABLE 6. Thiabendazole content (ppm)

Control				Dipped				Sprayed				
Outer		Inner		Outer		Inner		Outer		Inner		
Pulp	Skin	Pulp	Skin	Pulp	Skin	Pulp	Skin	Pulp	Skin	Pulp	Skin	
Shipment 3												
0·01	0·04	0·01	0·05	0·04	0·7	0·04	0·7	0·04	0·4	0·04	0·4	
				—	0·9	0·04	0·3	0·06	0·4	0·03	0·4	
				H 0·03	0·7			0·04	0·6			H
				0·02	0·7			0·04	0·6			
Shipment 4												
0·01	0·08	0·01	0·11	0·02	0·4	0·03	0·5	0·02	0·7	0·03	0·7	
				0·03	0·5	0·02	0·5	0·03	1·0	0·05	1·0	
				0·02	0·4	0·02	0·5	0·02	0·7	0·03	0·9	
				H 0·03	0·6	0·03	0·6	0·03	0·6	0·04	1·0	H
				0·04	0·5	0·04	0·7	0·06	1·6	0·03	0·7	
Shipment 5												
0·03	0·06	0·03	0·3	0·07	0·8	0·04	1·7	0·03	0·9	0·03	0·6	
—	0·05	—	0·08	0·09	1·2	0·07	1·2	0·06	0·8	0·08	0·8	
				0·04	1·0	0·11	1·3	0·11	1·3	—	—	
				H 0·03	1·0	0·03	1·0	0·05	0·8	0·04	0·5	H
				0·07	1·0	0·08	1·1	0·05	0·6	0·03	0·7	
Shipment 6												
0·03	0·14	0·03	0·2	0·04	0·6	0·06	1·1	0·03	0·4	0·03	0·5	
				0·05	0·8	0·04	1·1	0·03	0·4	0·03	0·8	
				0·11	1·2	0·06	1·1	0·06	0·4	0·05	0·5	
				H 0·16	1·3	0·12	1·1	0·05	0·6	0·07	1·1	H
				0·07	0·7	0·07	0·8	0·03	0·3	0·04	0·3	

Shipments 1 and 2 not examined

H= Results obtained from mixed half bananas.

Lowest content found in (treated) pulp 0·02 ppm. Highest content found in (treated) pulp 0·16 ppm (shipment 6, outer layer). Lowest content found in the skin 0·3 ppm. Highest content found in the skin 1·7 ppm (shipment 5, inner layer).

Conclusions

The treatment of hands of bananas with TBZ substantially reduced the damage caused by fungal rot. The fungi causing the rotting are currently under investigation, but so far the work is only preliminary and the results will be published elsewhere.

The residues found in all the bananas examined are well below the tolerance levels laid down by the FDA (i.e. 3·0 ppm on the skin, 0·4 ppm in the pulp). The more

TABLE 7. Average thiabendazole content (ppm)

Shipment		Average TBZ content (ppm)			
		Dipped		Sprayed	
		Pulp	Skin	Pulp	Skin
3	Outer	0·03	0·8	0·04	0·5
	Inner	0·04	0·5	0·04	0·4
4	Outer	0·03	0·5	0·05	0·9
	Inner	0·03	0·6	0·04	0·9
5	Outer	0·06	1·0	0·06	0·9
	Inner	0·07	1·2	0·04	0·7
6	Outer	0·09	0·9	0·04	0·4
	Inner	0·05	1·0	0·04	0·6
Overall average	Outer	0·05	0·8	0·05	0·7
	Inner	0·05	0·8	0·04	0·7

important of these levels is that found in the pulp, since the skin is not normally eaten, but the skin analysis provides a useful guide to the efficacy of the application. On average about 94% of the TBZ applied by either treatment is retained by the skin, the actual amount varying from 90 to 96%. The residues found in dipped bananas were marginally higher than those on sprayed bananas, but the overall difference was very slight. In the quality assessment the dipping treatment was found to be more effective than spraying. The possible cause of this difference may be that there was a more even distribution of penetration of the hands of those dipped than those sprayed.

The residue levels appear to have but little dependence upon the location of the fruit between outer or inner positions in the hand; three out of the four shipments examined showed only marginally higher residues on the skins of inner layer bananas from dipped fruit compared with the corresponding outer layer samples indicating no significant accumulation due to run off. In sprayed fruit also, there was no consistent difference in residue levels to indicate shielding of the inner layer.

The residues in dipped bananas from shipments 5 and 6 appeared to be considerably higher (by a factor of about two in some cases) than those found in shipments 3 and 4, indicating some change in the process or strength of the dip liquor. Likewise the residues on sprayed bananas from the fourth and fifth shipments were higher than those from the third and sixth.

The values for 'apparent' TBZ found in the untreated bananas showed some increase with time and it is thought that the samples may have been contaminated either at the origin of the trials or during transit. The results obtained were not corrected for the 'apparent' value as the first analyses showed these to be practically negligible.

This paper demonstrates that under the conditions pertaining in the banana trade from the Eastern Caribbean to the United Kingdom, the use of TBZ at levels which would be tolerated under American legislation is highly effective in controlling stem rot and further suggests that dipping may be a more efficacious method of application than spraying, even though residues are similar in both types of treatment.

Acknowledgments

The authors thank the Tropical Products Institute, Geest Industries Ltd and WINBAN for the co-operation and facilities provided.

The TBZ-containing material was 'Mertect 340' supplied by Merck, Sharp & Dohme Ltd. Use of this material in the experimental work described implies no official endorsement of its use, or criticism of possible competitors. The authors wish, however, to thank this firm for their co-operation over the supply of material and information.

References

(Anon 1968) Thiabendazole. *Federal Register* 33, No. 82, part 120.
Beaudoin, Ch., Champion, J. & Mallesard, R. (1969) *Fruits* **24,** 89.
Burden, O.J. (1967) *Qd agric. J.* **93,** 186.
Crivelli, G. (1966) *Feddo* **20,** 25.
Cuille, J. & Bur-Ravault, L. (1968) *Fruits* **23,** 351.
Edney, K.L. (1968) *Ditton Laboratory Annual Report* 1967/68, 50.
Eldon Brown, G. (1968) *Pl. Dis. Reptr* **52,** 844.
Eldon Brown, G., McCornack, A.A. & Smoot, J.J. (1967) *Pl. Dis. Reptr* **51,** 95.
Eldon Brown, G. & Wilson, W.C. (1967) *Proc. Fla St. hort. Soc.* **80,** 301.
Frossard, P. (1968) *Fruits*, **23,** 207.
Harding, P.R. (1967) *Pl. Dis. Reptr* **51,** 781.
Harding, P.R. (1968) *Pl. Dis. Reptr* **52,** 623.
Harding, P.R. & Schade, J.E. (1967) *Pl. Dis. Reptr* **51,** 51.
McCornack, A.A. & Eldon Brown, G. (1967) *Proc. Fla St. hort. Soc.* **80,** 232.
Phillips, C.A. & Spector, J. (1969) *Proc. Conf. trop. subtrop. Fruits* (In press).
Pierson, C.F. (1966) *Pl. Dis. Reptr* **50,** 913.
Primo Yufera, E. & Hernandez Gimenz, E. (1966) *Revta agroq. technol. Alimentos* 6, 369.
Robinson, J.J., Phares, H.F. & Graessle, O.E. (1964) *J. invest. Derm.* **42,** 479.
Scott, K.J. & Roberts, E.A. (1967) *Aust. J. exp. Agric. anim. Husb.* **7,** 283.
Simmons, N.W. (1966) *Bananas*, 2nd edn. Longmans Green, London.
Staron, T. & Allard, C. (1964) *Phytiat-Phytopharm.* **13,** 163.
Swarts, D.H., Jacobs, C. & Nel, T.G. (1969) *Fmg S. Afr.* **45,** 215.
Szalkowski, C.R. & Kanora, J.K. (1965) *J. Ass. off. agric. Chem.* **48,** 288.
Wardlaw, C.W. (1961) *Banana Diseases*, 1st edn. Longmans Green, London.

J. Fd Technol. (1970) **5**, 101–102

Book Review

Quality and Stability in Frozen Foods. 'Time–Temperature Tolerance' and its Significance. Ed. by W. B. VAN ARSDEL, M. J. COPLEY and R. L. OLSEN. New York and London: Wiley-Interscience, 1969. Pp. 384 + xv. £9 7s.

This book illustrates how parochial technology is: how limited to the circumstances and requirements of the industry in the area within which it originates. Here the requirements are those of the merchandizing of frozen foods; their storage and transport, their display and sale, and their performance in the kitchen and on the table. The critical theme is the evaluation of deterioration invoking such principles as 'just noticeable' or 'just perceptible' difference (JND or JPD) or 'just perceptible change' (JNC), which are the nearest that can be got to the objective evaluation of subjective sensations. The whole book, in fact, is based on a massive research operation on the Temperature–Time Tolerance of frozen foods mounted by the United States Department of Agriculture, the editors themselves having been responsible for the conduct of this operation. The various authors, however, are drawn from a wider spectrum, two of them, F. Bramsnaes and Mogens Jul reporting experiences of the applications of the JND method to fish and meat, respectively, in Denmark.

The price is, of course, astronomic, but quality and stability are assured by printing on paper with pH 6·5 or higher. This, we are told on a fly-leaf, 'will contribute to its longevity'. This is followed by a mysterious countdown from 10 to 1—does this mean that it is expected to have a lunar as well as a terrestrial distribution?

E. C. BATE-SMITH

Books Received

Confectionery Products Manufacturing Processes. By M. GUTTERSON. U.S.A.: Noyes Development Corporation, 1969. Pp. 323. $35.

Alcoholic Malt Beverages. By M. GUTCHO. U.S.A.: Noyes Development Corporation, 1969. Pp. 333. $35.

Soluble Coffee Manufacturing Processes. By NICHOLAS PINTAURO. U.S.A.: Noyes Development Corporation, 1969. Pp. 254. $35.

Baked Goods Production Processes. By MILTON GUTTERSON. U.S.A.: Noyes Development Corporation, 1969. Pp. 353. $35.

Journal of Texture Studies. Vol. No. 1, November 1969. Ed. by P. SHERMAN and A. S. SZCZESNIAK.
Dordrecht: Reidle, 1969. Pp. 129. Subscription price (4 issues). Dfl. 160 (U.S. $45).

Proceedings of the Second Conference for Feed Manufacturers 1968. Ed. by HENRY SWAN and DYFED LEWIS.
London: Churchill. Pp. 192.

Proceedings of the Third Conference for Feed Manufacturers 1969. Ed. by HENRY SWAN and DYFED LEWIS.
London: Churchill. Pp. 168.

Sugar Technology Reviews. Vol. 1. No. 1. December 1969. Ed. by G. H. JENKINS.
Amsterdam: Elsevier. Pp. 83. Dfl. 72.00 plus Dfl. 4.50 postage or equivalent (U.S. $20.00 + U.S. $1.25).

A major reference work

The Chemical Biology of Fishes

with a key to the literature

R. Malcolm Love

Torry Research Station
Aberdeen, Scotland

January 1970, xvi + 548 pp., 140s. ($7.00)
SBN 12.455850.X

This is a major reference work which brings together all the known factors which influence the composition of fish tissues, and identifies the chemical differences which distinguish one fish from another. The result is a biology of fish as seen through the medium of chemical analysis, with practical suggestions for a more physiological approach to the chemical study of fish.
The book is divided into three sections describing the dynamic aspects of fish chemistry. It gives complete bibliographical indexes to the levels of 250 chemical substances in different tissues of over a thousand species of fish. The entries are classified by chemical substance and by the names of the fish.

After describing techniques for sampling fish tissues, the author deals with intrinsic factors such as growth, maturity and habitual activity. He then discusses the many effects of the environment such as salinity, temperature and depth, as well as fishermen's lore on factors affecting the 'condition' of the fish. The book ends with a chapter on the effects of starvation.
This work is designed to meet a wide range of needs and should prove invaluable to marine biologists, biochemists, food technologists, nutritionists and those concerned with processing raw materials. They will find it a welcome reference to methods of analysis on fish tissues and a comprehensive study of chemical information in its biological and physiological context.

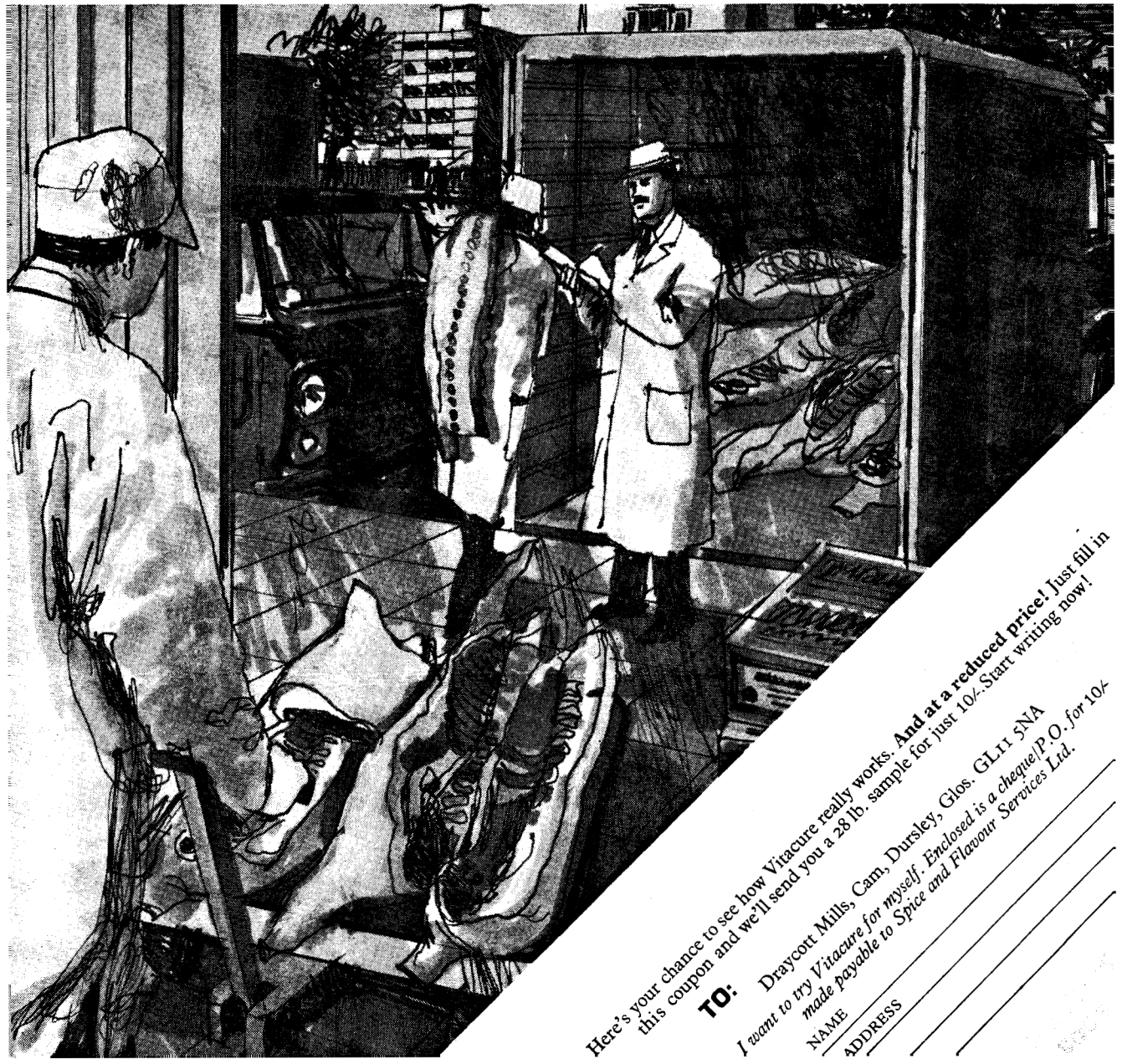
Contents

ACADEMIC PRESS

London and New York
Berkeley Square House, Berkeley Square, London WIX 6BA, England
111 Fifth Avenue, New York, N.Y. 10003, USA

The perfect solution to your curing problems.

No more quality control problems.
The results you get with Vitacure speak for themselves. An end to uneven curing and lost meat. **Every time.** A perpetual safeguard to your reputation. Without any of the comeback about uneven curing you run the risk of getting with your own curing agent. The secret of its success is in its manufacturing process. Tried and rigorously tested and developed in our new factory and laboratories. Try a sample of Vitacure for yourself. Try it now. Put it to the test. See if it doesn't live up to everything we've said about it. Just fill in the coupon and post it off today.



Here's your chance to see how Vitacure really works. **And at a reduced price!** Just fill in this coupon and we'll send you a 28 lb. sample for just 10/-. Start writing now!

TO: Draycott Mills, Cam, Dursley, Glos. GL11 5NA

I want to try Vitacure for myself. Enclosed is a cheque/P.O. for 10/- made payable to Spice and Flavour Services Ltd.

NAME

ADDRESS

JOURNAL OF FOOD TECHNOLOGY: NOTICE TO CONTRIBUTORS

The Journal of Food Technology publishes original contributions to knowledge of food science and technology and also review articles in the same field. Papers are accepted on the understanding that they have not been, and will not be, published elsewhere in whole, or in part, without the Editor's permission. Papers accepted become the copyright of the Journal.

Typescripts (two complete copies) should be sent to the Editor, Mr W. B. Adam, George and Dragon Cottage, Chipping Campden, Glos. Papers should be typewritten on one side of the paper only, with a 1½ inch margin, and the lines should be double-spaced. In addition to the title of the paper there should be a 'running title' (for page headings) of not more than 45 letters (including spaces). The paper should bear the name of the author(s) and of the laboratory or research institute where the work has been carried out. The full postal address of the principal author should be given as a footnote. (The proofs will be sent to this author and address unless otherwise indicated.) The Editor reserves the right to make literary corrections.

Arrangement. Papers should normally be divided into: (a) Summary, brief, self-contained and embodying the main conclusions; (b) Introduction; (c) Materials and methods; (d) Results, as concise as possible (both tables and figures illustrating the same data will rarely be permitted); (e) Discussion and conclusions; (f) Acknowledgments; (g) References.

References. Only papers closely related to the author's work should be included; exhaustive lists should be avoided. References should be made by giving the author's surname, with the year of publication in parentheses. When reference is made to a work by three authors all names should be given when cited for the first time, and thereafter only the first name, adding *et al.*, e.g. Smith *et al.* (1958). The '*et al.*' form should always be used for works by four or more authors. If several papers by the same author and from the same year are cited, a, b, c, etc., should be put after the year of publication, e.g. Smith *et al.* (1958a). All references should be brought together at the end of the paper in alphabetical order. References to articles and papers should mention (a) name(s) of the author(s); (b) year of publication in parentheses; (c) title of journal, underlined, abbreviated according to the *World List of Scientific Publications*, 4th edn and supplements; (d) volume number; number of first page of article. References to books and monographs should include (a) name(s) and initials of author(s) or editor(s); year of publication in parentheses; (b) title, underlined; (c) edition; (d) page referred to; (e) publisher; (f) place.

Standard usage. The *Concise Oxford English Dictionary* is used as a reference for all spelling and hyphenation. Verbs which contain the suffix ize (ise) and their derivatives should be spelt with the z. Statistics and measurements should always be given in figures, i.e. 10 min, 20 hr, 5 ml, except where the number begins the sentence. When the number does *not* refer to a unit of measurement, it is spelt out except where the number is greater than one hundred.

Abbreviations. Abbreviations for some of the commoner units are given below. The abbreviation for the plural of a unit is the same as that for the singular unless confusion is likely to arise.

gram(s)	g	second(s)	sec
kilogram(s)	kg	cubic millimetre(s)	mm^3
milligram(s)		millimetre(s)	mm
(10^{-3} g)	mg	centimetre(s)	cm
microgram(s)		litre(s)	l
(10^{-6} g)	µg	millilitre(s)	ml
nanogram(s)		pound(s)	lb
(10^{-9} g)	ng	gallon(s)	gal
hour(s)	hr	milliequivalent	mEq
minute(s)	min	R_F values	R_F

Figures. In the text these should be given Arabic numbers, e.g. Fig. 3. They should be marked on the backs with the name(s) of the author(s) and the title of the paper. Where there is any possible doubt as to the orientation of a figure the top should be marked with an arrow. Each figure must bear a reference number corresponding to a similar number in the text. Photographs and photomicrographs should be unmounted glossy prints and should not be retouched. Line diagrams should be on separate sheets; they should be drawn with black Indian ink on white paper and should be about four times the area of the final reproduction. Lines and lettering should be of sufficient thickness and size to stand reduction to one-half or one-third. Letters and numbers must be written lightly in pencil. Whenever possible, the originals of line diagrams, prepared as described above, should be submitted and not photographs. The legends of all the figures should be typed together on a single sheet of paper headed 'Legends to Figures'.

Tables. There should be as few tables as possible and these should include only essential data; the data should not be crowded together. The main heading should be in capitals with an Arabic number, e.g. TABLE 2. Each table must have a caption in small letters. Vertical lines should not be used.

Page proofs will be submitted to the contributors for minor corrections and should be returned to the Editor within 3 days. Major alterations to the text cannot be accepted.

Offprints. Fifty offprints will be issued free with each paper but additional copies may be purchased if ordered on the printed card which will be sent to the senior author with the proofs.

JOURNAL OF FOOD TECHNOLOGY
Volume 5, Number 1, March 1970

Contents

Printed in England by BPC Letterpress Limited at The Sidney Press Limited Bedford