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Subjective and objective assessments of the degree of cooking of potatoes heated by different methods

R. COLLISON, K. JOHNSON, OLUFOLAKIME O. OKIKIOLU AND ANN WEST

Summary

Standard potato slices were heated for various periods of time by three different methods: boiling water, steam under pressure, and a microwave oven. After heating, the internal temperature was measured together with textural characteristics to assess the degree of cooking, using both a taste panel and an Instron 1140 machine.

It was found that for a given method of heating the taste panel score is related to the instrumental measurements of rupture load and rupture energy. It was also found that the degree of cooking of a potato does not depend solely on the internal temperature reached, but is also dependent on the heating method and particularly on the rate of heating.

Introduction

Some heat processing procedures in the food industry have a primary aim which is well defined and relatively easy to measure. Thus, the prime aim in the pasteurization of milk is to reduce the bacteriological content to a certain level. By contrast, the primary aim in cooking potatoes is difficult to define and therefore to measure. However, an important feature is the acquisition of certain textural characteristics. Szczesniak, Branet & Friedman (1963) have subdivided textural characteristics of interest to the consumer into three principal categories: mechanical, geometrical, and a third category referring mainly to moisture and fat content.

When potatoes are cooked in boiling water or steam, heat is first transferred from the cooking medium to the surface of the food and then to the thermal centre. The time required for cooking is largely dependent on how quickly heat

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travels towards the thermal centre, and cooking procedures are sometimes calculated according to the time taken for the thermal centre to reach a specified temperature.

With microwave heating, because heat is generated within the sample, the centre can reach a high temperature in a matter of seconds. This raises the question as to whether the internal temperature is the only criterion or whether other factors, including time, should be taken into account. For example with meat (Roberts & Lawrie, 1974, the attainment of a given temperature by microwave heating produces properties different from those achieved by conventional heating.

The present investigation with potatoes was carried out with two aims in mind:

(a) to determine whether there was any relationship between instrumental measurement of degree of cooking and taste panel score
(b) to find to what extent the degree of cooking depends on the internal temperature reached.

In these experiments the geometrical characteristics are standardized and the changes during cooking are confined mainly to mechanical properties together with some variations in moisture content.

Experimental

Potato samples and cooking methods

All the experiments reported here were carried out during a period of 6 weeks in January and February 1976 on King Edward potatoes, stored at 6°C until used. Slices 3.0 cm thick and 5.0 cm diameter were cut from the central part of the tuber using a round metal cutter. The potato slices were heated either in 1000 cm^3 of unsalted boiling water, a household pressure cooker at 15 lb/in^2 excess pressure, or in a dry dish in a Litton Menu-master Microwave Oven.

Immediately after heating, the internal temperature at the centre of the slice (1.5 cm below the surface) was measured using a calibrated thermocouple. The samples were then kept in a hot cupboard at 60°C until they were tested.

Texture measurement

All cooked slices were tested after 30 min in the hot cupboard. (At this stage the internal temperatures were 60 ± 3°C).

Measurements were made using the Instron 1140 machine. Essentially this consists of two parts: (a) a drive mechanism which drives a moving cross head at a preselected speed, which in these experiments was 100 mm/min and (b) a load sensing and recording system.

A flat circular compressor of 10 cm^2 area was attached to the moving cross head, and the instrument adjusted to compress the potato slices beyond the point of rupture. The area of the potato slices was greater than 10 cm^2, so that in

effect we were recording the load applied to a potato area of 10 cm^2 as a function of compression. Four samples were tested for each method of heating.

Taste panel method

Catering Studies students were used throughout the experiment as tasters. Originally sixteen students were screened during panel selection tests over a period of 3 weeks and eight were finally selected as being sufficiently discriminating and consistent for use as permanent members of the panel. During this preliminary 3-week period, tasters were familiarized with the extremes of the tasting scale by sampling specimens of raw uncooked potato, and potatoes that had been boiled for 40 min. Tasting sessions took place regularly once per week at 12.15 p.m. which meant that samples were evaluated after spending 1 h in the hot cupboard.

The hot potato samples were served on disposable paper plates and disposable forks were provided. Sample preparation and size was identical to that for the Instron measurements. Each sample was coded using a three digit code. Each tester was presented with a number of coded samples (maximum six) corresponding to the varying lengths of cooking time. The tasters were asked to score the samples for texture on a scale which ranged from 10 (raw) to 0 (overcooked). Average scores for each sample were calculated, from 6 determinations for each method of heating.

Results

Analysis of Instron curves

Figure 1a shows a typical Instron curve of load versus compression for a raw potato slice. On compression, the load increases steadily until the potato

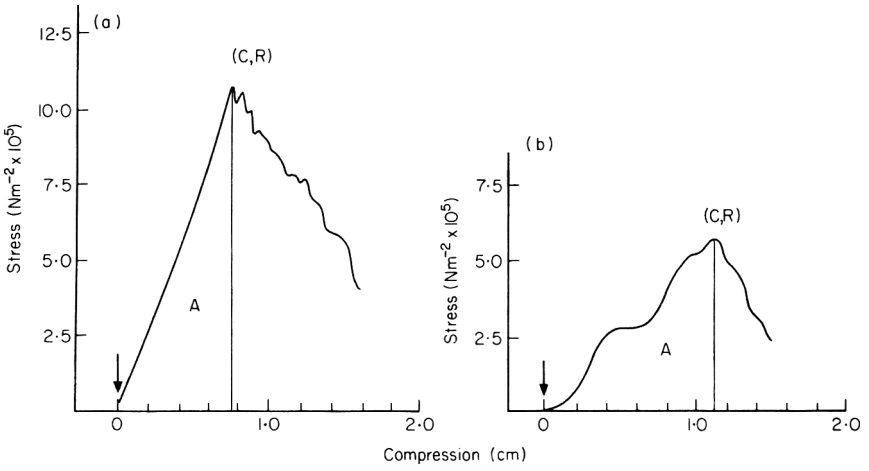

Figure 1. Load–compression curves for (a) raw potatoes, (b) potatoes heated for 15 min in boiling water.

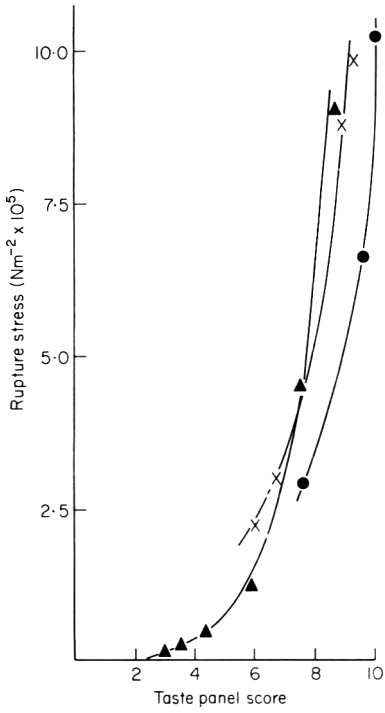

Figure 2. Rupture load and taste panel score (▲, Boiling water; ●, microwave oven; ×, pressure cooker.

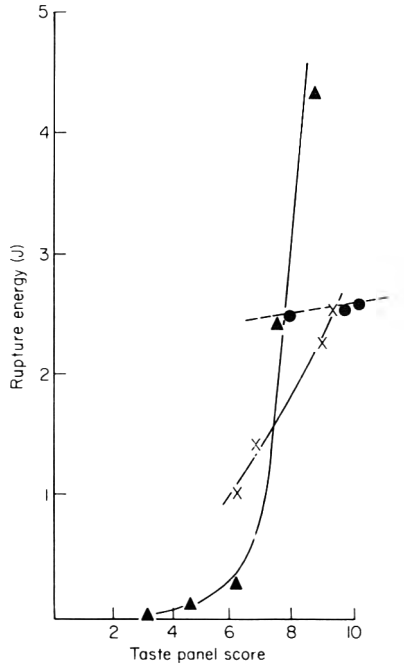

Figure 3. Rupture energy and taste panel score (▲, Boiling water; ●, microwave oven; ×, pressure cooker.

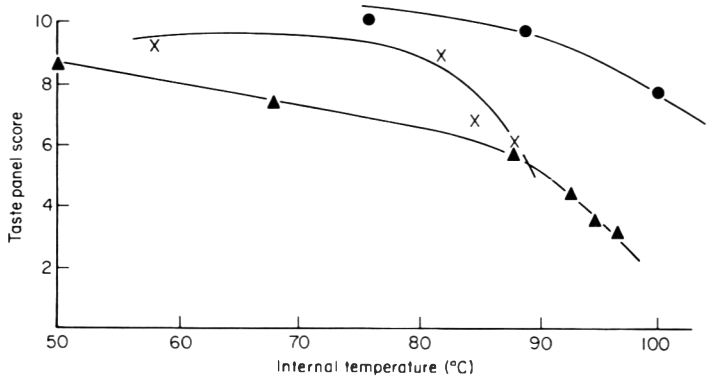

Figure 4. Taste panel score and internal temperature (▲, Boiling water; ●, microwave oven; ×, pressure cooker.

ruptures, at which point the load suddenly drops. The rupture point is, therefore, easily distinguished, and corresponds to a well defined rupture load and rupture compression. At this point, the Instron head penetrates the sample which begins to collapse. The rupture energy which was also calculated is proportional to the area (A) under the curve.

Values of rupture load were remarkably consistent for raw potatoes, all being in the range of 98 to 102 kg. Furthermore, the rupture load fell continuously during cooking by all three heating methods. The rupture energy also was continuously reduced during cooking although the results were not as consistent. On the other hand, the rupture compression varied erratically on heating and tended to increase at first (as in Fig. 1b) and then subsequently decrease. In view of this, attention is confined to looking at the relationship between the taste panel score and the rupture load and energy. These properties are also examined to discover if they bear any relationship to the internal temperature attained by the potato slices.

Instrumental measurements, taste panel results and internal temperatures

Figure 2 shows the plots of rupture load against taste panel score separately for each of the three methods of heating. For a given heating method there is a significant correlation. Furthermore, the curves for boiling water, and for pressure cooking are almost superimposed, although that for 'dry' microwave heating is displaced. Similarly the plots of rupture energy against taste panel score (Fig. 3) show a correlation for a given method of heating, although in this case the three curves are quite separate.

The internal temperature attained on heating has some bearing on the textural characteristics of the sample. For a given method of heating the taste panel score (Fig. 4), rupture load (Fig. 5) and rupture energy (Fig. 6), are all dependent on the internal temperature.

However, the attainment of a particular temperature, irrespective of the heating method, does not by itself, fix either the taste panel score or the

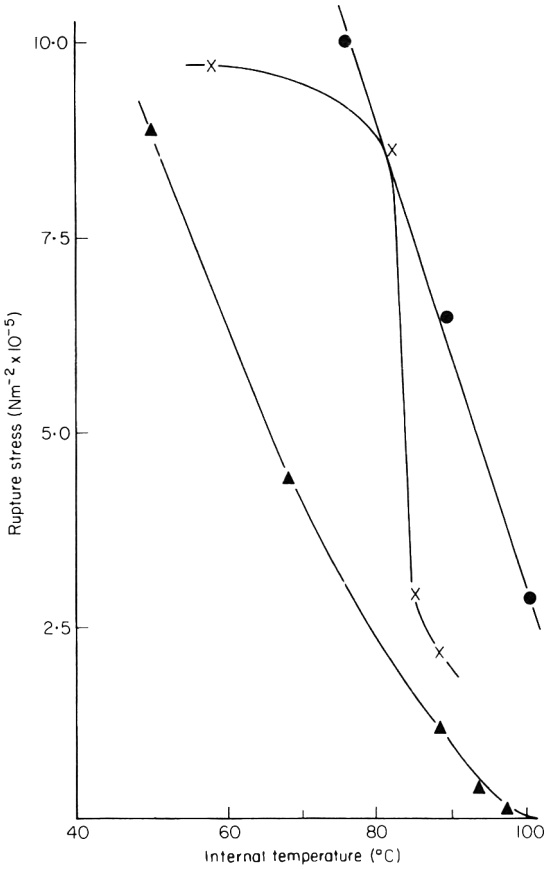

Figure 5. Rupture load and internal temperature (▲, Boiling water; ●, microwave oven; ×, pressure cooker.

instrumental measurements. It would be reasonable to suppose that other factors such as the time of heating and moisture loss or gain also affect the physical properties.

Discussion

Taste panel and instrumental measurements

In these experiments, the taste panel numbers have given a score on a scale ranging from raw (score 10) to overcooked (0). This assessment was based on feel in the mouth during eating. Szczesniak (1963) has proposed that a taster views textural characteristics according to a definite sequence of actions, viz. first bite, mastication and residual impression. Mechanically and physiologically this is a complicated situation. The assessment depends on a complex series of factors including mechanical properties and structure of the food, the shearing forces imposed on the food by the grinding action of the teeth, and the interaction between the food particles and the saliva.

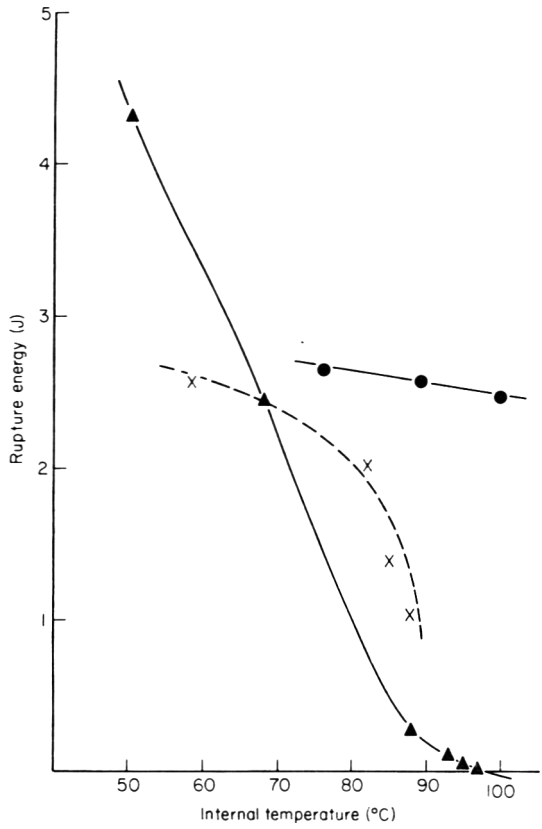

Figure 6. Rupture energy and internal temperature (▲. Boiling water; ●. microwave oven; ×, pressure cooker.

Similarly, the instrumental determination of textural characteristics is complex. Potato is viscoelastic in nature, (Voisey, Tape & Kock, 1969) that is when it is subjected to a force it undergoes two types of deformation, elastic or recoverable deformation and non-recoverable viscous flow. Both of these are time dependent and, therefore, the load compression curves of the type measured in this investigation will depend on the rate at which the food is compressed.

Rupture load and rupture energy, are not fundamental rheological properties, and can only be defined in terms of the instrumental conditions under which they were measured. There is the further complication that the mechanical action of the Instron machine on the food is different to that of eating.

Despite these difficulties the results presented here show a degree of correlation provided they are restricted to one method of heating at a time. This suggests that rupture load and rupture energy both contribute to the sensation which is experienced and evaluated by members of the taste panel.

Significance of internal temperature

Although for a given method of heating, instrumental measurement and taste panel results correlated with the internal temperature, the results show conclusively that the attainment of a certain internal temperature is not the overriding factor in determining the properties of the heated potato. Thus, a potato slice heated in boiling water was relatively cooked when the internal temperature had reached 93°C, whereas the sample heated in a microwave oven was comparatively raw even when it had reached 100°C.

Conclusions

It was found that the heating of potato slices by any of these heating methods (boiling water, steam under pressure, and microwave oven) caused a progressive reduction in the rupture load and rupture energy. Both these properties, correlated with taste-panel scores.

The internal temperature attained on heating correlated with the instrumental and taste panel measurements for a given method of heating. However, when considering all these heating methods, the changes depend not only on the temperature reached, but also on the heating method and on the time factor.

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Heat recovery in spray drying systems

C. R. HOLLAND AND J. B. McCANN

Summary

Identification and subsequent quantification of all energy losses in a spray drier system in a food production plant are shown to be obtained by the application of heat and mass balances. Heat recovery systems are reviewed and proposals are given for the introduction of such a system to optimize energy usage. Cost data for the application of a heat recovery unit and the use of economic thicknesses of insulation show that considerable annual savings can be achieved resulting in payback times of approximately one year.

Introduction

High fuel costs and the threat of dwindling fuel resources point to the need for energy conservation. This may be achieved by studies of energy utilization of process plants with the view to optimizing fuel usage. Any analysis of energy consumption must include all energy losses and the reasons for their existence. These losses will be in the form of either heat or mass losses. Heat losses may occur by conduction through, and convection from walls of vessels, in high temperature systems, as radiation, and as waste heat in effluent streams. Mass losses may occur as leakages, product carry over in exhaust streams and condensate streams to drainage.

The object of this investigation was to study energy utilization in a food processing plant, L. E. Pritchitt and Co. Ltd, Kiltonga Industrial Estate, Newtownards, County Down, with the view to optimizing fuel usage. The company produces a variety of wet and dry products, but this paper will only be concerned with the process producing dry milk powder from skimmed milk, concentrating on the spray drier and ancillary heat exchange equipment within the

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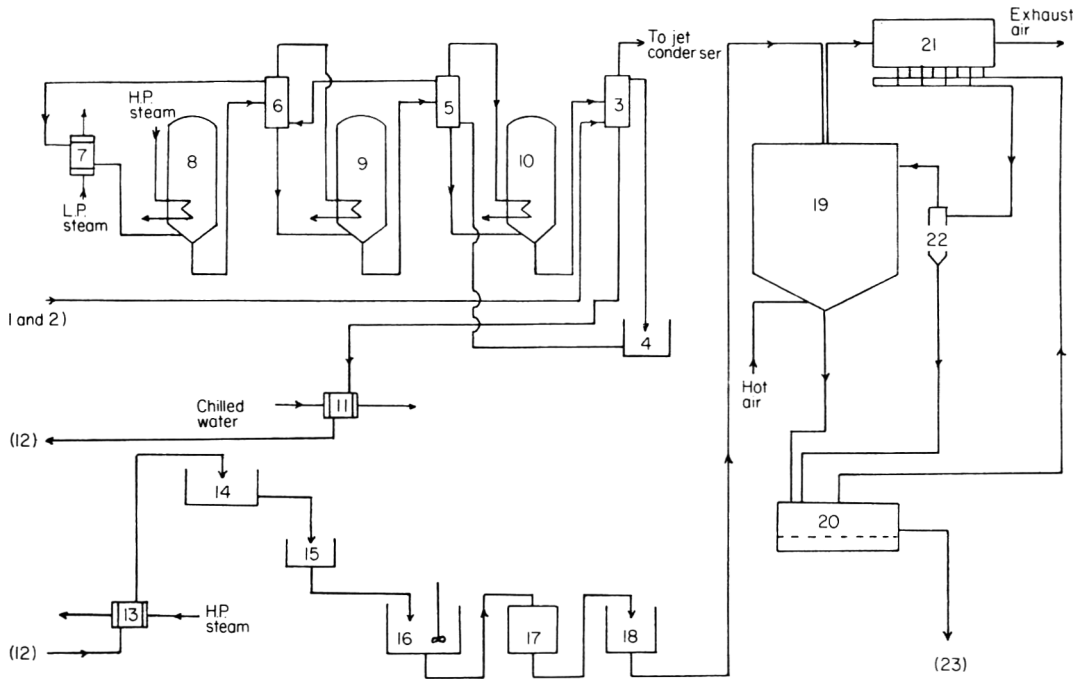

Figure 1. Flow diagram for dry product processing. 1, Receiving tank; 2, receiving tank; 3, 3rd effect separator; 4, holding tank; 5, 2nd effect separator; 6, 1st effect separator; 7, preheater; 8, 1st calandria; 9, 2nd calandria; 10, 3rd calandria; 11, evaporator cooler; 12, storage vessels; 13, preheater; 14, holding tank; 15, weight tank; 16, mixer; 17, homogenizer; 18, holding tank; 19, spray drier; 20, fluidized cooler; 21, cyclone bank; 22, final cyclone; 23, dry mixing and packing section.

process. Two objectives were kept in mind during the investigation: (1) to reduce the amount of energy required, and (2) to make more efficient use of the actual energy supplied. Energy required for the spray drier section of the process is in the form of heat carried by steam generated by oil fired boilers. All savings are, therefore, related to fuel oil costs.

Process description

A line diagram of the process is shown in Fig. 1. Skimmed milk, at a temperature of 7.0°C and solids content of 8.0%, is pumped from storage to the evaporator system which is a falling film, triple effect unit. The evaporator system concentrates the skimmed milk to approximately 45% solids. The concentrated milk is cooled and stored in a holding tank prior to pasteurization in a plate type heat exchanger. Fats and sugars are then added to the pasteurized milk in a series of agitated vessels. The resulting mixture is homogenized prior to being fed to the spray drier.

In the spray drier section of the plant (Fig. 2), the homogenized feed (76°C) is atomized to a fine spray by it being pumped through a rotating disc atomizer. The falling spray is dried to 3% moisture by counter current flowing hot air (150°C) which enters tangentially at the bottom of the spray drier through a series of louvres. The majority of the dried powder falls to the floor of the spray drier where it is swept into a collecting chute by means of brushes on the floor of the chamber. It is then transported by a screw conveyor to a fluidized bed cooler which reduces its temperature to 20°C. The powder then enters the packing section of the plant.

The drier exit air stream (80°C) contains entrained product fines which are removed in a series of cyclones. The fines removed in the cyclones enter a pneumatic conveying stream created by air drawn off the top of the fluidized bed cooler.

The hot air, required in the spray drier, is heated in an air heater which, as can be seen in Fig. 3, consists of two parts. The major part of the heating process is achieved by the air flowing over a bank of finned pipes through which is passing 10.6 bar steam. The resulting condensate is flashed at 5 bar pressure and this steam is used in the preheating part of the air heating process.

Method of approach

The general procedure adopted was to establish, firstly, detailed heat and mass balances for each item of equipment in the spray drier section of the plant, and secondly, to determine the sources and magnitude of all heat losses that were occurring.

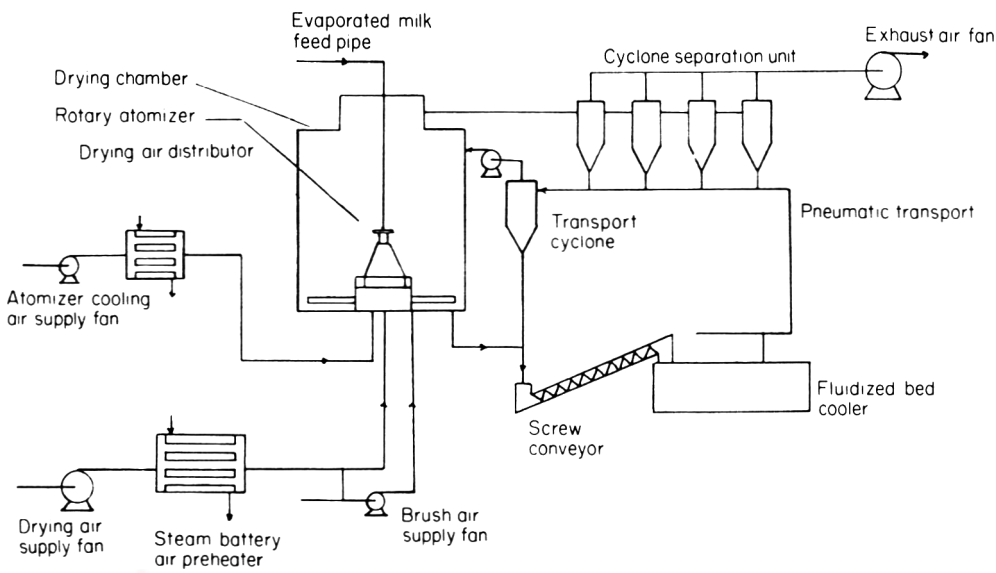

Figure 2. Spray drier system.

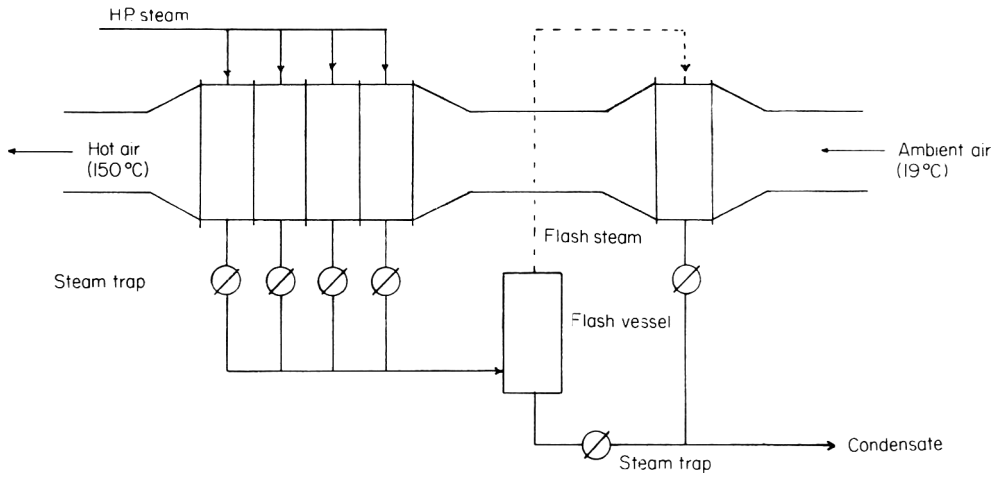

Figure 3. Flash steam recovery in air preheater.

The type of measurements taken on the plant were: (i) air flow rates and (ii) temperatures.

Air flow rates had to be measured using pitot tubes, as instrumentation for flow on the plant was limited.

Temperature measurements were required for the following reasons: (i) to determine the heat transfer characteristics of the equipment; (ii) to determine physical properties of process streams, i.e. densities, viscosities and heat capacities; (iii) to determine the humidity of the process streams.

The temperatures of all process streams and the surface temperatures of vessels, pipes and ducting were taken using a copper/constantan thermocouple system. Wet and dry bulb temperatures of process air streams were measured using an Assmann Hygrometer enabling the humidities to be calculated in terms of (kg of water/kg of dry air).

Results

The results of a complete heat and mass balance for the spray drier are summarized in Table 1.

Total heat IN = 3510 kW
Heat OUT = 2873 kW
Heat lost in drying chamber = 637 kW

Heat may be lost: (i) conduction through and convection from the insulated walls of the chamber; (ii) conduction through and convection from the uninsulated top of the drier; and (iii) air leakages.

Table 1. Heat and mass balance on the spray drier

Flows in	Temperature (°C)	Flow rate (kgs^{-1})	Humidity (kgH_2O/kg dry air)	Heat content ($kJ\ kg^{-1}$)	Heat flow (kW)
Evaporated milk feed	62	0.45		285.50	128.47
Hot inlet air	150	18.41	0.0072	172.52	3176.10
Atomiser cooling air	40	0.89	0.0035	49.24	43.82
Brush air stream	64	1.09	0.0072	83.34	90.84
Pneumatic transport stream	28	0.89	0.0200	79.18	70.47
Flows out					
Powder product	69	0.24		63.79	15.31
Exit air stream	83	21.28	0.019	134.27	2857.25

The total heat lost from a surface is calculated by the equation:

$$Q = h_c A \Delta t$$

where

Q = total heat transfer
h_c = heat transfer coefficient
A = surface area
Δt = temperature difference between the vessel surface and ambient.

The heat transfer coefficient, h_c, is calculated using expressions of the following form.

$$Nu = c(Gr.Pr)^n$$

where

Nu = Nusselt number, $\frac{h_c L}{\kappa}$;

Pr = Prandtl number, $\frac{c_p \mu}{\kappa}$;

Gr = Grashof number, $\frac{\beta g \Delta t L^3 \rho^2}{\mu^2}$;

β = coefficient of cubic expansion of air
g = acceleration due to gravity
ρ = density of bulk air
μ = viscosity of bulk air
L = characteristic dimension of the hot surface
c_p = heat capacity of air
κ = thermal conductivity of air.

Evaluating the physical properties of the air at a mean bulk temperature of 19°C, the following simplified correlations for h_c for various geometrical shapes can be found: (i) vertical planes and large cylinders, $h_c = 1.58\Delta t^{1/3}$; (ii) horizontal or vertical cylinders, $h_c = 1.22\Delta t^{1/3}$; (iii) horizontal plane facing upwards, $h_c = 1.7\Delta t^{1/3}$.

Heat loss due to convection from the spray drier may be listed:

Source	Heat loss (kW)
Chamber walls	4.09
Drier top	3.34
Evaporated milk feed pipe	0.34
Total	7.77

Convection only accounts for 7.77 kW of the total heat loss of 637 kW. The remainder of the heat loss is associated with leaks in the system and air stream leaving the drier chamber with the powdered product.

Steam battery air heater

The flow rate of high pressure steam to the heater was unknown but could be predicted by conducting a heat balance on the unit.

The heater consists of two parts: (i) the main heater fed by high pressure steam (10.6 bar); (ii) the preheater fed by low pressure steam (5.0 bar).

The low pressure steam was produced by flashing the condensate from the high pressure steam giving rise to 6.12×10^{-2} kg of 5.0 bar steam per kg of 10.6 bar steam.

The heat provided by steam in the heater is usefully gained by the air to be used in the spray drier and wastefully lost by convection from the heater surfaces. The heat gained by the air (the difference between inlet and outlet heat contents) was calculated at 2456 kW. Heat lost by convection from the outer surface of the heater was assumed to occur from three surfaces only, since the fourth surface supported the heater on the ground. The results are summarized below.

Surface	Heat loss (kW)
Top	1.32
Front side	2.74
Rear side	2.74
Total	6.80

Assuming no other heat losses occur the high pressure steam requirement was found to be 1.15 kg^{-1}.

Drier efficiency

The overall thermal efficiency, η, is defined as the fraction of total heat supplied to the drier used in the evaporation process. It can be approximated to the following relationship.

$$\eta = \frac{(T_1 - T_2)}{(T_1 - T_0)} \times 100$$

where

T_0 = ambient air temperature, 19°C
T_1 = hot inlet air temperature, 150°C
T_2 = exit air temperature, 83°C.

$$\eta = \frac{150 - 83}{150 - 19} \times 100 = 51\%$$

Discussion

In the spray drying section of the plant the heat is produced by steam giving up its latent heat to form condensate. The condensate will contain sensible heat, i.e., approximately 20 to 25% of the heat originally added to the water in the boiler house by burning fuel oil. By careful attention to flash steam recovery and returning all condensate to the boiler house, where it can be usefully employed as boiler feed or process hot water, most of this heat can be fully recovered.

The application of heat and mass balances on the plant will establish the sources and magnitudes of the heat losses. Two major areas of heat loss were established: (i) the heat content of the exhaust air stream leaving the spray drier; (ii) the heat lost by convection from all hot surfaces.

Heat recovery

The heat contained in the exhaust air stream could be most conveniently utilized to preheat the incoming fresh air required in the spray drier. This would involve the use of a heat recovery device consisting of an air to air heat exchanger. Several systems are commercially available and a brief review is given below.

Rotating wheel heat exchangers. Rotating wheel heat exchangers are in principle very simple but yet highly effective recovery units. The exhaust and fresh air streams are ducted on a counter flow principle through a slowly revolving wheel (0–10 rpm). The principle of operation is shown diagrammatically in Fig. 4. The exhaust and fresh air flow through separate ducts. The hot air gives up its heat to a matrix within the duct. This matrix acts as the heat transfer medium, giving up its heat to the cooler air stream during a later phase in the wheels revolution. Various materials are used for the matrix, e.g. ceramics, plastics, knitted wire mesh, inorganic fibrous materials etc.

A typical metal wheel is the Ljundstrom wheel which has a stainless steel or aluminium matrix constructed in the form of alternate thin strips of flat and corrugated foil. The specific heat transfer area is estimated at 3000 m^2 per m^3 of the rotor material with the foil only occupying 15% of the face area.

In order to prevent contamination of the fresh air by exhaust air the outer casing usually contains a purge section in which the flutes filled with exhaust air are purged by supply air before they enter the supply air duct. Figure 4c shows exhaust air entrained in the flutes of the rotor being carried over into the supply air stream. The carry over is of the order of 2–4% of the main air flow. By equipping the heat exchanger with a purging sector (Fig. 4d) the carry over can be drastically reduced.

These types of wheel are primarily designed to remove sensible heat, and manufacturers claim thermal efficiencies for sensible heat transfer may be as high as 80% for equal mass flow rates.

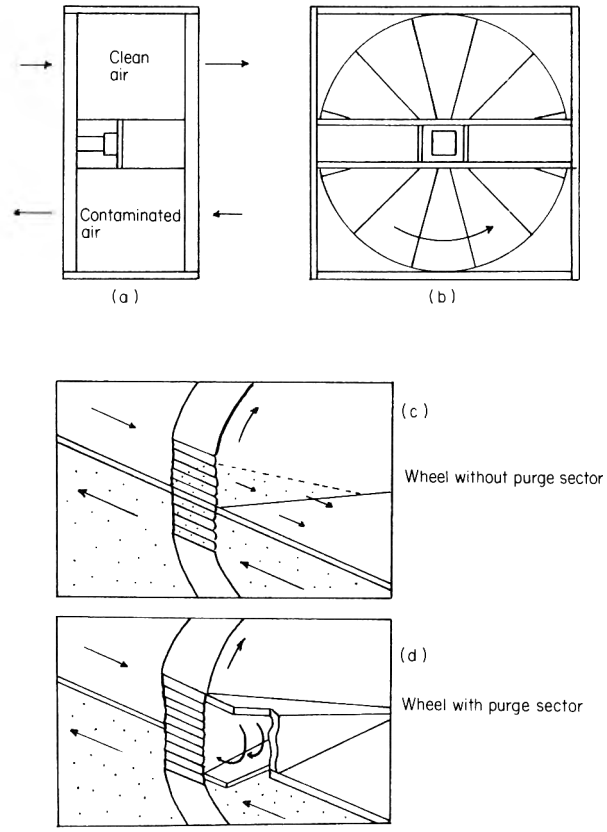

Figure 4. Rotating wheel regenerative heat exchanger.

Heat pipes. Heat pipes are closed evaporation-condensation systems capable of transferring thermal energy at a high rate. A refrigerant and a capillary wick are permanently sealed inside a metal tube setting up a liquid to vapour to liquid loop (Fig. 5). Thermal energy applied to either end of the pipe causes the refrigerant to vaporize. This vapour then travels to the other end of the pipe where the thermal energy is removed. The vapour condenses back to a liquid, then flows back to the opposite end through the capillary wick. A continuous evaporation-condensation cycle is set up provided there is a heat source along one end of the pipe and a heat sink along the other end.

In a heat pipe thermal recovery unit a number of heat pipes are set horizontally in a frame, with each pipe extending across the total width of the unit which is vertically separated into two ducts. Thermal energy is transferred horizontally through the pipes from the warm air in one duct to the counter flowing cool air in the other duct.

Many banks of tubes are required for high efficiencies. As the hot air stream from the spray drier will contain some milk powder, a system of this kind would be prone to fouling, requiring regular shutdown for cleansing.

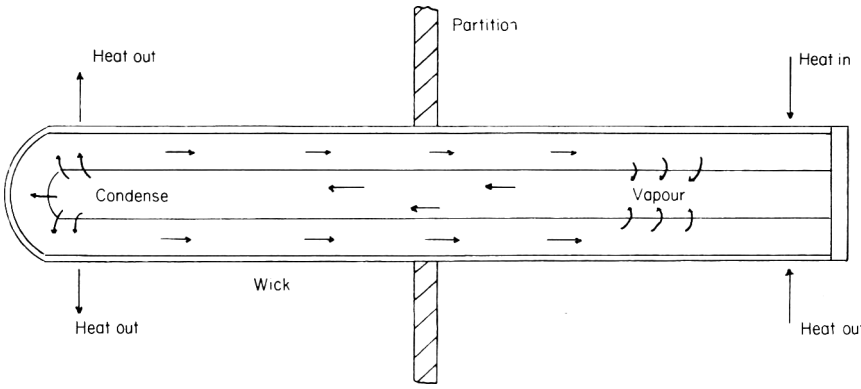

Figure 5. Heat pipe.

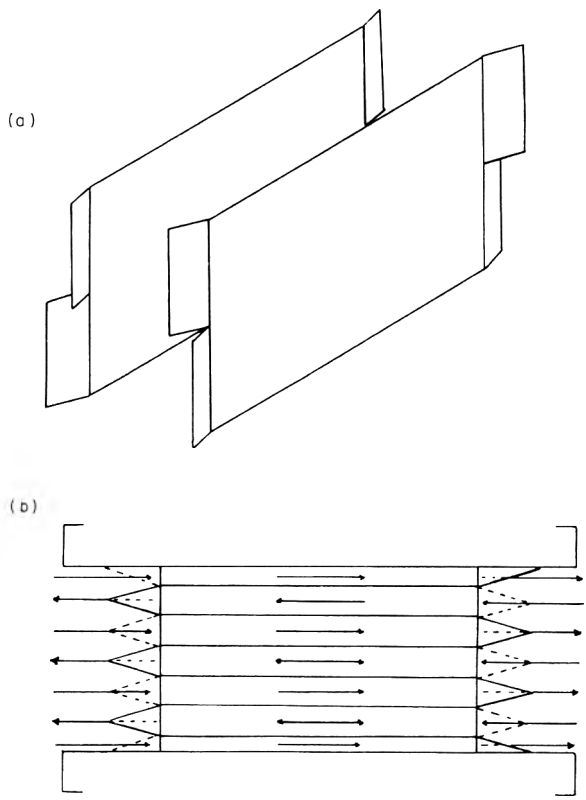

Figure 6. Recuperator plates and air flow.

Plate type heat exchangers. These air to air heat exchangers have no moving parts and are very simple in construction and easy to clean. In principle they comprise an open ended box filled with a matrix (usually metal) which is formed into a multiplicity of narrow linear passages where rows of those transporting exhaust air alternate with those carrying fresh air (Fig. 6). Heat energy is passed through the matrix walls from one air stream to the other. If the air is cooled below its dew point, condensation will occur and the condensate formed escapes via a drain in the bottom of the casing.

The particular advantages of this type of exchanger are: (i) high efficiency; (ii) no moving parts; (iii) ability to cope with dust ladened air as this type is easily inspected and cleaned.

Liquid coupled, indirect contact regenerative exchanger. The system, as shown in Fig. 7, consists of two heat exchangers, one in the exhaust duct and one in the supply duct, connected by a pipe loop. Liquid, usually water with an antifreeze additive, is pumped around the loop. Sensible heat is transferred to the liquid in the exhaust duct liquid-air exchanger and is then in turn, in the supply air duct exchanger, passed to the cooler incoming air.

Total heat efficiencies are usually of the order of 30% to 50% and often the energy used in operating the system can be as high as the energy being transported. The low efficiencies and possibility of fouling of the exchangers by milk powder makes this an unattractive proposition.

Proposed heat recovery system

The milk powder content and the dew point of the hot exhaust stream present problems with regard to the selection of the heat recovery device. The system

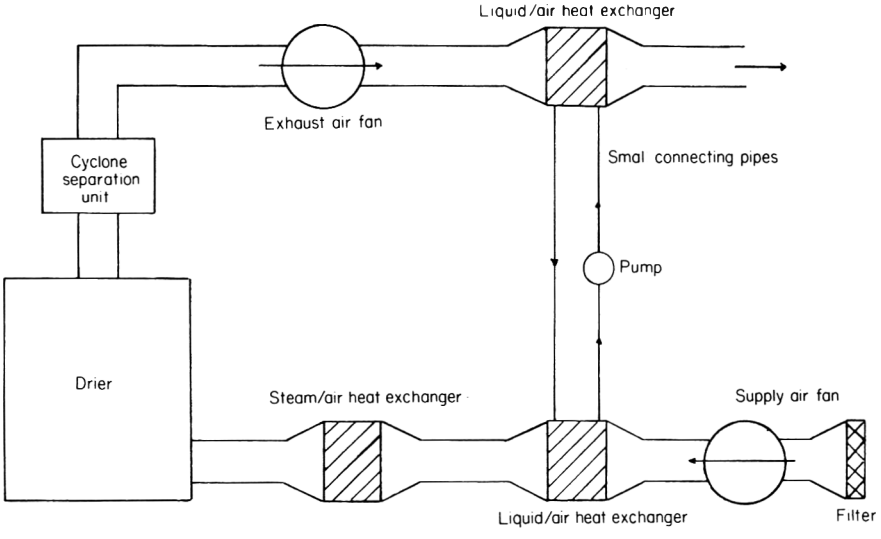

Figure 7. Waste heat recovery by liquid coupling.

has to be easily cleaned which can be a considerable problem if the exhaust temperature is below the dew point, when condensation occurs.

Heat regenerative systems have been installed (D. Applegate, pers. comm.), with encouraging results, in systems where the exhaust air temperature remains above the dew point. Problems have been encountered with cleaning and cross-contamination and therefore, if a heat wheel type heat exchanger is used it will render the product unfit for human consumption (C. N. Gordon, pers. comm.).

If the drier is very efficient, giving high dew point temperatures and condensation is likely to occur, then a heat recuperator or a heat pipe unit, where the two airstreams are completely separated, would seem better alternatives.

The units must be capable of being cleaned automatically and manually. Considerable problems have been encountered with installed heat pipe units with regard to cleaning. In these situations, the best selection seems undoubtably to be the heat recuperator.

Current cost and performance data were obtained for a recuperator to handle an exhaust volume of 15.1 $m^3 s^{-1}$ at 80°C.

The installation costs of a heat recovery unit are between two and three times the basic cost, in this situation, a value of 2.5 is taken. The annual labour and maintenance costs are estimated at 60% of the basic costs. The proposed system, using a recuperator because of its ease of cleaning and the absence of any possibility of cross-contamination, is shown in Fig. 8.

An approximate costing can be achieved by undertaking a heat balance for the proposed system. The presence of milk powder in the exhaust will necessitate that the air is not cooled below its dew point (24.5°C) and, therefore, inlet and exit temperatures are set at 80 and 35°C respectively. An inlet temperature of 80°C is assumed to allow for any heat loss in the ducting before the air reaches the exchanger.

Flow rate of exhaust air = 21.28 kg s^{-1}
Sensible heat available = 47.01 kJ kg^{-1}
Assume 75% heat transfer efficiency,
Heat transferred to supply air = $21.28 \times 47.01 \times 0.75$
= 750.3 kW

The supply air, which enters the heat exchanger at a temperature of 19°C and flow rate 18.41 kg s^{-1}, by absorbing the above quantity of heat will increase its temperature to 59°C. This represents a saving of 750.3 kW of steam energy.

Table 2. Recuperator costs

	Aluminium	Stainless Steel
Purchase price (£)	9500	16,000
Installation (£)	23,750	40,000
Labour and maintenance (£)	5700	9600
Total (£)	38,950	65,600

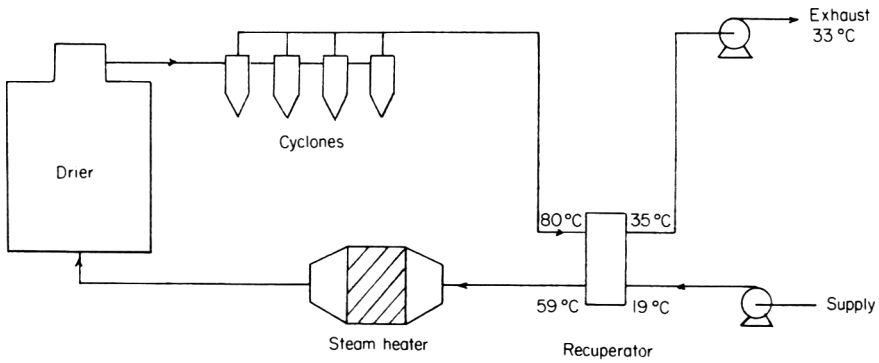

Figure 8. Proposed heat recovery unit.

Assuming an overall efficiency of 70% in the boiler house and the calorific value of the fuel used to generate steam as 30,212 kJ kg^{-1}, the following savings can be achieved:

$$\text{fuel savings} = \frac{750.3}{30212 \times 0.7} = 3.55 \times 10^{-2} \text{ kg s}^{-1}$$

$$\text{cost of fuel} = 6.18 \text{ pence kg}^{-1}$$

$$\text{saving} = 6.18 \times 3.55 \times 10^{-2} = 0.22 \text{ pence s}^{-1}$$

yearly saving (assuming 8,000 hours production)

$$= \frac{0.22 \times 3600 \times 8000}{100}$$

= £63,360

Considering the total costs in Table 2, and the estimated yearly savings, it can be seen that the payback times for the aluminium system is less than one year, and just over a year for the stainless steel system. The evidence has clearly shown that a capital investment into a heat recovery device seems a worth-while proposition.

Use of thermal insulation

The use of thermal insulation is only justifiable on surfaces of temperatures where the application of insulation will significantly reduce heat loss. As a rough guideline, any surface having a temperature above 50°C should be considered.

Two areas in the spray drier section of the plant would benefit from the application of insulation:

(a) *Drier top*. At the top of the drier chamber there is a cylindrical ducting which directs the exit air from the drier to flow tangentially from it. This is uninsulated and has a temperature of 72°C.

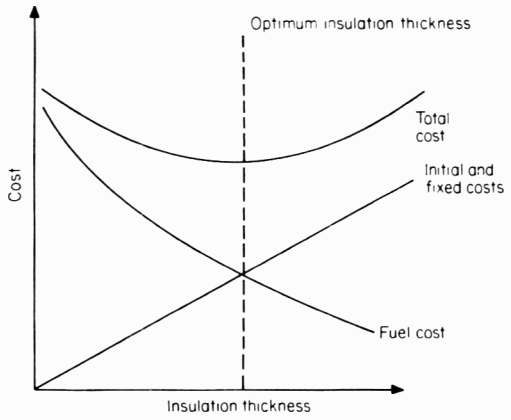

Figure 9. Optimum thickness of insulation.

(b) *Rear wall of drier steam battery*. All the surfaces of the drier steam battery are insulated except the rear side where the steam mains enter. This surface has a temperature of 69°C and loses a significant amount of heat by convection.

The optimum thickness of insulation required is determined on economic grounds. The heat loss is related to the cost of the fuel required to produce the amount of heat. The lower the heat loss, the greater the thickness and initial cost of the insulation that is required. The fixed annual charges of maintenance and depreciation also increase with increasing thickness of insulation. An optimum is, therefore, achieved between fuel savings and costs of insulation, (Fig. 9).

The savings, s, obtained by the application of insulation may be represented:

s = (cost without insulation) − (cost with insulation)

(i) The cost without insulation is the cost of the fuel required to produce the amount of heat lost from the uninsulated surface. (ii) Cost with insulation is the cost of the fuel required to produce the amount of heat lost from the surface, insulated to an arbitrary thickness, Y. It must also include the initial and fixed annual costs of the insulation again as a function of its thickness, Y.

To obtain the maximum saving the equation is differentiated with respect to the thickness, Y, and equated to zero. This mathematical procedure will enable the calculation of the optimum thickness of insulation which is obtained at the maximum saving.

The results of an analysis, as outlined above, are given in Table 3. The insulation material considered was rock wool, having thermal conductivity of 0.042 $Wm^{-1}\ K^{-1}$, in the form of slabs, faced with aluminium foil. It is worth noting at this point that the optimum thickness of insulation calculated for various surfaces in the plant correlated reasonably well with commercially recommended thicknesses for similar temperature differences.

The net savings of column eight at first do not seem particularly attractive. They relate to the first year of operation, but obviously the insulation will last for many years giving rise to improved subsequent savings.

Table 3. Savings using economic thicknesses of insulation

Surface	Surface area (m^2)	Fuel savings kW	Fuel savings (£/year)	Economic thickness of insulation (mm)	Insulation cost (£ m^{-2})	Insulation cost (£)	Net saving (£/year)
Drier top	8.92	0.371	174.61	52	1.95	17.40	157.21
Steam battery	3.72	0.211	154.70	80	2.98	11.08	143.62

Conclusions

The main test of any heat recovery proposition is its economic viability. The study outlines the possibility of good yearly savings on fuel costs and a payback time of the capital investment of approximately 1 year.

Energy losses from plants can never be eliminated but by the application of heat recovery techniques they may be reduced to an acceptable level.

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Cloud stabilization in citrus beverages by low methoxyl pectin

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Summary

Cloud in citrus beverages containing 40–65% total soluble solids (TSS) is stabilized by the addition of 0.05–0.1% ammonia deesterified low methoxyl pectin (LMP) containing 4.5% methoxyl, and 2–6 mg of calcium per 100 g of the beverage. The concentration of LMP and calcium required decreased as the TSS increased. The stabilization of cloud is based on the principle that calcium added at concentrations much lower than that required for gel formation results in considerable increase in the viscosity of the LMP solution. Heat inactivation of pectin esterase (PE) in the juice is not essential for cloud stabilization.

Introduction

Cloud loss in citrus beverages like squashes, crushes, syrups, etc., which contain 25% juice and 20–65% TSS, is a serious problem to bottlers. The pulp and the serum separate within a few hours of preparation imparting an unattractive appearance to the product.

Cloud in orange juice originates from (i) the structural tissues like albedo, rag and pulp which are high in cellulosic components and (ii) from the juice vesicles which are high in protein, lipid, nitrogen and phosphorus containing components, natural pigments and flavouring oil (Scott, Kew & Veldhuis, 1965). The loss of cloud has been mainly attributed to the action of PE (Bissett *et al.*, 1957; McColloch *et al.*, 1956; Moore, Rouse & Atkins, 1962; Rothchild & Karsenty, 1974).

In citrus beverages, natural cloud is retained by the addition of sodium hexametaphosphate and locust bean gum (Stevens & Britcheff, 1957). Krop & Pilnik (1974) considered that the loss of cloud in citrus juices is due to the deesterification of pectin by PE and formation of insoluble calcium pectates. In the presence of polygalacturonase (PG), the polygalacturonides formed by PE are converted to low molecular uronides which would not form insoluble

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calcium pectates and thereby ensure the stabilization of cloud. In the U.K., the juice is flash-pasteurized and the finished product is homogenized to overcome pulp separation. Ranganna & Raghuramaiah (1970) showed that mere pasteurization and addition of high methoxyl pectin or sodium alginate did not stabilize the cloud in orange juice beverages containing 40–60% TSS. The authors developed a procedure for effective stabilization of cloud in such beverages by pasteurizing the juice and increasing the viscosity of the finished product by adding low density propylene glycol ester of alginic acid.

Investigations carried out to stabilize the cloud in orange and lime juice beverages containing 20–65% TSS by the addition of LMP and calcium form the subject matter of this paper.

Materials and methods

Preparation of orange juice beverage

Loose-jacketted mandarin oranges were washed, cut into halves in a halving machine and the juice extracted in a rosing machine. The juice was screened through a screw-type juice extractor with a 1 mm screen. One portion of the juice was pasteurized for 2 min at 92°C and cooled. Both pasteurized and unpasteurized juices were preserved using 1000 ppm of sodium benzoate or 700 ppm of sulphur dioxide until required.

The juice was extracted from limes by hand pressing or in a rosing machine, screened and preserved as in orange juice.

The prepared beverage, hereafter called 'squash' irrespective of the TSS, contained 25% juice, 1.5% acidity (as anhydrous citric acid) and 1000 ppm of sodium benzoate or 350 ppm of sulphur dioxide. The TSS varied from 20–65%. The calculated quantity of sugar was added as 70° Brix syrup and citric acid as 50% stock solution.

Exploratory studies on cloud stabilization

Orange squash was prepared from pasteurized and unpasteurized juice. The pulp separated within a few hours of preparation of the squash, and the serum became clear after 2 months of storage. In squashes containing 20–55% TSS, the pulp settled down at the bottom whereas at 55 and 65% TSS, the pulp floated at the top. On adding 0.05 to 0.3% of ammonia deesterified LMP having 4.5% methoxyl groups prepared from lime peel (*Citrus aurantifolia*) as described in our previous paper (Padival, Ranganna & Manjrekar, 1979a), the pulp separated in squashes having 20–50% TSS; between 55 and 65% TSS, the pulp remained in uniform suspension at LMP concentrations of 0.05–0.1%.

Effect of low methoxyl pectin and added calcium concentrations on viscosity of sugar syrup, serum squash and whole juice squash

Squashes having 20–65% TSS were prepared using the serum obtained by centrifuging the juice (hereafter called serum squash) and whole juice (here-

after called juice squash). Syrups having the same TSS as in the squashes were used as control. Whole juice or serum, aliquots of sugar syrup, citric acid, LMP solution, orange oil and preservative were mixed together in required proportions and made to a known weight with water. The calcium concentration in syrup, serum squash and juice squash was increased from 0 to 20 mg at the rate of 2 mg per 100 g after every 24 hr and the changes in viscosity noted. With added calcium, a slight increase in the viscosity was observed after overnight storage as compared to the viscosity measured immediately. The calcium chloride solution used contained 10 mg of calcium per ml.

The squashes were prepared using pasteurized and unpasteurized orange juice with required amounts of LMP and calcium to ensure cloud stability, filled into bottles, stoppered and stored for one year at room temperature (25–30°C). The extent of cloud stability and variations in viscosity at different TSS and at optimum concentrations of LMP and calcium were determined in five replicates. The results are expressed as mean standard error (SE) and coefficient of variation (CV).

Pectin esterase activity

PE activity in orange and lime juice was determined by the method of Owens *et al.* (1952).

Viscosity measurement

The viscosity of syrups and squashes was measured at room temperature (25 ± 1°C) in a Brookfield Synchro-lectric viscometer using spindles No.1 and 2 at 30 rpm.

Measurement of cloud stability

In some squashes prepared with added LMP and calcium, the pulp tended to settle down or rise to the top gradually during storage leaving a clear serum. Therefore, the total height (H) of squash and the height (h) to which the pulp was held in suspension were measured and the extent of cloud stability was calculated using the expression: Cloud stability (%) $= h/H \times 100$ (Ranganna & Raghuramaiah, 1970).

Results and discussion

Changes in viscosity of sugar syrup, orange serum squash and orange juice squash

The viscosity of sugar syrup, serum squash and juice squash increased with the TSS between 20 and 65% (Table 1). The extent of increase was extremely high beyond 55% TSS. The order of increase in viscosity was: juice squash > serum squash > sugar syrup. The slight increase in the viscosity of serum squash as compared to sugar syrup was due to the pectin and other constituents

Table 1. Effect of added LMP on the viscosity of sucrose syrup, orange serum squash and orange juice squash

	Viscosity without LMP			Viscosity with LMP			
TSS of squash (%)	Sugar syrup (cp)	Serum squash (cp)	Juice squash (cp)	Concentration of LMP (%)	Sugar syrup (cp)	Serum squash (cp)	Juice squash (cp)
20	4.5	5.0	5.5	0.10	5.0	7.0	8.0
				0.20	7.0	7.0	7.5
				0.30	8.0	8.0	9.0
30	6.0	6.5	7.5	0.10	8.0	9.0	10.0
				0.20	9.0	9.0	9.5
				0.25	10.0	10.0	11.0
40	8.0	9.0	12.0	0.10	13.0	15.0	23.0
45	12.0	13.0	15.0	0.10	21.0	29.0	65.0
50	17.0	20.0	23.5	0.10	26.5	60.0	120.0
55	27.0	29.0	32.0	0.10	36.0	120.0	190.0
60	51.0	52.0	55.0	0.05	120.0	130.0	200.0
				0.10	190.0	200.0	360.0
65	110.0	120.0	130.0	0.05	200.0	270.0	290.0
				0.10	350.0	390.0	530.0

naturally present in the serum. The whole juice, in addition, contained suspended pulp solids and hence, the viscosity was still higher.

Addition of LMP increased the viscosity further (Table 1). TSS being the same, the extent of increase in the viscosity of sugar syrup, serum squash and juice squash followed similar pattern. Concentration of LMP being the same, the viscosity increased with TSS which was very high at 40% and above, but not so at 20 or 30%.

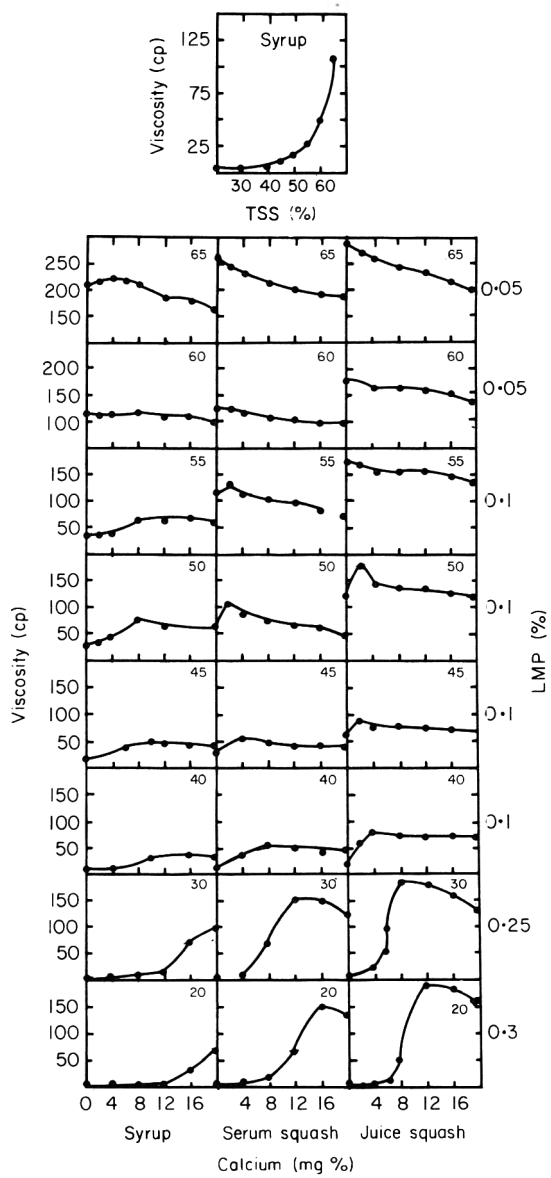

Figure 1. Effect of LMP and calcium on the viscosity of sugar syrups, orange serum squashes and orange whole juice squashes having 20–65% TSS.

Table 2. LMP and calcium requirement for maximum viscosity and for stabilization of cloud in orange squash

TSS (%)	Optimum concentration of LMP (%)	Added calcium concentration required for maximum viscosity		
		Sugar syrup (mg %)	Serum squash (mg %)	Juice squash (mg %)
40	0.10	12	8	4
45	0.10	10	4	4
50	0.10	8	2	2
55	0.10	8	2	0
60	0.05	0	0	0
65	0.05	0	0	0

When calcium was added along with LMP, the viscosity increased to a greater extent up to 55% TSS, but decreased at 60 and 65% TSS. The effect of increasing concentrations of added calcium on the viscosity at the optimum level of LMP is shown in Fig. 1.

The concentrations of LMP and calcium required for maximum increase in the viscosity of sugar syrup, serum squash and juice squash are given in Table 2.

Low methoxyl pectin and calcium requirements for stabilization of cloud in orange and lime squashes

Changes in pectinesterase activity during storage: PE activity in orange and lime juices was dependent upon the mode of extraction of the juice. The activity in lime juice extracted using a hand-operated lime squeezer was less than that of

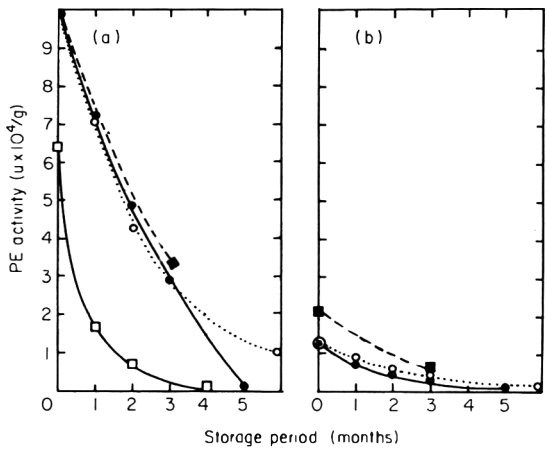

Figure 2. Changes in pectin esterase (PE) activity in lime juice and orange juice during storage. (a) Lime juice; (b), orange juice. Frozen (■), sulphited (●), and benzoated (○) lime and orange juice extracted in a rosing macnine; sulphited (□) lime juice using a hand-operated lime squeezer.

the juice extracted using a rosing machine (Fig. 2a). During frozen storage, the enzyme activity decreased gradually. In orange juice, the activity was less than that of lime juice, but the residual activity was seen even after three months of frozen storage (Fig. 2b).

In sulphited lime and orange juices extracted using a rosing machine as well as in lime juice extracted using a squeezer, the residual PE activity was not found after 6 months of storage. The benzoated lime and orange juice had 11.5 and 25% respectively of the initial PE activity at the end of 6 months (Fig. 2).

In the preparation of squash, although the juice screened through 1 mm mesh was used, the pulp particles were irregular in shape and of varying sizes. The size distribution of the particles varied widely from 150 to 1000 μm, and irrespective of the size, the pulp tended to separate from serum (Ranganna & Raghuramaiah, 1970). Mere heating of the juice to inactivate the pectic enzymes as in the case of fruit juices and concentrates was found to be insufficient to render the cloud stable in bottled beverages like squashes, crushes and syrups wherein the TSS varied from 40 to 60%.

Table 3. Effect of added LMP and calcium on the cloud stability of orange and lime juice beverages stored for one year at room temperature

Particulars of squash			Extent of cloud stability	
TSS (%)	Concentration of added LMP (%)	Concentration of added calcium (mg %)	Orange squash (%)	Lime squash (%)
20	0.10	20	67.4	
20	0.30	6	99.7	98.0
20	0.30	10	95.6	
20	0.50	6	20.0	
30	0.20	8	81.0	
30	0.25	6	99.7	98.2
40	0.10	4*	100.0	
40	0.10	6	97.7	99.4
45	0.10	2*	100.0	
45	0.10	4	95.0	98.9
45	0.10	6	90.0	
50	0.10	0	99.8	
50	0.10	2*	100.0	95.7
50	0.10	4	96.5	
55	0.10	0*	100.0	96.0
55	0.05	2*	100.0	
		4	90.0	
60	0.10	0*	100.0	
60	0.05	2*	100.0	100.0
65	0.10	0*	100.0	
65	0.05	2*	100.0	100.0

*Optimum level of calcium for cloud stability during prolonged storage.

In orange squash prepared from a fresh (PE active) or pasteurized mandarin orange juice without any cloud stabilizing agent, the pulp separated after a few hours of preparation. In squashes containing 20 and 30% TSS, concentrations of 0.1 and 0.2% LMP and up to 20 mg% of added calcium were insufficient to stabilize the cloud as observed immediately; hence, 0.25–0.3% LMP was added. However, these squashes showed gelling after 3 months of storage at room temperature. This aspect requires further study.

Between 40 and 55% TSS, 0.1% LMP was sufficient to stabilize the cloud. At 60 and 65% TSS, 0.05% LMP was sufficient as the increase in the viscosity was extremely high with 0.1% LMP (Table 1).

The concentration of calcium required for uniform stability of cloud in orange squash varied with TSS (Table 3). The squashes prepared using varying concentrations of LMP and added calcium were stored for one year at room temperature (25–30°C). During this storage period, a slight separation of the serum occurred at the top resulting in 1–5% cloud loss in samples having calcium concentration lower or higher than the optimum (Table 3). Homogenization of the juice and/or beverage may possibly overcome this. The viscosity of the squashes having 20–45% TSS increased during storage, remained more or less the same when the TSS were 50, 55 and 60%, but decreased when the TSS was 65% (Table 4). Although addition of calcium is not actually necessary for cloud stability in squashes containing 55–60% TSS, during prolonged storage, a small portion of the serum separates at the bottom. This is overcome by adding 2–4 mg calcium per 100 g squash.

The cloud stability being nearly 100% in squashes containing 40–65% TSS at the optimum concentrations of LMP and calcium, the mean ± SE showed very significant consistency within the replicates (CV ranging between 0 and 1.01) (Table 4). The mean viscosity varied less than 10% within the replicates (CV ranging between 4.71 and 9.28) and was positively correlated ($r = +0.97$; $P < 0.01$) to TSS and negatively correlated ($r = -0.82$; $P < 0.05$) to concentration of calcium.

Table 4. Cloud stability and viscosity in orange squash at different levels of TSS, LMP and calcium

Particulars of squash			Cloud stability (%)		Viscosity (cp)		
TSS (%)	Concentration of LMP (%)	Concentration of added calcium (mg %)	Mean ± SE	CV	Mean ± SE	CV	After storage
40	0.10	4	99.60±0.89	0.92	70.80±3.77	5.32	100
45	0.10	2	100.00±0	0	82.10±7.42	9.04	135
50	0.10	2	100.00±0	0	117.17±10.87	9.28	140
55	0.10	0	98.00±0	0	180.20±13.81	7.66	180
55	0.10	2	100.00±0	0	187.80±8.84	4.71	180
60	0.05	0	99.00±0	0	190.20±17.41	9.15	200
65	0.05	0	100.00±0	0	244.00±15.05	6.17	225

Lime juice develops bitterness on heating and hence, the squashes were prepared only with fresh, PE-active juice. The concentrations of LMP and calcium required for uniform cloud in lime squashes (40–65% TSS) were similar to those found for orange squashes (Table 3).

The TSS of 40–65% in fruit squashes, crushes and syrups render the specific gravity of serum higher than that of the suspended pulp particles resulting in the latter to rise to the top. In such beverages, the cloud could be stabilized by increasing the viscosity of the serum which would retard the floating of the pulp (Ranganna & Raghuramaiah, 1970). Low density propylene glycol ester of alginic acid has been used to increase the viscosity of orange squash having 40–60% TSS. This additive is not permitted for use in some countries. LMP, could safely be used, since the pectin is a natural ingredient of fruit juices.

Gel formation involves the transformation of sol state of LMP to gel state caused by added calcium (Padival, Ranganna & Manjrekar, 1979b). Gel formation occurs only at the optimum concentration of LMP (~ 1% LMP) and calcium (20–30 mg). Calcium added to LMP solution at concentrations much lower than that required for gel formation causes considerable increase in the viscosity of the LMP solution (Table 5). The procedure developed in this study for cloud stabilization in orange and lime juice beverages makes use of this property of increase in the viscosity of the LMP solution at suboptimal concentrations of calcium. The concentrations of LMP (0.05–0.10%) and calcium (2–6 mg per 100 g squash) required, are considerably lower than those required for gel formation. PE activity in the juice does not affect cloud stability.

Table 5. Relationship between added calcium concentration and viscosity of acid, NaOH and NH_3 deesterified low methoxyl pectins

Methoxyl content (± 0.1%) (%)	Calcium concentration (mg/g LMP)	Viscosity of 1% solution*		
		Acid deesterified LMP (cp)	NaOH deesterified LMP (cp)	NH_3 deesterified LMP (cp)
3	0	16	10	22
	10	20	20	39
	15	30	60	100
	20	50	210	400
4	0	13	10	17
	10	18	20	33
	15	25	124	90
	20	47	Soft gel	505
5	0	10	17	14
	10	15	37	19
	15	20	55	40
	20	35	Soft gel	290

*Viscosity was determined after adjusting the pH of the 1% LMP solution to pH 3.0.

For stabilization of cloud in the present study, LMP prepared from lime peel (*Citrus aurantifolia*) by ammonia deesterification was used. Table 5 shows that the viscosity of LMP solutions with added calcium varies considerably for acid, sodium hydroxide and ammonia deesterified LMP, and also with the methoxyl content of the LMP. Hence, the LMP and calcium concentrations required should be standardized to ensure uniform cloud stability in the commercial manufacture of citrus beverages.

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Relative volatilities of some onion flavour components

G. MAZZA

Summary

The volatilities of propanethiol, 2,5-dimethylthiophene, methyl propyl sulphide, dimethyl disulphide, dipropyl disulphide, allyl methyl sulphide, diallyl sulphide, diallyl disulphide, acetaldehyde, propionaldehyde, methanol, ethanol, 1-propanol and 2-propanol in dilute water solutions were studied experimentally by gas chromatography. The volatilities of these compounds varied appreciably. They were higher for thiols, thiophenes, and monosulphides, than disulphides, aldehydes or alcohols. The results for aldehydes and alcohols confirm earlier theoretical predictions by other authors that at 25°C the volatility, in very dilute solution, increases as the carbon chain gets longer.

Introduction

The characteristic flavour of onion is due mainly to its sulphur-containing volatile constituents. These compounds together with a number of alcohols and aldehydes have been identified by Semmler (1892), Challenger & Greenwood (1949), Niegisch & Stahl (1956), Carson & Wong (1961), Spare & Virtanen (1961), Saghir *et al.* (1964), Brodnitz, Pollock & Vallon (1969), Brodnitz & Pollock (1970), Boelens *et al.* (1971) and others. The literature dealing with onion flavour constituents up to 1976 has been reviewed and documented by Whitaker (1976) and Abraham *et al.* (1976).

More recently Mazza & LeMaguer (1979) studied the retention of onion volatiles during dehydration and observed that the percentage retention varied with the compound investigated. An attempt to relate the difference in behaviour amongst the compounds to their volatilities could not be made when a review of the literature revealed very little information in this area, especially in relation to sulphur-containing compounds.

Very significant work, however, was carried out by Butler, Ramchandani & Thompson (1935), who studied water solutions of the homologous series of

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alcohols from methanol to octanol, and by Buttery, Ling & Guadagni (1969) and Buttery *et al.* (1971) who studied the volatilities in dilute water solution of some members of the homologous series of alkanals, alkan-2-ones, and methyl alkanoates from C_3 to C_9 and some alkyl pyrazines and unsaturated aliphatic aldehydes. Both groups found that the volatilities in the dilute water solutions gradually increased with increasing molecular weight. Pierotti, Deal & Derr (1959) determined the activity coefficients (γ) of a number of organic compounds in water, using a variety of methods. They also determined the vapour pressure of some of the pure compounds, P, and from the calculation of the product of γ and P were able to determine the volatilities of homologous series of paraffins, ethers, alcohols, and acids in diluted water solution.

The present work was undertaken to determine experimentally the volatilities of some onion flavour components using a simple gas chromatographic procedure.

Materials and methods

The organic compounds used were obtained from reliable commercial sources (Aldrich Chemical Co., Milwaukee, WI. and ICN K & K Labs Inc., Plainview, N.Y.) and checked for their purity by gas chromatography (GC) before use. The water was distilled and then boiled to remove volatile impurities and air. The GC apparatus was a Hewlett Packard Model 5710A with a dual flame ionization detection. The dual columns were 2.44 m × 3.175 mm o.d. stainless steel packed with Chromosorb 101, 80/100 mesh, and operated at temperatures ranging from 80°C for ethanal to 180°C for dipropyl and diallyl disulphides. Nitrogen was used as the carrier gas and the flow rate was 30 ml/min. Hydrogen flow rate was 25 ml/min and air flow rate 275 ml/min. Hamilton gas-tight and conventional glass cylinder and barrel type syringes were used to inject the vapour and liquid phases into the GC unit.

For the determination of the partition coefficient, a volume of the chemical under test, which would give a concentration of 5–500 ppm (w/w) was added to 135 ml of boiled distilled water at room temperature in a 270 ml Teflon bottle. The bottle was closed immediately, shaken vigorously and placed in a 25°C constant temperature water bath for 15 min or more to equilibrate. The needle of a 2.5 ml gas-tight syringe was then pushed through the rubber cap of the bottle and the headspace gas forced into the syringe by squeezing the bottle. The vapour phase sample, 2.0–2.5 ml, was then injected directly into the GC apparatus through the silicon rubber septum injector. Solution samples, 2.5–10.0 µl, were taken out of the bottle, used for the vapour samples, and injected immediately in the GC unit. Solution and vapour samples were injected alternately, so that a change in the concentration of the solution due to vapour removal would be compensated. The injector temperature was maintained at 200°C, to ensure rapid vaporization of the solution, and the detector temperature was 250°C. The air/water partition coefficients were determined

as k = (weight of solute per ml of air)/(weight of solute per ml of solution) at 25°C and 1 atm.

The GC peak area of the solution and vapour peaks were measured with a Hewlett Packard 3380A electronic integrator. The injection of both solution and vapour allows the cancelling out of the GC peak area to weight conversion factors and simplify the calculation to:

$$k = \left(\frac{\text{Peak area (vapour)/vapour sample volume}}{\text{Peak area (liquid)/liquid sample volume}} \right) \quad (1)$$

For each compound, k was calculated as the average of at least four determinations. From the values of k the relative volatility of each compound, i.e., the ratio of the volatility of that compound and the volatility of water at the same temperature, was calculated directly as:

$$\alpha_{io} = \frac{y_i/x_i}{y_o/x_o} = k \cdot \left(\frac{RT\rho^{L}{}_{W}}{M_W P^{S}{}_{W}} \right) = k \cdot \frac{\rho^{L}{}_{W}}{\rho^{G}{}_{W}} = k \cdot 4.333 \times 10^{4} \quad (2)$$

where y_i and y_o are, respectively, the concentrations in mole fraction of aroma component and water in the vapour in equilibrium with the liquid phase in which their concentrations x_i and x_o; $P^{S}{}_{W}$, saturation pressure of pure water at 25° = 3.169×10^{3} Pa; T = 298.16 K; $\rho^{L}{}_{W}$, density of liquid H_2O = 997.11 kg/m^3; R, gas constant = 8.3143×10^{3} J/K k mole; M_W, molecular weight of water = 18; and $\rho^{G}{}_{W}$, density of water vapour at 25°C = 2.3062×10^{-2} kg/m^3.

Equation (2) was derived from simple vapour-liquid equilibria considerations as shown in the Appendix.

Results and discussion

Table 1 lists the relative volatilities found for the compounds examined together with the partition coefficients, boiling points and molecular weights. The air/water partition coefficients are given to allow for the rapid calculation of an unknown concentration in one medium when the concentration is known in the other medium. The boiling points and molecular weights have been taken from the *Handbook of Chemistry and Physics* (1973).

Upon examining the results in Table 1 it is immediately obvious that the volatility of the compounds studied varied appreciably. Propanethiol, for instance, was about fifteen thousand times more volatile than methanol and over one hundred times more volatile than propanal. Also, dipropyl disulphide was four times less volatile than methyl propyl disulphide and over two and one half times less volatile than diallyl sulphide. Less obvious is the fact that while the volatility of aldehydes and alcohols increased gradually with the molecular weight and boiling point, the volatility of the sulphur-containing compounds followed the opposite trend. This may be due to their difference in solubility in water, as well as to the unique properties of the sulphur atom. The introduction of two double bonds, dipropyl disulphide *vs.* diallyl disulphide, increased the

Table 1. Relative volatilities, air/water partition coefficients, molecular weights and boiling points of fourteen onion volatiles

Compound	Molecular weight*	Boiling point* (°C)	Air/water partition coefficient (k)	Relative volatility (α_{io})
Propanethiol	76.2	67.5	4.48 ± 0.25† $\times 10^{-1}$	19413
2,5-Dimethylthiophene	112.2	136.7	1.08 ± 0.20 $\times 10^{-1}$	4680
Methyl propyl sulphide	90.2	95.5	9.37 ± 0.75 $\times 10^{-2}$	4040
Dimethyl disulphide	94.2	109.0	4.69 ± 0.02 $\times 10^{-2}$	2032
Dipropyl disulphide	150.3	193.3	2.25 ± 0.20 $\times 10^{-2}$	975
Allyl methyl sulphide	88.2	92.0	8.05 ± 0.65 $\times 10^{-2}$	3488
Diallyl sulphide	114.2	139.0	5.66 ± 0.34 $\times 10^{-2}$	2453
Diallyl disulphide	146.0	—	5.38 ± 0.50 $\times 10^{-2}$	2331
Ethanal	44.1	20.8	2.48 ± 0.25 $\times 10^{-3}$	107
Propanal	50.1	48.8	3.43 ± 0.25 $\times 10^{-3}$	149
Methanol	32.0	64.9	3.02 ± 0.50 $\times 10^{-5}$	1.3
Ethanol	46.1	78.5	6.52 ± 1.00 $\times 10^{-5}$	2.8
1-Propanol	60.1	97.4	10.81 ± 0.87 $\times 10^{-5}$	4.7
2-Propanol	60.1	82.4	19.61 ± 1.60 $\times 10^{-5}$	8.5

**Handbook of Chemistry and Physics* (1973).
†Standard deviation.

volatility by two and one half times. This may be due to the partial shifting of the electron pair and, hence, to the lack of hydrogen bond between water and sulphur.

There are no published volatility data of sulphur-containing compounds to compare the figure obtained in this work with, but a comparison of the volatility figures for acetaldehyde and propionaldehyde with those of Buttery *et al.* (1969) was made and the difference was found to be within the experimental error.

The high relative volatility values obtained for some of the most important onion flavouring components (e.g., propanethiol, dipropyl disulphide) indicates that these compounds will reach the olfactory sensors more abundantly when fresh onion is cut and that the potential loss during dehydration is very high. This is because flavour components in liquid foods, or foods with low dry matter content, undergoing drying have the tendency to evaporate much faster than water. After partial evaporation of water, if the vapour removed is in equilibrium with the liquid and if there is no concentration gradient in the solution, the retention of a flavouring component, i, can be expressed by the

$$\frac{M_i}{M_{io}} = \left(\frac{M_W}{M_{Wo}}\right)^{\alpha_{io}} \tag{3}$$

where M_{io} and M_{wo} are the amounts of flavouring component and water initially present in the solution and M_i and M_w are the amounts left after partial evaporation (Menting *et al.*, 1970). According to this equation, with α_{io} values of the magnitude shown in Table 1, drying of onion will result in a very rapid depletion of the flavour. This can be illustrated by the following example. The retention of dipropyl disulphide, a compound with rather intermediate volatility will be 5.6×10^{-3}% when only 1% of water is evaporated, and 2.4×10^{-43}% when 10% of the water is evaporated. The retention of 1-propanol, a compound with low volatility, will be much higher than dipropyl disulphide, 95 and 61% for 1 and 10% of the water evaporated, respectively. Fortunately, equation (3) holds only if the evaporation at the surface is not limited by the mass transport in the liquid phase. In the dehydration of onion, this condition can only be fulfilled at the very beginning of drying. At low water concentrations the diffusion coefficients in the liquid and solid phases are very low (Thijessen, 1971) and thus the resistance to mass transfer in these phases becomes much greater than that in the gas phase, hence even after over 95% of the water has been removed from onion slices there is still sufficient flavour to give dehydrated onions the well-known flavour capacity.

Appendix

Derivation of Equation (2). By definition y, the mole fraction in the gas phase, equals the product of x, the mole fraction in the liquid phase, and a coefficient, k. If y_i is the mole fraction of a volatile, i, in the gas phase, and x_i, the mole fraction of i in the liquid phase, and if y_o and x_o denote the mole fractions of water in the gas and liquid phase, respectively, the relative volatility, α_{io}, is defined by $\alpha_{io} = k_i/k_o$.

If the total volume of the headspace system used in this work is denoted by V_T and the volume of the space occupied by the gas and liquid phases by V_G and V_L, respectively, and if it is assumed that the total pressure of the system, P_T, equals the sum of the atmospheric pressure, P_o, and the saturation pressure of pure water, P^S_w, it follows that $V_T = V_G + V_L$ and $P_T = P_o + P^S_w$. As half of the system was liquid and half was vapour $V_L = V_G = \frac{1}{2} V_T$.

The injection of known volumes of liquid, v_L, and vapour, v_G, phases in the GC unit results in a peak area, A_L, for i in the liquid phase, and a peak area, A_G, for i in the gas phase. The mass of i in the gas phase, m^i_G, is equal to kA_G, and the mass of i in the liquid phase, m^i_L, is equal to kA_L. From this, it follows that the concentration of i in the gas phase, C^i_G, is equal to kA_G/v_G and the concentration in the liquid phase C^i_L, is equal to kA_L/v_L kg/m^3. Consequently, the mass of i in the gas phase equals the product of C^i_G and V_G and the mass of i in the liquid phase equals the product of C^i_L and V_L. The number of moles of i in V_G, n^i_G, equals m^i_G/M_i, and that in V_L, n^i_L equals m^i_L/M_i where M_i is the molecular weight of i.

The concentration of the volatile, i, in the solutions was very small (5–500 ppm), hence, if it is neglected, the number of moles of water in the solution, n^{o}_{L}, equals $V_L\ \rho_W/M_W$, where ρ_W and M_W are the density and molecular weight of water, respectively. The total number of moles of i and o in the gas phase, n^{T}_{G}, equals $P_T V_G/RT$, where P_T is in P_a, V_G in m^3, R = 8.314 × 10^3 J/K kmole, and T in K. The mole fraction of volatile, i, in the gas phase, y_i equals n^{i}_{G}/n^{T}_{G} and the mole fraction of i in the liquid phase, x_i, equals n^{i}_{L}/n^{o}_{L}. Also, y_o equals P^{S}_{W}/P_T and $x_o \simeq 1$. Substituting,

$$k_i = \frac{y_i}{x_i} = \frac{n^{i}_{G}}{n^{T}_{G}} \cdot \frac{n^{o}_{L}}{n^{i}_{L}} = \left(\frac{A_G}{v_G} \cdot \frac{v_L}{A_L}\right) \cdot \frac{RT\rho_W}{M_W P_T} \qquad \text{(A-1)}$$

$$k_o = \frac{y_o}{x_o} = \frac{P^{S}_{W}}{P_T} \qquad \text{(A-2)}$$

$$\alpha_{io} = \frac{k_i}{k_o} = \left(\frac{A_G}{v_G} \cdot \frac{v_L}{A_L}\right) \cdot \frac{RT\rho_W}{M_W P^{S}_{W}} \qquad \text{(A-3)}$$

But if it is assumed that the water vapour follows the gas law, the density of water vapour at T, ρ^{G}_{W}, equals $M_W \cdot (P^{S}_{W}/RT)$; the term $RT\ \rho_W/M_W P^{S}_{W} = \rho^{L}_{W}/\rho^{G}_{W}$ and at 25°C $\alpha_{io} = k \cdot 4.333 \times 10^4$.

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A rapid batter expansion method for testing the baking quality of wheat flours

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Summary

A rapid batter expansion method has been described for testing the quality of wheat flour. Batter is prepared by thoroughly mixing wheat flour, baking powder and water which is then transferred to a graduated cylinder. The cylinder is kept in water bath at 40°C and the reading at the maximum expansion is noted down. It has been observed that the batter collapses after reading the maximum expansion, and leaves a mark on the cylinder which also helps in reading the maximum expansion. The results indicate that the batter expansion is highly correlated with bread volume and protein content.

Introduction

The quality of wheat flour for the purpose of breadmaking may be evaluated by various physical dough tests and physico chemical methods. The former require the use of sophisticated and costly instruments like the Brabender Farinograph and Extensograph, Chopin's Alveograph, Swanson's Extensometer and Mixograph etc. In addition to being time consuming these need specially trained persons to operate them.

Rapid physico chemical methods like Zeleny's sedimentation tests (Zeleny, 1947), dough expansion test (Winton & Winton, 1947), wheat flour fermentation time test (Pelshenke, 1930, 1933; Cutler & Worzella, 1931; Winter & Gustafson, 1934) are much in use for testing the wheat quality. Zeleny's sedimentation is not a direct measure of protein quality but of grain hardness. It does not give reproducible results if performed on the same flour with difference in particle size. The dough expansion method takes from one to three hours to note the rise in the volume of dough made with flour, sugar, yeast and

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Table 1. Proximate composition and farinographic studies of wheat flour of 75% extraction.

Constituents	%	Farinographic Studies	
Moisture	13.5	Water absorption	68.2%
Protein	11.7	Dough development time	3¾ minutes
Dry gluten	11.3	Dough stability	1½ minutes
Fat	0.3	Mixing tolerance	5¼ minutes
Crude fibre	0.3	Dough softening units	60 B.U.
Ash	0.5		
Carbohydrates	73.6		

water. The author suggests that the dough prepared from strong wheat flour exhibits more expansion than that prepared from soft wheat flour. In this method the yeast converts sugar (present in the flour as well as added) into CO_2 which is responsible for the expansion of the dough. This method is affected by the original content of fermentable sugars and diastatic activity of the flour and flours with the same quality and quantity of protein but different sugar content would give different levels of sugar in the flour . The wheat flour fermentation time test is influenced by many factors like proteases, fineness of flour, amount of mixing, temperature, length of storage between grinding and testing the original content of fermentable sugars and diastatic activity of the flour. Recently a gel protein method (Feillet, Fevre & Jeanjean, 1976) for evaluating the baking properties of soft wheats has been reported. In this method, the flour is extracted twice by water, then by chloroethanol 70%. After centrifugation, a residual gel called 'gel protein' is formed above the starch layer. It is shown that height of gel is highly correlated to baking quality. This test is also time consuming and requries about 18 h for one test.

This paper describes a rapid batter expansion method for the evaluation of wheat quality. Essentially it is the dough expansion method with the modification that yeast has been replaced by baking powder.

Materials and methods

Commercial wheat flour of 75% extraction purchased from the market was used for the standardization of the method and its compositional analysis and farinographic properties are given in Table 1. Samples of indigenous wheat varieties i.e. C-273, C-591, Indus-66 and Panjamo-62, were obtained from the Punjab Agricultural Research Center, Lyallpur, Pakistan. The varieties were milled separately in a Brabender mill to get flour of 75% extraction. All the chemicals used were of A.R. grade. Moisture, protein, fat, fibre, carbohydrates, dry gluten, were determined according to the methods of AOAC (1965).

Table 2. Batter expansion, protein content and bread volume of blends of wheat flour and corn starch.

Blend of Wheat Flour/Corn Starch		Protein content (%)	Bread volume (ml)	Batter expansion (ml)
Wheat flour	Corn starch			
100	—	11.5	319	480
75	25	8.4	260	370
50	50	5.5	180	264
25	75	2.8	110	162
—	100	—	85	110

Preparation of baking powder

Sodium bicarbonate and glucono-delta-lactone were thoroughly mixed in 1:2.25 ratio by sieving several times. It was kept in Kilner jars. Bread was prepared by a straight dough method as described earlier (Khan & Elahi, 1972) and bread volume was measured by the seed displacement method.

Description of the method

Different parameters such as quantity of baking powder for a definite quantity of wheat flour, temperature and volume of water for batter making which would give maximum expansion, were studied and the following method was finally developed.

Wheat flour (50g) and baking powder (10g) were mixed thoroughly by sieving five or six times and transferred to a plastic bowl. Water (60 ml) at 15–20°C was added and stirred with a glass rod to make a uniform batter which was then transferred to a one litre graduated cylinder. The cylinder was kept in a water bath at 40°C. The batter reading is recorded at the maximum expansion. The batter collapses after reaching the maximum expansion and leaves a mark on the cylinder which also helps in reading the maximum expansion. It takes about 5–10 min for reaching the maximum expansion.

Table 3. Batter expansion, protein content and bread volume of 75% extraction flour of different wheat varieties.

Wheat variety	Batter expansion (ml)	Protein content (%)	Bread volume (ml)
C–273	470	11.4	315
C–591	418	10.6	290
Indus-66	385	10.3	265
Panjamo-62	323	10.2	226

The reliability of the method was checked with blends of wheat flour and corn starch and different indigenous wheat varieties. The results are included in Tables 2 and 3 respectively.

Discussion

Table 2 indicates the batter expansion, bread volume and protein content of various blends of wheat flour of 75% extraction and corn starch. It will be seen that with the decrease in protein content of wheat flour resulting from the addition of corn starch, the bread volume and batter expansion are also decreased. Pure wheat flour has the maximum protein, bread volume and batter expansion while corn starch the minimum.

Table 3 includes the protein content, bread volume and batter expansion of 75% extraction flours of different indigenous wheat varieties. It will be observed that C-273 has the maximum batter expansion, bread volume and protein content, while Panjamo-62 the minimum, which shows that batter expansion is highly correlated to bread volume and protein content.

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The prediction of water activity of aqueous solutions in connection with intermediate moisture foods

III. a_w Prediction in multicomponent strong electrolyte aqueous solutions

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Summary

A study was made on the theoretical prediction of water activity (a_w) in multicomponent aqueous solutions of strong electrolytes, in the range of a_w of most interest for intermediate moisture foods (IMF). A simplified model proposed by Ross (1975) is tested against a rigorous model equation developed on the basis of recent statistical theories of electrolytes. As a result of this study a new simple and very accurate model equation is proposed for predicting a_w in aqueous solutions of mixed strong electrolytes in the a_w range of most interest to IMF.

Introduction

It is well known that choosing a solute for water activity (a_w) control in intermediate moisture foods (IMF) is a difficult task because many factors have to be considered, as discussed in Part I (Benmergui, Ferro-Fontán & Chirife, 1979). Sometimes one may take advantage of using a combination of solutes instead of a single one; this may lead to a reduced flavour impact, improved texture or reduced cost. The combination of solutes may include electrolytes as well as non-electrolytes.

This work is concerned with prediction of a_w in multicomponent aqueous solutions of 'food additive-like' strong electrolytes in the range of a_w of most interest to IMF. With this purpose an examination is made of some literature models for predicting a_w in multicomponent electrolyte mixtures. A simplified model proposed by Ross (1975) which gained popularity in the food area is critically tested against a rigorous model equation developed by Pitzer & Kim (1974) on the basis of recent statistical theories of electrolytes. This last model

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proved to yield very accurate predictions of properties of mixed aqueous electrolytes.

As a result of this study, a new simple model equation is proposed for predicting a_w in aqueous solutions of mixed strong electrolytes in the a_w range of most interest in IMF.

Results and discussion

There exists a number of empirical, semi-empirical and theoretical methods for predicting the water activity (or other thermodynamic properties) of multicomponent strong electrolyte solutions. Most of these methods were reviewed by Sangster & Lenzi (1974).

Zdanovskii (1936) proposed an empirical rule for electrolyte solutions under isopiestic equilibrium. For a multicomponent solution of individual solutes at concentrations m_i in isopiestic equilibrium with binary solutions of molality m_{oi} the corresponding equation is:

$$1 = \sum_i \frac{m_i}{m_{oi}} \text{, at constant } a_w \qquad (1)$$

The unknown water activity is that for which eqn (1) is satisfied and has to be found by a method of successive approximations. This method, of course, neglects specific solute-solute effects. Chen *et al.* (1973) found that Zdanovskii's (1936) equation gave good results for predicting the a_w of ternary solutions of strong electrolytes which may be of interest in IMF, like NaCl, KCl and $CaCl_2$. They found, however, that the agreement between predicted and measured a_w data was satisfactory only up to an a_w of about 0.85; at total ionic strengths corresponding to lower a_w values the predictions were not very satisfactory. Similar results were reported by Sangster & Lenzi (1974).

Robinson & Bower (1965) proposed an additivity rule for the vapour pressure lowering of ternary aqueous solutions. In terms of a_w the predictive equation may be written as:

$$(1 - a_w)_{\text{mixture}} = m_1 [(1 - a_{w1})/m_{1,1}] + m_2 [(1 - a_{w2})/m_{2,1}] \qquad (2)$$

where, I is the ionic strength of the mixed solution, m_1 and m_2 are component molalities, and $m_{1,1}$, $m_{2,1}$, a_{w1}, a_{w2} are the molalities and water activities respectively of the binary solution of ionic strength I. Chen *et al.* (1973) and Sangster & Lenzi (1974) also tested eqn (2) for ternary mixtures including NaCl, KCl, $CaCl_2$, Na_2SO_4 and the like, and reported that this equation predicts very well the a_w of the solutions tested. Significant deviations in the predictions were observed, however, at total ionic strengths involving a_w s of below about 0.85.

Reilly, Wood & Robinson (1971) used the equations of Reilly & Wood (1969) for the prediction of free energy to derive expressions for the osmotic coefficient of many components in charge-asymmetric mixtures of electrolytes.

In a first level of approximation only data on single-salt solutions were used, and in the full equations data on common ion mixtures of electrolytes were used. The full equations were applied to mixtures of three cations with common anions, like LiCl – NaCl – KCl, and the predictions agreed with the experimental measurements to within the experimental error. Sangster & Lenzi (1974) tested the Reilly–Wood–Robinson equation using only single-salt data, against ternary solutions of strong electrolytes including, NaCl, KCl, Na_2SO_4, etc. and found very good agreement with experimental data. However, this equation showed no consistent advantage over less complicated ones, like eqn (1) and eqn (2).

The model of Pitzer & Kim (1974)

In a first paper (described in Part I of this work) Pitzer (1973) gave the theoretical basis for the treatment of mixed electrolytes. On that basis, Pitzer & Kim (1974) developed an equation for the accurate representation and prediction of the thermodynamic properties of aqueous strong electrolyte mixtures.

For common ion mixtures (MX – NX) the equation for the osmotic coefficient, φ, is:

$$\varphi - 1 = \frac{1}{\sum_i m_i} [2\,If + m_M m_X B_{MX} + m_N m_X B_{NX} + m^2_X(m_M C_{MX} + m_N C_{NX}) + m_M m_N \theta_{MN} + m_M m_N m_X \psi_{MNX}] \quad (3)$$

where,

$$f_{(at\ 25°C)} = -0.392 \left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}}\right] \qquad B_{ij} = \beta_{oij} + \beta_{1ij} \exp(-2\sqrt{I})$$

C_{MX}, C_{NX}, θ_{MN}, and ψ_{MNX} are constant for each solute.

Pitzer & Kim (1974) showed that eqn (3) was a very accurate description of measured data for aqueous electrolyte mixtures.

Ross equation (1975)

When a given solute or a mixture of them are incorporated into an IMF it is necessary to predetermine the final a_w of the product in order to formulate the food to the desired a_w with a minimum of product development time. Based on this premise, Ross (1975) developed a very simple equation for estimating the water activity of complex solutions. Ross' method involves simplifying assumptions with respect to the Gibbs–Duhem equation,

$$\sum_i n_i \, d \ln (a_i) = 0$$

where n_i : number of moles of component i, a_i : activity of component i.

Ross (1975) assumed that interaction effects between different solute components cancel on the average and with this condition Gibbs-Duhem equation reduces to the simple expression:

$$a_w = (a_w{}^0{}_1) \cdot (a_w{}^0{}_2) \cdot (a_w{}^0{}_3) \qquad (4)$$

which is Ross' equation. This equation says that the water activity of a complex solution becomes simply the product of the water activity values of the aqueous solutions of each component, when measured at the same molality as in the complex solution. In other words, the a_w of the mixture is a product of each component water activity $(a_w{}^0{}_1), (a_w{}^0{}_2), (a_w{}^0{}_3)$ . . . as if they were dissolved in all of the water in the system independently of the others. Ross tested the validity of his equation by measuring the a_w of solutions of sucrose with KCl and NaCl, at various molalities covering the range of most interest to IMF, that is about 0.96 to 0.80 (Bone, Shannon & Ross, 1975). He indicated that the percentage error between measured and calculated a_w using his equation was less than 1%. Other workers in the food area (Sloan & Labuza, 1976; Chuang & Toledo, 1976; Chirife, 1978) also tested Ross' equation in systems of interest in IMF, but none of the systems examined contained mixed strong electrolytes; they consisted of non-electrolyte – electrolyte (always NaCl) systems.

Development of a new model equation

Clearly, the main advantage of Ross' (1975) equation is its extreme simplicity. However, as will be shown later, this simplicity is obtained through a loss of accuracy in the predictions. For this reason it would be desirable to have a similar simple equation but which is able to yield better predictions of a_w in mixed strong electrolytes. This is done in the following way:

$$a_w = \exp \{- (\varphi \cdot 0.018 \Sigma m_i)\}$$

The osmotic coefficient, φ , may be expressed as,

$$\varphi = 1 + \frac{1}{\Sigma m_i}\{(2\ If) + \sum_{ij} B_{ij} m_i m_j + \sum_{ijk} B_{ijk} m_i m_j m_k\}$$

In this way

$$a_w = \exp \{-0.018 (\Sigma m_i + 2\ If + \Sigma_{ij} + \Sigma_{ijk})\}$$

and neglecting second and higher orders in the molalities,

$$a_w \cong \exp \{-0.018 [\sum_i m_i + 2\ If\ (I)]\}$$

Now, we note that $\sum_i m_i$ and ionic strength are additive functions of the number of solutes, i.e.

$$\sum_i m_i = \sum_s (\sum_i m_i)_s \equiv \sum_s m_s \qquad 2I = \sum_i m_i z_i^2 = \sum_s (\sum_i m_i z_i^2)_s \equiv 2 \sum_s I_s$$

and consequently,

$$a_w \cong \prod_s \exp \{-0.018 [m_s + 2I_s f(I)]\}$$

Since the ratio $2 I_s/m_s$ is a constant for each solute, equal to its mean squared ionic charge $|z_+ z_-|_s$, one can conveniently scale the exponents in this equation up to total ionic strength I by just multiplying by an adequate factor

$$a_w \cong \prod_s \exp \left\{-0.018 [m_s(I) + 2 I f(I)] \frac{I_s}{I}\right\}$$

where $m_s(I) = \frac{I}{I_s} m_s$ is the total (dissociated) molality of solute s which affords an ionic strength equal to that of the mixture. To the same degree of approximation, one can summarize this result by writing,

$$a_w \equiv \prod_s [a_{ws}(I)]^{I_s/I} = \prod_s [a_{ws}(I)]^{m_s/m_s(I)} \qquad (5)$$

which is the equation proposed in this work. It has some resemblance with the one developed by Meissner & Kusik (1972). However, in four-ion systems eqn (5) is simpler than theirs. A more detailed comparison of both equations will be published elsewhere.

One should note that by taking the natural logarithm on both sides of eqn (5), and approximating the logarithm by the first two terms of its series expansion near $a_w = 1$ one gets

$$1 - a_w \simeq \sum_s \frac{m_s}{m_s(I)} [1 - a_{ws}(I)]$$

which is Robinson and Bower's (1965) equation for mixtures. Since this involves an additional (numerical) approximation, we consider it is superseded by the proposed equation (5).

The only difference in eqn (5) with that of Ross is that the activity of each electrolyte must be taken at the total ionic strength and then raised to the $m_s/m_s(I)$ power.

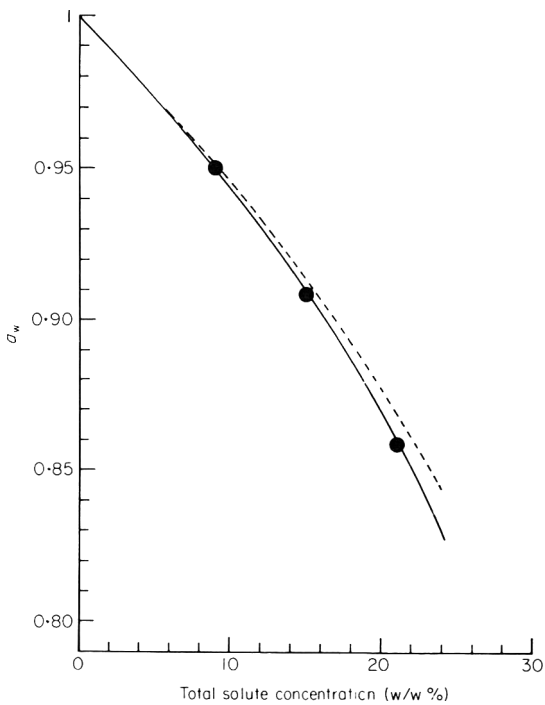
Test of Ross' (1975) and the proposed model equations

The validity of Ross' equation and the proposed new one, will be now tested against the 'exact' model developed by Pitzer & Kim (1974) for aqueous electrolyte mixtures. As this model has been proved to be a very accurate

description of measured properties, it is used here as a direct representation of experimental data.

The following electrolyte mixtures will be examined: (1) NaCl–KCl, (2) KCl–$CaCl_2$, (3) KCl–$MgCl_2$, (4) NaCl–$CaCl_2$, (5) NaCl–$MgCl_2$, (6) $CaCl_2$–$MgCl_2$ and (7) Na_2SO_4–NaCl. The electrolytes considered involve 1–1, 2–1 and 1–2 type inorganic salts, most of which are currently used as food additives. All the calculations were performed for a 1:1 dry weight ratio of solutes. The results of the calculations were expressed as a_w of the mixture versus total solute content for the a_w range of most interest to IMF. The results are shown in Figs 1 to 7; they show the predicted a_w using Ross' (1975) equation and the proposed new equation as compared to the exact model (hitherto identified with experimental data) of Pitzer & Kim (1974). The a_w data of the single electrolytes needed to apply either Ross' (1975) or the proposed equation, were taken from Pitzer & Mayorga (1973).

The most obvious conclusion is that the proposed equation is much better than Ross' one; it predicts the a_w of the mixtures with a high degree of accuracy in the whole range of a_w examined. Ross' equation give good predictions only down to about 0.95 a_w and significant deviations between measured and predicted values are observed at lower water activities. One interesting conclusion which can be drawn from Figs 1 to 7 is that in all cases Ross' equation predicts a_w values higher than measured.



Figures 1–7. ---, Ross; ———, Pitzer & Kim; ●, proposed model.

Figure 1. Comparison of a_w predictions in aqueous mixtures of NaCl–KCl (1:1 dry weight ratio) at 25°C.

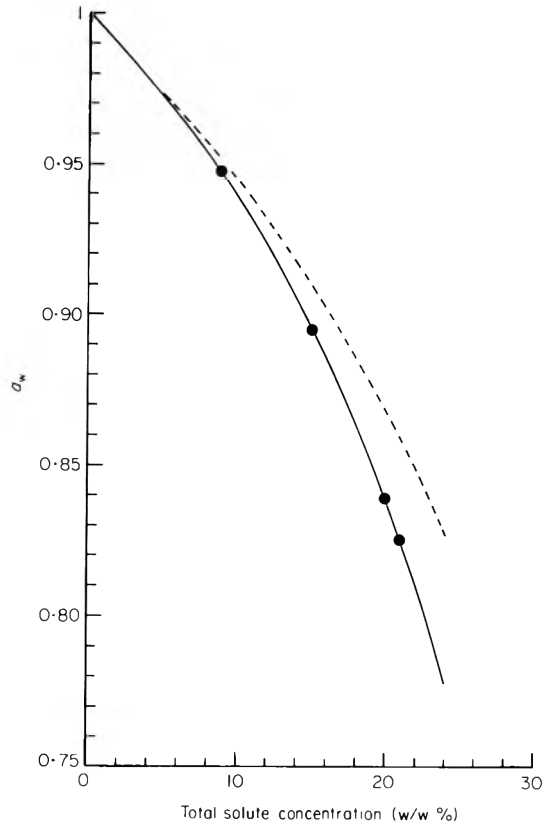


Figure 2. Comparison of a_w predictions in aqueous mixtures of NaCl–$CaCl_2$ (1:1 dry weight ratio) at 25°C.

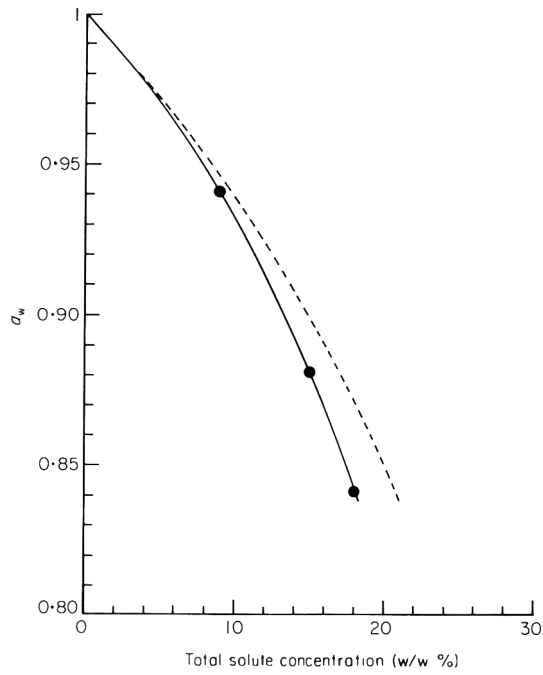


Figure 3. Comparison of a_w predictions in aqueous mixtures of NaCl–$MgCl_2$ (1:1 dry weight ratio) at 25°C.

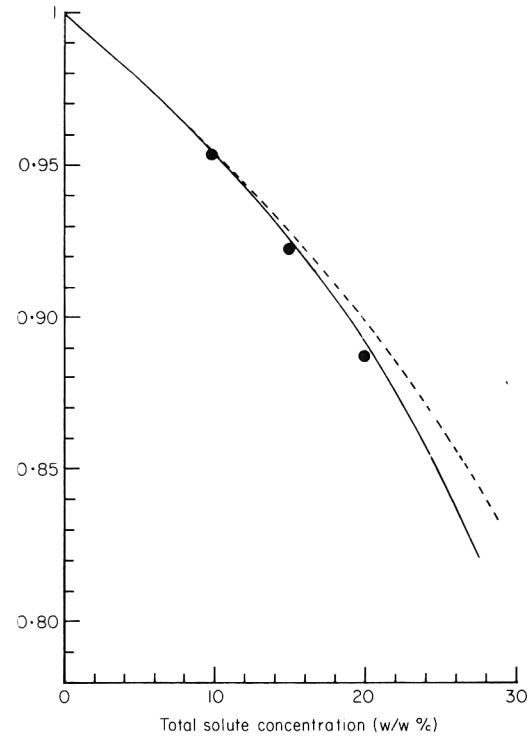


Figure 4. Comparison of a_w predictions in aqueous mixtures of NaCl–Na_2SO_4 (1:1 dry weight ratio) at 25°C.

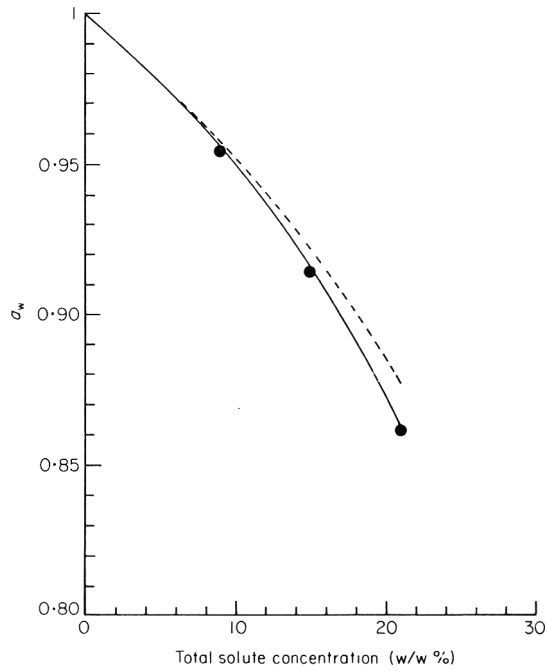


Figure 5. Comparison of a_w predictions in aqueous mixtures of KCl–$CaCl_2$ (1:1 dry weight ratio) at 25°C.

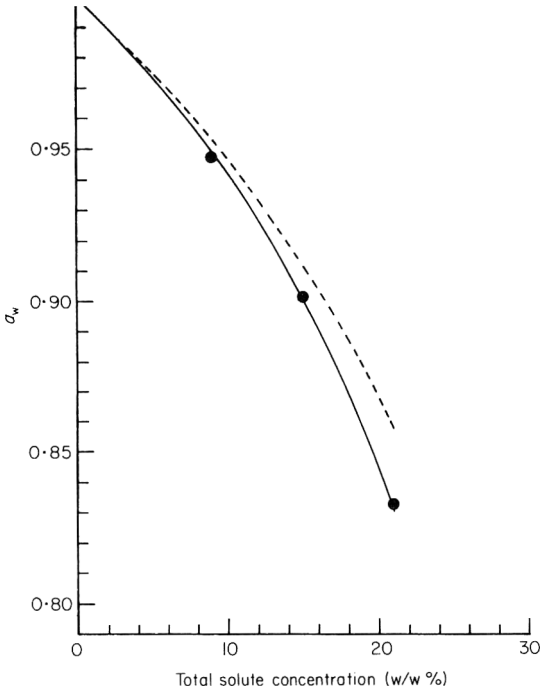


Figure 6. Comparison of a_w predictions in aqueous mixtures of KCl–$MgCl_2$ (1:1 dry weight ratio) at 25°C.

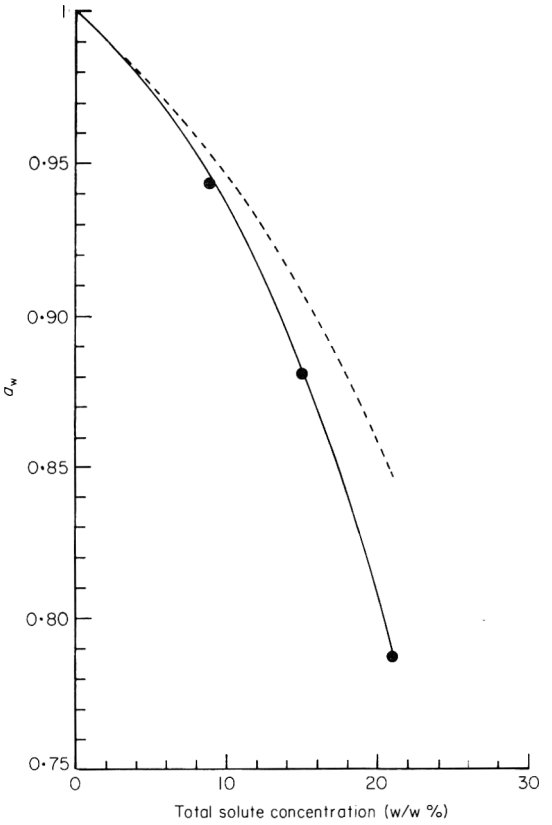


Figure 7. Comparison of a_w predictions in aqueous mixtures of $CaCl_2$–$MgCl_2$ (1:1 dry weight relation) at 25°C.

From the point of view of microbial inhibition in IMF, this means that Ross' equation has some sort of 'built-in' safety factor. It is also interesting to note that the only system for which Ross' equation gives a prediction which may be of comparable accuracy to that obtained with eqn (5), is NaCl–KCl. As a matter of fact, this system is the electrolyte-electrolyte mixture tested by Ross (Bone *et al.*, 1975) to the validity of its model.

At this point it is important to define more clearly what is understood by 'accurate' prediction of a_w in an IMF; certainly this concept would have different meanings to a physical chemist or a food technologist. Experimental methods utilized in the physical chemistry area usually permit the expression of a_w values to 3 or 4 decimal figures (Sangster & Lenzi, 1974). In the food area, however, a_w values are usually rounded to the second decimal figure, mainly if they are measured with electric hygrometers as is usually done (Labuza *et al.* 1976). Thus concerning an IMF, it would be desirable and sufficient to predict the a_w of a multicomponent electrolyte mixture within about $\pm$ 0.01 a_w. The results presented in the figures show that this is not always the case when applying Ross' equation to strong electrolyte mixtures; in the low region of a_w considered, the predictions may give errors as high as 0.03–0.04 a_w. Of course, whether or not this error may be tolerated depend on the objectives of the user; for instance, if the final a_w will be experimentally checked and the prediction is only used to reduce the number of experimental trials, it may be used.

Usually the errors in a_w prediction are expressed as percentage errors in the quantity of a_w. However, it would be more realistic to define the error percentage as:

$$\text{percentage error} = \frac{(a_w)_{\text{Pred}} - (a_w)_{\text{Obs}}}{1 - (a_w)_{\text{Obs}}} \times 100$$

This is the error in the quantity $1 - a_w$, and is more significant than the error in a_w itself since it gives directly the error in the a_w lowering (Sangster & Lenzi, 1974). Furthermore, this is more useful from the point of view of IMF, because most microbial inhibition occurs throughout the $1 - a_w$ range of water activity.

From the deduction of eqn (5) one should not conclude that its range of validity is limited by the smallness of the solute-solute interaction terms. In fact, as the figures show, it is quite good up to the higher molalities here considered, where interactions are certainly not negligible.

Comparing eqn (5) using for the activities in the right hand side the Pitzer & Mayorga (1973) equations with the full interaction terms, with the Pitzer & Kim (1974) activity formula for mixtures, one sees that, in fact, eqn (5) is constructed in such a way that an effective cancellation among interactions takes place. More quantitatively, one can express the ratio

$$\frac{a_w \text{ (Pitzer \& Kim)}}{a_w \text{ eqn (5)}} = \exp\left(-2 \times 0.018\, m_{MX}\, m_{NY}\, D\right)$$

in terms of a generic 'discrepancy function' D. We study elsewhere this function, which for the simpler case of a mixture in which both electrolytes are of the same ionic type turns out to be,

$$D = (B_{MY} - B_{MX}) - (B_{NY} - B_{NX})$$

It is in fact a cancellation of two terms, which are themselves cancellations of virial coefficients. If, for example, there is a common electrolyte in this mixture, D vanishes and eqn (5) is thus exact up to third order in the concentrations. This is far from the truth for the Ross discrepancy function. At high ionic strength we show that

$$D_{Ross} \approx \nu_M \nu_Y B_{MY} + \nu_X \nu_N B_{NX}$$

It is now easy to understand the procedure by which Ross arrived at his equation. It amounts to neglecting all kinds of interaction terms in the equations above, including the Debye–Hückel contribution. Though this is reasonable (up to second order in the concentrations) for non-electrolytes, it is certainly unjustified for electrolyte mixtures, which explains the general disagreement of Ross' method with experimental results for these systems.

Conclusions

Ross' (1975) equation has been applied for predicting the a_w of aqueous mixtures of strong electrolytes in the range of a_w of most interest to intermediate moisture foods. Electrolytes studied included NaCl, KCl, $CaCl_2$, $MgCl_2$ and Na_2SO_4, which may be considered 'food additive-like' compounds. The results indicated that a_w predictions using Ross' equation significantly differed from experimental data at a_w values of less than about 0.95 for the systems under study.

A new simple model equation of much higher accuracy than Ross' one is proposed and may be of value for a_w prediction in the range of a_w of most interest to IMF.

A theoretical analysis is made to explain the behaviour of Ross' and the new equations.

Acknowledgments

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Nomenclature

I: ionic strength $= \frac{1}{2} \Sigma\, m_i\, z^2_i$

m_i: molality of species i

z_i: charge of species i in electronic units

I_s: ionic strength of solute s $= \frac{1}{2}\, \nu_s\, m_s |z_+\, z_-|$

m_s: molality of solute s

ν_s: number of moles of ions produced by one mole of s

J. Fd Technol. (1980) **15**, 59–70

The prediction of water activity in aqueous solutions in connection with intermediate moisture foods

IV. a_w Prediction in aqueous non electrolyte solutions

J. CHIRIFE*, C. FERRO FONTAN†‡ AND E.A. BENMERGUI†

Summary

A systematic survey was made of water activity reduction in single non electrolyte aqueous solutions together with an examination of the theoretical aspects of a_w predictions. The prediction of a_w in multicomponent aqueous solutions of non electrolytes as well as of mixed strong electrolyte–non electrolyte solutions was also studied.

Introduction

As was mentioned in Part I of this work (Benmergui, Ferro Fontan & Chirife, 1979) non-electrolytes may be also used to depress water activity in IMF. It is the purpose of the present paper to make a systematic survey of water activity reduction in single non-electrolyte aqueous solutions as well as an examination of the theoretical aspects of a_w predictions. This work is also concerned with the prediction of a_w in multicomponent aqueous solutions of non-electrolytes as well as of mixed strong electrolyte–non-electrolyte solutions. With this purpose the simplified model of Ross (1975) (discussed in Part III, Ferro Fontan, Benmergui & Chirife, 1979) is tested against a diversity of literature experimental data of a_w in multicomponent solutions.

Results and discussion

Survey of a_w lowering in binary non-electrolyte solutions

Teng & Lenzi (1974) collected experimental data on water activity (a_w) for several non-electrolytes which are of interest in IMF technology. Most of those data were obtained through accurate isopiestic vapour pressure measurements

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Table 1. List of non-electrolytes studied

Amino-acids and urea amides
(1) α-Alanine
(2) β-Alanine
(3) α Amino-n-butyric acid
(4) Glycine
(5) Glycolamide
(6) Glycylglycine
(7) Lactamide
(8) Urea
(9) Dl-Valine
Polyols
(10) Erythritol
(11) Glycerol
(12) Mannitol
(13) Sorbitol
Simple sugars (monosaccharides) and oligosaccharides
(14) Glucose syrup DE 32
(15) Glucose syrup DE 42
(16) Glucose
(17) Maltose
(18) Raffinose
(19) Sucrose
(20) Xylose

performed by researchers studying the thermodynamic properties of aqueous solutions. Teng & Lenzi (1974) used polynomial expressions to fit the complete range of available a_w data for various non-electrolyte binary systems. They represented the data in the form,

$$a_w = 1 + \sum_{i=1}^{k} A_i \, m^i \qquad (1)$$

where m is the solute molality, k the degree of polynomial, A_i the coefficient of the polynomial and σ the standard deviation. The optimum fit was obtained by increasing k until a minimum σ of regression was attained.

Teng & Lenzi (1974) listed the A_i for the solutes in question, together with the σ_{min}, which was less than 0.0002; i.e. the accuracy of their method of representation was of the same order as that of the experimental data. They also reported the maximum molality to which the data were fitted by expression (1), which proved to be useful also with concentrated solutions (for example $a_w < 0.95$). It was concluded that Teng & Lenzi's (1974) compilation constituted an excellent source of data for our purposes, and expression (1) was used to generate the a_w versus concentration data for non-electrolytes of interest in IMF technology.

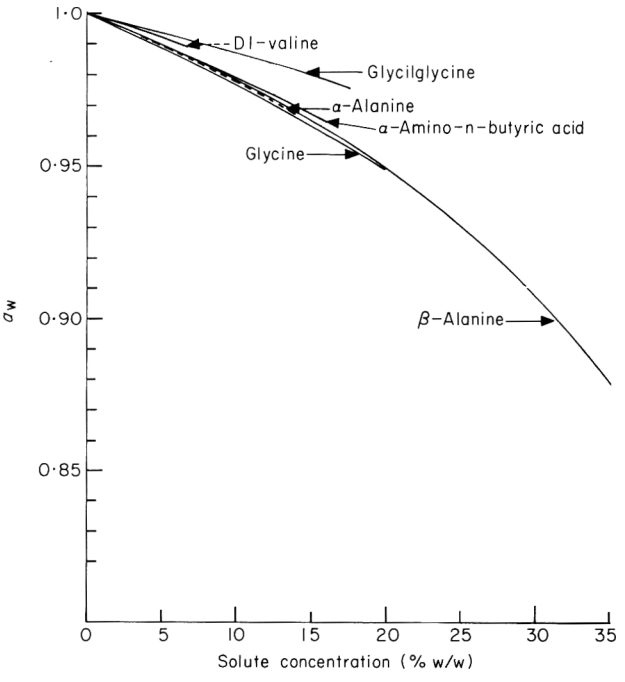


Figure 1.

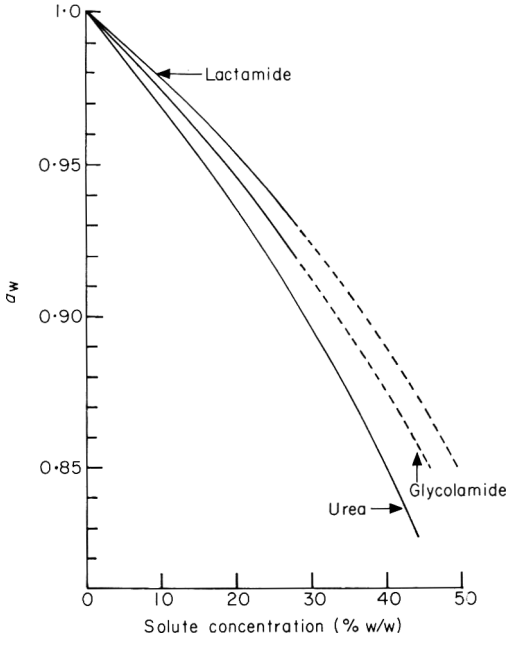


Figure 2.

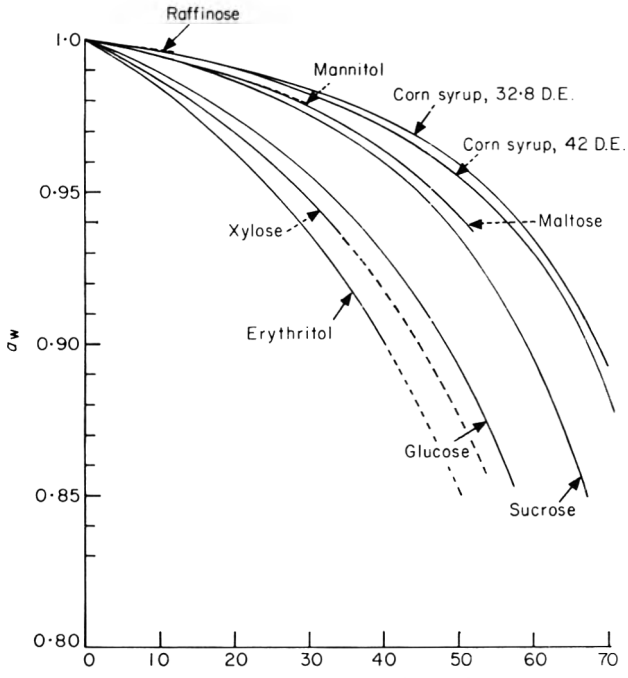


Figure 3.

On p. 62 in Fig. 3 the a_w-concentration curve for mannitol has been drawn incorrectly; however, the a_w-lowering behaviour of mannitol can be calculated correctly by Equation (2) with K = 0.906 as indicated in Table 4.

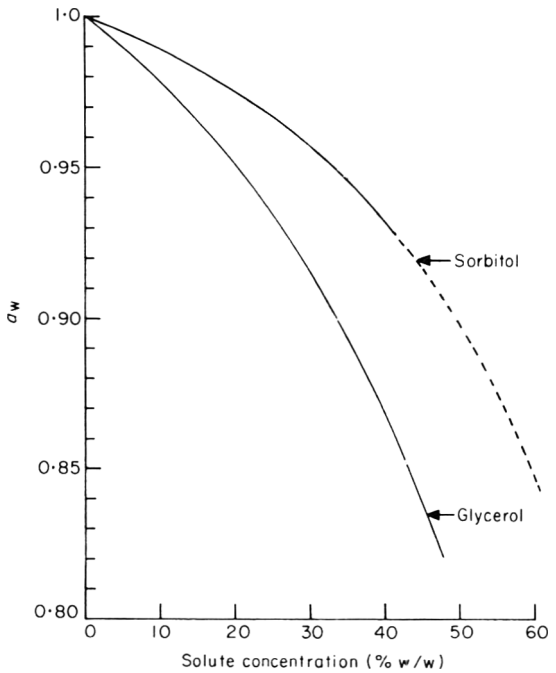


Figure 4.

Figures 1 to 4. Water activity as a function of solute concentration for various single aqueous non-electrolyte solutions at 25°C.

Table 2. Solute concentration (w_s) in single aqueous non electrolyte solutions having an $a_w = 0.85$ at 25°C

Solute	w_s (% w/w)
Urea	39.7
Propylene-glycol	40.0
β-Alanine*	40.0
Glycerol	43.0
Glycolamide	45.6
Lactamide†	49.5
Erythritol†	50.3
Xylose†	54.0 (at $a_w = 0.856$)
Glucose	58.0
Sorbitol†	59.5
Sucrose	67.0
Glucose syrup DE 42	74.2

*Slightly extrapolated
†Extrapolated

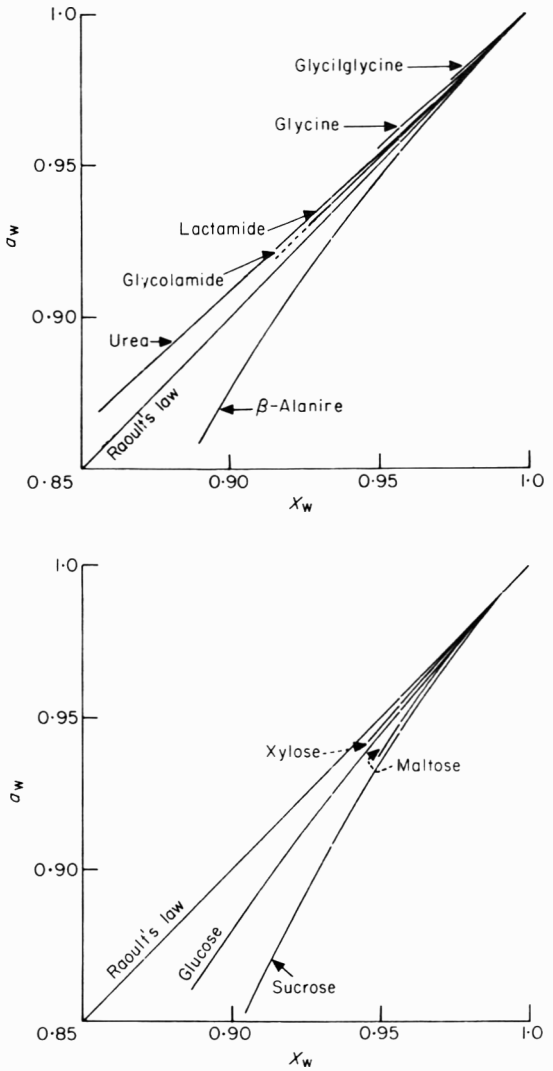
Non-electrolytes considered included amino-acids and amides, polyols, monosaccharides and oligosaccharides.

Table 1 lists the twenty compounds studied. Most of them may be considered as 'food additive'-like compounds. Data corresponding to glucose syrups (corn-syrup') reported by Norrish (1966) are also included, although it should be noted that these are multicomponent mixtures, rather than binary systems.

Figures 1 to 4 show the variation of a_w with solute concentration for the different compounds at 25°C. Solute concentration was expressed on total weight basis instead of molality because it may be more illustrative for technological purposes. The curves were drawn in most cases only up to the maximum concentration indicated by Teng & Lenzi (1974) and this is shown by the full lines. In some cases, however the curves were extrapolated (provided that the solubility limit had not been reached) and this is indicated using dotted lines. The extrapolation procedure will be discussed later. Following the reasonings in Part I (Benmergui *et al.*, 1979), Table 2 shows the weight concentration of each individual non electrolyte needed to achieve a 'safe' water activity of 0.85. The origin of data corresponding to propylene glycol will be referred to later. As expected, Table 2 reveals that the solute concentration in the aqueous phase is relatively much higher than that needed when using most electrolyte solutes (Benmergui *et al.*, 1979). Of course, these high solute concentrations are expected to adversely affect taste and other physical properties of the IMF.

Comparison with Raoult's law

The behaviour of some of the solutes here studied, with respect to that predicted by Raoult's law is shown in Figs. 5 and 6. It is noteworthy that sugars



Figures 5 and 6. Comparison of a_w depression by various non-electrolytes with depression expected from Raoult's law at 25°C.

(mono- and disaccharides) give significant negative deviations as well as β-alanine.

Theoretical analysis

Based on a simple thermodynamic analysis of solutions Norrish (1966) proposed a correlating equation for binary systems which he applied to some sugar and polyol solutions. Norrish's (1966) equation may be written

$$a_w = X_1 \exp(-K X^2_2) \quad (2)$$

Table 3. Values of K eqn 2) for amino-acids and amides

Substance	K
α-Amino-n-butyric acid	2.59 ± 0.14
β-Alanine	2.52 ± 0.37
Lactamide	−0.705 ± 0.066
Glycolamide	−0.743 ± 0.079
Urea	−2.02 ± 0.33
Glycine	−0.868 ± 0.11

Table 4. Values of K (eqn 2) for sugars and polyols

	K
Sugars	
Sucrose	6.47 ± 0.06
Maltose	4.54 ± 0.02
Glucose	2.25 ± 0.02
Xylose	1.54 ± 0.04
Polyols	
Sorbitol	1.65 ± 0.14
Erythritol	1.34 ± 0.05
Glycerol	1.16 ± 0.01
Mannitol	0.906 ± 0.27

where X_1 and X_2 are molar fractions of water and solute respectively, and K is the correlating constant. Norrish (1966) reported K values for sucrose, invert sugar, glucose syrups, glycerol and sorbitol (Norrish's original equation was defined on $\log_{10}$ basis).

A computer program was prepared to calculate the best K values when applying eqn (2) to the a_w data of non-electrolytes collected in this work. The standard deviation of the fit as well as the error in the correlating constant K were also calculated but only the latter is reported. The results are shown in Tables 3 and 4. Our results for sorbitol, sucrose and glycerol differ somewhat (between about 7 to 25%) from those of Norrish (in order to compare, K values here reported have to be divided by 2.303). However, we believe that the present data should be preferred because the experimental data on which they are based seem to be more rigorous. On the other hand comparison of the standard deviation of our fit with the graphical representation of Norrish (1966) results also support this preference. Moreover, present data for sucrose and glycerol are very close to recent determinations of Chuang & Toledo (1976).

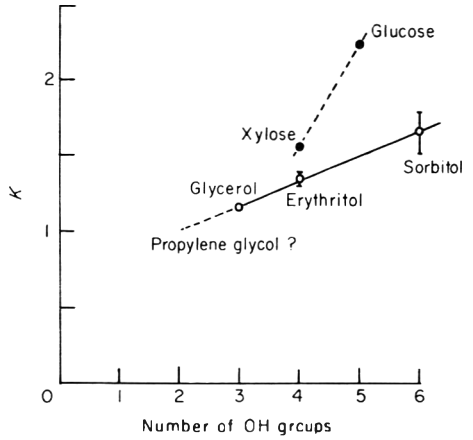


Figure 7. The dependence of K on the number of hydroxyl groups in the molecule.

Extrapolations of some of the a_w-concentration curves shown in Figs 2, 3 and 4, were performed using eqn (2) with the corresponding K values. Certainly, the most remarkable virtue of eqn (2) is its extreme simplicity which needs only one parameter to characterize the a_w reduction curve. Norrish (1966) also suggested that the K constant might be correlated with the number of hydroxyl groups in the molecule for the case of sugars and polyols. He also advanced the possibility that in the case of substances containing 'effective groups' (those able to form hydrogen bonds with water) other than hydroxyl it might be possible to separate the effects of the different groups. This predictive potential of equation (2) is tested using the results shown in Tables 3 and 4. Figure 7

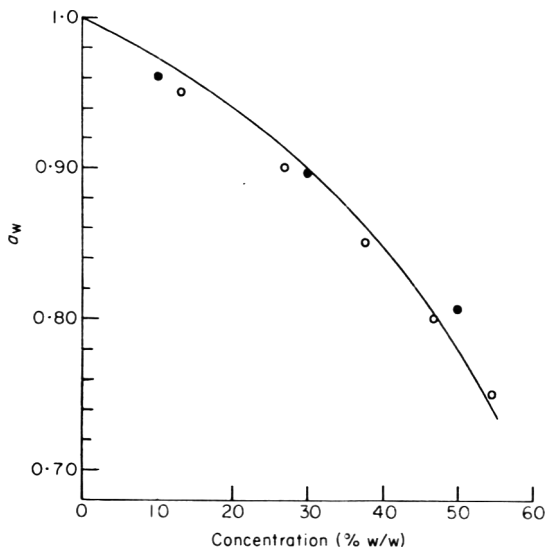


Figure 8. Comparison of predicted and observed a_w depression by propylene glycol solutions. ●. Verlinde *et al.* (1975); ○. Sloan & Labuza (1975b); ——. predicted.

Table 5. Comparison of observed and calculated (Ross' equation) a_w for various ternary non-electrolyte aqueous systems (m : molality)

	m_1	m_2	a_w (obs.)	a_w (calc.)	Percentage deviation (on 1-$a_{w\,obs}$)	Reference
(a) Sucrose (1)–Sorbitol (2)	1.693	1.0593	0.943	0.945	3.5	Stokes &
	1.2683	1.5709	0.943	0.946	5.3	Robinson
						(1966)
(b) Sucrose (1)–Glucose (2)	2.3504	1.0996	0.926	0.929	4.1	,,
	1.7391	1.8737	0.925	0.930	7.1	,,
(c) Sucrose (1)–Glycerol (2)	2.0405	1.3615	0.930	0.933	4.5	,,
	1.5022	2.065	0.930	0.932	3.0	,,
(d) Sucrose (1)–Mannitol (2)	2.5321	0.3874	0.936	0.937	1.6	Robinson &
	2.2820	0.6829	0.936	0.938	3.1	Stokes
	1.9707	1.0494	0.936	0.939	4.7	(1961)
	3.4904	0.176	0.915	0.915	—	,,
	3.0949	0.6557	0.915	0.918	3.5	,,
	5.2913	0.2669	0.863	0.864	0.75	,,
	5.1174	0.4889	0.863	0.866	2.2	,,
	4.953	0.7051	0.863	0.866	2.2	,,
(e) Urea (1)–Sucrose (2)	0.243	3.6375	0.912	0.910	2.3	Ellerton &
	5.6473	0.2461	0.912	0.910	2.3	Dunlop
	0.2843	4.2556	0.875	0.893	1.9	(1966)
	6.9685	0.3037	0.895	0.892	2.9	,,

shows the aforementioned correlation for polyols from which it is seen that the relationship is linear. This suggests that the effect of hydrogen bonding is dominant in determining the properties of these solutions. However, not all hydroxyl-containing molecules can be brought to the same correlation, as advanced by Norrish (1966). For instance, the data for glucose and xylose (4 and 5 OH-groups) are also plotted in Fig. 7 and do not appear to fit the same correlation. The data for maltose and sucrose (not plotted) also do not fit with any of the other groups (monosaccharides and polyols). So, it may be supposed that in addition to the number of OH-groups other molecular characteristics also play a significant role.

The a_w lowering characteristics of propylene glycol (1-2 propanediol) were reported by Loncin (1975), Sloan & Labuza (1975a,b), and Verlinde, Verbeeck & Thun (1975). There is, however, considerable disagreement between these data. Loncin (1975) indicated that propylene glycol has a very strong negative deviation from Raoult's law, having in this aspect a better a_w lowering ability (on molar basis) than glycerol. The data of Sloan & Labuza (1975b) did not agree with those reported previously (Sloan & Labuza, 1975a) but they

Table 6. Comparison of observed and calculated (Ross' equation) a_w for various ternary electrolyte – non-electrolyte aqueous systems (m : molality)

	m_1	m_2	a_w (obs.)	a_w (calc.)	Percentage deviation (on 1-a_w obs)	Reference
(a) Mannitol (1)–NaCl (2)	0.7285	5.8359	0.761	0.756	2.1	Kelly,
	1.0482	5.7784	0.761	0.755	2.5	Robinson
	0.8191	5.1642	0.791	0.787	1.9	& Stokes
	1.1401	5.0904	0.791	0.785	2.9	(1961)
	0.6707	4.9609	0.801	0.798	1.5	"
	0.9096	4.9023	0.801	0.797	2.0	"
(b) Urea (1)–NaCl (2)	4.4403	3.4657	0.814	0.813	0.54	Bower &
	8.7605	2.079	0.814	0.813	0.54	Robinson
	5.662	4.0765	0.776	0.775	0.45	(1963a)
	11.262	2.4182	0.776	0.775	0.45	"
(c) Glycine (1)–KCl (2)	0.9836	1.1473	0.948	0.946	3.8	Bower &
	2.0131	0.6521	0.948	0.946	3.8	Robinson
	1.3494	0.787	0.954	0.951	6.5	(1965)
(d) Mannitol (1)–KCl (2)	1.1056	4.2921	0.845	0.842	1.9	Robinson
	1.4379	4.0715	0.848	0.844	2.6	& Stokes
	1.3907	3.9376	0.852	0.849	2.0	(1962)
(e) Mannitol (1)–NaCl (2)	0.9096	4.9023	0.801	0.797	2.0	Kelly *et al.*
	1.1401	5.0904	0.791	0.785	2.8	(1961)
	1.0482	5.7784	0.761	0.755	2.5	"
(f) Sorbitol (1)–NaCl (2)	1.1079	5.7672	0.764	0.754	4.2	Bower &
	0.7941	5.812	0.764	0.756	3.4	Robinson
	1.1349	5.0802	0.793	0.786	3.4	(1963b)
	0.950	3.7575	0.851	0.846	3.4	"

stated that their last data were more accurate. The data of Sloan & Labuza (1975b) as well as those of Verlinde *et al.* (1975) are plotted together in Fig. 8. It can be seen that they are in reasonable agreement. The data of Loncin (1975) (not plotted), however, are in disagreement. This controversy may perhaps be elucidated using the predictive value of constant K.

Based on the number of OH-groups in the molecule it could be expected that the a_w lowering ability of propylene glycol should not be better (on molar basis) than that of glycerol. If the straight line showed in Fig. 7 is extrapolated a value of K = 1.0 may be tentatively assigned to propylene glycol. The a_w *vs* concentration curve of propylene glycol may be now predicted and this is shown in the same Fig. 8. It can be seen that the predicted curve fits reasonably well the experimental data of Sloan & Labuza (1975b) and Verlinde *et al.* (1975).

Although not enough data are available, some ideas may be advanced to interpret the K values obtained for the amino acids and amides.

It appears that the amino group favours a_w lowering, as shown by the relatively high values of K for β-alanine and α-amino n-butyric acid. The presence of an amido group, however, does not produce the same effect and this is shown by the small values of K obtained for urea, lactamide and glycolamide, all of them showing positive deviations from Raoult's law.

a_w prediction in multicomponent mixtures of non electrolytes and strong electrolyte–non electrolyte solutions

In part III of this work (Ferro Fontán *et al.*, 1979) we have discussed the problem of a_w prediction in solutions of mixed strong electrolytes. It has been shown that Ross' equation (Ross, 1975) may give significant deviations from reality, mainly at reduced a_ws (i.e. $a_w < 0.95$). We are now examining the ability of Ross' equation to estimate the a_w of multicomponent non-electrolyte and electrolyte – non-electrolyte solutions. Literature experimental data on thermodynamic properties of multicomponent aqueous solutions (mainly reported as osmotic coefficients) are now utilized to test the validity of Ross' equation. Most of data were obtained through accurate isopiestic vapour pressure measurements, by workers in the physical chemistry area. Solutes tested include combinations of sorbitol, sucrose, glucose, glycerol, mannitol, glycine, urea, NaCl and KCl. Tables 5 and 6 show the results of the application of Ross' equation to various non-electrolyte and electrolyte–non-electrolyte ternary aqueous systems in the range of most interest in IMF. The deviation between observed and calculated values is expressed on $1 - a_w$ basis rather than on a_w (Ferro Fontán *et al.*, 1979). It can be seen that the agreement between measured and predicted a_w values is very good for all systems examined. This is attributed to the smaller solute-solute interactions prevailing in mixtures of non-electrolytes or single electrolyte–non-electrolyte. If more than one electrolyte is present deviations may occur as discussed in part III (Ferro Fontán *et al.*, 1979).

Acknowledgments

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Emulsifying properties of undenatured potato protein concentrate

F. HOLM AND S. ERIKSEN

Summary

The emulsifying properties of an undenatured potato protein concentrate (PPC) have been studied in a model system. Emulsification capacity, emulsion activity and stability and emulsion viscosity were studied under a wide variety of conditions.

PPC proved to be superior in all cases to commercial soy isolate except for emulsion viscosity with the same amount of oil added. The emulsification capacity of PPC could be even further improved (50%) by removal of low molecular components by dialysis. The present results indicate that PPC might be considered as a replacement for soy isolate in food formulations.

Introduction

To-day, potato protein is produced as a by-product from most potato starch factories by heat and acid precipitation of the protein in the fruit water (Knorr, 1977; Wilhelm & Kempf, 1977).

The protein is primarily precipitated to reduce the nitrogen load of the waste water on the recipient, and the dried coagulate is used as a special feed, the biological value of potato protein being very high compared to other vegetable protein sources (Kofrányi, 1971, Mørup, 1976; Rexen, 1976).

Because of low solubility and functionality of the denatured potato protein, a more careful processing method is necessary, if potato protein is to have a future as an additive in food formulations.

Production of undenatured potato protein is possible by spray drying of ground potatoes with subsequent dry separation into a protein concentrate (PPC), a starch concentrate and a fibre-rich product (Holm, 1979).

The produced PPC is used for demonstration of the fat emulsifying properties of potato protein in food formulations. The emulsifying properties of an added vegetable protein are important in foods such as sausages, soups, luncheon meat, mayonnaise, coffee creamer and salad dressing.

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Usually, the emulsifying properties of a vegetable protein are examined in a model system consisting of water, oil and protein and are often compared to the properties of a standardized soy protein as the results very much depend upon experimental conditions such as emulsification method, temperature, pH, salinity and protein concentration (Kinsella, 1976: Tornberg & Hermansson, 1977; Puski, 1976).

In the present study, the emulsification properties, emulsification capacity, emulsion activity, stability and viscosity, have been determined and compared with those of other vegetable proteins, particularly soy protein.

Materials

The undenatured PPC (40% protein) has been produced in pilot experiments. Washed potatoes were homogenized into a pulp, spray dried and separated into three fractions (starch, protein and fibres) by sieving and air classification (Holm, 1979). In some experiments, the properties of the protein fraction (43.4% protein dry wt) were compared with those of dried fruit water produced by spray drying of the supernatant of centrifuged potato pulp (61% protein dry wt). All spray dryings were performed with an inlet air temperature of 200°C and an outlet air temperature of 95°C. A commercial denatured potato protein (Roquette Freres, France) was included for comparison (83.9% protein dry wt). All protein percentages were calculated as N% × 6.25. Five purified, protein-rich products were produced on the basis of PPC.

Protein I. A suspension (20%) was dialyzed against deionized and distilled water for 24 h. The dialysate was freeze dried (67.5% protein dry wt).

Protein II. PPC was extracted with deionized water and the extract was freeze dried (45.9% protein dry wt).

Protein III. PPC was extracted as under II, but pH was adjusted to 4.0 with HCl with subsequent stirring for 30 min prior to freeze drying of the suspension (44.5% protein dry wt).

Protein IV. As III, but the temperature was increased to 80–85°C during the 30 min stirring time (45.3% protein dry wt).

Protein V. As II, but the suspension was dialyzed against deionized and distilled water for 24 h prior to freeze drying (85.2% protein dry wt).

Soy isolate (Purina 500 E) (92.4% protein dry wt) and soy concentrate (Aarhus Oliefabrik) (70.7% protein dry wt) were used as reference proteins.

Methods

Emulsification capacity

The procedure for determination of emulsification capacity is shown in Fig. 1 and is based on a Swift titration (Swift, Lockett & Fryar, 1961). The protein product was suspended in a 0.5 M NaCl solution (0.5 g/100 ml) and stirred for 2 min; pH was checked or adjusted with 0.1 M HCl. Enough soy oil was added prior to homogenization so that the volume at the inversion point totalled about

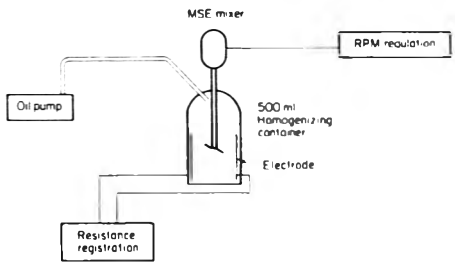

Figure 1. Experimental set up for measuring emulsification capacity.

200 ml, and so that the homogenizing time was approximately constant (3 min). A MSE mixer was used (MSE Scientific Instruments, England). The homogenizing time prior to oil addition from the dosing pump was 30 sec, and the addition rate was 18.5 ml/min (pump type ABU 11, Radiometer, Copenhagen). By means of the variable transformer, the revolution speed of the homogenizer could be varied. Recording of inversion point took place manually or automatically by measuring the electric resistance in the emulsion (Webb *et al.*, 1970). The capacity was calculated as ml oil/gram crude protein.

Emulsification activity and stability

The protein was suspended in 100 ml 0.5 M NaCl by stirring for 2 min. Then 50 ml of soy oil was added with subsequent homogenization at 10,000 rpm with

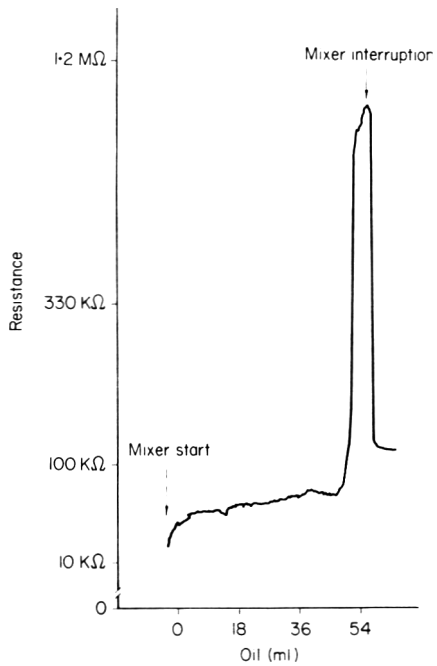

Figure 2. Example of continuous recording of resistance during emulsification.

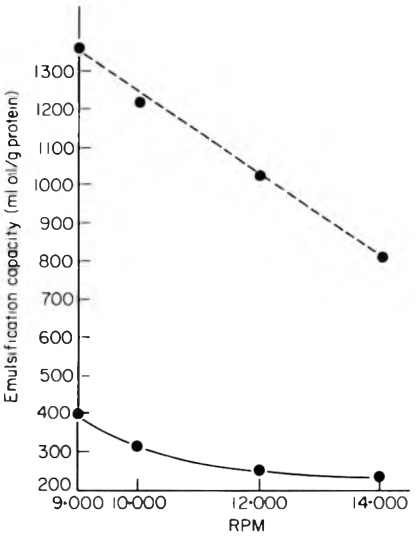

Figure 3. Effect of the rate of mixing on the emulsification capacity of PPC and soy isolate stabilized emulsions; 0.25 g protein/50 ml 0.5 M NaCl. ---, PPC; ——, soy isolate.

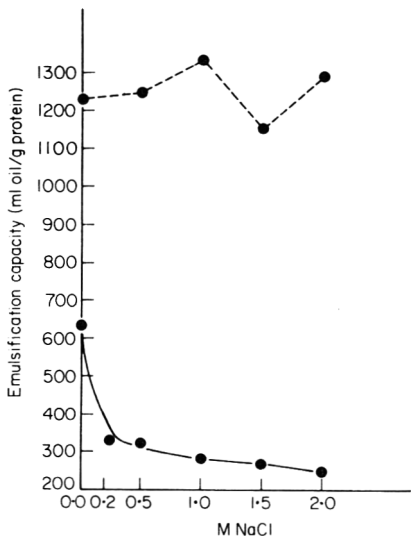

Figure 4. Effect of NaCl concentration on the emulsification capacity of PPC and soy isolate stabilized emulsions; 0.25 g protein/50 ml, speed of mixing 10,000 rpm; ---, PPC; ——, soy isolate.

the MSE mixer. At the same time the oil dosing pump was started (18.5 ml/min). This pump was switched off after addition of another 50 ml of oil. The homogenizer was disconnected after 3 min total time and then part of the emulsion was poured into two 50 ml measuring bottles. Total volume and volume of the aqueous layer after 1, 3 and 24 h standing were recorded. Activity was calculated as the volume of the emulsion after 24 h standing . . . as percentage of total volume.

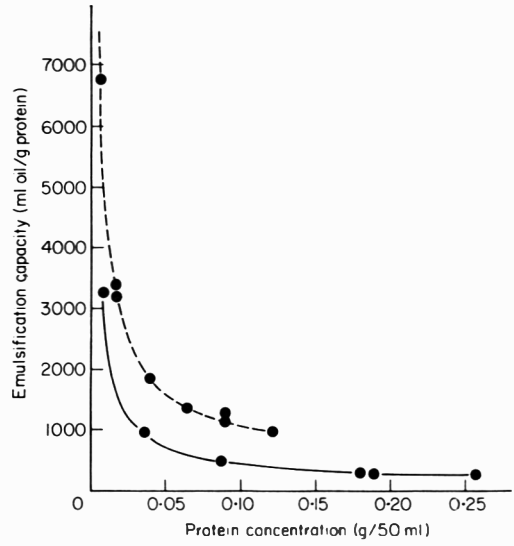

Figure 5. Effect of protein concentration on the emulsification capacity of PPC and soy isolate stabilized emulsions. Speed of mixing 10,000 rpm. ---, PPC; ——, soy isolate.

After 24 h the measuring bottles were heated for 10 min in a water bath at 80°C, cooled in iced water to room temperature and the stability was calculated as was the activity.

Emulsion viscosity

The protein was suspended in a 0.5 M NaCl solution by stirring for 2 min. The oil was added with subsequent homogenization at 10,000 rpm with the MSE mixer for 2 min. Total volume was 200 ml.

The added oil quantity totalled 50 or 90% v/v of the oil quantity determined by the capacity measurements.

The viscosity was measured on a Brookfield Viscometer (RVT) as a function of time from the start of the viscometer. The speed of the viscometer was 100 rpm or variable. Spindle 2 was used unless otherwise stated.

Results

Capacity

In some experiments the capacity was measured with a recorder by continuous monitoring of the resistance in the homogenizing cell. A typical example is shown in Fig. 2. The sudden resistance increase can be taken as an indication of inversion of the oil in water emulsion. The standard deviation of the capacity determination was determined to 3.1% of the mean value at 800 ml of oil/gram protein.

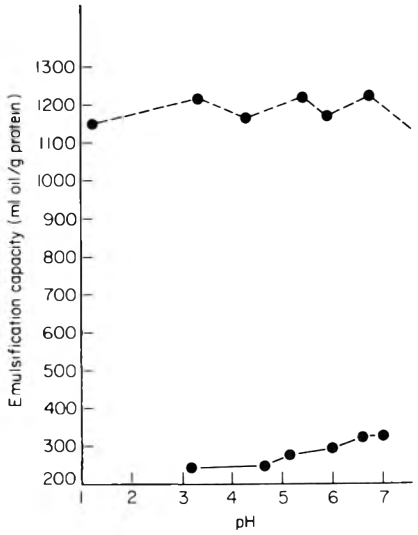

Figure 6. Effect of pH on the emulsification capacity of PPC and soy isolate stabilized emulsions; 0.25 g protein/50 ml 0.5 M NaCl. Speed of mixing 10,000 rpm. ---, PPC; ——, soy isolate.

The influence of the speed of the MSE mixer on the emulsification capacity of PPC and soy isolate in 0.5 M NaCl can be seen in Fig. 3. The very high capacities for potato protein were general for the complete study.

The capacity dependence of the NaCl concentration in the aqueous phase is shown in Fig. 4. Whereas the emulsifying ability of the soy isolate decreases strongly with increased NaCl concentration no significant change in the emulsification capacity of the potato protein is demonstrated. Because of the high emulsification capacity of the potato protein and consequent high viscosity near inversion it has been practically difficult to determine capacities of protein concentrations above 0.2 g PPC/50 ml of 0.5 M NaCl solution. This results in

Table 1. Effect of refining of PPC on the emulsification capacity

Protein product	Treatments	Protein percentage dry wt	Emulsification capacity (ml oil/g protein)	Capacity change after treatment (%)
PPC	None	43.9	1134	0
I	Dialysis	67.5	1712	+51.0
II	Extraction	45.9	1176	+ 3.7
III	Extraction + acid	44.5	857	−24.4
IV	Extraction + acid and heat	45.3	500	−55.9
V	Extraction + dialysis	85.2	1627	+43.5
Purina 500 E	None	92.4	321	—

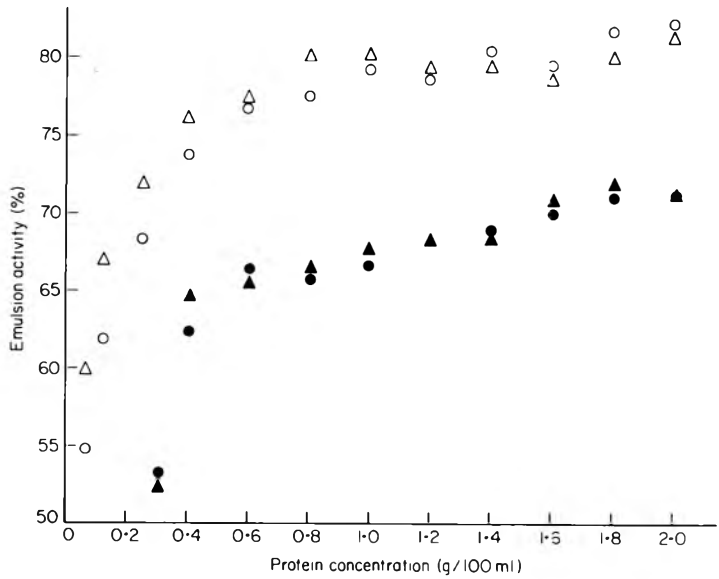

Figure 7. Effect of protein concentration on emulsion activity/stability of PPC and soy isolate stabilized emulsions. △, PPC; ○, PPC after heat treatment; ▲, soy isolate; ●, soy isolate after heat treatment.

increased standard deviations with increased PPC concentrations. Figure 5 shows the dependence of protein concentration on the emulsification capacity.

The pH-dependence on the emulsification capacities of PPC and soy isolate is shown in Fig. 6. Near the isoelectric point of the soy isolate, the emulsification capacity is low, whereas PPC does not show a significant decline at the isoelectric point (pH = 4.0).

The effect of dialysis, extraction, heat and acid treatments can be seen in Table 1.

The emulsification capacities of dialyzed samples (I and V) increase, whereas the removal of insoluble ingredients has no influence. The combination of heat and acid results in a more complete and irreversible denaturation than acid alone.

Activity and stability

Activity and stability of oil in water emulsions (50% v/v) stabilized by varying amounts of PPC and soy isolate are shown in Fig. 7. PPC has a high activity and stability compared to soy isolate and both proteins result in an excellent stability after heat treatment.

Table 2 shows activity, stability and capacity of various proteins at pH 4.5 and at the natural pH values of the proteins.

The activities and stabilities marked with an asterisk have at 50% v/v oil exceeded the inversion points because of the low capacity of the protein in question. Only undenatured potato protein has satisfactory stabilities at the given protein concentration.

Table 2a. Emulsifying properties of selected proteins. 0.15 g protein/50 ml o.5 M NaCl; pH = 4.5

Protein	pH	Activity (%)	Stability (%)	Capacity (ml oil/g protein)
PPC	4.5	75.8	73.6	847
Spray dried fruit water	4.5	74.4	72.3	799
Coagulated potato protein	4.5	52.2*	51.3*	261
Soy concentrate	4.5	52.7*	51.8*	274
Soy isolate	4.5	52.6*	51.8*	259

*Emulsification capacity is exceeded.

Table 2b. Emulsifying properties of selected proteins. 0.15 g protein/50 ml 0.5 M NaCl; Natural pH values

Protein	pH	Activity (%)	Stability (%)	Capacity (ml oil/g protein)
PPC	5.8	74.5	71.4	781
Spray dried fruit water	5.6	72.5	69.0	706
Coagulated potato protein	5.0	50.6*	50.3*	241
Soy concentrate	6.6	50.7*	50.0*	278
Soy isolate	6.8	52.2	52.4	350

*Emulsification capacity is exceeded.

Viscosity

The influence of different protein stabilizers on viscosity of oil in water emulsions was measured. The amount of added oil equals 90% of the emulsification capacity. Figures 8a and 8b show the time-dependent variation of the emulsions at pH 4.5 and at the natural pH values of the protein products.

The viscosity declines with time until an equilibrium value is reached. This is the case for all proteins except soy isolate, having an increased viscosity.

With an increasing oil content in the emulsions the equilibrium viscosity increases strongly until inversion point (Fig. 9). With the same percentage volume of oil in unbroken emulsions with PPC and soy isolate, the viscosity is highest for soy isolate emulsions.

If the protein concentration in emulsions containing oil corresponding to 90% of the capacity is increased, increasing viscosity is also found (Fig. 10).

Figure 11 shows the viscosity of the emulsions as function of 'shear rate'. The results show the pseudoplastic nature of the emulsions.

Discussion

The emulsifying properties of an unconventional protein are some of the most important functional properties when the protein is to be mixed in foods. The

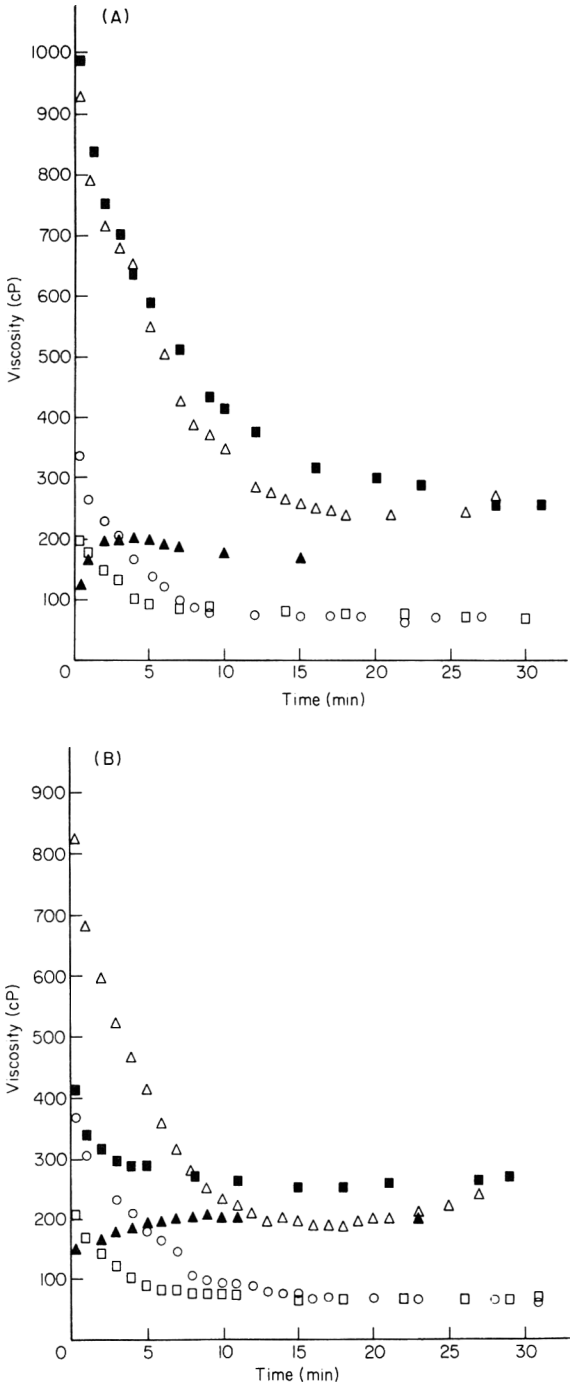

Figure 8. Effect of time on the viscosity of selected protein stabilized emulsions; 0.15 g protein/50 ml 0.5 M NaCl. (A): pH 4.5, spindle no. 4 is used for PPC and spray dried fruit water. (B): pH as in Table 2b, spindle no. 3 is used for PPC and spray-dried fruit water. △, PPC; ▲, soy isolate; ■, spray-dried fruit water; □, soy concentrate; ○, coagulated potato protein.

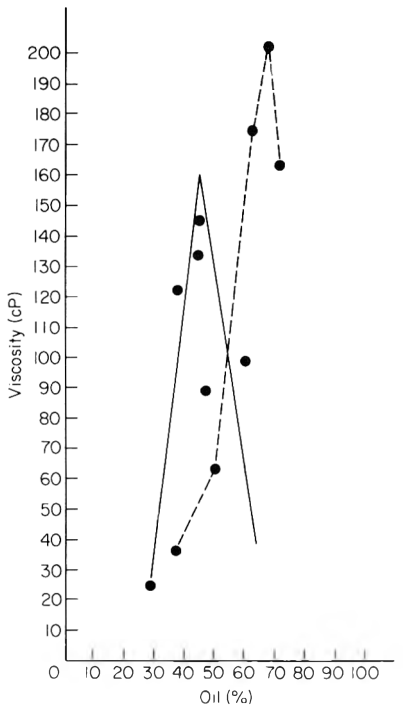

Figure 9. Effect of oil % on viscosity of protein stabilized emulsions for PPC and soy isolate; 0.1 g protein/50 ml 0.5 M NaCl. ---, PPC; ——, soy isolate.

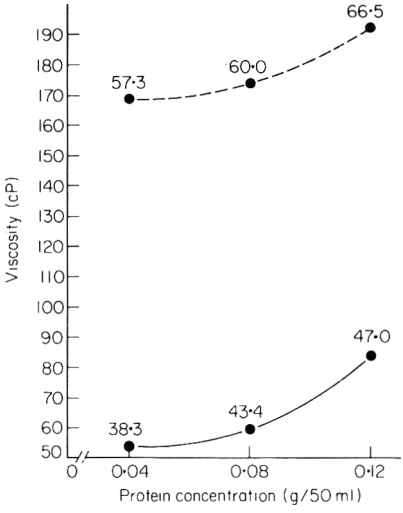

Figure 10. Effect of protein concentration on the viscosity and oil percentage (oil is added to 90% of emulsification capacity). Oil percentage at the different protein concentrations is shown in the figure. ---, PPC; ——, soy isolate.

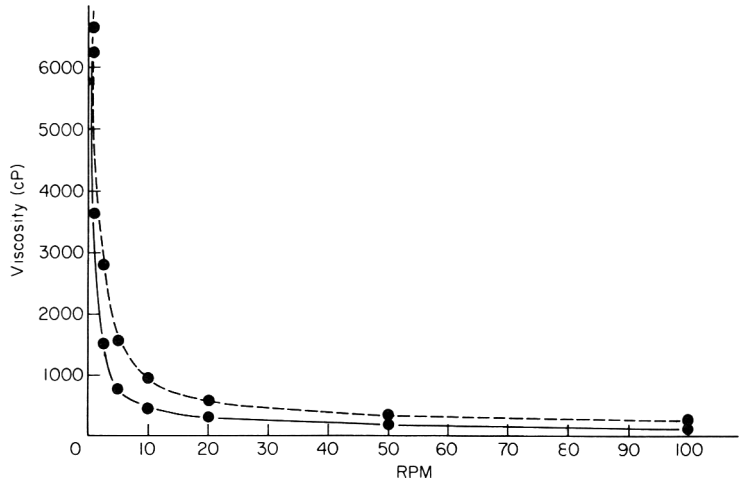

Figure 11. Effect of shear rate on viscosity of PPC and soy isolate stabilized emulsions. ---, PPC; ——, soy isolate.

results obtained with potato protein generally show that undenatured PPC is superior to a commercial soy protein product, which to-day is used to an increasing extent.

Emulsion capacity

Effect of mixing. Figure 3 shows a decrease in emulsification capacity with increased speed of mixing. These observations have previously been reported for meat emulsions (Swift *et al.*, 1961) and recently by Ramanatham, Ran & Urs (1978) for groundnut protein isolate emulsions. The superior capacity of potato protein is striking.

Effect of salt and pH. From a food point of view, it is interesting that the emulsification capacity of potato protein is independent of NaCl concentration and pH values (see Figs. 4 and 6). Usually vegetable proteins show poor emulsification properties at and around their isoelectric points (Ramanatham *et al.*, 1978).

The observed results for potato protein are due to the extreme high solubility (above 60%) of potato protein at the isoelectric point.

At increasing NaCl concentrations the emulsification capacity decreases considerably for soy isolate (Fig. 4). Similar results are reported for alfalfa protein (Wang & Kinsella, 1976) and groundnut protein concentrates (Ramanatham *et al.*, 1978). They also observed an increased emulsification capacity at very low NaCl concentrations.

Effect of protein concentration. The effect of increasing protein concentration on the emulsification capacity is shown in Fig. 5, where a progressive decrease is

noted. This effect has also been reported for soy protein (Franzen & Kinsella, 1976), caseinate, non-fat dried milk (Pearson *et al.*, 1965) and groundnut protein (Ramanatham *et al*, 1978).

Effect of purification. The results of different treatments of the potato protein concentrate on the emulsification capacity are summarized in Table 1. Dialysis which removed low molecular material has a high positive effect on the emulsification capacity (50% increase). Removal of water insoluble material has very little effect. The insoluble material mainly consists of starch granules and fibre material. Yatsumatsu *et al.* (1972) reported a negative correlation between emulsification capacity and fibre content of soy bean products.

Acid treatment, especially in combination with heat, of the protein extract decreases the emulsification capacity considerably. Even though the emulsification capacity is halved compared to no treatment it is still around twice as high as commercial soy isolate under the same experimental conditions.

Emulsion activity and stability. Figure 7 shows the emulsion activity and stability of PPC and soy isolate with increasing concentrations of the protein in the aqueous phase. The emulsion activity is higher for PPC than for soya and is most pronounced at low protein concentrations ($< 0.4\%$).

The emulsion stability of either protein after heat treatment is good. The emulsion stability of PPC stabilized emulsions is lower at very low protein concentrations. The emulsion activity and stability of different protein concentrates at a given protein concentration (0.3%) at pH = 4.5 and at natural pH values are shown in Table 2. PPC has the highest activity and stability of the tested concentrates. The values for soy isolate at least would have been higher, if a fixed protein concentration of 0.4% or higher was chosen (see Fig. 7).

Viscosity

Effect of time. It is well known that protein-stabilized oil in water emulsions show thixotropic characteristics. Figures 8a and 8b show the decrease, with time in viscosity to a final value.

The different behaviour of soy isolate is probably due to physical effects. The solubility of this concentrate in the aqueous phase prior to emulsification is dependent on the energy of dispersion for a given time. Although highly soluble this slow solubility process in combination with the slow diffusion of soy proteins to the interface (Tornberg, 1978) might explain the behaviour of soy isolate.

Effect of oil. The viscosity increase with increasing amounts of added oil at a given protein concentration (0.1 g/50 ml) in the aqueous phase is shown in Fig. 9. The sharp points at the curves illustrate the viscosities at the inversion points which coincide with the emulsification capacity. Transformation of oil percen-

tage (67% and 45% for PPC and Purina 500 E, respectively) to actual added ml of oil/g protein (1000 and 410 ml/g for PPC and Purina 500 E, respectively) produces results that fit the curves in Fig. 5.

With the same levels of oil added soy protein-stabilized emulsions show a much higher viscosity (prior to inversion) than PPC stabilized emulsions. This is probably due to the bridging effect of soy protein (Tornberg, 1978). The bridging concept means that a protein already adsorbed on a fat particle can extend far out in the continuous medium and adsorb on another fat globule creating an increase in the apparent viscosity.

Effect of protein. The effect of increasing amounts of protein in the aqueous phase on viscosity and oil percentage at 90% capacity of the protein-stabilized emulsions is seen in Fig. 10. For either protein concentrate the oil percentage and viscosity increase with increasing protein concentration. Similar results are reported by Crenwelge *et al*. (1974) for soy, cottonseed and non-fat dried milk.

Effect at shear rate. The viscosity very much depends on shear rate. Figure 11 shows the viscosity of protein-stabilized emulsions at different speeds of the viscometer. The decrease in viscosity with shear rate shows the pseudoplastic nature of these emulsions, which was also noted by Ramanatham *et al*. (1978) in the case of groundnut protein.

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Processing of maize and sorghum in Nigeria for human consumption

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Summary

Sorghum and maize are two of the major food grains grown and eaten in Nigeria. Production of these two crops averages about 4.5 million metric tons, this value representing approximately 56% of the total cereal grains produced in Nigeria for the past three years.

Although the production of these cereals has increased over the years, the effect has not been felt because of inadequate post-harvest technology especially in the area of processing. Maize and sorghum processing in Nigeria as in many other African countries is still by the traditional method of pounding in a mortar and winnowing. This method is usually performed by women, and is the major occupation for many of them. It is time consuming in that less than 2 kg of flour/hour/woman at an extraction rate of about 60% can be produced. The flour produced normally has a moisture content of 25–40% and with the rather hot climate the keeping quality is usually poor. The efforts being made through research and development to improve milling efficiency, increase the quantity of available cereal products, increase the shelf-life and eventual diversification of processed grains to replace fully or partially imported cereals for domestic and industrial uses are discussed.

Introduction

The strength of a nation depends on the wealth of food it can provide for its people. Feeding the millions of people in Nigeria has now become a problem of immense magnitude. The importation of food and live animals in 1970 amounted to a value of approximately 58 million naira (£50m sterling) while in 1974 the amount rose to 155 million naira (£123m sterling). The value of whole wheat and flour was 16 million naira in 1970 but increased significantly to 52 million naira (£41m sterling) in 1974 (Federal Office of Statistics, 1975). Barley, baby food, corn flour and semolina among others have also increased

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greatly. The recent programme of 'Operation Feed the Nation' launched by the Federal Government in 1976 showed the government's concern for the huge and unnecessary investment in importation of food to the detriment of agricultural and technological development. It is not a healthy reflection on the economy of a developing country to invest in the importation of food which can either be grown in the country and processed or for which suitable substitutes either partially or wholly are available.

Sorghum, rice, millet and maize constitute staple food grains available in Nigeria. In 1977 the total production of these cereal grains was 8.6 million metric tons grown over 13 million hectares of land. Sorghum is the main cereal crop in Nigeria, occupying 46% of the area applied to cereal cultivation and 44% of the total cereal production. Maize accounts for only 13% of the total harvest.

The processing of local cereal grains has not changed during recent years. Apart from the pilot plant milling of some of the local cereals at Maiduguri Pilot Flour Mill, milling of cereals is carried out by pounding in a wooden mortar and winnowing, as well as by small scale processing using motor operated mills located in corners of local markets (Muller, 1970). Our experience at the Federal Institute of Industrial Research and the reports of other workers (Perten, 1976) have shown that less than 2 kg of flour can be produced per hour per woman at an extraction rate of about 60% of the grain. Some water is usually added to facilitate milling, but this leads to an increase in the moisture content of the flour to about 25–40%. In tropical countries like Nigeria with high ambient temperatures, the keeping quality of such flour is very limited. The indigestible fibre is high because of this inefficient processing and this hinders the digestion of other constituents of the diet.

The rather low capacity of the traditional processing limits the quantity of locally processed cereal products available in the markets. Consumers therefore buy flours and grits of imported cereal grains. Steckle & Ewanyk in 1974 showed the preferential demand for local cereal grits and flour in a consumer preference study in grain utilization carried out at Maiduguri. Industrial processing and uses of local cereals in Nigeria is not carried out because of inadequate information on appropriate processing equipments and procedures.

Hahn (1969) reviewed the dry milling methods that have been tried on sorghum. They include roller milling, pearling, impacting, fine grinding and air classification. Unlike maize where the necessary commercial processing procedures have been documented (Stiver, 1954; Easter, 1969; Brekke & Kwolek, 1969) comparable commercial processing of sorghum for human consumption is not available.

For some time now, the Federal Institute of Industrial Research has been engaged in cereal processing research, during which useful information on the appropriate village and possible commercial processing of grains into products suitable for human food and for industrial uses has been obtained. This paper discusses some of the pilot plant processing trials of local cereals for diverse utilization and import substitution.

Materials and methods

Farmers' varieties of both maize and sorghum obtained from local dealers were used for this study.

Cleaning

A Shaw Wallace grain cleaner, No. 75101001, and the aspirator type MVSB were used for the cleaning.

Conditioning

At least 45 kg of the different types of cereal grains were conditioned by the addition of 2.5 and 3% water to maize, and 2 to 4% to sorghum and both rested for 10–15 min.

De-branning and degerming

The Buhler MKDA – 44/100 maize decorticator and the modified Ostad rice huller were used separately for maize processing. For the debranning of sorghum, two Binny Satake rice polishers were used one on top of the other. For convenience the first machine in which the first polishing was done was denoted machine 1, while the second which did the final polishing was denoted machine 2.

Drying, aspirating and grinding

An air dryer set between 50 and 60°C was used whenever necessary in drying the tailings and throughs from the degerming machine. A Buhler grain aspirator was used for the aspiration. The grits obtained were separated into various particle sizes by passing through a plansifter containing wire meshes of different sizes. Further reduction to flour and smaller grits was by grinding in either the Chakki type plate grinder or the Buhler Laboratory Flour Mill type MLU – 202. The yield in each case was recorded and samples taken for analysis.

Chemical Analysis

The AACC (1969) methods of analyses were used in the determination of dry matter, protein, oil, ash and crude fibre.

Industrial uses

The methods reported by Olatunji (1977) were used for bread-making and the determination of hot water extract.

Table 1. Chemical composition of local farmers' varieties of maize and sorghum (whole kernel)

	Maize	Sorghum
Moisture (%)	10.8	10.9
Protein ($N \times 5.7$) %	9.7	11.2
Ash (%)	1.4	1.7
Oil (ether extract) (%)	4.4	4.0
Fibre (%)	1.9	1.8

Results and discussion

The chemical composition of the varieties of maize and sorghum used in this study is shown in Table 1. There were slight differences in the relative proportions of protein, ash; oil and crude fibre.

Results of using two different machines and moisture additions on yield of debranned and degermed maize grits are presented in Table 2. Yield of grits with less than 1% oil was about 60%. There was an additional 5–10% increase in yield when oil was around 1.5%. These results are similar to previous reports by Wyss (1974) and Olatunji (1977). The yields reported for the modified Ostad Huller were higher than the corresponding values for the maize decorticator. The difference might be related to the capacities of the two machines and the quantities of grains used. The capacity of the decorticator is 1500 kg/hr while the Ostad Huller is 200 kg/hr. The decorticator now sells for about ₦ 6000 while the Ostad Huller is about 6% of this amount. The relatively low cost of the Ostad Huller, the high efficiency of the machine coupled with simplicity of operation makes it an ideal machine for small scale industries especially in the villages.

Sorghum milling results (Table 3) show the suitability of the Satake rice polishers for polishing sorghum. Yields of over 80% were obtained for the three different moisture levels investigated, and polishing in all cases was above

Table 2. Average yield of maize grits with different moisture additions and different processing equipment

		Maize decorticator MKDA 44/100		Modified Ostad Rice Huller	
Weight of corn used	(kg)	56.0	56.0	57.7	57.7
Moisture added	(%)	2.5	3.0	2.5	3.0
Grit yield with less than 1% oil	(%)	60.0	59.5	59.5	58.9
Grit yield with between 1 and 1.5% oil	(%)	70.4	69.2	74.8	74.0
Degree of polishing	(%)			above 98 for all	

Table 3. Average yield of polished sorghum with different moisture additions.

		1	2	3
Weight of sorghum used	(kg)	47.0	46.5	47.0
Extra moisture added	(%)	2	3	4
Polished sorghum	(%)	85.0	83.1	81.3
Bran removed 1st machine	(%)	8.9	10.3	11.2
2nd machine	(%)	6.1	6.6	7.5
Degree of polish				
1st machine	(%)	72	75	80
2nd machine	(%)		above 96 for all	
Percent breakage				
1st machine	(%)	2.0	2.3	3.1
2nd machine	(%)	7.6	8.6	9.8

96%. Kapasi-Kakama (1976) and Viraktamath, Raghavendra & Desikachar (1971) obtained comparable results using a Cecoco model F grain polisher and a rice polisher respectively.

The grinding of decorticated maize and sorghum is a technique for pulverizing the grains to the desired granulation, which varies for different uses. In the preparation of local dishes such as couscous, koko and tuwo cereal grains of different granulations are needed.

Various granulations are similarly required for industrial uses such as flour for bread production and grits in beer brewing. Two major products, flour and pollard are obtained by using the Buhler laboratory mill but many products of different particle sizes are possible with the Chakki plate grinder (Table 4).

Table 4. Average grinding results with Chakki plate grinder and Buhler mill.

	Maize (%)	Sorghum (%)
Chakki plate Grinder		
−44 Sieve size and above	10.0	11.4
−30 + 44 ,,	47.2	47.0
−22 + 30 ,,	25.9	26.5
−22 ,,	16.9	15.1
Buhler mill (2 runs)		
Flour	53.1	54.6
Pollard	41.8	42.4
Bran Section	5.1	3.0

Table 5. Effect of debranning and degerming on the chemical composition of sorghum and maize.

	Oil (%)	Protein (%)	Crude fibre (%)	Ash (%)
Sorghum (unpolished)	4.0	11.2	1.8	1.7
Polished sorghum (machine 1)	3.6	11.0	0.9	1.4
Polished sorghum (machine 2)	2.4	10.8	0.7	1.1
Maize (not processed)	4.4	9.7	1.9	1.4
Maize (debranned)	4.1	10.0	1.2	1.0
Maize degermed less than 1% oil	–	8.2	0.7	0.3
Maize degermed between 1–1.5% oil	–	8.8	0.9	0.6

Products that pass through the −44 sieve contain the flour and fine meal suitable for preparing koko, tuwo and bread. The product from the −30 + 44 wire mesh is the semolina. The −22 + 30 sieve size products with some of the smaller particle sizes are suitable as adjuncts for beer brewing, and used locally for the preparation of burabusco.

The effect of processing on the chemical composition of sorghum and maize is presented in Table 5. Perten (1976) and Desikachar (1976) have shown reductions in oil, protein, crude fibre and ash contents of processed cereal grains. However, pearling seems to improve the appearance of the grains and the traditional dishes prepared by using the flours and grits have improved eye and taste appeal.

Goussault & Adrian (1976) showed that the reduction in the indigestible glucide materials during pearling as shown in Table 5 enhanced higher digestibility of the pearled products.

Results of the industrial utilization of maize and sorghum (Table 6) show the possibility of using the flour of both maize and sorghum in breadmaking. Substitution of the wheat flour with 10% sorghum or maize flour gave acceptable bread. The corn grits (brewers grits) tested for beer brewing also showed encouraging results as previously reported by Olatunji (1977).

Conclusion

Our investigations have shown that the application of today's technological knowledge in grain milling can be purposefully adapted to replace local processing procedures. The processed products have improved appearance and acceptability because of the removal of almost all the bran. The reduction in oil is an indication that the products will keep for a long time and can successfully be used for products desiring low oil content. As a result of the large production capacities of the machines, more processed products will be available for household and diverse industrial utilization and reduce the reliance on imported cereal grains.

Table 6. Results on trials with dry-milled maize and Sorghum products for industrial uses

		Gluten (%)	Specific volume of bread (cc/g)	Total Bread Score (%)	Acceptability of bread	Hot water extract lb/quarter of malt (336 lb)	Specific Gravity 20°/20°
Composite Flour							
10% Sorghum	+ 85% GP + 5% SF	10.3	3.6	76	Acceptable	–	–
20% ,,	+ 75% ,, + 5% ,,	8.9	3.1	60	Not acceptable	–	–
* 10% Maize	+ 85% ,, + 5% ,,	10.3	3.4	77	Acceptable	–	–
* 20% ,,	+ 75% ,, + 5% ,,	8.9	2.8	56	Not acceptable	–	–
* 100% GP		12.4	4.0	83	Acceptable	–	–
Combinations of barley malt and corn grits (brewers grits)							
* 50% CG	+ 50% BM	–	–	–	–	88	1025.9
* 40% CG	+ 60% BM	–	–	–	–	88	1025.9
* 100% Malt		–	–	–	–	92	1027.2

* Source Olatunji 1977.
GP = Golden Penny flour; SF = soy-bean flour; CG = corn grits; BM = barley malt.

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Applications of high pressure liquid chromatography* to food analysis

R. MACRAE

Summary

High pressure liquid chromatography (HPLC) is becoming widely accepted as an invaluable technique for the analysis of many food components. In many instances HPLC methods have replaced laborious analyses and, in general, the chromatographic methods are more specific and precise, coupled with a significant reduction in analysis times.

A number of articles, e.g. Battaglia (1977), Rapp & Ziegler (1975), Wildanger (1975a) and Saxby (1978a,b), have been written reviewing the applications of HPLC to food analysis, but these have not covered the literature comprehensively. This is attempted here, preceded by a brief description of the methodology and instrumentation of HPLC.

Methodology and instrumentation

The basic HPLC chromatograph consists of a solvent supply, a pump, an injection system, a column and a detector coupled to a chart recorder, as shown in Fig. 1.

The solvent reservoir may be any convenient vessel, but provision must be made for degassing the solvent, either by application of vacuum or heat or by ultrasonification. Failure to degas solvents, particularly protic solvents, may lead to air bubble formation in the detection cell, with consequent disruption of the chromatogram.

Chromatographic pumps are of two main types, constant pressure or constant displacement. Usually the former is air driven and pneumatically amplified and the latter reciprocating and electrically driven. Constant pressure pumps often have a large 'hold-up' column, which makes rapid changes of solvent difficult;

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*The terms 'high pressure liquid chromatography', 'high performance liquid chromatography' and 'highspeed liquid chromatography' are synonymous. In this paper the abbreviation HPLC is used to cover these, and all other expressions, describing chromatography with microparticulate columns.

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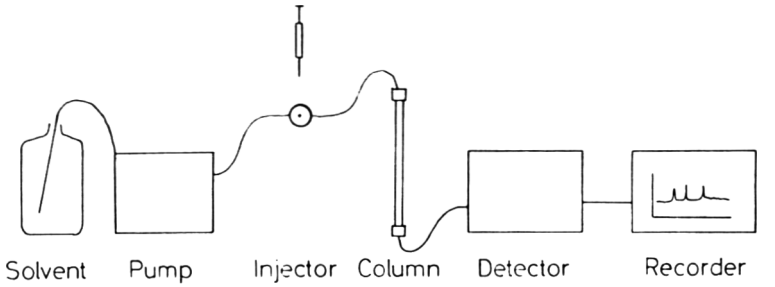

Figure 1. Basic HPLC system.

also they are less suitable for gradient programming. Single-headed constant displacement pumps give rise to a pulsed output and a pulse dampener is required. Alternatively, a twin-headed pump may be used with the pistons 180° out of phase to give an essentially pulse free output. The flow produced by this type of pump is governed by the speed of the electric motor, which is readily controlled electronically to provide a gradient (see below). A three piston pump has been produced which is reported to provide a more uniform flow (Mori, 1977).

Most pumps, of either type, provide a maximum flow of 10 ml min^{-1}, which is adequate for the vast majority of applications using analytical columns (4–5 mm i.d., 25 cm long). Maximum operating pressures are in the order of 400 bar. In general, constant displacement pumps give greater reproducibility and, apart from their increased cost, are to be preferred.

Sample injection onto the column may be carried out by one of two main methods, 'on column' or via a valve. The former mode, septum or septumless, allows the sample to be discharged from the syringe directly onto the top of the column. In this way the column can operate in the infinite diameter mode, which can lead to greater resolution than with valve injectors, Bristow (1976). The disadvantages associated with the use of septa include leaching from the septum material, leakage and needle blockage.

Injection valves, in which the sample is introduced into a holding-loop prior to application to the column, are more convenient in operation and can readily be automated, usually by pneumatic activation. However, the sample is further diluted before it reaches the column and it is not possible to take advantage of the infinite diameter effect. It is difficult to obtain reduced plate heights of two or three with valve injection, even on a column that is known to have this efficiency when used with a septum injector, Bristow (1976).

Analytical HPLC columns are usually constructed from stainless steel with zero dead-volume reducing unions at the ends. Typical lengths are 100–500 mm, most commonly 250 mm, with internal diameters of 3–5 mm. Larger diameter columns, 8 and 25 mm i.d., are used for preparative work. The range of column packing materials is described below.

A large range of detectors are currently available for use with HPLC systems, but of these only the ultraviolet detector, the fluorescence detector and the differential refractometer are in common use.

Ultraviolet detectors can operate at a fixed wavelength, usually 254 nm with a mercury lamp, or over the whole ultraviolet range, using a deuterium lamp. The fixed wavelength detector has a higher sensitivity, because of the greater intensity of incident radiation, but its applicability is limited. The variable wavelength detector can be adjusted to the wavelength of maximum absorption of the compounds of interest and in addition, some variable wavelength detectors have a tungsten source which extends detection to the visible region.

Fluorescence detectors are of limited applicability, but for those compounds that exhibit fluorescence the detection limit is often considerably lower than for ultraviolet detection Schroeder, Lechnir & Daun (1977). The sensitivity of the detector is significantly increased by using a flow cell packed with a solid support Zimmerli (1977a).

The refractometer has been called the universal detector, as it responds to all compounds that cause the refractive index of the column eluent to be different from that of the solvent. However, its sensitivity is considerably less than that of ultraviolet or fluorescence detectors and thus is only used when these detectors are not suitable, for example, in the analysis of sugars or oils.

Several other detectors have been used in HPLC including electrochemical devices and transport systems coupled to flame ionization detectors and more recently mass spectrometers.

The output from the detector is fed to a chart recorder or possibly, where routine analyses are being carried out, to a data handling/integration system.

The versatility of HPLC can be extended by gradient elution in which the composition of a binary solvent mixture is changed throughout the chromatographic run. A second pump is usually required, and the shape of the gradient is governed by the rate of change of pumping speed of each pump. A typical gradient system is shown in Fig. 2. Such a system can also be used for flow-programming, in which the rate of flow of the solvent, rather than its composition, is changed throughout the analysis. This is particularly useful where refractive index detection is employed, as gradient elution is clearly not possible.

The majority of HPLC analyses are carried out with the column at room temperature. However, there is clear evidence e.g., Macrae (1978), that temperature has a significant effect on the chromatographic parameters, so that for reproducible chromatography it is essential that a constant column temperature is maintained. This is particularly important where quantification depends on peak height comparisons. Column temperatures may be maintained by ovens, heated blocks or water jackets.

The wide range of chemical compounds that are analysed as food components means that a wide range of differing column packing materials come into consideration. The most commonly used stationary phase is silica, which may be used unmodified, where the chromatographic process is one of adsorption, or a

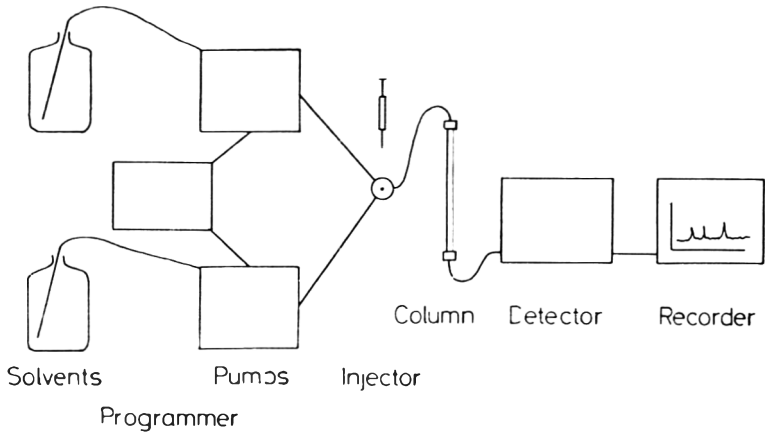

Figure 2. Gradient elution HPLC system.

silica modified by bonding functional groups to the silanol groups to give a partition system. Silica can be used with a wide range of solvents covering a large polarity range, although very polar compounds, such as amino acids or sugars, are more conveniently chromatographed on modified silica phases. When the group bonded to silica is hydrophobic in nature, for example a C_{18} group, the stationary phase operates in a reverse phase mode, where the less polar (more hydrophobic) compounds are more stronly retained.

The bonded functional group may possess ion exchange properties, for example, a sulphonic acid group, and these stationary phases are used for ionic food components, such as amino-acids or nucleotides. Alternatively ionic compounds can be chromatographed as ion-pairs using an appropriate counter-ion and a reverse phase column.

Gel-filtration is not common in HPLC, mainly because of the lack of suitable rigid stationary phases, although some separations using controlled pore glass have been attempted.

Carbohydrates

Simple sugars, mono- and disaccharides, can readily be analysed by gas chromatography after conversion to the more volatile trimethylsilyl derivatives. However, oligosaccharides, for example raffinose and stachyose, are not so amenable to this technique and a precision of only *ca* 10% is obtained (Delente & Ladenburg, 1972). HPLC does not require derivatization prior to analysis with the result that the speed of analysis and precision is improved.

The majority of analyses, both for simple sugars and oligosaccharides, use partition chromatography on a silica bonded phase, either with amino functionality (Conrad, 1975; Conrad & Palmer, 1976a,b; Jones, Burns & Sellings, 1977), or cyano-functionality (Rabel, Caputo & Butts, 1976), although some

earlier work used partition chromatography with ion-exchange resins in the salt form (Lawrence, 1975; Rapp, Bachmann & Ziegler, 1975). The most commonly used detector is the differential refractometer, (for example, Conrad, 1975), although it is possible to use ultraviolet detection at 190–200 nm (Gibson, 1978). Greatly improved sensitivity may be obtained by preparing derivatives that absorb strongly in the ultraviolet or visible regions (Nachtmann & Budna, 1977). However, the increased sensitivity is coupled with an increase in complexity of the method.

HPLC does not provide the answer to all sugar analyses in foodstuffs, as even some simple sugars are not readily separated by this technique, for example D-glucose and D-galactose (Linden, 1976).

The major problem in applying HPLC, or any other chromatographic technique, to the analysis of sugars in food materials is in obtaining an extract free of interfering compounds. This may involve the removal of fat (Celga & Bell, 1977) or protein (Macrae & Zand Moghaddam, 1978). In certain instances it is possible to use a pre-column to remove the intefering compounds (Timbie & Keeney, 1977; Fitt, 1978), in this way the column life is also greatly extended.

HPLC has been used for the analysis of sugars in many food commodities, including fruit juices (Schwarzenbach, 1977a; Conrad, 1975; Linden, 1976) wines (Rapp, Backmann & Ziegler, 1975), beverages (Conrad & Palmer, 1976a; Schwarzenbach, 1977), confectionery (Nachtmann & Budna, 1977; Hunt *et al.*, 1977; Hurst & Martin, 1977; Timbie & Keeney, 1977), honey (Schwarzenbach, 1977; Thean & Funderburk, 1977; Conrad & Palmer, 1976a, 1975; Fitt, 1978), legumes – mainly soya (Conrad & Palmer, 1976a; Havel *et al.*, 1977; Black & Bagley, 1978; Jones *et al.*, 1977; Macrae & Zand Moghaddam, 1978), dairy products (Conrad & Palmer, 1976a, 1966b; Lawrence, 1975; Hurst & Martin, 1977; Jones *et al.*, 1977), cereals (Jones *et al.*, 1977) and oil seeds (Celga & Bell, 1977).

HPLC has also been used extensively to study the breakdown of polysaccharides both for the production of syrups and the utilization of carbohydrate wastes (Wu *et al.*, 1976; Andren, Mandels & Medeiros, 1975, 1976; Richter & Woelk, 1977).

Lipids

The separation of lipids into their various classes, based on differences in polarity, has been achieved by a number of workers, (e.g. Aitzetmueller, 1975; Kiuchi, Ohta & Ebine, 1975). However, individual lipid classes have not been extensively studied by HPLC, mainly because alternative methods of analysis, in particular g.c., have proved adequate, although in some areas it has been shown that HPLC can provide additional information.

Triglycerides may be chromatographed directly with the degree of retention depending both on the number of carbon atoms in the molecule and the extent of unsaturation (Wada, Koizumi & Nonaka, 1977; Aitzetmueller, 1977; Platt-

ner, Spencer & Kleiman, 1977; Karleskind *et al.*, 1978). Furthermore it is possible to isolate the pure triglycerides for determination of their fatty acid composition after conversion to their corresponding methyl esters. The latter part of the analysis may conveniently be carried out by g.c. (Plattner, Spencer & Kleiman, 1977).

A number of papers have shown the ability of HPLC to separate *cis/trans* isomers, for example the separation of all *cis* linoleic acid (Kroll & Mieth, 1977). Another area where HPLC has been used to study isomeric mixtures is in the analysis of the products of oxidation of unsaturated fatty acids (Chan & Levett, 1977a,b; Chain, Prescott & Swoboda, 1976). In these studies it was possible to detect the hydroperoxides formed, which would not have been possible at the elevated temperatures required for g.c. A further example of this advantage is the analysis of epoxy glycerides in trivernolin (Plattner, Wade & Kleiman, 1978).

Most of the recently published separations make use of reverse phase microparticulate partition columns, although some of the earlier work used pellicular reverse phase columns (Scholfield, 1974, 1975a,b). Refractive index detectors are most commonly used, but with the advent of variable wavelength detectors capable of operating at 200 nm a number of separations using ultraviolet detection have been published (Perkins, 1977).

Other applications of HPLC to lipid analysis include vegetable oil unsaponifiables (Cortesi *et al.*, 1977), Jojoba liquid wax esters (Spencer, Plattner & Miwa, 1977), fats (Siouffi, 1974), fatty acids (Cooper & Anders, 1975) and phospholipids (Hax & Geurts Van Kessel, 1977; Fager, Shapiro & Litman, 1977; Cavina *et al.*, 1972).

Vitamins

Vitamin analysis is one of the main areas of expansion in HPLC methodology. In general vitamins are not amenable to g.c. analysis and bio-assays are time consuming with poor reproducibility. Consequently the high speed and precision of HPLC should have a large impact on this area of analysis (Kirk, 1977).

The complete range of vitamins, from the water soluble vitamin C to fat soluble vitamin A, can be separated in a single chromatographic run using a reverse phase packing and a wide polarity gradient (Saxby, 1978b). However, in most food applications the extracts are contaminated with other compounds and thus it is more usual to develop a chromatographic procedure for a specific vitamin, or a group of chemically similar vitamins.

Ultraviolet detectors are most commonly used with the wavelength chosen to correspond to the maximum absorption of the compound of interest. However, for those vitamins that show fluorescence a large increase in sensitivity is obtained by using a fluorimeter as detector, for example the sensitivity of the analysis of riboflavin is greatly increased in this manner (Slavin, Williams & Adams, 1977).

The water soluble vitamins are commonly analysed by ion exchange chromatography. In this way ascorbic acid, thiamine, riboflavin and nicotinic acid have been determined in a variety of foods (Floridi *et al.*, 1976; Williams, Daker & Schmitt, 1973; Baker, Williams & Steichen, 1974). Riboflavin, as mentioned above, has a native fluorescence, but thiamine must be oxidized to thiochrome with alkaline ferricyanide before detection by fluorescence. Folic acid, and natural folates, have also been studied using anion-exchange, (e.g. Clifford & Clifford, 1977; Reed & Archer, 1976). In addition to ion-exchange chromatography paired ion chromatography has been used for the determination of water soluble vitamins. The acid is converted into a hydrophobic ion-pair by salt formation with a quaternary ammonium ion containing hydrophobic groups, for example cetyltrimethylammonium. The ion-pair is then chromatographed in a reverse phase mode. This method has been applied to the determination of ascorbic acid, and other vitamins, in a variety of foods (Sood *et al.*, 1976; Wills, Shaw & Day, 1977).

Early methods used to study the fat soluble vitamins, in particular carotene stereoisomers in vegetables utilized columns of calcium and magnesium hydroxides (Sweeney & Marsh, 1970a,b). However, many more recent papers have been published for the determination of vitamin A and carotene isomers on a variety of columns, including alumina (Van De Wierdhof, Wiersum & Reissenweber, 1973), silica (Dennison & Kirk, 1977) and reverse phase material (Thompson & Maxwell, 1977; Soderhjelm & Andersson, 1978). Vitamin A has a natural fluorescence and this is the method of detection to be used where possible, although a large number of papers have been published using ultraviolet detection, (e.g. Dennison & Kirk, 1977; Maruyama *et al.*, 1977). Isolation of vitamin A from foodstuffs involves extraction of the unsaponifiable material with ether or hexane. The extract is then used directly for chromatography, though in some instances a further pre-column clean-up may be necessary. The above methods have been applied to a wide range of foods including; butter and margarine (Egberg, Heroff & Potter, 1977), orange juice (Reeder & Park, 1975; Stewart, 1977a,b) and eggs, cereals and infant foods (Dennison & Kirk, 1977).

In the analysis of vitamin D it is the determination of the bio-active form D_3 that is required. Colorimetric methods are not specific to vitamin D_3 and consequently do not measure the true amount of active vitamin D present. A number of papers have been published showing the separation of vitamin D_3 from D_2 and its precursors (Wiggins, 1977; Hofsass *et al.*, 1976; Antalick, Debruyne & Faugere, 1977) and also certain papers where total vitamin D is determined (Thompson, Maxwell & Abbe, 1977; Rueckemann & Ranfft, 1977). Columns used in the determination of vitamin D include silica (Rueckemann & Ranfft, 1977), octadecylsilane reverse phase material (Wiggins, 1977) and ion-exchange material used in a partition mode (Hofsass *et al.*, 1976). Detection is normally by ultraviolet absorption.

In order to obtain a sufficiently clean extract to realize the fine separation between vitamins D_2 and D_3, the crude extract must be further treated before

analysis by HPLC. The methods used include chromatography on silica-gel (Wiggins, 1977), Hyflo supergel and magnesia (1:1) followed by alumina (Antalick, Debruyne & Faugere, 1977), or celite followed by Florex XXS (Rueckemann & Ranfft, 1977). In general the nature of the clean-up process must be dictated by the food to be analysed. HPLC determination of vitamin D compares favourably with established techniques and is more rapid (Hofsass *et al.*, 1976). The method has been applied to milk (Thompson, Maxwell & Abbe, 1977), oils (Hofsass *et al.*, 1976), vitamin concentrates (Rueckemann & Ranfft, 1977).

The large number of components of vitamin E, α-, β-, γ and δ-tocopherol and the four tocotrienols, complicates the analysis of this vitamin. However, early papers, for example Williams, Schmit & Henry (1972) and Van Niekerk (1973), met with partial success and subsequently methods allowing separation of all eight forms of vitamin E on a silica column have been published (Van Niekerk, 1974). HPLC has been used for the determination of tocopherols in vegetable oils (Abe & Katsui, 1975; Abe, Yuguchi & Katsui, 1975) using partition chromatography and fluorimetric detection. In addition the technique has been used to study the thermal dimerization of tocopherols during the course of oxidation of saturated and unsaturated triglycerides (Fujitani & Ando, 1977a,b).

Flavour and odour compounds

The majority of the important flavour and odour compounds are volatile and hence amenable to analysis by g.c. In particular the high resolution realized by capillary column g.c. has been used to advantage in the analysis of many complex mixtures of odour and flavour compounds. However, there are certain groups of compounds with low volatility but nonetheless possessing important flavour properties, and it is in these cases that HPLC will prove to be more useful than g.c. One area where extensive use of HPLC to the analysis of flavour compounds has been made (Siebert, 1972; Conrad & Fallick, 1974), is in the brewing industry. The amounts of humulones and lupulones in hops is of importance to the final quality of the beer. A large number of papers have been published studying these acids and other flavour compounds in hops, wort and beer, for example, Bellean & Dadic (1974), Bruckner *et al.* (1974), Erdal & Hartlev (1973), Charalambous (1974), Charalambous *et al.* (1974a,b), Charalambous (1973), Palamand & Aldenhoff (1973), Bruckner *et al.* (1973), Molyneux & Wong (1972, 1973) and Slotema, Verhagen & Verzele (1977). The published separations utilize both adsorption and reverse phase partition chromatography, mainly with ultraviolet detection.

Furanocoumarins, of which bergapten is the most widely distributed example, are toxic and their determination in a variety of foods, particularly in essential oils, is frequently required. Shu *et al.* (1975) published a method using an octadecyl bonded stationary phase. However, it was found that silica gave a clearer separation from other compounds present in some essential oils Shu,

Walradt & Taylor (1975). An earlier paper by Stermitz & Thomas (1977) described the separation of furanocoumarins in parsley. Coumarin itself has also been determined in vodka (Benk & Treiber, 1977) and with vanillin in a variety of foods (Kamata *et al.*, 1976).

The determination of naringin and limonin, the bitter components in grapefruit, has been published in a series of papers using reverse phase partition chromatography (Fisher, 1975, 1978; Fisher & Wheaton, 1976).

Further examples of the use of HPLC in the analysis of flavour compounds include piperine in peppers (Lee *et al.*, 1976; Galetto, Walger & Levy, 1976; Cleyn & Verzele, 1972, 1975), methyl anthranilate in grape beverages (Rhys Williams & Slavin, 1977), beef aroma (Schmit, Henry & Williams, 1972; Lee & Chang, 1975; Chang, 1972; Charalambous *et al.*, 1973), citrus fruit essential oils (Schmit, Williams & Henry, 1973), sesame oil (Takei *et al.*, 1969), cinnamon oil (Ross, 1976), purple passion fruit (Murray, 1972), flavour chemicals (Walradt & Shu, 1972), quinine in soft drinks (Frischkorn & Frischkorn, 1976), marigold extracts in orange products (Wild & Dobrovolny, 1976a,b; Benk, Treiber & Bergmann, 1976), cheese (Piergiovanni & Volonterio, 1977) and groundnuts (Wu, 1977).

A further area that has been extensively studied is the determination of alkaloids in beverages. Methods have been published for the analysis of alkaloids in tea (Hoefler, 1976), coffee (Madison, Kozarek & Dame, 1976), cocoa beans (Timbie, Sechrist & Keeney, 1978) and chocolate (Wildanger, 1975b, 1976).

Nucleotides are important flavour compounds and have been studied, mainly by ion-exchange techniques by a number of workers, e.g. Weatherby (1975), Bennett (1977) and Heyland & Moll (1977).

Toxic compounds

(a) Mycotoxins

The most widely encountered mycotoxins in foods are the aflatoxins, metabolites of *Aspergillus flavus*. The determination of these compounds in a wide variety of foods has formed the basis of a large number of papers. An early paper by Seitz (1975) showed that the four naturally occurring aflatoxins could be separated on a microparticulate column of silica. Ultraviolet detection was used but an increase in sensitivity for the two G toxins can be achieved by the use of fluorescence detection. Several similar separations using silica have been published, e.g. Garner (1975) and Pons (1976) and also some papers using reverse phase partition, e.g. Takahashi (1977a,b).

Zimmerli (1977a) and Panalaks & Scott (1977) have shown that a considerable improvement in sensitivity for aflatoxins can be realized by using a fluorimeter flow cell packed with silica gel. Detection limits of 0.02 μg/litre in wine are claimed Zimmerli (1977a).

Aflatoxins have been determined in a wide range of foods including milk (Zimmerli, 1977b); groundnuts (Kmieciak, 1976; Panalaks & Scott, 1977; Diprossimo, 1976; Blanc, Midler & Karleskind, 1976; Karleskind, 1977; Lansden, 1977; Baker, Williams & Steichen, 1974), almonds (Zimmerli, 1977b), oils (Karleskind, 1977), rice (Lansden, 1977), corn (Seitz, 1975; Stubblefield & Shotwell, 1977; Diebald & Zare, 1977; Rao & Anders, 1973), cotton seed (Pons & Franz, 1977) and wines and fruit juices (Zimmerli, 1977a).

Several more general papers on the determination of aflatoxins in foods have also been published, e.g., Engstrom, Richard & Cysewski (1977), Williams, Baker & Larmann (1974) and Steichen (1975).

In addition to the extensive literature on the study of aflatoxins several other naturally occurring toxins have been investigated. These include patulin in apple juices (Ware, 1975; Tanner & Zanier, 1976; Stott & Bullerman, 1976), sterigmatocystin in corn and oats (Ito *et al.*, 1976; Stack *et al.*, 1976), rubratoxin (Engstrom, Richard & Cysewski, 1977), pimaricin in cheese (Frede, 1977), *alternaria* metabolites in grain and sorghum (Seitz & Mohr, 1976) and tenulin in milk, derived from *helenium amarum* (Ivie, Witzel & Rushing, 1975). These methods use mainly silica columns but in some cases reverse phase partition chromatography has also been employed.

(b) Nitroso-compounds

There is considerable interest in the quantification of specific nitroso-compounds in foods. Whereas g.c. can be used for the determination of volatile nitrosamines HPLC has found application for both volatile (e.g. Cox, 1973) and ionic compounds (e.g., Ross *et al.*, 1977). A comparison of g.c. with HPLC, even for volatile nitrosamines, has shown the latter method to be more rapid and at least as accurate as the former (Cox, 1973). A wide range of detectors have been used for nitroso-compounds, both non-specific, e.g., ultraviolet radiation (Green *et al.*, 1977) and specific, e.g., thermal energy analyses (Fine *et al.*, 1976a; Green *et al.*, 1977; Fine *et al.*, 1977a; Ross *et al.*, 1977). Other detection methods involve photohydrolysis, coupling the cleaved nitrite to a Griess reagent followed by detection of the dye formed at 548 nm (Green *et al.*, 1977; Hansen *et al.*, 1977; Singer, Singer & Schmidt, 1977). A further method employs pre-column derivitization of amines, formed from the nitroso-compounds, with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole and subsequent detection by fluorimetry (Wolfram *et al.*, 1977). The use of HPLC for the determination of nitroso-compounds has mainly been applied to bacon, e.g., Wolfram *et al.* (1977), Hansen *et al.* (1977), Green *et al.* (1977) and Fine *et al.* (1976b), although all the references cited above contain methods applicable to foods.

(c) Polynuclear aromatic hydrocarbons

HPLC has been widely applied to the determination of polynuclear aromatic hydrocarbons in foods. Due to their strong fluorescence certain of these com-

pounds can be detected at levels below 1 ng (Klimisch & Ambrosius, 1976; Schroeder, Lechnir & Daun, 1975). However, ultraviolet detection is adequately sensitive for many analyses (Schroeder, Lechnir & Daun, 1975).

The majority of the published methods use silica column, e.g., Guerrero, Biehl & Kenner (1976), although (Hunt, Wild & Crosby (1977) have developed a chemically bonded phase (phthalimidpropylsilane) specifically for the analysis of polynuclear aromatic hydrocarbons.

Applications of HPLC in this area include: drinking water (Johnson, Abu-Shumays & Abbott, 1977; Kasiske, Klinkmuelbr & Sonneborn, 1978), sea foods (Guerrero, Biehl & Kenner, 1976; Hunt, Wild & Crosby, 1977) and smoke condensates (O'Hara *et al.*, 1974; Radecki *et al.*, 1978).

(d) Pesticide residues

Over forty papers describing the application of HPLC to the analysis of a variety of pesticides have been published. All these references will not be detailed here as they will be included in a subsequent review.

Gas chromatography using an electron capture detector is more sensitive than HPLC for the determination of organochlorine pesticides (Lawrence, 1976). However, certain specific detectors, e.g. an electrolytic conductivity detector, have been used for the determination of organochlorine pesticides on lettuces (Dolan, 1976).

Many herbicides and insecticides are not amenable to g.c. analysis and it is in these cases that HPLC has proved most useful. For example the separation of a number of carbamate pesticides has been reported by several workers (Moye, 1975; Frei *et al.*, 1974; Lawrence, 1977; Dorough & Thorstenson, 1975). A series of papers has also been published on the determination of biphenyls and their metabolites in a variety of citrus products (Reeder, 1975).

Colourants and pigments

Many naturally occurring pigments have been studied by HPLC, e.g. pigments in citrus fruits (Stewart & Leuenberger, 1976) or spinach (Eskins, Scholfield & Dutton, 1977). In addition natural colourants used in processed foods have also been studied, e.g. carotenoid-containing plant extracts in orange drinks (Wild, 1976). However, the major interest has been in ascertaining whether synthetic dyes present in foods are permitted or not (Noda & Nishiki, 1977). A further important use of HPLC is the detection of impurities, which may be toxic, in synthetic dyes. Dyes that have been extensively studied include; tartrazine (Wittmer, Nuessle & Haney, 1975), F D and C Yellow No. 6 (Singh, 1974a; Marmion, 1975, 1977; Bailey & Cox, 1975) F D and C Red No. 40 (Bailey & Cox, 1976; Singh, 1974b), F D and C Red No. 2 (Singh, 1977a), F D and C Blue No. 2 (Singh, 1975) and Orange B (Singh, 1977b).

Most of the food colourants are water soluble acid dyes and hence are amenable to paired-ion chromatography using reverse phase partition columns. This would appear to be the most useful technique e.g. Wittmer, Nuessle &

Haney (1975). Dyes may be detected in the ultraviolet or visible regions but for those compounds which exhibit native fluorescence fluorimetry provides greater sensitivity.

Artificial sweeteners

Considerable interest has recently been directed to the possible toxicity of artificial sweeteners. Cyclamates have already been removed from the list of permitted sweeteners and there have been reports that saccharin also may not be entirely safe. Thus the detection and quantification of these compounds in foods is important and several methods have been published, mainly concerning saccharin, e.g. Nelson (1973, 1976), Smyly, Woodward & Conrad (1976), Ueta & Mazaki (1977), Tanaka *et al.* (1975), Eng. Calayan & Talmage (1977), Ciraolo, Calapaj & Clasadonte (1977) and Tenebaum & Martin (1977). Several of these papers, e.g. Ciraolo, Calapaj & Clasadonte (1977), Nelson (1973) and Ueta & Mazaki (1977), also report the quantification of benzoic acid. Other artificial sweeteners which have been analysed by HPLC include hesperetin (Seitz & Wingard, 1978) neohesperidin dihydrochalcone (Fisher, 1977) and aspartame (Fox, Anthony & Lau, 1976; Nizhizima *et al.*, 1976). The ionic nature of many of the artificial sweeteners leads to the successful application of ion-exchange chromatography.

Food additives (preservatives, antioxidants and emulsifiers)

Other food preservatives that have been studied by HPLC in addition to benzoic acid mentioned above, include sorbic acid in the following foods; bread (Terweij-Groen & Kraak, 1977), citrus juices (Bennett & Petrus, 1977) and wine (Eisenheiss, Weber & Ehlerding, 1977; McCalla, Mark & Kipp, 1977). A limited number of papers have appeared on the detection of antioxidants in fats and oils, e.g. Graciani (1975) and Lichtenthaller & Ranfelt (1978) and one paper on the analysis of naturally occurring antioxidants in rosemary and sage (Chang *et al.*, 1979).

Surface active compounds (emulsifiers) have similarly received only brief attention with two papers published Baur (1973) and Brueschweiler (1977).

Organic acids

In addition to the acids used as food preservatives naturally occurring organic acids can also be determined by HPLC (Mabrouk, 1976). Foodstuffs that have been analysed for their acidic components include: grape must (Stahl & Lamb, 1973; Rapp & Ziegler, 1976), hops (Vanhertum & Verzele, 1973), and raw sausage (List & Askar, 1976).

The use of malic acid as a food acidulant has been proposed with analysis being carried out by HPLC (Anon, 1977). Other applications in this area are the determination of quinic acid in bilberry juices as a criterion of authenticity

(Tanner & Peter, 1978) and monitoring insect infestation in cereals by determining traces of uric acid (Pachla & Kissinger, 1977).

Several methods for amino-acid analysis using HPLC have been proposed using reverse phase columns but in general dedicated amino-acid analysers using ion-exchange columns, many of which now use HPLC concepts, provide better resolution and more reliable analyses, e.g. Murren, Stelling & Felstead (1975). However, in some specific areas of amino-acid analysis HPLC has proved useful, e.g. the analysis of betaine in sugar products (Steinle & Fischer, 1978).

Miscellaneous

A large number of less important food components have also been studied using HPLC. The wide range of compound types that can be successfully analysed demonstrates the versatility of the technique, these include phenolic compounds (Wulf & Nagel, 1976; Tanaka *et al.*, 1976; Felice, King & Kissinger, 1976), sterols (Hesse, Pietrzik & Hoetzel, 1977; Kikuchi & Miki, 1978; Seitz *et al.*, 1977; Seitz & Paukstelis, 1977), anthocyanidins (Wilkinson, Sweeny & Lacobucci, 1977), gallotanin (Beasley, Ziegler & Bell, 1977), isoflavones in soybeans (West, Birac & Pratt, 1978), polyhydric alcohols in apple juice (Schwarzenbach, 1977b) and amine components in fish (Mietz & Kasmas, 1977, 1978).

Conclusion

Instrumentation and column packing materials available for HPLC have greatly improved in the last decade and advances in these areas will doubtless continue. However, in the majority of analyses of food components it is in the areas of extraction and sample preparation where there is greatest need for development. The chromatographic separation of standards is often readily achieved and problems are only encountered when food extracts are chromatographed.

Further improvements in detection systems can also be expected, in particular in the fields of 'universal detection' and fluorescence labelling.

HPLC has already made a significant contribution to the methodology of food analysis and this contribution will doubtless increase in the future.

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The aerobic microflora of the Scotch haggis

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Summary

The aerobic microflora of freshly purchased Scotch haggis was dominated by organisms identified with *Bacillus. Lactobacillus, Staphylococcus,* yeasts and moulds were also detected in significant numbers. On storage at 5,30 or 37°C for 3 weeks, spoilage of the haggis was accompanied by a drop in pH and a tenfold increase in numbers of general contaminants and lactic acid bacteria.

Introduction

The haggis is a Scottish dish traditionally prepared from the sheep's pluck (liver, lights and heart) mixed with fat, cereals and seasoning and cooked in the stomach bag. Nowadays haggis is produced on a large scale from whatever offals are most readily available. The offals are cooked, weighed, minced and mixed with the other ingredients. The mix is then extruded into the casing, which may be natural (i.e gut) or synthetic, the open ends are tied fast and the haggis is cooked at about 80°C, cooled by spraying with cold water and allowed to dry before distribution for sale.

The legislation which at present governs the haggis is reviewed in the *Food Standards Committee Report on Offals in Meat Products* (Anon., 1972). In this report, offal is considered in two categories. Prohibited offal is defined as brain, feet, fries, gut (including chitterlings), manifolds, paunches, udders, sweetbreads, tripe, melts, spinal cords, uteri, pigs' maws and calves' vells. These offals are prohibited in open uncooked meat products. Permitted offal is defined as any offal other than offal prohibited for use in open uncooked meat products.

An open meat product is defined as any product manufactured from meat and

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other ingredients, and which has not been canned. Uncooked is defined as being not subject to a process of cooking so as to render unnecessary any further cooking before human consumption. Haggis is quite clearly an open uncooked meat product. Nevertheless, it contains prohibited offals and the report (Anon., 1972) emphasizes that the traditional products, haggis and black pudding, are exempt from the restrictions which apply to the use of prohibited offals.

The rationale behind the creation of a category of prohibited offals is that these carry a higher bacterial load than meat itself and that the usual methods of handling and slaughter do not reduce that load. The nature of these ingredients and the method of manufacture of haggis suggest that the haggis may bear a substantial microflora, nonetheless to our knowledge there are no published accounts of the microbiology of haggis. This investigation set out to determine the numbers and types of microorganisms making up the dominant microflora of the Scotch haggis.

Materials and methods

The haggis used in this study were obtained from various retailers around Edinburgh. They varied in weight from 275 g to 650 g, all had natural casings.

Sampling

Haggis were sampled immediately on receipt in our laboratories or after storage at 5, 30 or 37°C for 3 weeks. A sterile scalpel was used to peel off a band of casing approximately 3 cm wide around the girth of the haggis. Samples weighing 5 g were aseptically taken either from the peripheral regions of the haggis (no more than 5 mm deep) or from the centre of the haggis.

Each sample of haggis was homogenized with 100 ml of ¼-strength Ringer's solution for 30 sec in a Colworth Stomacher 400. Serial dilutions were made in ¼-strength Ringer's solution.

Measurement of pH

Ten g of haggis were homogenized in 90 ml of distilled water and the pH measured using an E.I.L. 7020 pH meter.

General counts

General counts of the numbers of microorganisms in haggis were obtained by spreading 0.2 ml aliquots of the homogenate or dilutions thereof on well-dried plates of plate count agar (Oxoid). Plates were incubated at 25°C for 48 h.

Individual colonies were picked off plate count agar (PCA), checked for purity and streaked on slopes of nutrient agar. The morphology, colony characteristics and gram-reaction of each isolate was recorded.

Gram-negative types were identified according to the scheme used by Halls & Board (1973). Glucose breakdown was tested in the medium of Hugh & Liefson (1953). Motility was determined by the examination of a hanging drop preparation of an 18h peptone water culture using phase contrast microscopy, and the oxidase test was carried out according to the method of Kovac (1956).

Gram-positive rod-shaped bacteria were identified with *Bacillus* on the evidence of spore formation when cultures were examined microscopically. Catalase-negative rod-shaped gram-positive bacteria showing no evidence of spore formation were identified with *Lactobacillus*

Gram-positive cocci were examined for catalase production to distinguish catalase-negative lactic streptococci from species of *Staphylococcus* and *Micrococcus*. The catalase-positive types were distinguished from each other by the method of Baird-Parker (1966).

Selective Counts

Lactic acid bacteria were recovered on Rogosa agar. One ml aliquots of the homogenate or dilutions thereof were mixed with 15 ml of Rogosa agar and poured as plates, each plate once set was overlayed with a further 5 ml of Rogosa agar and incubated at 25°C for up to 5 days.

Yeasts and moulds were recovered in Rose Bengal chlortetracycline agar (Jarvis, 1973) incubated at 25°C for 7 days.

Staphylococcus aureus was recovered on mannitol salt agar (Oxide Code CM85) and on Baird-Parker (1962) medium. Inoculated plates of these media were incubated for 24 or 48 h at 37°C. Presumptive staphylococci were examined for coagulase production by the slide coagulase test of Williams & Harper (1946).

Faecal streptococci were counted by the most probable number method in tubes of azide dextrose broth (Difco Code B387) incubated at 45°C for 24 h.

A presumptive coliform count was done by the most probable number method in minerals modified glutamate medium (Oxoid) incubated at 37°C for 48 h. Enterobacteriaceae were also sought on plates of violet red bile agar incubated at 37°C for 24 h.

Results

Distribution of microorganisms in haggis

Table 1 shows the general counts on PCA from one freshly purchased haggis. Three samples were taken from the peripheral regions of this haggis and three from the centre. These counts were examined by analysis of variance. The hypothesis of no difference in counts between peripheral and central samples was rejected at the 5% level. The hypothesis of no difference between the individual central or individual peripheral samples could not be rejected. In

Table 1. The distribution of viable aerobic microorganisms recovered from a freshly purchased haggis

Region of haggis sampled	Colony counts/0.2 ml of 10^{-1} dilution of haggis homogenate spread on PCA	Mean estimate of numbers of viable aerobic microorganisms/g of haggis.
Peripheral (<5mm deep)	4, 14, 25	1.4×10^4
" " "	19, 22, 36	2.6×10^4
" " "	11, 23, 47	2.7×10^4
Central region	6, 7, 8	7.0×10^3
" "	6, 9, 22	1.2×10^4
" "	2, 2, 8	4.0×10^3

Analysis of variance of these data rejects at the 5% level the hypothesis of no difference between samples taken from peripheral and central regions. The hypothesis of no difference between replicate samples taken from the peripheral region alone or the central region alone cannot be rejected.

other words there was a heterogeneous distribution of microorganisms within the haggis. These findings were borne out by analysis of variance of general counts obtained from other haggis in this study.

Numbers and types of microorganisms recovered from haggis

Samples of six newly purchased haggis, examined with the object of establishing the common range of organisms associated with the product revealed those with identities given in Table 2.

Gram-positive aerobic spore-forming bacteria identified with *Bacillus* were the predominant bacteria found in all of the haggis examined. Lactic acid bacteria (mainly *Lactobacillus*) were the second most frequently occurring types recovered on PCA, in Rogosa agar they were recovered at levels of 10^3–10^4/g, somewhat higher counts being obtained from the central regions rather than the peripheral regions of the haggis.

Yeasts and moulds were detected in small numbers on PCA and were selectively recovered at levels of 10^2–10^3/g of haggis. Yeasts mainly were detected on the selective medium.

Gram-positive cocci were not encountered on PCA plates taken from freshly purchased haggis but they were detected at levels of 10^2–10^4/g on selective media. Counts on mannitol salt agar were somewhat higher than on Baird-Parker agar due to false-positive colonies of *Bacillus* which tolerate the high salt concentration in this medium. On the other hand, all black colonies which were taken from Baird-Parker medium for confirmatory examination proved to be coagulase-positive, gram-positive cocci identifiable with *Staphylococcus aureus*. Insignificant numbers of faecal streptococci were recovered in azide dextrose broth.

Table 2. Microbiological survey of freshly purchased Scotch haggis (mean of 6 haggis).

Organism sought	Medium and methods	Principal organisms recovered	No. present/g of haggis
General bacterial contaminants	PCA, 48 h at 25°C	*Bacillus* and *Lactobacillus*	10^4–10^5
Lactic acid bacteria	Rogosa agar, 5 days at 25°C	*Lactobacillus*	10^3–10^4
Yeasts and moulds	Rose Bengal chlortetracycline agar, 7 days at 25°C	Mainly yeasts	10^2–10^3
Staphylococcus aureus	Mannitol salt agar, 48 hr at 37°C	*S. aureus* and *Bacillus*	10^2–10^4
	Baird-Parker agar, 48 hr at 37°C	*S. aureus*	10^2–10^3
Faecal streptococci	Azide dextrose Broth, 24 hr at 45°C		< 1
Coliforms	Minerals modified glutamate medium, 48 hr at 37°C.	Presumptive coliforms	*ca* 10
	Violet Red Bile Agar 24 hr at 37°C	None detected	< 100

Gram-negative bacteria did not make a significant contribution to the microflora of haggis. Only low numbers of coliforms were detected in minerals modified glutamate medium, none were detected on violet red bile agar. The examination of isolates from the general counts on PCA however suggested that more gram-negative fermentative organisms may occur in fresh haggis than were revealed on the selective media. Non-fermentative gram-negative types identified with *Pseudomonas* and *Acinetobacter* were recovered only in very low numbers on PCA.

In summary the aerobic mesophilic microflora of freshly purchased haggis was principally gram-positive with *Bacillus* and *Lactobacillus* as the dominant genera. Additionally, yeasts, coliforms and *S. aureus* were always present in haggis.

Changes in stored haggis

Haggis from the same batch used to obtain the data presented in Table 1 were stored in sterile Kilner jars for 3 weeks at 5, 30 or 37°C before examination. The haggis stored at 5°C remained acceptable as far as its visual appearance and

Table 3. Microbiological survey of haggis stored for 3 weeks before examination using the media and methods outlined in Table 2.

Organism sought	Temperature of storage	Principal organisms recovered	No. present/g of haggis. Peripheral region	Centre of haggis
General bacterial contaminants	5°C	*Bacillus*	9.3×10^5	2.6×10^5
	30°C	*Bacillus*	9.1×10^5	3.1×10^5
	37°C	*Bacillus* and lactic streptococci	NT*	9.6×10^5
Lactic acid bacteria	5°C	*Lactobacillus*	5.5×10^4	1.2×10^5
	30°C	*Lactobacillus*	6.7×10^4	1.5×10^5
Yeasts and moulds	5°C	Yeasts	2.6×10^4	1.0×10^3
	5°C	Moulds	1.6×10^4	6.7×10^2
	30°C	Yeasts	5.3×10^2	1.3×10^4
	30°C	Moulds	5.3×10^2	2.7×10^3
Staphylococcus aureus	37°C		NT	2.0×10^4
Faecal streptococci	5°C		100(27–300)*	360(120–1280)
	30°C		10(5–37)	14(4–31)
Coliforms	5°C	Presumptive coliforms	10(3–38)	3(<1–6)
	30°C	"	2(<1–4)	2(<1–4)

NT = not tested

*95% confidence limits of most probable numbers of organisms present are given in parentheses.

odour was concerned. The haggis stored at higher temperatures were very obviously spoiled. They carried a substantial mould flora on their exterior, their interiors were slimy and there was a strong aroma of butyric acid. The pH of fresh haggis was typically around 6.4 with very little variation, whereas the pH of refrigeration haggis dropped to 5.8–5.9 over 3 weeks and the pH values of the obviously spoiled haggis were lower than 5.0.

Table 3 shows that the general counts on stored haggis had risen to around 10^5 or 10^6/g, *Bacillus* remained the dominant genus in these haggis but large numbers or lactic streptococci were also recovered from plates of PCA used in conjunction with haggis stored at 37°C. In general the number of lactic acid bacteria increased during storage and it was evident from counts on Rogosa agar that somewhat higher number were present in the central rather than the peripheral regions of the haggis. It may be inferred that the drop in pH during storage is associated with the increase in number of lactic acid bacteria.

Staphylococcus spp. and *Micrococcus* spp were evident on general counts of stored haggis. *Staphylococcus aureus* was recovered in larger numbers from haggis stored at 37°C than from freshly purchased haggis. Faecal streptococci which had not been detected in fresh haggis made a significant contribution to the microflora of the haggis stored at 5°C and 30°C.

The almost negligible gram-negative microflora of the haggis was not affected by storage.

Discussion

This study has shown that the Scotch haggis bears a substantial aerobic microflora. It is difficult to find other meat products with which one can validly compare the haggis. The general counts in the haggis are similar to those reported by Dowdell & Board (1971) for the British fresh sausage which like the haggis contains minced meat, cereals and spices. Gardner (1966) reports somewhat higher general counts (10^6–10^8/g) in pork sausage, and it is perhaps not surprising that a product such as the haggis which is cooked twice during manufacture should have fewer bacterial contaminants than the sausage.

No doubt the dominance of *Bacillus* in the microflora of the haggis is a function of the cooking process, the temperature of 80°C at which haggis are manufactured would be insufficient to inactivate the heat-resistant endospores of this genus. It is well known for *Bacillus* to be present in large numbers on products such as milled cereals (Halls & Tallentire, 1978) and spices (Tjaberg, Underdal & Lunde, 1972; Christensen *et al.*, 1967) which are used as ingredients of haggis. Moulds and yeasts are also frequently encountered in these ingredients. Lactic acid bacteria are frequently found in meat and meat products, and presumably also on offals although we have found only one reference to substantiate this (Shelef, 1975). Spoilage of the haggis seems to be principally associated with an increase in numbers of these organisms. It is likely that their survival in the haggis is due to low heat penetration during manufacture. The heterogeneous distribution of microorganisms in the haggis supports the assertion.

The low level of coliform organisms and faecal streptococci in freshly purchased haggis is indicative of generally good hygienic practice during manufacture. However the presence of *S. aureus* and *Bacillus* spp. suggests that the haggis could be a potential source of food poisoning, therefore proper cooking of the haggis may be necessary to prevent any likelihood of health hazards. Nonetheless there is no standard method of preparing haggis for the table in Scotland today. It is to be assumed that the traditional method of cooking was to boil the haggis. Nowadays it is seen fried and deep-fried in batter; it is seen in bulk on cafeteria hot-plates. It might be cautious to suggest that mass catering may overtake the traditionally safe haggis and bring it into the ranks of suspect foods.

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Book Reviews

United States Food Laws Regulations and Standards. Ed. by Y. H. Hui New York: John Wiley & Sons, 1979. Pp. xv + 616. £21.40.

An English person new to the Americans' way of controlling the quality and safety of their food supply is apt to regard the multiplicity of Federal Agencies, the enormous quantities of printed paper (both regulations and advisory documents) they each produce and the seemingly endless litigation between Agencies and industry with the same bewildered incomprehension with which the Victorian lady viewed Sarah Bernhardt's exotic Cleopatra. He too may conclude 'how different, how very different, from our own dear MAFF!' but he ought not to persuade himself that it is just a fascinating spectacle with no bearing on our own affairs. Whatever criticisms we have of the American system (some justified, many not) we cannot ignore what they do.

The Americans have tended either to recognize or experience problems earlier than the rest of the world and have made very considerable efforts to create a detailed legislative system of control. The result has been, that many countries, and even individual food companies, have used the American regulations as a model or guide where they have no specific ones of their own. The American regulatory system then has an interest for us beyond that which we might have for a country where we sell our products; and any book explaining their system is likely to be welcomed.

The author of this work is Associate Professor of Nutrition in the Department of Home Economics at Humboldt State University, California. He has set out to give the reader a basic understanding of the way in which the major food regulatory agencies in the United States control the quality, safety and advertisement of the food supply. In this he has succeeded very well.

A separate chapter is devoted to each of the seven Federal Agencies with some statutory responsibilities for enforcing food laws. These are the Department of Agriculture (USDA), the Department of Commerce, the Food and Drug Administration of the Department of Health Education and Welfare (FDA), the Treasury, the Consumer Product Safety Commission, the Environmental Protection Agency and the Federal Trade Commission. The most important Agency to food manufacturers is the Food and Drugs Administration and a great deal of information is provided in the chapter on the FDA about the organization of the agency and the nature and limits of its statutory responsibilities. A summary of regulations promulgated is given which will considerably assist anyone who needs to find his way through the mass of paper which comprises Title 21 of the Code of Federal Regulations. The

system of enforcement and the FDA's relationship with other Government Agencies and the State Authorities are described. Sources of information including relevant Government and private publications are listed and much other miscellaneous information is included.

The book contains a vast amount of useful information and it is a pity that the index is not more comprehensive. However, in spite of some difficulty in finding any particular piece of information this is a very useful book which will be of value to anyone with an interest in the general subject of food law, as well as to exporters to the U.S.A.

Margaret Andrews

Nutrition in the Community. The art of delivering services. By R. T. Frankle, and A. Y. Owen.
Saint Louis: The C. V. Mosby Company. 1978 Pp. xv + 395. £9.00.

The aim of this publication is to act as a reference book for students, teachers and 'practitioners' (my quotes) assigned to the task of designing and working a community nutrition programme. The information comes over as a mixture of nutrition and sociology practised in a U.S. setting.

The subjects dealt with are: Nutrition: is a national nutrition policy needed?; Role of the public health nutritionist: Who? Where? How? How well?; The art of programme planning; The community: assessment, elements in planning process and setting priorities; Community nutrition programmes: strategies at the local level; The action plan and behavioural change; Nutritional assessment and surveillance; Tools of nutritional assessment; Evaluation: how to measure outcome; Budgeting: how to manage finances; Legislation; Grant and grantsmanship: where the money is; The outlook for nutrition services: where do we go from here?

Of the thirteen chapters, I found that only four were interesting and of use. Others were written in a style which was difficult to read and reminiscent of some of the evaluation documents produced by various United Nations bodies, with an excessive use of jargon. Admittedly there was a large glossary at the end of the book to aid interpretation, but at times I found even this difficult to follow.

The first chapter on nutrition policy was well written giving an excellent background to the McGovern report, and in this chapter a brief mention was made of Norwegian nutrition policy – one of the few references to nutrition activity outside the U.S. Of the other chapters, that on the nutritional assessment and surveillance and that on tools of nutritional assessment were also well thought out. Useful examples of dietary questionnaires for dietary surveys were given, which could act as the basis of similar questionnaires for surveys in other countries. The section on the interpretation of dietary information with respect to Recommended Allowances (U.S.) was also well done. The material in this

section was treated in a more critical manner with a discussion of the limitations of the methodologies – an approach which was not in evidence in many sections of the book.

The case histories of dietary surveys in the U.S. indicate a disjointed approach to the determination of exactly what the nation is eating, and emphasize the important and wide scope of our own National Food Survey, which is not even given a mention in this book. Too much emphasis was placed on the role of undernutrition in the community. Admittedly this may be important in a Western Society when dealing with faddist groups or alcoholics, but the main nutritional problem as it was stated early in the book, that of overnutrition and the associated degenerative diseases, was not emphasized in the main body of the text.

In conclusion I would say that the book would be useful for any nutritionist intending to work in the United States (in the Chapter on Legislation there is even a table giving a nutritionist guide to telephone numbers in Washington), but has limited use for those outside.

Ann F. Walker

Fundamentals of Freeze Drying. By J. D. Mellor.
London: Academic Press 1978. Pp. xxvii + 386. £20.50.

The book is divided into three main sections, General principles (five chapters), Cyclic pressure applications (three chapters) and Applications (six chapters). Chapter one gives a brief description of the development of freeze-drying, together with a useful introduction to the major stages in the freeze-drying process, namely prefreezing, primary drying, secondary drying and rehydration. Chapters two to five then deal in considerable mathematical detail with sublimation, heat transfer, vapour transfer and drying rates. Good reviews are provided in each of the subject areas and there are appendices offering mathematical treatment for diffusion, heat conduction with moving interface, molecular collisions in porous materials and desorption.

Chapters six to eight deal with pressure cycle operation, obviously a research field of particular interest to the author. The advantages of the process, the equipment involved and analysis of pressure temperature effect during drying are all discussed.

The application section is very interesting. Subject areas covered are laboratory apparatus and techniques, drying plant and equipment, foodstuffs, quality aspects of freeze drying (e.g. shrinkage, volatile retention, rehydration), biological aspects and a chapter on miscellaneous aspects. A comprehensive list of over 400 references is given, divided into two sections – 'References' and 'Additional Research References'. Subject and author indexes are also provided.

This is more than just a book on the freeze drying process. The book has a strong practical element with details on the measurement of thermal conductivity, diffusion rates, prorosity, permeability, moisture content and the melting and freezing characteristics of food materials, as well as the measurement and control of temperature and drying end point. There is discussion of other unit operations that are closely associated with freeze drying, such as evaporation, freeze-concentration and freezing, as well as the use of microwaves in freeze drying.

The units are almost exclusively S.I. and the book would provide valuable reference material for students, engineers and technologists interested in the physical properties of food materials. Despite the fact that freeze drying has never caught the imagination of the food industry, there continue to be many research publications and several recent text books on the subject. So many of the books today consist of poorly edited collections of scientific papers in a particular area. The major advantage of this particular book is that a very competent review of the subject is given without undue repetition.

M. J. Lewis

Moulds, Toxins and Food. By Claude Moreau, translated by Maurice Moss. Chichester: John Wiley & Sons. 1979. Pp. xiii + 477. £21.00.

This is a translation of the book *Moisissures Toxiques dans l'Alimentation* by Claude Moreau, published in 1974 by Masson et Cie, Paris. The extensive coverage provided in the original work by Moreau can be discerned from the inclusion of no fewer than 2,938 references to the literature up to 1972. Maurice Moss has extended the review to include the period 1976 to early 1978 with some references from 1973–75, by adding a further Chapter, 13, 'Recent developments in the study of mycotoxins' which consists of 34 pages and incorporates a further 151 references.

The first two introductory chapters discuss the incidence, nature and consequences of mould contamination of foods, and general aspects of mycotoxins and mycotoxicoses. The next nine chapters are organized systematically on the basis of the major mycotoxicoses: aflatoxicosis; clavacitoxicosis; other aspergillotoxicoses; islanditoxicosis; diverse *Penicillium* toxicoses; fusariotoxicoses; sporidesmiotoxicosis; stachybotryotoxicosis; and finally 'other mycotoxicoses'. It is worth remarking that Moreau takes the term 'mycotoxin' in its commonly used restricted definition of 'extracellular zootoxic metabolites produced by moulds in food consumed by man or animals'. This book therefore does not cover the intracellular toxins of the macrofungi, or the toxins produced by plant parasitic microfungi such as *Claviceps purpurea*.

A considerable amount of information has been packed into this volume. The morphological descriptions of the toxin-producing fungi are provided, with useful line drawings of their microscopic appearance. Chemical and analytical

data include the structural formulae of the toxins and in many cases the biosynthetic pathways and information such as melting points and R_f values in appropiate TLC systems. References to the application of nuclear magnetic resonance, high pressure liquid chromatography and other techniques are frequently given.

The nature of the toxicity of each toxin is described, with LD_{50} values and descriptions of the signs and symptoms of acute and chronic intoxications in a number of animals including man. Histopathological findings are listed where known. Obviously, in this rapidly advancing field of knowledge, some of these aspects have not yet been elucidated for a number of the toxins listed.

The stated aim of the book is to help provide 'mycologists, doctors, veterinarians, biochemists, toxicologists, nutritionists, dieticians, hygienists and food technologists' with access to information concerning work on all relevant aspects of the production of toxic metabolites by moulds. However, the range of topics covered in the book and the method of treatment would seem to make this book of limited use to most nutritionists, dieticians and hygienists. For example, the subject index mainly lists chemical compounds and toxins, and clinical and pathological manifestations with a separate taxonomic index of the fungal species described.

Summing up, this can be thoroughly recommended as an invaluable source book for those biochemists, food scientists, and workers in the medical and veterinary sciences, who are concerned with the problems of mycotoxicoses.

W. F. Harrigan

Books received

New Protein Foods. Vol. 3. Animal Protein Supplies. Part A. Ed. by Aaron M. Altschul and Harold L. Wilcke.
New York: Academic Press. 1978. Pp. xvi + 408. $39.50.

This volume examines the use of animal protein in the human diet in the context of the increasing world population and the resulting constraints on land, water and energy.

Plant Regulation and World Agriculture. Ed. by Tom K. Scott. NATO Advanced Study Institutes Series A: Life Sciences, Vol. 22. Proceedings of a NATO Advanced Study Institute held in Turkey, 1978.
New York: Plenum Press. 1979. Pp. xi + 575. $47.50.

A work which discusses plant physiology in relation to agricultural improvement by plant breeding and use of plant hormones.

Journal of Consumer Studies and Home Economics

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Book review

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Abbreviations. Abbreviations for some commoner units are given below. The abbreviation for the plural of a unit is the same as that for the singular. Wherever possible the metric SI units should be used unless they conflict with generally accepted current practice. Conversion factors to SI units are shown where appropriate.

SI UNITS

gram	g	Joule	J
kilogram	kg = 10^3 g	Newton	N
milligram	mg = 10^{-3} g	Watt	W
metre	m	Centigrade	°C
millimetre	mm = 10^{-3}m	hour	hr
micrometre	μm = 10^{-6} m	minute	min
nanometre	nm = 10^{-9} m	second	sec
litre	l = 10^{-3} m^3		

NON SI UNITS

inch	in	= 25·4 mm
foot	ft	= 0·3048 m
square inch	in^2	= 645·16 mm^2
square foot	ft^2	= 0·092903 m^2
cubic inch	in^3	= 1·63871 × 10^4 mm^3
cubic foot	ft^3	= 0·028317 m^3
gallon	gal	= 4·5461 l
pound	lb	= 0·453592 kg
pound/cubic inch	lb in^{-3}	= 2·76799 × 10^4 kg m^{-3}
dyne		= 10^{-5} N
calorie (15°C)	cal	= 4·1855 J
British Thermal Unit	BTU	= 1055·06 J
Horsepower	HP	= 745·700 W
Fahrenheit	°F	= 9/5 T°C + 32

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. 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'.

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