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# EQUILIBRIUM RELATIVE HUMIDITY OF FOODSTUFFS.

By E. W. Hicks.

## 1. Meaning of Term.

Almost all foodstuffs contain water and water soluble materials, and they can be regarded as equivalent to aqueous solutions of definite concentrations. This means that they have definite osmotic pressures, definite freezing points, and definite vapour pressures at fixed temperatures. All these properties are related to one another and to the concentration of the aqueous solution in the foodstuff, or more precisely, to the activity of water in the system. For many purposes the most direct and most convenient measure of the activity of water in a foodstuff is the *equilibrium relative humidity*, i.e., the relative humidity of an atmosphere in which the foodstuff will neither gain nor lose water. If a material is stored in an atmosphere above its equilibrium humidity it will absorb water and continue absorbing it until equilibrium with the storage atmosphere is attained. Similarly, foodstuffs stored in atmospheres below their equilibrium humidity will evaporate water until they are concentrated to restore equilibrium.

The equilibrium humidity of most foodstuffs varies with temperature, but generally this variation is too small to be of much practical importance over the range of ordinary storage temperatures. The equilibrium humidity varies with the water content and with the concentration and composition of the soluble materials. For instance, in a foodstuff rich in carbohydrate, e.g., jams, sweets, cakes, etc., the main factors affecting the equilibrium humidity will be

(a) water content ;

(b) the ratios starch: sucrose: monosaccharides.

For a given total carbohydrate, the higher the ratio of sugars to starch the lower the equilibrium humidity. Also the higher the ratio of monosaccharides to total sugar, the lower the equilibrium humidity because what may be called the equilibrium humidity deficit (i.e., 100% minus equilibrium humidity) is roughly proportional to the number of particles (molecules and ions) in solution in a given quantity of water.

The equilibrium humidities of common foodstuffs cover a wide range, e.g.,

Fresh beef, 99.3%

Fresh vegetables generally, > 98%

Jams, 79-83%

Cakes, 73-85%

Pre-cooked flaked cereals, 25% (approx.)

Dried milk, 20 % (approx.).

## 2. Practical Importance.

(a) *Gain or loss of water.*

The average relative humidities taken over the whole year for a number of Australian towns are shown in the following table:—

*Relative Humidity for various towns (per cent.)*

| | | | | | |
|---|---|---|---|---|---|
| Perth | 63 | Melbourne | 68 | Brisbane | 68 |
| Broome | 59 | Mildura | 65 | Camooweal | 41 |
| Adelaide | 53 | Sydney | 70 | Cairns | 72 |
| Bendigo | 63 | Bourke | 56 | Darwin | 68 |

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There are many foodstuffs with equilibrium humidities well above 80%, e.g., meats, fruits, vegetables, bread, etc., and these will tend to dry out almost everywhere in Australia, though the rate will vary in different places.

Another group of commodities have equilibrium humidities below 40% and cannot be allowed to take up more than a very limited amount of water without adverse effects on quality, e.g., flaked cereals, dried milk, etc. Everywhere in Australia these require packages with a high resistance to transfer of water vapour.

Another large group of foodstuffs can be allowed to take up or lose water to maintain equilibrium with the storage atmosphere provided that they do not become wet enough to support mould growth. Among these are flour, cornflour, custard powder, rice, macaroni, spaghetti, pepper and spices. These commodities rarely present water exchange problems except in the wet season in some tropical coastal regions.

There are other commodities which normally contain little or no water but which become damp at very high humidities, e.g., sugar and salt. The limiting humidity for dampening of these materials is the equilibrium humidity of a saturated solution, e.g., sugar 80%, salt 75%.

(b) *Growth of bacteria, yeasts and moulds.*

The equilibrium humidity of a commodity is a reliable measure of the availability of water to micro-organisms which might grow on it, and the prevention of microbial attack by controlling the composition to ensure an equilibrium humidity too low to permit their growth is often possible. This is, in fact, standard practice in many food industries.

The lowest equilibrium humidities at which various types of organism can grow vary with the composition of the material and other factors, but rough limits can be specified. Thus bacterial growth is nearly always impossible below 95 % relative humidity and the growth of most yeasts below 90%, but some osmophilic yeasts are reported to grow as low as 69%. These are important in confectionery. Unfortunately the limits for mould growth are rather variable. Some authorities have set the limit at 80%, and this is apparently valid for jams and certain other foodstuffs, though there may be some species of mould able to grow on jam at this equilibrium humidity. Mould growth has, however, been observed on some commodities at 75% equilibrium humidity.

The reasons for variations in the limit for different commodities are not known and are probably complex.

## 3. Methods of Measurement.

(a) *Using sulphuric acid solutions as standards.*

The relation between the concentration of sulphuric acid solutions and their equilibrium humidities is accurately known. This relation is shown in the following table, based on data given in International Critical Tables.

Screw-top glass jars are suitable for use as constant humidity chambers for checking equilibrium humidities. If a material known to have an equilibrium humidity of the order of 75% is to be studied, a satisfactory procedure is to set up three bottles, one containing ½ in. to 1 in. of acid to give a humidity of 80%, one with the same quantity of acid to give 75% R.H., and the third 70%. Approximately equal quantities of material are weighed accurately into each of 3 standard-sized dishes and one placed on a glass triangle above the acid in each bottle. A suitable size of sample is generally 2 to 5 grams. The bottles are held at a well-controlled constant temperature and the dishes re-weighed at appropriate intervals. It is not necessary to wait for the materials to attain

equilibrium at the three humidities. A good estimate of the equilibrium value can be obtained by plotting the total weight change of each sample over a period of two days at 30°C. or 37°C., against the relative humidity of the storage atmosphere, drawing a curve (generally not a straight line) through the three points and taking the humidity corresponding to zero weight change on the curve as the equilibrium value. If high precision is required the test should be repeated using a narrower range of humidities, e.g., if the first test as above indicates a value of 76%, appropriate humidities for the second test would be 78%, 76%, 74%. Care must be taken that the quantity of water transferred is too small to affect the acid concentrations appreciably. If possible all the work (including weighings) should be done in a constant temperature room, but it is possible to work with a good incubator or other small constant temperature space. It is difficult to give any general specification of the accuracy of temperature control necessary. Fluctuations large enough to cause condensation on the walls of the bottle used will certainly lead to error and must be avoided.

(b) *Using salts as standards.*

Crystals of salts become damp and ultimately liquefy if they are held at humidities above the equilibrium humidity of their saturated solutions. Consequently suitably selected salts may be used as indicators in estimating equilibrium humidities. A useful micro method using this principle is described by Pouncey and Summers *J. Soc. Chem. Ind.* 58 (1939) 162.

(c) *By measurement of dew point of air in equilibrium.*

Hughes (*Chem. & Ind.* 61 (1942) p. 106) outlined a method in which air is equilibrated with the material to be tested and the dew point of this air measured. This is much faster than the first method suggested above, but may be more troublesome to carry out, particularly in laboratories where only occasional checks of equilibrium humidity are required. To obtain accurate results with this method, accurate temperature control is necessary and also the apparatus must be so proportioned that the amount of water condensed on the thimble is only a small proportion of the water content of the air in the system.

*Relation between density and Concentration of $H_2SO_4$ Solutions and Relative humidity.*

| Relative Humidity. | Density at— | | | | Gms. $H_2SO_4$ per 100 gms. solution. | |
|---|---|---|---|---|---|---|
| | 0° C. | 10° C. | 20° C. | 30° C. | 0° C. | 30° C. |
| 95 | 1·081 | 1·075 | 1·061 | 1·054 | 10·5 | 8·5 |
| 90 | 1·131 | 1·124 | 1·116 | 1·108 | 17·2 | 16·6 |
| 85 | 1·171 | 1·164 | 1·158 | 1·152 | 22·5 | 22·5 |
| 80 | 1·204 | 1·197 | 1·191 | 1·184 | 26·5 | 26·5 |
| 75 | 1·231 | 1·225 | 1·219 | 1·211 | 30·0 | 30·0 |
| 70 | 1·255 | 1·250 | 1·243 | 1·236 | 32·7 | 32·9 |
| 65 | 1·278 | 1·273 | 1·266 | 1·259 | 35·4 | 35·7 |
| 60 | 1·300 | 1·295 | 1·288 | 1·281 | 37·9 | 38·3 |
| 55 | 1·321 | 1·317 | 1·309 | 1·301 | 40·2 | 40·8 |
| 50 | 1·340 | 1·336 | 1·330 | 1·328 | 42·6 | 43·1 |
| 45 | 1·361 | 1·356 | 1·350 | 1·344 | 44·8 | 45·7 |
| 40 | 1·383 | 1·378 | 1·375 | 1·366 | 47·0 | 48·0 |
| 35 | 1·406 | 1·401 | 1·397 | 1·390 | 49·4 | 50·3 |
| 30 | 1·430 | 1·425 | 1·420 | 1·414 | 51·8 | 52·8 |
| 25 | 1·455 | 1·450 | 1·445 | 1·440 | 54·3 | 55·5 |

# THE USE OF SYNTHETIC ASCORBIC ACID.

By F. E. Huelin.

Ascorbic acid (vitamin C) is now produced in considerable quantities synthetically, and the synthetic product is available to supplement natural sources of the vitamin. The desirability of using synthetic ascorbic acid in peace-time Australia is rather a controversial subject, but it can be stated definitely that natural sources of the vitamin should always be used in preference to the synthetic product, as fresh fruits and vegetables may contain other valuable nutritive constituents, both known and unknown, as well as ascorbic acid.

In war-time, particularly in the services, it is sometimes difficult to supply sufficient ascorbic acid from natural sources, and the synthetic product is of definite value. It can be taken directly as tablets, but certain fortified foodstuffs and beverages are generally more attractive. It is essential to consider the stability of ascorbic acid in selecting products for fortification, as the rate of destruction is influenced by pH, low concentrations of copper, and access of oxygen to the pack, as well as other factors. The stability is considerably increased as the pH is reduced, i.e., as the acidity is increased. Hence the more acid products, e.g., fruit juices, cordials, and jams have generally been prepared for fortification, in order to lose as little of the added ascorbic acid as possible before the product is consumed. The exclusion of air is very important, and canned products should have the headspace reduced to a minimum.

Fortification of canned apple juice to a level of 28 mg. per 100 ml. was carried out in this laboratory by adding ascorbic acid tablets to each can, as it was filled with hot pasteurised juice. The cans were then closed, inverted for two minutes, and cooled in water. In this way the oxidation of ascorbic acid during canning was reduced to a minimum. About 2 mg. per 100 ml. was lost during canning, and the subsequent loss was 1 mg. per 100 ml. per month at 70-80°F. and 2 mg. per 100 ml. per month at 100°F. Fortification in bulk appears to be quite practicable, and has been carried out in Canada, but would involve strict precautions in excluding air and in pasteurising and canning the juice as rapidly as possible.

Marshall in Canada has fortified strawberry, raspberry, plum and peach jams with synthetic ascorbic acid. After six months the retention was about 85 per cent. at 60°F., 75 per cent. at 75°F., and 50 per cent. at 100°F.

The fortification of chewing gum has been carried out by Andrews in New Zealand and by Marshall and Hopkins in Canada. Andrews found that the retention of ascorbic acid depended primarily on the thickness of the coating and its freedom from cracks. Marshall and Hopkins found the retention of ascorbic acid after six months in sealed containers to be 86 per cent. at 60°F., 84 per cent. at 75°F., and 75 per cent. at 100°F.

Marshall and Hopkins have also fortified hard candy and found the retention of ascorbic acid after six months' storage in sealed containers to be 96 per cent. at 60°F., 91 per cent. at 75°F., and 73 per cent. at 100°F. Exposure of both chewing gum and hard candy to moist atmospheres (95 per cent. humidity) more than doubled the rate of loss.

Lime tablets containing about 0.5 per cent. of synthetic ascorbic acid have been prepared locally. Analyses made in this laboratory have indicated at least 90 per cent. retention after twelve months at 100°F. The high retention is probably due to the low moisture content (maximum one per cent.).

Investigations have been carried out in this laboratory on the fortification of artificial lemon and orange cordials. Syrups containing sugar (50%), lactic acid (1-1.5%), sodium benzoate (0.23%), dyestuff (100 p.p.m.) and flavouring essence were fortified with 200 mg. of synthetic ascorbic acid per 100 ml. Both syrups and beverages were stored in sealed bottles. After three months at 86°F., the syrups lost about 10 per cent. of the original ascorbic acid, and the diluted beverages about 30 per cent.

One difficulty in the fortification of artificially coloured products is the tendency of many dyes to fade in the presence of ascorbic acid. Of nine dyes tested, only Orange II, Carmoisine, and Tartrazine were found to be reasonably stable. Orange I, Brilliant Scarlet, Auramine, Magenta, Eosin, and Indigo all showed serious fading. The lemon syrup was prepared to contain 100 parts per million of Tartrazine and the orange syrup 90 parts per million of Orange II and 10 parts per million of Carmoisine.

# EXTENDING THE STORAGE LIFE OF APPLES WITH SKIN COATINGS.

By S. A. Trout and E. G. Hall.*

In the March, 1942 and March, 1943, issues of the *Quarterly,* investigations on skin coatings were described and the precautions to be observed in the treatment of apples were outlined. Since then, a further range of skin coatings has been tested and some of the troubles previously encountered have been overcome. *However, the investigations have not yet reached a stage where it is possible to recommend a universal coating which could be applied successfully to all varieties of apples under various storage conditions.* It may be stated in general terms that under favourable conditions certain coatings will prolong the storage life of a particular variety grown in a certain locality.

The solution of castor oil and shellac in alcohol has been very effective with most varieties under cool conditions, but it has induced alcoholic flavours in immature fruit stored at relatively high temperatures. Alcohol has sometimes caused lenticel spotting, but no other solvent has been found to be an effective substitute. Emulsions are less likely to cause alcoholic flavours as their films are more permeable to the respiratory gases, oxygen and carbon dioxide.

Wax emulsions have been the most effective coatings for reducing weight loss, but have caused calyx injuries to certain varieties because injurious concentrations of soap are required for their emulsification.

A heavy medicinal paraffin oil has been more effective than lighter mineral oils or vegetable oils in controlling wilting and in itself is not toxic to the fruit. However, both the efficiency of an oil emulsion and its toxic effect on fruit depend more on the composition and concentration of the emulsifying agent than on the oil itself. Emulsions with a low concentration of soap are the most effective but must be reasonably stable when diluted with water for use. The breaking of an emulsion during use results in the deposition of a heavy layer of oil on the fruit, severely restricting the diffusion of oxygen with the subsequent development of abnormal alcoholic flavours.

Prior to 1939 extensive experiments had been conducted on the factors associated with the keeping quality of fruits, and it was found that the growing conditions, maturity of the fruit at the time of picking, size of the fruit and of the crop, and storage conditions after picking, largely determined the length of storage life of a particular variety of apple.

Skin coatings retard the normal processes of respiration and thus extend the life of fruit mainly by restricting the diffusion of atmospheric oxygen into the tissues. The rate of respiration is dependent so much on the factors associated with keeping quality that these factors must be taken into account in the testing of a particular skin coating. Furthermore, because of the possibility of disturbing the normal metabolism of fruit with the consequent risk of abnormal fermentation and serious internal disorders, and because materials used in the coatings may be toxic to certain varieties under some conditions inducing injuries such as lenticel spotting and calyx injury, long and careful investigations are necessary before a coating can be recommended for general use.

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The rate of oxygen consumption increases with rising temperature, and thus any skin coating is more effective at high temperatures. This means that the thickness of the coating used has to be related to the temperature at which the fruit will subsequently be stored. To obtain equally effective results a thicker coating has to be used in cool than in common or unrefrigerated storage. The danger of using thick coatings lies in the fact that oxygen consumption rapidly increases on removal of the fruit to warmer atmospheric temperatures, and the coating may restrict the oxygen supply so effectively that all normal respiratory processes will cease. This will result in the development of abnormal alcoholic flavours and serious breakdown of the tissues. Maturity of the fruit at the time of picking is perhaps of greater importance in the storage of fruit treated in the skin coatings than in untreated fruit, because immature fruit does not develop normal flavour after treatment and is likely to develop alcoholic flavours as a result of induced anaerobic respiration. Over-mature fruit is also more susceptible to mould and breakdown after treatment.

Fruit for treatment should be at the optimum maturity for cool storage when picked, free from injuries and of normal size. Treatment should be done immediately after picking, but should be avoided during hot weather.

Growers who contemplate treating apples are advised to seek the advice of C.S.I.R. or their local Department of Agriculture regarding the coatings which should be used, as indiscriminate use of skin coatings may lead to serious losses.

# SPECTROGRAPHY IN FOOD RESEARCH.

By H. A. McKenzie.

In recent years classical chemical methods of investigation have been increasingly supplemented by the newer physical methods. It is, therefore, not surprising to find these methods playing an important role in the food industries. A well-known example is that of redox potential measurements, which have proved of particular value in the dairy industry.

The spectrographic method has been fairly widely applied abroad, but has received insufficient attention in this country. The criticism usually levelled at this method is that the cost of the equipment involved is high. Admittedly the initial outlay is considerable, but the results achieved in the long run amply justify this initial expenditure.

Before considering the applications of spectrography in the field with which we are concerned, it may be as well to give a simple account of the general principles of the method. Spectra are classified as:—

(a) emission spectra

(b) absorption spectra.

Emission spectra are produced directly by an excited source, whereas, in the case of absorption, light emitted by an external source is absorbed by the medium under consideration. The light emitted or absorbed is broken up into a spectrum by an instrument which is called a spectroscope if the spectrum is observed visually. Nowadays the spectroscope has been largely replaced by the more elaborate spectrograph in which the spectrum is recorded on a photographic plate and the result so obtained is known as a spectrogram.

## Emission Spectra.

The more usual methods of excitation are arc, spark and flame. The arc is the most widely used of these three and in general is found to be the most satisfactory. Both the low voltage D.C. and the high voltage A.C. arcs are employed. Condensed and uncondensed sparks have been used, but the condensed is usually the more satisfactory. The subject of the choice of spectrographs and the principles involved in them is too big to consider here. Emission spectra have been applied in the qualitative analysis for many metals and a number of non-metals and in the quantitative analysis for these elements when they are present in small amounts. Thus many types of substances have been successfully analysed by the spectrographic method. The identification of metals is mainly due to the research of de Gramont, and may be accomplished by measuring the wave-lengths of several spectra lines and making a comparison with known spectra or tables. This comparison has been facilitated by the introduction of the so-called R.U. powder.* This powder contains about fifty elements, and when its spectrum is produced by burning in an arc about a half-dozen of the sensitive lines of each element appear. Hence if the spectrum of R.U. powder be photographed on the same plate as that of the unknown sample, the elements in the unknown may be readily identified.

* R.U. = Rils ultimes = sensitive lines.

As a quantitative method it is usually only suitable for determining components present to the extent of less than one per cent. The analysis for a number of metals can be carried out in an exceedingly short time, and in competent hands, high accuracy is obtained. A further advantage is that a sample of a few milligrammes is sufficient for the analysis. An adequate discussion of the technique of modern quantitative analysis is beyond the scope of this article but the following will give an indication of the methods employed. The intensity of the spectral line due to the constituent being determined is measured relative to that of a line due to the second component that is present in constant amount. The latter component is known as the internal standard. The intensities of the lines are measured by photometric methods. Recently, further improvements have been made with the introduction of a device known as the log sector.

**Absorption Spectra.**

Absorption spectrophotometry has not received anything like the attention by industry that it deserves, and whenever it has been employed by industry it has usually been only as "glorified colorimetry." These spectra may be used for quantitative analysis for certain metals and acid radicals, for determination of structure and many other investigations. The principle of absorption spectrophotometry is briefly this: The light absorbed by the solution of substance is proportional to the amount of substance and to the thickness of the solution, and there is a definite law (The Lambert-Beer Law) which gives the relation between these entities. Absorption spectrophotometers are so designed that a measurement of the absorbed light may be made. Modern spectrophotometers are mainly of the photo-electric type.

From the above general discussion of the various types of spectra, some of the applications to food research will now be fairly obvious. Since the spectrographic method has been found to be ideally suited for trace metal analysis, it is not surprising to find that it has been successfully applied to such determinations in foods. It is often difficult to convince the uninitiated that a few parts per million of certain metals can cause a serious reduction in the quality of products. Thus, it took years to convince the dairy industry that certain off-flavours in its products were due to traces of contaminating metals. The importance of these trace elements cannot be over-emphasised. For instance, off-flavours can be produced in concentrated fruit juices by the presence of only minute amounts of some contaminating metal, copper for example. Not only do the trace metals frequently cause flavour degradation, but they may cause highly undesirable colour changes. For these reasons alone, constant checking of products for the trace elements is most necessary. There is another aspect of trace metal analysis of foods which is highly important, namely, analysis to determine if the product conforms to Pure Foods Acts and to generally accepted specifications. For instance, the generally established limit for lead in foods in the U.S.A. is 2 p.p.m. and 0.3 p.p.m. for beverages and products can be readily analysed for lead by the spectrographic method.

Some American manufacturers have found the addition of a trace of some harmless substance to their product useful for identification purposes. A spectrogram of a suspected spurious product is made and compared with one of their own product and positive identification is then possible.

Frequently, foods are packed in tin or aluminium containers, and the extent of corrosion of the container may exert an appreciable influence on the subsequent palatability of the product. The corrosion of tinplate is markedly dependent on the composition of the base plate, and that of aluminium on the traces

of impurities present in it. Therefore it is not surprising to find that the spectrographic method has been applied with considerable success in the field of canned foods.

The method has been applied to the determination of metals in spray residues on fruits, etc., and the determination of metals in brewery products (traces of metals can cause turbidity in beer, etc.).

As well as constant supervision of products there is a need for research work on the effects of trace metals, particularly to determine the nature of the reactions they so readily catalyze, and the spectrographic method can play a big part in such research.

Investigations of oils, lacquers and the like have been carried out using the absorption method. These substances are now very important in the canning industry. The method has also been found useful in vitamin assay and the determination of pH.

The scope of this article is such that it has been impossible to make even passing references to many of the applications of spectrography in the food field, but from what has been described it is hoped that some idea of the magnitude of the contribution of spectrography to the food industries may be realised.

# BLACK DEPOSITS ON JAM CANS.

By J. F. Kefford.

An Australian jam manufacturer requested this laboratory to investigate the nature and causes of black deposits occurring on the external and internal surfaces of jam cans.

## External Black Deposits.

A number of observations had been made on this problem over a considerable period and the facts appeared to be as follow:—

1. After varying periods in the stacks jam cans showed brownish-black sticky deposits on the external surfaces. The black material appeared to exude from the can at the cannery end which is always uppermost in the stacks. The exudate ran down the can, collected around the bottom seam and eventually overflowed to drop on to the upper end of the can beneath.
2. The appearance of the black deposit was associated with periods of warm, humid conditions.
3. Cans on the outside of stacks were less affected than cans within the interior of the stacks.
4. Cans packed immediately into cases and stored in the cases did not develop the black exudate, but black material was detectable in the edge of the seam at the cannery end.
5. The products chiefly affected were:

   Marmalade
   Apple Jelly
   Quince Jelly.

In the experience of this manufacturer other jams are not affected, but in the past other manufacturers have experienced the black deposits on cans of other jams.

## Investigation.

A working hypothesis suggested by these facts is that the exudate from the seams consists of jam which has been occluded in the seam during the filling and sealing operations. Under humid conditions this jam takes up moisture, becoming more fluid, and flows down the cans onto cans below. The dark colour is probably due to reaction between the jam and the metal of the can. This hypothesis was tested in a short experimental investigation.

Scrapings of black deposits from the exterior of cans were analysed and found to contain 3% (30,000 p.p.m.) of iron. This strongly supports the view that the black colour is due to organic iron compounds of the "iron tannate" type. Samples of jam, one taken from the centre of the pack and the other taken from in contact with the tinplate surface contained only 5 p.p.m. and 65 p.p.m. of iron respectively.

A storage experiment was arranged with 3 dozen cans of marmalade jam. These cans were taken from the line after filling, washing (30 sec. in water at 200°F.)

and cooling 20 secs. in water at 105°F.) and brought immediately to this laboratory. Half of the batch was washed further by immersion in boiling water for 5 minutes. Then, samples of the re-washed cans and of the untreated cans were held under each of the following storage conditions:—

(a) 86°F., low humidity.

(b) 86°F., 90 % relative humidity.

(c) 50°F., 90% relative humidity.

(d) Room temperature (65-75°F.), low humidity.

Some of the stored cans were stacked cannery end up and the others cannery end down.

*Results.*

After 5 days at 90% R.H., both at 86°F. and at 50°F. the untreated cans showed typical black exudate from the seams. On the cans stacked cannery end up the black material had run down the cans and dripped off. On the cans stacked cannery end down the exudate was visible all round the bottom seam, and in a few cases it had overflowed and dripped off.

Under the same conditions the re-washed cans showed the exudate to a significantly less extent. In cans stacked either end up black material was visible round the edge of the seam, but in no case had it run down or dripped off the cans.

At low humidities, both at room temperature and at 86°F., no exudates were visible after 25 days.

By tearing down the seams of cans showing exudates it was possible to see clearly the material occluded in the seam between the body of the can and the coverhook. The seams were normal commercial seams.

These results confirm the ideas already expressed that under humid conditions hygroscopic jam material, occluded in the seams, liquefies and runs down the cans. The material picks up iron from the can and in the presence of atmospheric oxygen it becomes an unsightly black deposit.

The greater incidence of black deposits on cans of jelly products is probably due to the greater fluidity of these products at filling temperatures which permit the product to be occluded in the seam more readily. This material is not removed by washing unless special precautions are taken. It is suggested that a boiling water wash with some positive scrubbing or strong spraying action is necessary.

## Internal Blackening.

The second related problem concerns the appearance of a brownish black deposit on the internal surface of the cannery end (headspace end) of jam cans. The deposit appears within a few days of canning and gradually increases in intensity. It is usually most prominent round the expansion rings. After longer storage, some stripping of the tinplate with exposure of the baseplate is observed over small areas on the headspace end of the can. The stripping is only extensive in cans of low vacuum.

It is considered that the black material appearing within the can is formed by essentially the same mechanisms as the external deposit. The jam takes up iron from the can, particularly at points where the plate is strained, e.g., at the expansion rings, and in the presence of residual oxygen in the headspace black compounds of the "iron tannate" type are formed.

The cans used in the above storage experiment were also examined for internal blackening. All cans opened showed the black deposit round the expansion rings and also in some instances on the body, at the headspace end, whether this end was the cannery end or the can maker's end.

If, however, the cans are inverted after the black deposit has formed it tends to re-dissolve in the jam.

It is suggested that the internal black staining problem may be circumvented by inverting the cans at the time of labelling. The consumer is then presented with a clean end, and in addition, the jelly is attractively moulded at the opened end.

A more positive solution is to avoid the black staining by internal lacquering of the cannery end of the cans. This would also assist to eliminate the corrosion which occurs at this end during longer storage.

# "YELLOW SPOTS" IN PICKLED ONIONS.

Pickled onions are sometimes affected by a condition characterised by the appearance of small spots and diffuse areas coloured bright yellow on the external surfaces and also in the internal tissues. The causes of this condition and the nature of the material constituting the yellow spots have not been completely elucidated.

Onions grown on limed soils are stated to be particularly susceptible to "yellow spots" and varietal influences also operate. High salt contents during brining are also said to encourage the appearance of this condition.

Samples of sweet pickled onions showing yellow spots were examined at this laboratory some time ago (unpublished data, C.S.I.R. Division of Food Preservation Canning Memo. No. 55 (1943) ). Microscopical and cultural tests gave no evidence that the condition was associated with microbial contamination. In microscopical section some cells of the onions were found to be opaque with yellow-brown inclusions, while neighbouring cells were quite transparent. The pigmented tissues, extracted with alcohol, yielded a yellowish residue which dissolved in alkali to give a strong yellow solution and was reprecipitated by hydrochloric acid. The precipitate was insoluble in water, soluble in alcohol, glacial acetic acid and 50% acetic acid, sparingly soluble in 20% acetic, and insoluble in benzine. A sodium fusion test indicated that sulphur was absent. The substance was not further identified.

Campbell (Campbell, H. Food Research 4, 397-9 (1939) ) investigated the nature of a yellow deposit in jars of home-canned green asparagus and found that it was most probably a flavone or flavonal glucoside. Flavone derivatives commonly occur as yellow colouring matters in plant products. From the few characteristics noted above the yellow deposit in pickled onions could also be of this nature.

At the present stage of our knowledge, therefore, it appears that yellow spots in pickled onions are caused by an unidentified organic substance which may be a flavone derivative. We do not know what mechanisms operate to cause the deposition of this material. The yellow spots are harmless and have no significance in relation to the wholesomeness or edibility of the product.

# AN INTERNAL VACUUM LEAK TEST FOR CANS.

By R. S. MITCHELL.

This article describes a method developed in these laboratories for testing leaks in cans, by the application of an internal vacuum to cans containing water, using an apparatus which permits air bubbles inside the can resulting from leaks to be seen.

The standard internal pressure test for leaks has been subject to criticism on the grounds that a differential pressure outwards is employed whereas leaks causing loss of vacuum and microbial contamination result from a differential inward pressure.

The method described was developed in an endeavour to overcome this serious objection and at the same time to have a test which would still show the actual points of leakage and still be sufficiently rapid.

## Previous Methods

Methods of testing cans by applying an internal vacuum have been used previously but are slow and inconvenient.

E. Gabriel Jones (Chemistry & Industry, Vol. 60, pp. 855-858) describes a method which consists of first removing the can contents, cleaning and then soldering of a brass tube over the hole. The can is half filled with water, a vacuum applied and the can partially immersed in a fluorescein solution and held at 60-70°C. for two to three hours. Leaks were detected by examining a sample of the water from inside the can under an ultra-violet lamp.

A circular issued by the Department of Supply and Shipping (July, 1944) describes a vacuum retention method whereby cans filled with liquid are sealed under vacuum, stored and examined later for vacuum.

Other methods include gaseous diffusion and solution diffusion. An example of gaseous diffusion consists of placing a lead acetate paper inside the can and subjecting the closed can to an atmosphere of hydrogen sulphide.

For solution diffusion, alakali outside the can and a suitable indicator in water inside the can shows penetration of the seam by a change in colour of the indicator.

## Description of Apparatus.

The essential parts of the apparatus developed in this laboratory are a specially constructed head to cover the opened can and a clamping device consisting essentially of a plate which can be raised or lowered by a cam thus clamping the can and head tightly together.

The head consists of a wooden block having a 1½ inch diameter hole cut through the centre and three holes drilled from the edges to connect with this large hole,

The large hole is sealed on the top by a glass plate suitably gasketed and clamped. Two of the small holes are connected to the vacuum pump and vacuum gauge respectively and the third carries the leads to a torch bulb mounted on the underside of the block. A rubber gasket on the lower surface completes an air-tight joint between the can top and the head. By placing a rubber gasket below the can, cans open at both ends may be tested, and by reversing the can both end seams may be examined independently.

**Operation.**

The can is prepared by thorough washing and drying as for the internal pressure test (Food Pres. Quarterly Vol. 3, No. 1) and then clamped between the head and the lower plate and the light bulb leads connected to a battery. Vacuum is applied by means of a water pump until about 20 inches of vacuum is obtained. The water to the suction pump is then turned off allowing water to run into the can. The pump is again turned on and observations made for streams of air bubbles which would indicate leaks. The points of leakage are marked on the outside of the can as exactly as possible.

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Sydney: Thomas Henry Tennant, Government Printer—1945.