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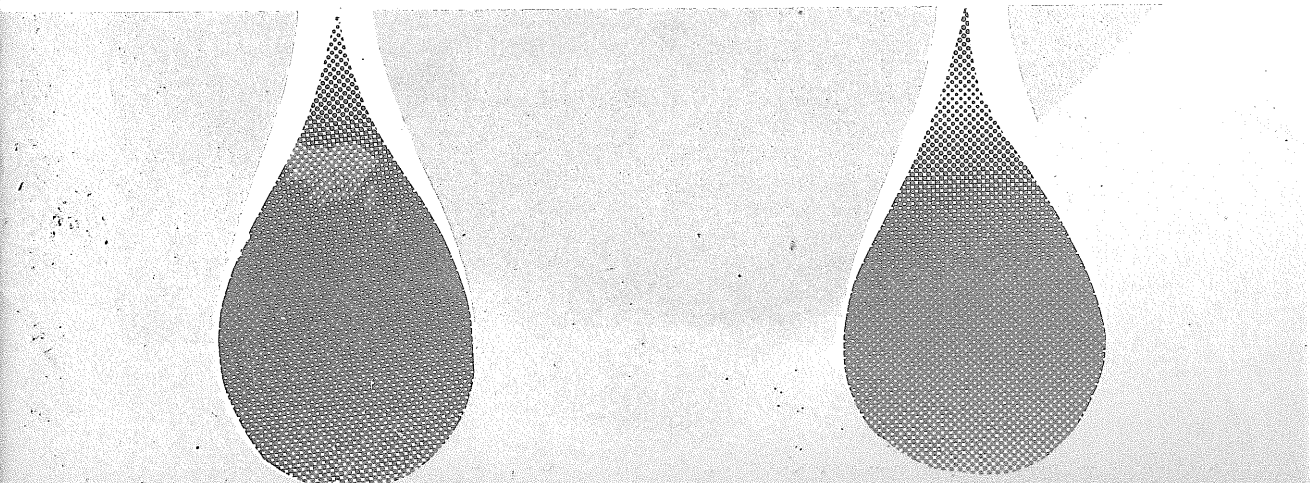

Meat chilling

By P. V. Harris

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A review of advances and problems, based on a lecture at the conference at MRL, 1974, on advances in meat science and technology

It is an unfortunate fact that the tenderness of meat is highly variable. Much of the variability can be attributed to the use of incorrect procedures for chilling the carcass. Important biochemical events occur in muscle after the death of an animal until the muscle has set (or rigor mortis is fully developed). During this period, though the animal is dead the flesh is still a biologically functioning system which becomes progressively more acid. The rate and severity of chilling affects the degree to which biochemical changes occur and is reflected in the two main structural components of muscle, the main contractile mechanism (the myofibrils) and the connective tissue, and also in the ultimate pH of the meat. The toughness of meat is due to the interaction between the connective tissue and the myofibrillar structures. While it can be said, and with good reason, that it is changes in the myofibrillar component during pre-rigor chilling which affect tenderness, this does not diminish the importance of the connective tissues as a structural component. Muscle with high connective-tissue strength, either as a result of the age of the animal or of anatomical location, will still be tough regardless of myofibrillar contraction state.

In order to discuss the factors which may cause contraction of the myofibrillar structure, and to understand how these factors can be either avoided or reduced, it is necessary to have some knowledge of meat structure and of how tenderness is assessed.

Meat structure

In the simplest terms, meat can be described as a series of minute approximately parallel rods—representing the meat fibres or myofibrillar structure—bound together into bundles by the network of connective tissue (Fig. 1). These bundles, in turn, are bound into the muscle by the thicker fibres of the epimysial connective tissue. The sheaths of connective tissue link up to the tendons which connect the muscle to the skeletal framework. The mechanical strength of such a system would be related to the strength of these rods, or meat fibres, as well as to the strength of the connective tissue. The strength of the myofibrillar rods increases with contraction and cooking, while aging and enzyme treatment weaken them. The strength of connective tissue increases with the age of the animal and varies also with the location of the muscle.

The detailed features of the myofibrillar structures can only be seen with an electron microscope. The basic repeating unit in the myofibril (seen in Fig. 1) is the sarcomere, which is made up of actin filaments and myosin filaments (Fig. 2). Myofibrillar contraction increases the interdigitation of the actin and myosin filaments. Shear-force values obtained for cooked meat increase with decrease in sarcomere length (Fig. 3).

Assessment of tenderness

Subjective (taste panel) and objective (mechanical) measurements are used to assess the tenderness of cooked meat. Subjective tests vary greatly in complexity and in the number of people who have to be involved. By using a small number of highly specialized and trained panellists, laboratory workers can evaluate the quality characteristics of the structural components of meat that result in toughness. In this way such a panel can assess the effects of different treatments on meat. Consumer taste panels, which consist of many people chosen at

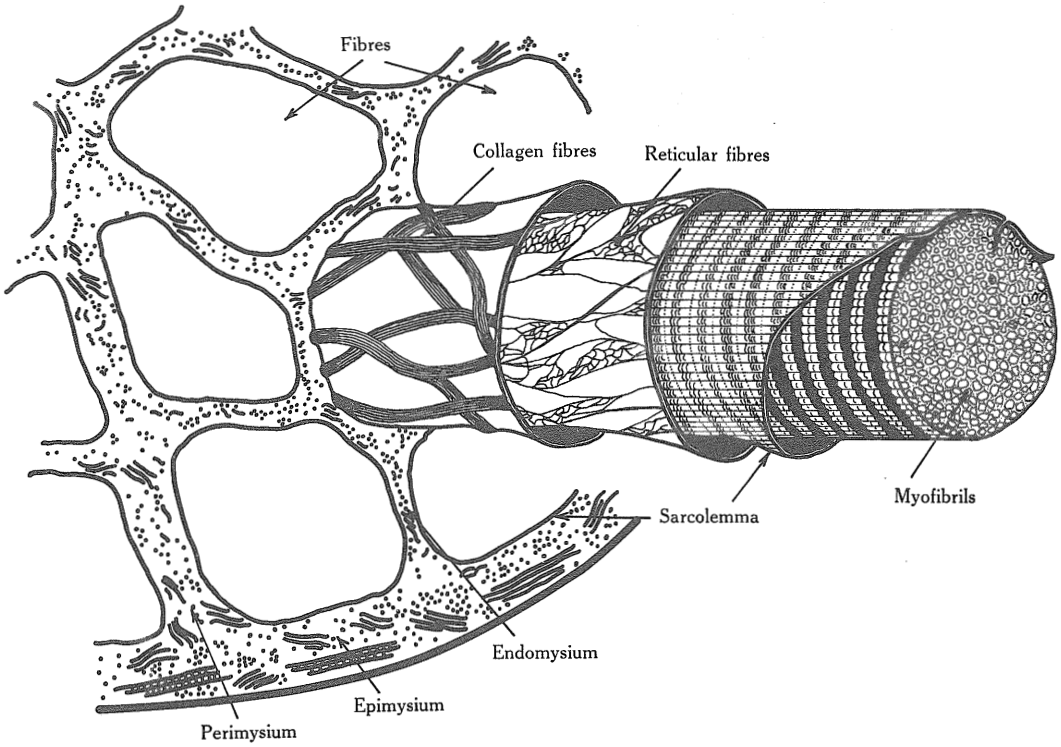


Fig. 1. Schematic diagram of a muscle fibre and some associated structures, showing how the fibres are held together by the endomysial, perimysial and epimysial connective tissues. The banding pattern on the muscle can be seen with a light microscope.

random, are unsuitable for the analytical approach pursued by laboratory-trained taste panels and are used mainly to assess acceptability and marketing prospects.

The most commonly used of the objective methods is the Warner-Bratzler shear test which measures the force required to pull a blunt knife through a meat sample of known size. At the Meat Research Laboratory an Instron Universal Testing Machine is used for testing compression and tensile strength and, more recently, for measuring shear. This machine is now linked with a computer so that the breakdown characteristics of the meat sample can be obtained by detailed analysis of the force deformation curve. The tensile tests measure both fibre tensile strength and adhesion between the meat fibres, the latter giving an index of the strength of the connective tissue.

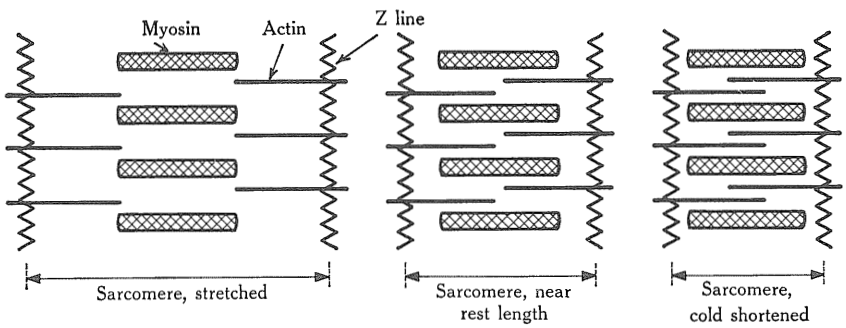


Fig. 2. The basic repeating unit on the myofibril is the sarcomere. Figure shows the interdigitation of the actin and myosin filaments and how this changes on contraction.

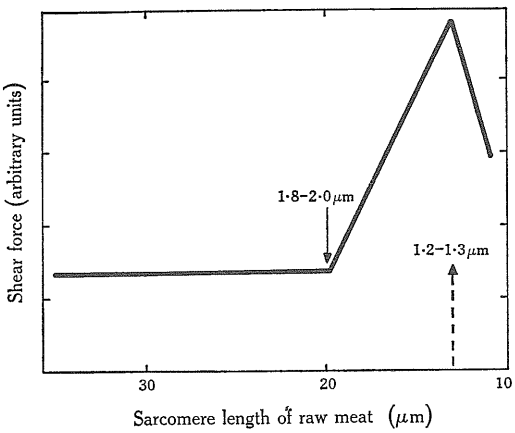


Fig. 3. Change in shear-force values (arbitrary units) with sarcomere length. Shear-force values start to increase at *c.* 1·8–2·0 μm, reach their peak at 1·2–1·3 μm and then decrease for sarcomere lengths below 1·2 μm.

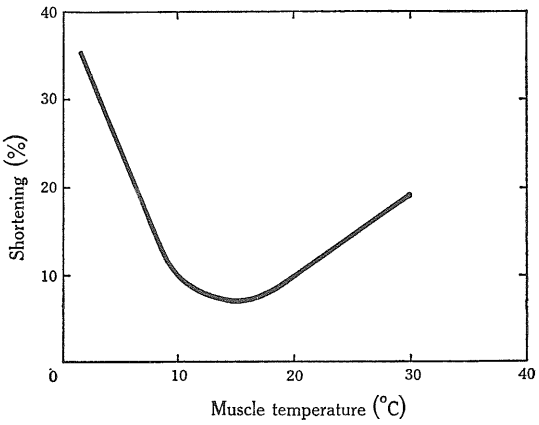


Fig. 4. Approximate relationship between percentage shortening and muscle temperature pre-rigor.

Tenderness measurements on raw meat are not as yet sufficiently reliable for us to advocate their use in a meatworks. The Armour Tendermeter* has been used in the United States but its correlation with taste panel measurements on the cooked meat is low. Other disadvantages relate to its inability to detect large differences in animal age and to the fact that it is influenced by the size of loin eye area. Measurements of sarcomere length on the raw meat, with a laser, could prove useful but such a measurement again takes no account of the effect of animal age.

*Registered trade name.

Factors that can produce myofibrillar contraction

The factors have been reviewed in more detail elsewhere (Newbold and Harris 1972; Macfarlane *et al.* 1974). Shortening (contraction) of muscle after slaughter is highly dependent on temperature and is least at about 15°C (Fig. 4). The shortening that results from keeping muscle at high temperatures (i.e. greater than 15°C) is called rigor shortening and that resulting from keeping it at lower temperatures is known as cold shortening. The sooner after slaughter the muscle temperature is lowered below 10°C, the more pronounced cold shortening will be. Once the pH of the muscle has fallen below 6·2, the tendency for the muscle to cold-shorten is much reduced. In lamb carcasses there is continued improvement in tenderness with increased time (up to 16 h) of holding the pre-rigor carcasses at 18–24°C before chilling. At this temperature pH would have decreased to 6·2 or less within about 8 h.

Laboratory measurements relating percentage shortening to toughness were carried out on small strips of muscle removed from the carcass. Obviously, when attempting to apply these results to muscle still on the carcass, one has to allow for muscle temperature which will depend on location, carcass size, fat cover and chilling conditions. Chilling rate is related to air temperature, air speed and humidity, and is not easy to predict or measure under commercial conditions. For example, the first few carcasses put into an empty chiller may chill faster than the carcasses put last into a full chiller, since air temperatures and air-flow rates may be very different.

Variations in chilling rate at different locations in a modern chiller have recently been convincingly demonstrated by MRL scientists. Deep butt temperatures in mutton carcasses ranged from −5° to +4°C at 24 h post-mortem and the time taken to reach 7° ranged from less than 4 h to 12 h.

Possible methods of overcoming cold or rigor shortening

Conditioning

Conditioning, in this context, means a temperature treatment applied to the carcass in the pre-rigor period, which is normally taken as the first 24–48 h after slaughter.

As an illustration of the effects of chilling temperature on tenderness, sheep muscles

Table 1. Mean shear-force values (kg) obtained for groups A, B, C and D muscles in mutton

Muscle group	Removed post-rigor after hanging 2 days at 0–1°C	Removed post-rigor after hanging 1 day at 15–16°C	Removed pre-rigor and stored 2 days at 0–1°C	Removed pre-rigor and stored 1 day at 15–16°C
A	10·97	5·37	14·91	5·16
B	8·50	5·27	14·61	5·20
C	6·39	5·99	10·92	6·03
D	4·23	4·19	9·13	4·09

were conditioned at 15–16°C and at 0–1° either while still on the carcass or after removal from the pre-rigor carcass. The results are shown in Table 1.

Group A muscles, semimembranosus (SM), gluteus medius (GM), biceps femoris (BF) and longissimus dorsi (LD), can readily shorten on pre-rigor carcasses hung from the Achilles tendon. Group B muscles, adductor (A) and vastus lateralis (VL), cannot shorten to the same extent as the group A muscles. Group C muscles, semitendinosus (ST) and rectus femoris (RF), and group D, triceps brachii (TB), supraspinatus (SS) and infraspinatus (IS), are prevented from shortening by their skeletal attachments.

It will be seen that, if muscle temperatures can be reduced to 15–16°C before rigor sets in, it does not matter whether the muscles are subject to skeletal restraint or not. In group A muscles conditioned at 0–1°, cold shortening occurs even when they are still attached to the carcass. The group B muscles, which were only partially restrained from shortening, were appreciably tougher when conditioned at 0–1°. For the group A muscles, which are able to cold-shorten and which in beef would include the commercially very important cuts of the rump, topside, striploins and cube roll, conditioning temperatures are obviously vitally important.

Conditioning and aging

It could be argued that conditioning carcasses at too low (or too high) a temperature is not particularly important since any loss in tenderness could be compensated for by aging the meat at 0–1°C. The effects of aging at 0–1° on the tenderness of muscles conditioned at 15–16° are shown in Table 2.

The group A muscles conditioned at 0–1° were aged for 3 weeks before the shear-force values were similar to those obtained after conditioning at 15–16° for 1 day. The group B muscles required about 1 week of aging when conditioned at 0–1° to bring values down to those obtained with conditioning at 15–16°. The other muscle groups are not significantly affected by conditioning temperature because they contain muscles which are restrained from shortening. If more severe shortening had been produced by using faster chilling rates then aging would have had much less effect. It is hopeless to expect that aging will compensate for any increase in toughness caused by too rapid chilling.

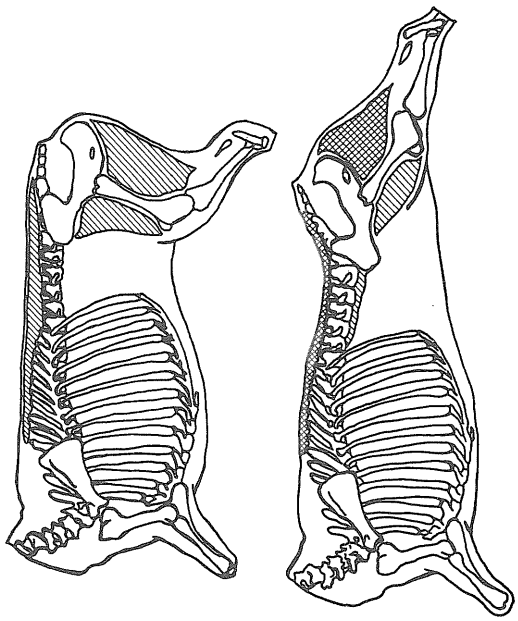


Fig. 5. Carcass shapes resulting from suspension from the aitch-bone or pelvis (*left*), and the Achilles tendon (*right*), showing the muscle areas affected. Hatching, relaxed (tender) muscle; cross-hatching, contracted (tough) muscle.

'Altered posture' suspension

Carcasses are normally hung from the Achilles tendon after slaughter and this method of hanging restrains some muscles (group C) from shortening (see Table 1).

Table 2. Mean shear force (kg) obtained for selected mutton muscles subjected to various post-slaughter aging and conditioning treatments

	Conditioning temperature (°C)					
	0–1	0–1	0–1	15–16	15–16	15–16
Aging time at 0°C (days)	0	7	21	0	7	21
Group A muscles (SM,* GM, BF, LD)	10·89	7·26	6·21	6·17	4·77	3·77
Group B muscles (A, VL)	7·81	5·44	4·28	5·55	4·62	3·50
Group C muscles (ST, RF)	5·83	4·12	3·75	5·37	4·81	3·31

*Group A: SM, semimembranosus; GM, gluteus medius; BF, biceps femoris; LD, longissimus dorsi. Group B: A, adductor; VL, vastus lateralis. Group C: ST, semitendinosus; RF, rectus femoris.

However, it has been shown (Hostetler *et al.* 1970, 1972, 1975) that other important muscles of the back and leg can be restrained from shortening by hanging carcasses from the obturator foramen or pelvis instead of from the Achilles tendon (Fig. 5).

The technique of using 'altered posture' suspension has been more actively investigated in New Zealand and Australia than in the United States where the technique originated. The muscles which are made effectively independent of conditioning temperature include commercially important cuts in the rump (GM), striploin and cube roll (LD), and topside (SM).

It is evident from the results in Table 3 that those muscles which had shortened on carcasses hung from the Achilles tendon were stretched when the carcasses were hung from the pelvis. The effects of these changes in sarcomere length on shear-force values are illustrated by the mean shear-force values listed in Table 4. It is evident that pelvic (or aitch-bone) hanging has markedly reduced shear-force values.

Conditioning compared with aging and 'altered posture'

So far, it has been shown that conditioning at 15–16° will avoid cold shortening and that aging will remove some of the toughness associated with conditioning at too low a temperature (Bouton *et al.* 1973). However, if cold shortening has been too severe, aging will not improve tenderness to any great extent, if at all. Altered posture has been shown to prevent cold shortening and thus avoid toughening owing to incorrect conditioning. However, aging at 15–16° is considered microbiologically unsound and the highest hygienically acceptable temperature is 7–8°, since salmonella and other food-poisoning organisms do not grow at or below these temperatures. Moreover, cooling to 7° is required under the regulations of the European Economic Community.

Table 3. Mean sarcomere lengths of selected muscles from beef and mutton carcasses hung (pre-rigor) either from the Achilles tendon or the pelvis and conditioned at 0–1°C

Selected muscle	Mutton		Beef	
	Achilles tendon	Pelvis	Achilles tendon	Pelvis
Group A				
SM*	1·71	2·62	1·70	2·76
GM	1·71	2·48	1·68	2·39
LD	1·72	1·80	1·80	2·00
BF	1·74	2·91	1·78	2·93
Group B				
A	1·81	2·78	1·83	3·21
VL	1·95	2·58	1·74	2·80

*SM, semimembranosus; GM, gluteus medius; LD, longissimus dorsi; BF, biceps femoris; A, adductor; VL, vastus lateralis.

Table 4. Mean shear-force values (kg) obtained for the muscles whose sarcomere lengths were listed in Table 3

Selected muscle	Mutton		Beef	
	Achilles tendon	Pelvis	Achilles tendon	Pelvis
Group A				
SM	10·85	4·81	8·35	5·13
GM	8·29	4·47	7·99	4·00
LD	10·17	6·36	11·12	5·72
BF	9·01	4·34	—	—
Group B				
A	7·76	5·24	—	—
VL	5·58	4·38	8·81	5·36

Experiments were therefore designed to compare the effects of conditioning at 0–1° and 7–8° with those of aging, and of suspension from the Achilles tendon and suspension from the pelvis. The centre of the LD muscles reached 1° in 9 h when conditioned at 0–1° and 8° in 8 h when conditioned at 7–8° (Bouton *et al.* 1974).

The results in Table 5 show that carcasses conditioned by hanging from the Achilles tendon at 7–8° give very similar results to those obtained for carcasses hung by the pelvis and conditioned at 0–1°. However, the values were slightly higher than those obtained for pelvis-hung carcasses conditioned at 7–8°. These results indicate that conditioning at 7–8° for 1 day need not cause excessive toughening. Aging reduced the shear values, although the group A muscles from carcasses hung by the Achilles tendon and conditioned at 0–1° still had high values.

Electrical stimulation

Work in New Zealand has indicated that post-mortem glycolysis, and hence the onset of rigor mortis, can be accelerated by electrical stimulation of lamb carcasses almost immediately after slaughter (Carse 1973). In these trials, carcasses at the bleeding rail were electrically stimulated by 3-kV pulses at 5 Hz for *c.* 2 min. As a result, they could be frozen 40–60 min later without cold shortening. Even with this technique, however, tenderness was much improved by also using altered posture (Davey 1973).

Hot boning

Hot boning for table meat purposes is a feasible proposition provided that the hot muscles are prevented from excessive shortening. This can be done by keeping the muscles at 15–16° until in rigor, but such conditions would not be bacteriologically sound. However, if methods of physical restraint were used—for instance, packing into a carton or heat shrinking a plastic film around the muscle or cut of meat—then fast chilling to low temperatures (0° or lower) might allow standards of bacteriological safety to be met while avoiding deleterious effects on tenderness (McLeod *et al.* 1974).

Conclusion

The implications to the meat industry of the results produced in research institutes both here and overseas seem clear. It has been shown that chilling conventionally hung carcasses too quickly (i.e. too efficiently) to 0–1° will certainly produce tough meat and that this toughness will not always be compensated for by aging (Bouton *et al.* 1973). Conditioning at 7° (the maximum temperature acceptable to the European Economic Community) may be done without producing excessive toughening (Bouton *et al* 1974). However, it has also been shown that if the hanging posture is altered, chilling rates no longer affect tenderness and carcasses may even be blast-frozen immediately after dressing without toughness occurring (Davey and Gilbert 1973, 1974). Thus where altered posture is used, chilling rates can be chosen that will improve shelf life by reducing microbial growth and yet have no effect on tenderness. Whenever prolonged storage of meat is required, e.g. to enable transport to overseas markets, control of microbial growth is obviously important. For local markets, and particularly where aging is not economically feasible, altered posture should generally improve the overall quality of the meat. When the choice of

Table 5. Warner-Bratzler shear-force values obtained for group A and group B muscles from mutton carcasses hung from the Achilles tendon or the pelvis and conditioned at 0–1° or 7–8°C for 1 day. Aging was carried out at 0–1° for 2 weeks in Cryovac* bags

Selected muscles†	Suspension method	Fresh		Aged	
		Conditioning temperature (°C)			
		0	7	0	7
Group A	Achilles tendon	11·82	5·35	6·30	3·29
	Pelvis	5·10	4·28	3·56	3·37
Group B	Achilles tendon	8·03	5·03	3·78	3·05
	Pelvis	5·02	4·58	3·50	3·66

*Registered trade name.

†Group A: semimembranosus, gluteus medius, biceps femoris, longissimus dorsi; group B: adductor, vastus lateralis.

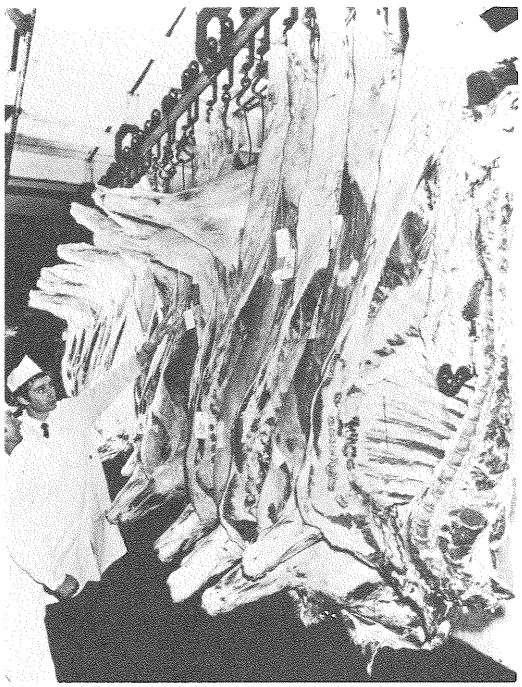


Fig. 6. Beef carcasses in a commercial chiller, hung from the aitch-bone or pelvis (*left*) and the Achilles tendon (*right*).

either method of hanging is being considered, it should be appreciated that the results obtained from altered posture will only be equivalent to those which would have been obtained by conditioning at 15–16°.

Hence the alternatives open to the meat industry at present appear to be:

- to continue hanging carcasses from the Achilles tendon and allow tenderness to be determined by the vagaries of the chilling process; or
- to hang carcasses from the pelvis and accept as a consequence that the altered shape could require changes in cutting-down procedures.

Adopting the second course should reduce overall variability in quality and in conjunction with a suitable system of carcass grading should offer the best guarantee of tenderness.

The use of electrical stimulation, in conjunction with altered posture, would seem to offer the possibility of turning out tender lamb within a few hours of killing (Davey 1973). Electrical stimulation techniques have so far not been used on beef carcasses and it is conceivable that the extremely rapid glycolysis could create further problems, although perhaps not to the same extent as occurs in pork, where difficulties with pale soft exudative muscle are very troublesome. Development of better and acceptable techniques for hot boning could allow more efficient use of chilling space, particularly as the bones in the skeleton would not have to be cooled.

References

Bouton, P. E., Harris, P. V., Shorthose, W. R., and Baxter, R. I. (1973). A comparison of the effects of aging, conditioning and skeletal restraint on the tenderness of mutton. *J. Food Sci.* **38**, 932–7.

Bouton, P. E., Harris, P. V., Shorthose, W. R., and Smith, M. G. (1974). Evaluation of methods affecting mutton tenderness. *J. Food Technol.* **9**, 31–41.

Carse, W. A. (1973). Meat quality and the acceleration of post-mortem glycolysis by electrical stimulation. *J. Food Technol.* **8**, 163–6.

Davey, C. L. (1973). Strategy on the future development and application of the principles underlying the conditioning of lamb. Fifteenth Meat Ind. Res.

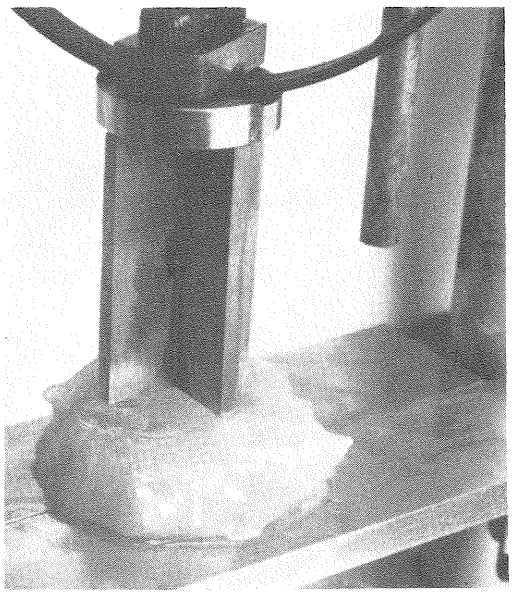
Inst. Conf., Hamilton, N.Z. pp. 41–4.
Davey, C. L., and Gilbert, K. V. (1973). The effect of carcass posture on cold, heat and thaw shortening in lamb. *J. Food Technol.* **8**, 445–51.
Davey, C. L., and Gilbert, K. V. (1974). Carcass posture and tenderness in frozen lamb. *J. Sci. Food Agric.* **25**, 923–30.
Hostetler, R. L., Landmann, W. A., Link, B. A., and Fitzhugh, H. A., Jr (1970). Influence of carcass position during rigor mortis on tenderness of beef muscles: comparison of two treatments. *J. Anim. Sci.* **31**, 47–50.
Hostetler, R. L., Link, B. A., Landmann, W. A., and Fitzhugh, H. A., Jr (1972). Effect of carcass suspension on sarcomere length and shear force of some major bovine muscles. *J. Food Sci.* **37**, 132–5.
Hostetler, R. L., Carpenter, Z. L., Smith, G. C., and Dutson, T. R. (1975). Comparison of post-mortem treatments for improving tenderness of beef. *J. Food Sci.* **40**, 223–6.
Macfarlane, J. J., Harris, P. V., and Shorthose, W. R. (1974). Manipulation of meat quality, particularly tenderness, by the processor. *Proc. Aust. Soc. Anim. Prod.* **10**, 219–26.
McLeod, K., Gilbert, K. V., Fairbairn, S. J., and Locker, R. H. (1974). Further experiments on the hot-cutting of lamb. *J. Food Technol.* **9**, 179–84.
Newbold, R. P., and Harris, P. V. (1972). The effect of pre-rigor changes on meat tenderness. A review. *J. Food Sci.* **37**, 337–40.

Apricot breakdown

Californian workers have confirmed Australian claims that fungal enzymes cause breakdown

Breakdown in the texture of canned apricots is a problem that has plagued the canning industry in California, South Africa, Europe and Australia.

It has been a difficult phenomenon to study because it is intermittent and unpredictable in occurrence and incidence. After it was first reported in Australia in 1958, apricot breakdown was investigated during several seasons by workers in the N.S.W. Department of Agriculture, commercial canneries and the CSIRO Food Research Laboratory. Eventually it appeared that the likely cause of breakdown was the following sequence of events: the mould *Rhizopus stolonifer* (formerly *nigricans*) is a widespread fruit pathogen and causes transit rot, a common post-harvest disease in stone fruit; in apparently sound apricots before the mycelium of this mould becomes externally visible a highly active pectolytic enzyme is generated in the skin and outer flesh of the fruit; this enzyme is sufficiently stable to heat to survive the normal canning process for apricots; then slowly during some months' storage of the canned apricots the enzyme breaks down the pectin that binds the tissue cells together and the apricot halves disintegrate. Convincing evidence was available for all steps in this sequence except for the recovery of active enzyme from canned apricots.



Measuring breakdown in apricots with a modified single-pin maturometer.

Substantial confirmation of the Australian observations has now been provided in studies by three separate groups at the University of California, Davis. The *Rhizopus* species *stolonifer*, *arrhizus* and *oryzae*, when grown on media containing pectin-polypectate, produced powerful polygalacturonases which caused rapid breakdown in the texture of canned apricots. Similar effects were obtained more slowly by adding a single fruit decayed by *R. arrhizus* or *R. stolonifer* to a 154 × 180·5-mm can of apricots before processing. Moreover, the extremely high heat resistance of *Rhizopus* polygalacturonase was also confirmed, some residual activity being detected even after heating at 100°C for 40 min.

However, the clinching observation has not yet been made: active pectolytic enzyme has not been recovered from a can of apricots showing breakdown. This is not really surprising because the slow rate of breakdown under conditions of normal contamination indicates that the amounts of surviving enzyme must be very small.

Further reading

Australian work

Harper, K. A., *et al. CSIRO Fd Res. Q.* (1971) **31,** 33–6; *J. Sci. Food Agric.* (1972) **23,** 311–20; *J. Sci. Food Agric.* (1973) **24,** 527–31; *Food Technol. Aust.* (1973) **25,** 130–3.

Californian work

Claypool, L. L. (1974). *Calif. Agric.* **28**(7), 4–8.

Packaging foods that contain sulphur dioxide

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In Australia, the National Health and Medical Research Council issues recommendations concerning the use of additives in foods. However, final decisions on the types of food to which they may be added and the amounts permitted rest with each State through its respective Pure Food Act. Sulphur dioxide (SO_2) is widely used as an additive because it reduces a variety of undesirable changes in foods. In addition to its well-known utility in decreasing microbial activity and inhibiting enzymes, SO_2 is also useful as an antioxidant and as a reducing agent, and it retards non-enzymic browning.

A useful guide to the SO_2 levels legally permitted in foods in the different States of Australia, and in Britain, has been published in an earlier issue of the *Quarterly* (Anon. 1974).

SO_2 is a gas at ambient conditions (b.p. −10°C). It is also a highly reactive substance and reacts with many food constituents. These properties present difficulties in the use of the preservative in foods since, to function successfully, enough to be effective must be retained in the food during its storage life. Loss of SO_2 occurs by a number of mechanisms during the processing and storage of foods (Ingles 1966; McBean 1967).

This paper provides an account of work done in the CSIRO Division of Food Research to study the influence of packaging materials and procedures on the loss of SO_2 from packaged foods. Although dried apricots were chosen as the test product, the principles involved are applicable to the packaging of other foods in which the preservative is used.

Permeation studies

When foods containing SO_2 are kept in sealed packages, some of the SO_2 accumulates as free gas in the headspace. If the containers are permeable to the gas then loss of preservative during storage will occur. Permeation of gases and vapours is rarely a

problem with glass or metal containers, but all containers made from plastic and cellulose are permeable to some degree. These latter materials in the form of flexible films and bottles are widely used for the packaging of foods, including those containing SO_2.

Permeation at high concentrations

Exploratory studies were done to examine the permeation of SO_2 through polymer films (Davis and Rooney 1971). Three films differing in chemical composition were chosen: low-density polyethylene, polyamide (Nylon 11) and polycarbonate (Bisphenol-A polycarbonate). Permeabilities were measured by a conventional concentration-increase method in which the test film was sealed in an all-glass cell. One compartment of the cell was filled with a known mixture of SO_2 and nitrogen, and the other compartment was filled with nitrogen. Permeability of the sample was calculated from the rate of increase in SO_2 concentration in the nitrogen-filled side of the cell; the concentration of SO_2 was measured by gas chromatography.

Initially, permeabilities of the three films were measured with a partial-pressure difference of 1 atm SO_2 across the film samples. These values were compared with the oxygen permeabilities of the same materials as measured by the volume-increase method (Davis 1964). This showed that all three materials were more permeable to SO_2 than to oxygen under comparable conditions. Furthermore, the ratio of the SO_2/oxygen permeabilities ranged from 7 for polyethylene to 47 for polyamide. Additional measurements were made on the three films with partial pressure differences for SO_2 ranging from 2·5 to 75 cmHg. The results, corrected to a unit partial pressure, showed that the permeability of SO_2 in all three films was pressure dependent.

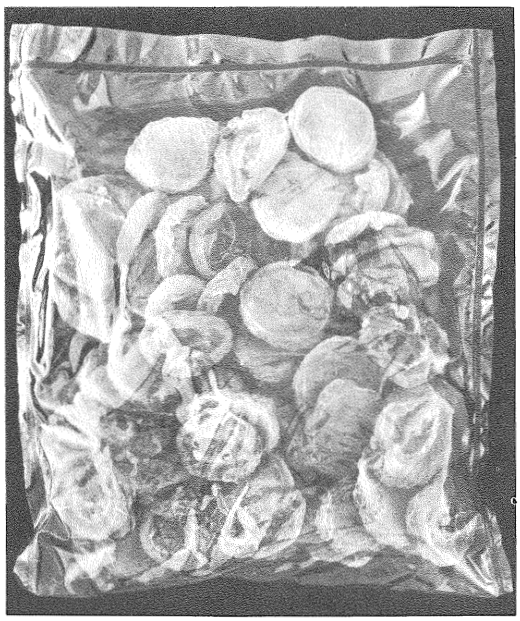

Fig. 1. A typical pouch pack of apricots. Like many other packaged foods its storage life depends to a considerable extent on how well the container retains added sulphur dioxide.

These observations suggest that the permeation of SO_2 in polymer films is anomalous, in contrast to that of the simple gases. For instance, Stannett *et al.* (1962) showed that the ratios of the permeabilities of any two of the simple gases oxygen, nitrogen and carbon dioxide in a wide range of polymers were approximately constant, and that the permeabilities of all these gases were independent of the partial pressures at which the measurements were made. However, the permeation behaviour of SO_2 is more like that of water vapour in hydrophilic materials and of organic volatiles in some polymer films.

The permeation of gases and vapours in polymers is not a fundamental property of the system, but depends on the two fundamental processes of solution and diffusion. The solution and diffusion of SO_2 in the three polymers were studied by means of a McBain sorption balance (Davis and Rooney 1971). In this procedure, a sample of the polymer is attached to a calibrated quartz helix suspended in a glass tube. The extension of the helix, as measured by a cathetometer, is directly proportional to the load. The tube and ancillary connections were evacuated, then SO_2 was admitted to a known pressure. The diffusion constant was calculated from the rate of sorption, and the solubility coefficient was calculated from the total amount of SO_2 sorbed at equilibrium.

These studies showed that the diffusion constants for the gas in all three polymers were pressure dependent, and that the solubility coefficients were pressure dependent with polycarbonate and polyamide but independent of pressure with polyethylene. These observations suggest reasons for the anomalous permeation

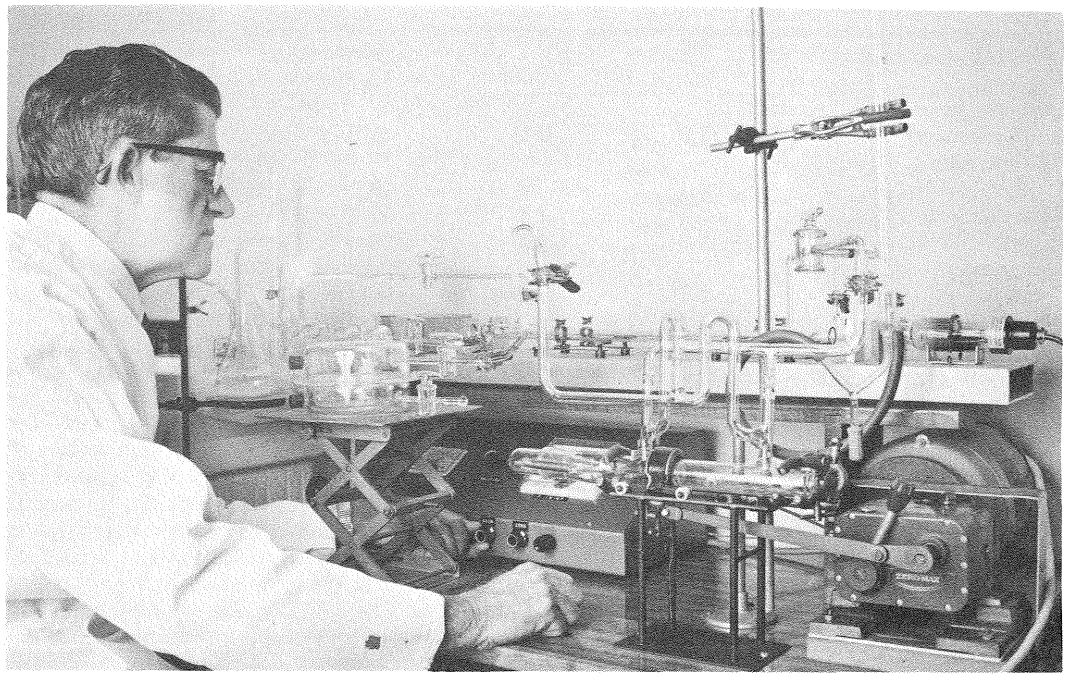

Fig. 2. Apparatus especially designed for measuring the permeability of flexible films to sulphur dioxide at extremely low partial pressures. See text for further description.

behaviour of SO_2 in the polymer films. In the case of polycarbonate, further work showed that sorbed SO_2 changes the physical structure of the polymer (Davis and Rooney 1972) as a result of the formation of molecular complexes between molecules of the sorbent and active sites on the polymer chains (Rooney *et al.* 1973).

Two points of practical importance are evident from the work discussed above. Firstly, the permeability of polymer films to SO_2 is high in comparison with permeability to oxygen and hence the loss of preservative by permeation from packaged foods could be appreciable. Secondly, the non-ideal permeation behaviour of SO_2 in polymer films means that permeability values measured at a specific partial pressure cannot be used to calculate values at other partial pressures, as can be done with simple gases.

Permeation at low concentrations

Preliminary measurements indicated that concentrations of free SO_2 up to 200 ppm (v/v) may be present in the headspace of packages of dried apricots containing 3000 ppm (w/w) of total SO_2. This level is equivalent to a partial pressure of 0·015 cmHg and represents, therefore, the partial pressure gradient available to cause loss of SO_2 by permeation from the package. It is also well below the lowest partial pressure of 2·5 cmHg at which permeability measurements could be made by the previous method based on gas chromatography. Consequently, a new apparatus was constructed in cooperation with the CSIRO Division of Chemical Physics to measure the permeability of flexible films to SO_2 at partial pressures down to 0·0015 cmHg.

The apparatus illustrated in Fig. 2 is described by Davis *et al.* (1975); it consists of the following three major components.

- An all-glass cell in which the film sample is sealed so that the cell is divided into two compartments.
- Means by which one of the cell compartments may be filled with a supply of SO_2 mixed at the required concentration with nitrogen.
- A detection system for determining the rate of increase in SO_2 concentration in the second nitrogen-filled compartment.

The supply of SO_2 was obtained by use of the permeation-tube technique described by

Table 1. Permeability of packaging materials to SO_2, oxygen, and water vapour at 25°C

Material	Thickness (mm × 10^2)	10^{10} × permeability* SO_2	O_2	H_2O†
Polyethylene (low density)	3·8	193	30·9	876
Polyethylene (high density)	2·1	56·8	10·5	305
Polycarbonate	2·5	210	15·4	> 10 000
Polystyrene	3·8	220	18·8	9280
Polyamide (Nylon 11)	4·1	21·6	1·40	2940
Polypropylene	2·5	7·13	6·81	303
Polyvinyl chloride (rigid)	14·5	1·16	0·667	2540
Polyester	1·3	2·01	0·339	1560
PVDC/polypropylene/PVDC	2·8	0·103	0·0697	212
PVDC/regenerated cellulose/PVDC	2·6	0·374	0·0398	202

*Units: cm^3 (STP) × mm × cm^{-2} × sec^{-1} × $cmHg^{-1}$
†Test method: B.S. 3177(1959) at 25°C, 75% R.H.

O'Keefe and Ortman (1966). This procedure depends upon the permeation of SO_2 from an FEP Teflon tube which is filled with liquid SO_2 and plugged at each end. The tube is then enclosed in a glass tube through which nitrogen flows at a known rate. The concentration of SO_2 in the effluent may be varied over a wide range by varying the dimensions of the permeation tube, the temperature of the tube and the rate of flow of nitrogen. Once equilibrated, the output from a permeation tube is remarkably constant and may be easily determined by gravimetric or chemical methods.

The detection system is based on the absorption of ultraviolet (UV) light by SO_2. The principle is similar to that of a double-beam spectrophotometer operating at a fixed wavelength of 213·8 nm where SO_2 absorbs strongly (Golomb *et al.* 1962). The light adsorption tube of the instrument is connected to the measuring compartment of the permeability cell via an all-glass pump (Duncan and Lawson 1967). These together comprise the measuring circuit.

In operation, the measuring circuit and reference tube of the detector are filled with nitrogen and the instrument is set at zero. The measuring circuit is then isolated and the test-gas mixture is admitted to the other cell compartment. SO_2 permeating through the sample is circulated by the pump through the sample tube, and the resultant UV absorption is plotted by a potentiometric recorder. The rate of permeation can then be calculated from the slope of the time-absorption curve.

In addition to providing a continuous supply of SO_2 for the permeability measurements, permeation tubes were also used to calibrate the detection system over the range 0–10 ppm (v/v). Based on a signal to noise ratio of 2:1, concentrations down to 0·5 ppm could be detected. This sensitivity permitted permeability measurements to be completed before the concentration of SO_2 in the measuring circuit exceeded 5 ppm.

Table 1 gives the permeability to SO_2 of a range of packaging films measured at partial pressures of less than 0·045 cmHg. For comparison, Table 1 also shows the permeabilities of the plastic materials to oxygen and water vapour measured by conventional procedures in this laboratory. It is interesting that the two PVDC*-coated materials showed lower permeabilities to SO_2 than the remaining uncoated materials. PVDC coatings are known to have good barrier properties to a wide range of gases and vapours, and the results observed on polypropylene show that this applies also to SO_2. For instance, the permeability to SO_2 of polypropylene coated on both sides with PVDC was 70 times less than the uncoated material of similar thickness.

*Copolymer of vinylidene chloride and vinyl chloride.

Test-pack studies

When foods containing SO_2 are packaged in containers that are permeable to gases and vapours, loss of the preservative may occur by the following mechanisms.

1. Conversion to sulphate by (*a*) oxygen adsorbed and absorbed by the food; (*b*) oxygen present in the headspace at the time the packages are sealed; and (*c*) oxygen permeating into the headspace during storage.
2. Reaction with the food constituents and disproportionation reactions.
3. Permeation through the package materials.

Two of these loss mechanisms, 1*a* and 2, are independent of packaging variables, but the remainder are directly related to three packaging variables—permeability of the package materials to oxygen and to SO_2, and the amount of oxygen in the headspace at the time the packages are sealed. Davis *et al.* (1973) studied the effect of these three variables on the rate of loss of SO_2 with sulphured dried apricots as the test product.

Test packs of sulphured apricots were prepared in pouches made from two types of material: low-density polyethylene (0·38 mm thick); and a laminate of paper (50 g/m^2), aluminium foil (0·013 mm thick) and heat-sealable polyester (0·05 mm thick). The first was chosen because it is highly permeable to both oxygen and SO_2 and the second was included because it has negligible permeability to gases and vapours. After being filled with apricots, half of the test pouches were flushed with air, sealed and stored in air at 25°C; the other half were flushed with nitrogen, sealed, and stored in nitrogen at 25°C. To avoid changes in moisture content, the storage atmospheres were controlled at 75% relative humidity which was close to the existing relative humidity of the product. At intervals over a storage period of 48 weeks, sample pouches were examined for total, combined and free SO_2 contents.

Table 2. Details of experimental treatments

Treatment code	Pouch material	Headspace and storage atmosphere	SO_2 loss mechanisms involved
PA	Polyethylene	Air	1*a*, 1*b*, 1*c*, 2, 3
PN	Polyethylene	Nitrogen	1*a*, 2, 3
FA	Foil laminate	Air	1*a*, 1*b*, 2
FN	Foil laminate	Nitrogen	1*a*, 2

The experiments thus comprised four treatments, and details of each treatment and of the various mechanisms of SO_2 loss applicable to each are summarized in Table 2.

Since mechanisms 1*a* and 2 are common to all treatments, the appropriate pairs of treatment combinations were compared to assess the importance of the other three mechanisms, each of which is associated with a specific packaging variable.

The concentrations of total, combined and free SO_2 observed at intervals over the storage period were converted to logarithms and plotted against storage time. These plots were linear and obeyed the relation

$$\log (SO_2) = a + bt,$$

where a is the logarithm of the initial SO_2 concentration, b is the rate of change of log (SO_2) with time, and t is the storage time. The rate figures therefore provided a convenient basis for isolating and comparing the various loss mechanisms.

The results, summarized in Table 3, show the percentage increase in the rates of loss of total, combined and free SO_2 attributed to the three packaging variables. These increases are expressed relative to the loss rates due to mechanisms 1*a* and 2 which are

Table 3. Relative importance of mechanisms for loss of SO_2 from packaged apricots during storage at 25°C

SO_2 loss mechanism	Associated packaging variable	Contribution to SO_2 loss rate (%)		
		Total	Combined	Free
1*a* and 2	None	41·6	35·3	46·2
1*b*	Headspace O_2	13·4	15·8	10·9
1*c*	O_2 permeation	30·5	33·1	30·0
3	SO_2 permeation	14·6	16·0	13·1
		100·1	100·2	100·2

unaffected by modifications to packaging treatments. Thus the use of a permeable pouch material such as polyethylene resulted in a higher rate of loss by permeation of SO_2 compared with an impermeable material, and the increase in loss rate as a result of this factor was similar to the increase arising from the presence of air instead of an inert gas in the pouch headspace. The effect of oxygen permeating into the packages was more important, since it resulted in an increase in loss rate which was approximately twice that resulting from SO_2 permeation or from the presence of headspace oxygen.

The results also show that the combined effect of the three packaging variables increased the rate of loss of SO_2 from dried apricots by more than 100% as compared with loss in an impermeable pack.

Conclusions

Packaging materials made of plastic and cellulose are permeable to water vapour, sulphur dioxide and oxygen, and these factors are of importance in the packaging of foods containing sulphur dioxide. There is no general relation between the permeation rates of any two of these compounds applicable to all packaging materials, and separate determinations are necessary for each material–penetrant system under realistic conditions of temperature and pressure. For instance, the permeation of SO_2 in polymers depends on its concentration and hence permeability values measured at pressures close to atmospheric pressure cannot be used to calculate values at the very low partial pressures that exist in the headspace of packaged foods. Such measurements should be made when the partial pressure of SO_2 is 1 cmHg or less.

Permeation of oxygen and SO_2 and the presence of oxygen in the headspace all increase the rate of loss of SO_2. Thus materials for the packaging of foods containing SO_2 should have low permeabilities to both oxygen and SO_2, and the packages should be sealed with a minimum volume of headspace air. Although dried apricots were chosen as the test product in the work described, similar principles would be expected to apply to the packaging of other foods containing SO_2.

References

Anon. (1974). Sulphur dioxide and foods. *CSIRO Food Res. Q.* **34**, 80–3.

Davis, E. G. (1964). The effect of relative humidity on the oxygen transmission rate of coated regenerated cellulose films. *Aust. J. Appl. Sci.* **15**, 309–20.

Davis, E. G., and Rooney, M. L. (1971). Transport of sulphur dioxide in polymers. *Kolloid-Z.* **249**, 1043–50.

Davis, E. G., and Rooney, M. L. (1972). Rigidity of polycarbonate in the presence of sulphur dioxide. *J. Polym. Sci. Polym. Phys. Ed.* **10**, 2325–31.

Davis, E. G., McBean, D. McG., Rooney, M. L., and Gipps, P. G. (1973). Mechanisms of sulphur dioxide loss from dried fruits in flexible films. *J. Food Technol.* **8**, 391–405.

Davis, E. G., Rooney, M. L., and Larkins, P. L. (1975). Permeability of polymer films to sulphur dioxide at low concentrations. *J. Appl. Polym. Sci.* **19**, 1829–35.

Duncan, S., and Lawson, F. (1967). A double-acting all-glass gas circulating pump. *J. Sci. Instrum.* **44**, 388.

Golomb, D., Watanabe, K., and Marmo, F. F. (1962). Absorption coefficients of sulphur dioxide in the vacuum ultraviolet. *J. Chem. Phys.* **36**, 958–60.

Ingles, D. L. (1966). Prevention of non-enzymic browning. *CSIRO Food Preserv. Q.* **26**, 39–44.

McBean, D. McG. (1967). Levels of free and combined sulphur dioxide in fruits during sulphuring and drying. *Food Technol. (Champaign)* **21**, 112–16.

O'Keefe, A. E., and Ortman, G. C. (1966). Primary standards for gas analysis. *Anal. Chem.* **38**, 760–3.

Rooney, M. L., Best, D. J., and Davis, E. G. (1973). Molecular complexes of sulphur dioxide with organic carbonates. *J. Polym. Sci. Polym. Chem. Ed.* **11**, 2601–13.

Stannett, V., Szwarc, M., Bhargava, R. L., Meyer, J. A., Myers, A. W., and Rogers, C. E. (1962). TAPPI Monogr. Ser. No. 23.

Control of the thermal process in flame sterilization

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This article is the second in a series on flame sterilization. The first article (*CSIRO Fd Res. Q.*, 1975, **35**, 34–9) described the design and operation of a flame sterilizer and discussed some general requirements of the process

In any method of processing canned products, precise control of the thermal process is essential if a commercially sterile canned product is to be achieved with a minimum of thermal degradation. An unnecessary increase in the time or temperature of a thermal process leads to an increase in the products of chemical reactions and usually to a lessened acceptability. As a thermal process is designed to inactivate spoilage organisms, a reduction in the process may result in spoilage of the product by surviving microorganisms, and even in food poisoning if the product is consumed. The effectiveness of a thermal process may be assessed in terms of its F value (or sterilizing value), which is defined as the number of minutes at 121·1°C that gives a process of equivalent microbial lethality to the process being evaluated.

In the CSIRO pilot-scale flame sterilizer, described by Casimir (1975), the thermal process consists of heating cans rapidly over gas burners to reach the desired temperature, holding the cans at this temperature until a process having the required F value is completed, and then rapidly cooling the cans. As the conditions induce high rates of heat transfer, the time taken to heat and cool the cans is short and does not contribute significantly to the overall F value of the process. Hence for practical purposes time taken in heating and cooling may be ignored, and the F value may be based simply on holding time and temperature; hence it may be expressed as

$$F = t \times 10^{(T - 121{\cdot}1)/z}, \qquad (1)$$

where F is the sterilizing value or the time (min) at 121·1°C which gives the same amount of sterilization as the process being evaluated, T is the holding temperature (°C), t is the holding time (min) and is equal to

$$\frac{\text{No. of cans in the holding section}}{\text{No. of cans per minute}},$$

assuming the temperature of the cans in the holding section remains constant, and z is the slope of the thermal death-time curve of the spores of the organism on which the process is based. For most process calculations for low-acid foods, z is assumed to be 10°C.

If the cans cool in the holding section, the process may be determined from the equation of Cheftel and Thomas (1963) as discussed by Casimir (1975). The two major factors therefore that may alter F values are the temperature of the cans in the holding section and the retention time of the cans in this section.

Determination of temperature of can

With the CSIRO pilot-scale flame sterilizer, an intermittent motion is imparted to the drag chain (Huntington and Casimir 1972), and this leaves the cans stationary in the holding section during the non-progression period of the drag chain. This stationary period allows time for a can to be removed from the drag chain for temperature measurement or for the use of a probe to measure the surface temperature of the can.

Stab temperature for process evaluation

The can is removed from the sterilizer

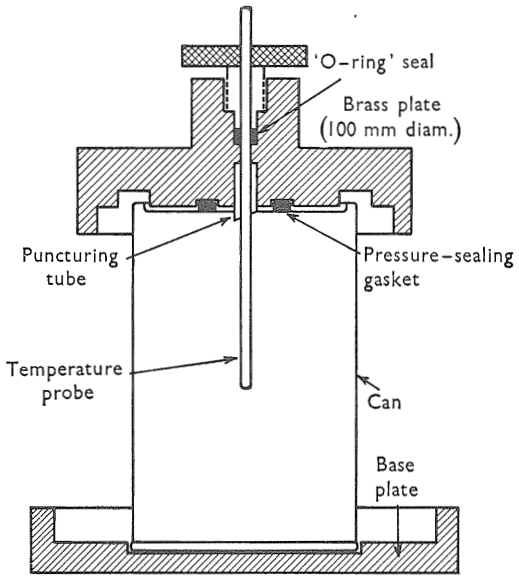

Fig. 1. Device for taking stab temperature measurements of the contents of a can.

after it has travelled through the flame heating section and is punctured without releasing the pressure. A temperature-sensing probe (Mettler Digital Thermometer, model TM15) is then inserted through the hole punctured in the end of the can (Fig. 1) and the temperature of the probe is indicated. This is, of course, a destructive procedure and is consequently not desirable for regular process control.

Surface temperature for process control

A number of devices for measuring surface temperature have been tried in an attempt to find a suitable method. An infra-red radiation detector was tried but it failed to give an accurate measurement of the temperature of the surface of the can because of the low emissivity of tinplate and because of stray radiation in the hot environment.

Commercially available probes of the thermistor or thermocouple type were found to have equilibration times in excess of the non-progression periods of the drag chain and hence the temperature of every can in the holding section could not be measured. However, an adequately fast response was obtained by forcing the unconnected thermocouple wires on to the can and thus using the metal of the can to form the hot junction. The response time of this method

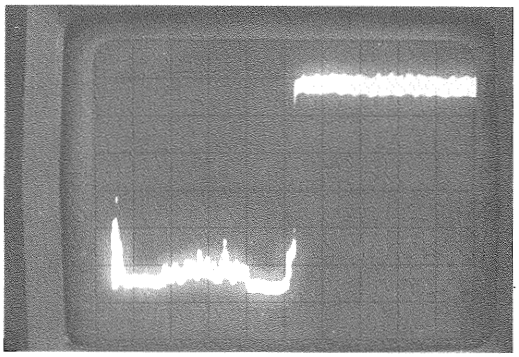

Fig. 2. Trace on a cathode ray oscilloscope showing a typical temperature–time response curve for the equilibration of the probe measuring surface temperature. Vertical axis, 1 mV/division; horizontal axis, 10^{-2} sec/division.

was in the order of 2×10^{-3} sec, as shown by the trace on a cathode ray oscilloscope (Fig. 2). The mechanism used to achieve this contact is shown in Fig. 3. The polytetrafluoroethylene (PTFE) head of the probe, containing the copper–constantan thermocouple wires, comes in contact with the surface of the can at a controlled pneumatic pressure.

The probe is timed to force the thermocouple wires on to the clean and dry surface of the can soon after the cans are discharged from the flame heating section, during a non-progression period of the drag chain. The temperature of the can may be either recorded by a potentiometric recorder or printed out, or else displayed as a temperature on a suitably calibrated digital

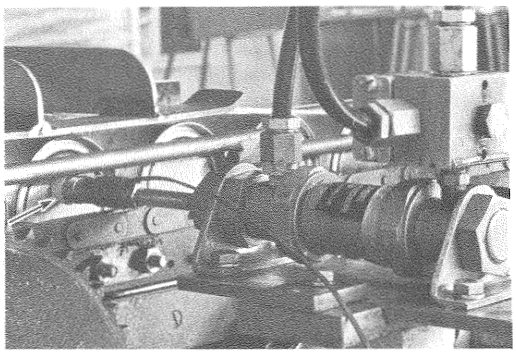

Fig. 3. A probe measures the temperature of the surface of a can. The arrow indicates the head of the probe in contact with the can.

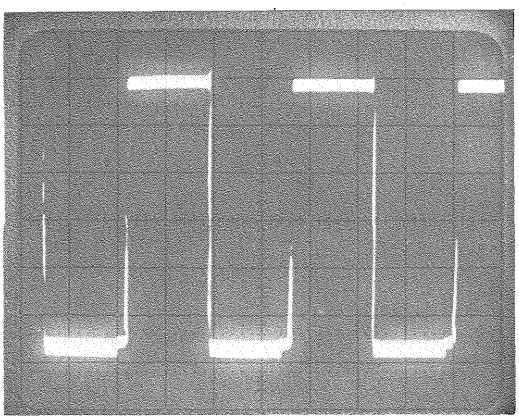

Fig. 4. Trace produced by a cathode ray oscilloscope of the temperature of individual cans, obtained by using the surface temperature measuring probe. Vertical axis, 1 mV/division; horizontal axis, 1 sec/division.

voltmeter. Typical temperature measurements on individual cans are shown in Fig. 4 by the trace on a cathode ray oscilloscope. The pilot-scale flame sterilizer was operated so that the throughput was 18 cans per min and the cans reached a temperature of 130°C when discharged from the flame heating section.

Temperature measurement of cans in flame sterilizers, which have a continuous drag chain progression, could be achieved by mounting the probe in such a way that it both contacts the surface of the can and moves with the can around a drag chain sprocket. An alternative mechanism is described (Anon. 1972) where every ninth to fifteenth can, depending on the speed of the conveyor, is removed from the track and held magnetically against a thermistor sensor for 8–15 sec, to allow time for temperature equilibration, and is then replaced into the track. Surface temperature measurements obtained by this procedure should be related to stab temperature measurements. For homogeneous products where agitation is adequate, surface and stab temperature differences are less than 1°C, but for thicker homogeneous products the surface temperature may be as much as 3°C higher than the stab temperature and this difference must be allowed for when computing F values.

Determination of process time

Process times in flame sterilizers are determined from temperature histories as in conventional retorting. As the temperature of the product increases linearly in the flame heating section, the heating rate may be expressed in °C/sec. Heating rates may be as high as 2°C/sec and a typical residence time in the flame heating section is about 30 sec. The F value of a process may thus be established for a flame sterilizer if the number of cans in the flame heating and the holding section is known, as well as the heating rate of the cans in the burner section, and the entry or exit temperature of cans from the flame heating section.

From this information the process may be calculated as follows

$$t = t_f \times N_h/N_f,$$

but $t_f = (T - T_i)/H$. Hence substituting in equation (1) we obtain

$$F = (T - T_i)/H \times N_h/N_f \times 10^{(T - 121{\cdot}1)/10}, \quad (2)$$

where t is the time (min) in the holding section, t_f is the time (min) in the flame heating section, T is the temperature (°C) of cans in the holding section, T_i is the temperature (°C) of cans entering the flame heating section, N_h is the number of cans in the holding section, N_f is the number of cans in the flame heating section and H is the heating rate in the flame heating section (°C/min).

In the CSIRO flame sterilizer there are 11 cans in the flame heating section and 33 cans in the holding section. If we assume the cans are heated to 90°C in the steam preheating section, enter the flame heating section at this temperature and are then heated at a rate of 1·0°C/sec or 60°C/min, we may make the following calculations of F value. The F value of the thermal process will be 11·5 min when the throughput, determined by the drag chain, is 17 cans/min; 12·7 min when the throughput is decreased by 1%, i.e. to 16·83 cans/min; and 10·4 min when the throughput is increased by 1% to 17·17 cans/min.

Hence under these conditions, if the F value is not to vary more than $\pm 1{\cdot}2$ min or $\pm 10\%$, the speed of the drag chain should not vary more than $\pm 1\%$.

To allow a wide variation in process value the CSIRO sterilizer has provision for varying the ratio of the number of cans in the holding section to the number of cans in

the flame heating section.

As seen from equation (2), a wide variation in the F values may be obtained by varying the ratio of cans in the holding section to cans in the flame heating section. This is achieved in the CSIRO sterilizer by shutting down a portion of the burner, reducing the capacity of the flame heating section from 11 to 8, 7, 4 or 3 cans.

Factors affecting the thermal process

Temperature of cans entering the flame heating section

As the rise in temperature in the flame heating section is linear with time, the cans will receive a heat treatment that results in a constant incremental rise in temperature, i.e. any temperature differences between cans will be maintained throughout the flame heating section. The F value of the process received by individual cans will only be the same if each can enters the flame heating section at the same temperature.

A constant entry temperature may be achieved by controlling the fill temperature precisely or else by preheating the cans in a steam heating section before they reach the flame heating section. The temperature of the canned product in the steam preheater increases logarithmically; hence even if the initial temperature varies appreciably between individual cans, can-to-can variation will be small when the temperature of the product is raised to within, say, 5–10°C of the temperature of steam.

Condition of the surface of the can

The surface of the can should be clean and dry when the cans enter the flame section. Burner energy is used to evaporate surface water from wet cans instead of heating cans and product. Cans may be dried by ducting a portion of the unwanted combustion gases countercurrent to the incoming cans.

Lithographed cans perform satisfactorily in the flame sterilizer, but the heating rates are dependent on the colour of the lithography since this influences the absorbtivity of the surface of the can. Moreover, plain cans heat at different rates from lithographed cans and hence the two types must not be processed at the same time.

Viscosity of the product

The purpose of imparting a reversing-spin action to the cans in the flame sterilizer is to agitate the product within the can. This agitation aids the transfer of heat from the inside of the can wall to the bulk of the product which therefore heats more rapidly and uniformly. With products of high viscosity, agitation within the container is less effective and may give rise to temperature gradients which are so severe that an adequate thermal process cannot be achieved during the flame sterilization procedure. In some products excessive thermal degradation and burn-on may occur at the can wall.

Headspace and thermal capacity of the can and contents

The proportions of solid, liquid and vapour, and the specific heat of these three components, influences the rate of heating and severity of agitation. These, in turn, determine the uniformity of the temperature throughout the contents. The proportions may vary from 70:10:20 by volume for vacuum packs, to 70:20:10 for brine, syrup or sauce packs. The proportions may change during the process if the container becomes distorted, or as a result of rehydration of solid particles such as pasta.

Particle size and pulse heating

Process times are based on the temperature history of the slowest heating point in the container. Hence a flame sterilization process for particles which heat by conduction in a low-viscosity liquid must be based on the temperature history at the centre of the largest particles. The liquid will heat uniformly and linearly in the flame heating section, but in the holding section heat will flow from the high temperature liquid to the cooler interior of the particles until an equilibration temperature is achieved. For products consisting of large solids in a liquid, time is required for the heat to conduct from the hot liquid to the centre of the solids. For such products a pulse or stepwise heating process may be used. The can is heated at a flame station and the temperature differential between the liquid and solid fraction of the can increases. The can is then transferred to the next station where the contents are agitated but not heated further and temperature equilibration proceeds. Before temperature equilibration is completed, i.e. before heat flow slows unduly because of decrease in the thermal gradient, the can is moved to the next flame heating station where the cycle is repeated.

Effect of empty pockets in the drag chain on the temperature of neighbouring cans and on the *F* value of the process received by these cans

	Cans before gap			No. cans	Cans after gap			
	3	2	1	missing	1	2	3	4
Temp. (°C)	130	130	123	1	125	128	130	
F	11·6	11·6	2·3		3·7	7·3	11·6	
Temp. (°C)	130	129	124	3	126	128	130	
F	11·6	9·2	2·9		4·6	7·3	11·6	
Temp. (°C)	130	129	126	12	124	126	128	129
F	11·6	9·2	4·6		2·9	4·6	7·3	9·2

Operation of the burners

The heating rate of cans depends to a large extent on the operation of the burners. The calorific output of a burner depends upon the amount of fuel burnt and on the maintenance of a stoichiometric air-to-fuel ratio for combustion. The combustion mixture must be at a steady and uniform pressure to give laminar flow (Reynolds number <2000) in the burner jets and the flame should have a well-defined blue internal cone. The tip of the blue cone is the hottest region of the flame and must be positioned adjacent to the can wall to give the maximum temperature gradient, and hence maximum heating rate. These points are discussed in Australian Patent Application No. 42814/72.

Effect of empty pockets in the drag chain

When the drag chain is completely filled with cans they form a uniform layer over the flame bed and the combustion gases cannot readily escape. If one or more cans are missing, hot combustion gases rise through the gap and reduce the heating efficiency of the burner. The data in the table illustrate the effect of gaps on the surface temperatures and *F* values of cans adjacent to and near the gaps. (The cans were in the holding section for 1·5 min.) To ensure that every can receives a similar thermal process it is necessary to run the sterilizer with the drag chain always completely filled. Probably this is best achieved by automatically feeding colour coded dummy cans into any gaps that result from fluctuations in production. These cans would be sorted out after cooling and returned to the entry point of the sterilizer ready for recycling. Alternatively, two or more cans on each side of a gap could be discarded as being underprocessed. If the throughput were slowed to give an adequate process to the cans adjacent to gaps, the other cans would be grossly overprocessed.

Conclusions

As heating and cooling rates in the reversing-spin flame sterilizer are rapid, precise process control is necessary if the sterilization process received by each can is to be adequate and uniform. The parameters which must be carefully controlled are those which affect the temperature of the can on leaving the flame heating section, and the time in the holding section.

Factors which influence the exit temperature from the flame heating section include fill control, temperature of the can when it enters the flame heating section, viscosity of the product, condition of the can surface, conditions of burner operation and the degree of success in filling all pockets on the drag chain.

Once these conditions are established satisfactorily and the number of cans in the flame heating and holding sections are settled, the *F* value of the process may be controlled by varying the speed of the drag chain which then determines both the temperature of the cans and the amount of time they spend in the holding section.

References

Anon. (1972). Records can temperature during heat processing. *Food Engng* **44**(4), 153.

Casimir, D. J. (1975). Flame sterilization. *CSIRO Food Res. Q.* **35**, 34–9.

Cheftel, H., and Thomas, G. (1963). Principles and methods for establishing thermal processes for canned foods. J. J. Carnaud & Forges de Basse-Indre. Res. Lab. Bull. No. 14. (Trans. from French by Israel Programme for Scientific Translations: Jerusalem, 1965.)

Huntington, J. N., and Casimir, D. J. (1972). Design, construction and operation of a reversing-roll pilot-scale flame sterilizer. *In* 'Flame Sterilization', Specialist Courses for the Food Industry (AIFST–CSIRO), No. 2, 33–5.

Electrodes for estimating sulphur dioxide

By D. Barnett

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Ion selective electrodes have been available for some years and recently electrodes have been produced commercially which respond to gases in aqueous solution. An electrode of this type which responds to sulphur dioxide (SO_2) could have applications in the food industry.

Two commercial electrodes for estimating SO_2 in aqueous solution have been examined in this laboratory. The essential features of their construction are shown in the accompanying figure. They consist of a tube of fluorocarbon polymer with a threaded end onto which the membrane that is permeable to SO_2 is fitted and sealed with a screw-on cap. A glass electrode of special design is inserted into the body of the tube and pressed against the membrane. The body also contains a reference electrode and is partially filled with a solution containing bisulphite and chloride ions. This solution forms a film between the end of the glass electrode and the membrane.

The operation of these electrodes depends on SO_2 in dilute solution obeying Henry's law, i.e. the partial pressure of SO_2 above a solution is directly proportional to the concentration of the gas in solution:

$$pSO_2 = K_H(SO_2)_{aq}.$$

Thus when a membrane that is permeable to gaseous SO_2 is immersed in an aqueous solution of this gas the amount of SO_2 that passes through the membrane is directly proportional to the concentration of SO_2 in the aqueous solution.

The filling solution on the inside of the electrode membrane contains a high concentration of bisulphite ions. Sulphur dioxide reacts with water according to the equation

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+, \qquad (1)$$

so that at equilibrium

$$K_{eq} = (HSO_3)(H^+)/(SO_2)(H_2O). \qquad (2)$$

When the concentration of bisulphite ions and water is large, (HSO_3^-) and (H_2O) in equation 2 may be considered to be constant and then

$$(H^+) = (SO_2) \times \text{constant}. \qquad (3)$$

The electrode therefore responds to changes in the concentration of SO_2 indirectly as a change in (H^+) or as a change in pH, according to the equation

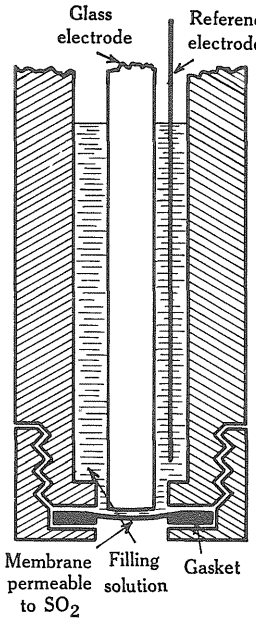
$$E_m = E_o + 2{\cdot}303(RT/F)\log_{10}(SO_2), \qquad (4)$$

where E_m is the measured potential in a solution containing SO_2; E_o is the potential measured with no SO_2 present and arises from the electrode components, i.e. glass electrode and reference electrode; and the temperature-dependent constant $2{\cdot}303RT/F$ has a value of 0·0591 V at 25°C. This constant is multiplied by the logarithm of the SO_2 concentration in the solution, which means that the measured potential will change by 59·1 mV for each decade change in concentration of SO_2. The electrodes therefore respond in a Nernstian manner and have an effective range from a few to some thousands of parts per million.

It is evident from equation (1) that the concentration of free SO_2 in a sample will depend on the pH and at pH values < 1, bisulphite ion is almost completely converted to SO_2.

Use of the electrodes is simple. First the sample is acidified with sulphuric acid. The membrane-carrying end of the electrode is immersed in the stirred solution which now contains a maximum concentration of free SO_2. The potential is read after a short interval to allow for equilibration. This potential may be compared with a calibration curve of potential *v.* SO_2 concentration and the level of SO_2 estimated in the original sample.

Carbonyl addition compounds of SO_2 are not dissociated at low pH so these electrodes estimate only the available or free SO_2 in foods, whereas the permitted legal limits are based on total SO_2 as determined by the



Essential features of an electrode designed to estimate SO_2 in aqueous solution.

Monier-Williams or similar methods. It is possible, however, by alkaline pretreatment to release much of the bound SO_2 to obtain a measure of total SO_2 in a sample.

Apart from the sensitivity of one of the electrodes tested to osmotic effects, they were remarkably free from interferences. The only likely source of interference would be from those substances capable of passing through the membrane and causing a change in the pH of the solution filling the electrode. Volatile acids are in this category, but the only such substance likely to occur commonly in foods is the acetic acid found in products such as pickles. Acetic acid vapour passing through the membrane will result in highly erroneous readings being obtained with such products.

The electrodes responded well in fruit juices and cordials. With dried foods it was difficult to obtain high reproducibility but the results would still be useful for quality control purposes. The best results in all instances were obtained by means of the standard addition technique. This requires only one standard solution and a knowledge of the response of the electrode, i.e. the number of mV per 10-fold change in concentration. When dealing with samples of the one kind of food it would be sufficient to develop a standard curve plotting millivolts against concentration of added SO_2 and then reading off the unknown concentration. The error in the measurements depends on a number of factors, including temperature, which is usually not difficult to control. The slope of the response curve varies from 56 to 60 mV per 10-fold change in concentration in the temperature range 10–30°C. Experience showed that errors of $\pm 5\%$ will occur even when conditions are carefully controlled; and much of this variability arises from uncertainty in reading the voltage. It is likely that such errors would be acceptable in many applications in the food industry in view of the convenience of using these electrodes and the time they would save.

Apart from an electrode, other equipment required for these measurements includes an expanded scale pH–mV meter capable of being read to less than 0·5 mV. It is essential to stir the sample, preferably with a magnetic stirrer, and the sample should be contained in a closed vessel. One of the commercial electrode assemblies has provision for flow-through operation which is most useful for clear liquid samples, although it requires a peristaltic or similar pump to deliver the sample at 2–5 ml per min.

To summarize, the electrodes are useful for rapidly estimating SO_2 in most foods, and particularly in liquid foods. Although the equipment is costly, the savings in time and the convenience of the method are attractive features. As described above, the general method of use will estimate free SO_2 only, but since this has been shown to be related directly to the preservative action of SO_2, this may be advantageous in many instances. Both electrodes were delivered with instruction manuals but neither contained all the information needed by users of the instruments.

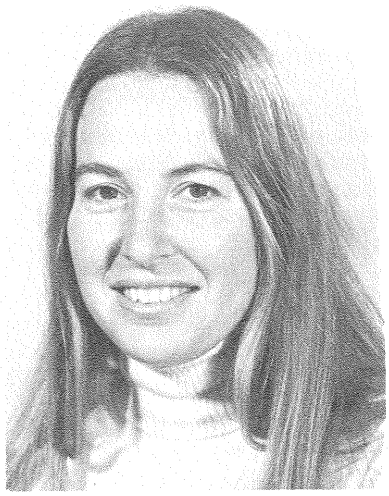
Note

The electrodes described in this article were the EIL Sulphur Dioxide Probe, model 8010-2, obtained from Kent Instruments (Australia) Pty Ltd, 70–78 Box Road, Caringbah, N.S.W. 2229; and the Orion Research Sulphur Dioxide Electrode, model 95-64, obtained from Watson Victor Ltd, 95 Epping Road, North Ryde, N.S.W. 2113.

News from the Division

Appointments

Mrs Evelyn White, B.A., was appointed Library Officer at FRL following Mrs Leida Piip's transfer, as Librarian, to the Division of Textile Physics. Mrs White has worked in libraries in Adelaide, Newcastle and Sydney and at Cambridge University, England; her most recent appointment was at Macquarie University.



Mr Grantley Chaplin, B.Sc.Agr., M.Sc., Experimental Officer, transferred to PPU (FRL) from the Division of Tropical Agronomy, Mareeba, Queensland.

Mr R. G. Hamilton, B.Appl.Sci., joined MRL's Industry Section as an Experimental Officer to work on the development of methods for the recovery of potentially valuable substances from abattoir wastes and for making more profitable use of those presently used in low-value products. Mr Hamilton was previously Product Development Chemist with Provincial Traders Pty Ltd.

A grant from the Australian Apple and Pear Corporation has enabled the Division to appoint Miss Helen Woods, B.Sc., as an Experimental Officer to work on apple and pear processing. And attention will be paid, first, to increasing the volume of apples processed by improving existing products and developing new ones.

Resignation

Mr P. L. Thomas, MRL's Liaison Officer and representative on the Editorial Committee of the *Quarterly*, has resigned from CSIRO. He becomes Officer-in-Charge of the Ciba-Geigy Cattle Tick Research Station at Beenleigh, Queensland. The Editorial Committee records its warmest appreciation of Len's contribution to the production of this journal; we wish him well in his new venture.

Award

Mr D. J. Casimir, of the Food Technology Section at FRL, was awarded a Ph.D. degree by the University of New South Wales in May 1975 for his thesis 'Technological aspects of the production of concentrates of passionfruit—*Passiflora edulis*'.

Work overseas

Dr W. B. McGlasson (PPU) was a principal speaker at the Gordon Research Conference on Postharvest Physiology at Santa Barbara, Calif. His paper, dealing with non-ripening tomato mutants, was contributed to the session on the biochemistry and physiology of ripening and senescence.

Dr J. H. B. Christian, Associate Chief, attended a meeting of the Codex Alimentarius Committee on Food Hygiene, held in Washington, D.C., in May.

New capital works at FRL

Work has commenced on the construction of a Plant Growth building to be situated on the south edge of the service road adjacent to the Food Science building. The new building will house special environmental cabinets for plant growth for use by staff of PPU and the Wheat Research Unit. The cabinets will be the first of their kind in Australia.

General

The Australian Government's Industries Assistance Commission is conducting an enquiry into the dairying industry. Drs B. S. Harrap and J. Czulak of DRL and Dr A. R. Johnson of FRL appeared as expert witnesses before the Commission in May. The particular matters under consideration were DRL's role in relation to assistance to the dairying industry and CSIRO's part in the development of ruminant products with modified fat content.

Selected publications of the Division

Readers' attention is drawn to a new Technical Paper (No. 40) from MRL, 'The validity and usefulness of subjective scales with special reference to food', by Dr A. Howard. This paper amplifies a two-part article written by Dr Howard for the *Quarterly* and entitled 'Taste panel techniques. I. Reproducibility, reliability and validity. II. A validation technique' (CSIRO *Fd Res. Q.*, 1972, **32**, 80–4; 1973, **33**, 8–14). Copies of Dr Howard's paper and of most of those listed below are available from the Librarian of the laboratory indicated.

From the Dairy Research Laboratory

Hamilton, J. S., Hill, R. D., and Leeuwen, H. Van (1974). A bitter peptide from Cheddar cheese. *Agric. Biol. Chem.* **38**, 375–9.

Henderson, J. O. (1974). A carbohydrate-free milk for infants. *Pace* **27**(4), 21.

Stewart, J. A.,* Muller, L. L., and Griffin, A. T.* (1974). Use of whey solids in calf feeding. *Aust. J. Dairy Technol.* **29**, 53–8.

Sullivan, J. J.,* Schlipalius, L. E.,* Mou, L., and Jago, G. R. (1974). Heat lability of starter cultures and its use in selecting potentially non-bitter strains. *Aust. J. Dairy Technol.* **29**, 71–4.

Sutherland, B. J. (1974). Control of salt absorption and whey drainage in cheddar cheese manufacture. *Aust. J. Dairy Technol.* **29**, 86–93.

From the Food Research Laboratory

Davis, E. G., McBean, D. McG., Rooney, M. L., and Gipps, P. G.* (1973). Mechanisms of sulphur dioxide loss from dried fruits in flexible films. *J. Food Technol.* **8**, 391–405.

Johnson, A. R. (1974). Biomanipulation of ruminant fats. *Food Manuf.* **49**, 19–22, 24.

McBean, D. McG., and Coote, G. G.* (1974). Quality tests of potato varieties in Australia. *Am. Potato J.* **51**, 165–9.

McGlasson, W. B., Scott, K. J.,* Raison, J. K., and Wills, R. B. H.* (1973). Physiology of apple fruits at low temperatures. Int. Inst. Refrig. Commn C2.

Marshall, B. J., Coote, G. G.,* and Scott, W. J. (1974). Some factors affecting the viability of dried bacteria during storage *in vacuo*. *Appl. Microbiol.* **27**, 648–52.

Middlehurst, J., and Parker, N. S. (1974). Condensation on canned foods during transport in ISO containers. *CSIRO Food Res. Rep.* **105**, 16.

Pitt, J. I. (1974). Resistance of some food spoilage yeasts to preservatives. *Food Technol. Aust.* **26**, 238–41.

Ruello, J. H. (1974). Handling and processing banana prawns of the gulf of Carpentaria. *Food Technol. Aust.* **26**, 186–90.

Ruello, J. H. (1974). Storage of prawns in refrigerated sea water. *Aust. Fish.* **33**, 6–9.

Sharp, A. K. (1974). Metabisulphite dipping machine. *Aust. Fish.* **33**, 10–11.

Sharp, A. K. (1974). Transient dropwise condensation of water vapour from air on to cylindrical food cans. Part I: Experimental determination of instantaneous values of the transfer coefficients. *Trans. Inst. Chem. Eng.* **52**, 17–22.

Sharp, A. K. (1974). Transient dropwise condensation of water vapour from air on to cylindrical food cans. Part II: An analogue model. *Trans. Inst. Chem. Eng.* **52**, 23–30.

Smith, M. B., Reynolds, T. M., Buckingham, C. P., and Back, J. F. (1974). Studies on the carbohydrate of egg-white ovomucin. *Aust. J. Biol. Sci.* **27**, 349–60.

Thomas, M. A.,* Baumgartner, P. A.,* Board, P. W., and Gipps, P. G.* (1973). Evaluation of some non-meat proteins for use in sausage. *J. Food Technol.* **8**, 175–84.

Tracey, M. V. (1974). Human needs for meat. *Proc. Aust. Soc. Anim. Prod.* **10**, 181.

From the Food Research Unit, Hobart

Eustace, I. J. (1974). Zinc, cadmium, copper and manganese in species of finfish and shellfish caught in the Derwent Estuary, Tasmania. *Aust. J. Mar. Freshwater Res.* **25**, 209–20.

Ratkowsky, D. A.,* Thrower, S. J., Eustace, I. J., and Olley, J. (1974). A numerical study of the concentration of some heavy metals in Tasmanian oysters. *J. Fish. Res. Board Can.* **31**, 1165–71.

Thrower, S. J., and Eustace, I. J. (1973). Heavy metal accumulation in oysters grown in Tasmanian waters. *Food Technol. Aust.* **25**, 546–53.

From the Meat Research Laboratory

Grau, F. H., and Smith, M. G. (1974). Salmonella contamination of sheep and mutton carcasses related to pre-slaughter holding conditions. *J. Appl. Bacteriol.* **37**, 111–6.

Johnson, B. Y. (1974). Some meat science aspects of chilling and freezing meat. Paper presented at Aust. Inst. Refrig. Air Condit. Heat Conf.

Lovett, D. A., and Herbert, L. J. (1974). Condensation in Australian abattoirs—its occurrence and control. Paper presented at Aust. Inst. Refrig. Air Condit. Heat. Conf.

MacFarlane, J. J. (1974). Pressure-induced solubilization of meat proteins in saline solution. *J. Food Sci.* **39**, 542–7.
MacFarlane, J. J., Harris, P. V., and Shorthose, W. R. (1974). Manipulation of meat quality, particularly tenderness, by the processor. *Proc. Aust. Soc. Anim. Prod.* **10**, 219.
Thornton, R. F., Shaw, F. D., and Hood, R. L. (1974). Marbling in feedlot cattle. *Aust. J. Exp. Agric. Anim. Husb.* **14**, 281–5.

*Not a member of the Division.

Book notice

'Cooling and ripening of fruits in relation to quality.' International Institute of Refrigeration, Commission C2. Bull. Annexe 1973-3.
(In French and English.)

This Bulletin contains 27 papers, and comprises reviews that were presented at the meeting of Commission C2 in Israel in 1973. The following topics are covered: control of ripening, controlled atmosphere storage, chilling, prestorage treatments including use of the gases carbon monoxide and acetaldehyde, packaging, and the effects of various treatments on the quality of stored products. Some information is also presented on the storage of eggplant and persimmons.

K.J.S.