# 16

# Water activity and its measurement in food

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## 16.1 Definition

Food should be stable and must be safe. These requirements mean that the products must not endanger the health of the consumer with micro-organisms or their toxins, or deteriorate owing to enzymic or microbial activity, at any stage from production through storage and retail to consumption. Factors determining microbial deterioration may be differentiated as intrinsic factors, process factors and extrinsic factors. Intrinsic factors include water activity $a_w$, pH value and redox potential $E_h$, and extrinsic factors cover temperature and humidity as well as atmospheric influences and partial pressures of gases during food storage. The techniques in food technology that affect shelf life by altering the conditions for microbial growth in the product are described as process factors. The control points critical for production can be deduced by analysing the hygienic risks of a food. Then measurements of the critical variables can be taken as part of process control, compared with standard levels and corrected where necessary. This concept of process control is known as Hazard Analysis and Critical Control Point (HACCP) (Kaufmann and Schaffner 1974; Bonberg and David 1977; Bryan 1980; Brown 2000; Directive 93/43/EEC).

For food, there are several factors that have a bearing upon any assessment of microbiological stability, and thus upon the shelf life and safety of a product. Water activity $a_w$ is a particularly important parameter for risk analysis as defined by the HACCP concept, as are the pH value, the $F_0$ value and the redox potential (see Section 1.2). These intrinsic factors of a food can be measured more or less accurately. Of the physical parameters, the pH value, the redox potential value (Rödel and Scheuer 1999a,b; 2000a,b) and the water activity of food may be reliably determined; equipment suitable for measuring the $a_w$ level has been developed in recent years. As a consequence, the concept of water activity with all its significance has become ever more widely established in research and especially in industrial applications (Giese 1997).

Water is essential for the growth and metabolic activity of micro-organisms. But not all of the water present in food is in fact available for the biological activity of micro-organisms or for other chemical and enzyme reactions. The concept of ‘water activity’

(Scott 1957) has generally been accepted as a parameter for the concentration conditions in the aqueous part of food. The water activity is defined as the ratio

$$a_w = p/p_0$$

where $p$ represents the actual partial pressure of water vapour and $p_0$ the maximum possible water vapour pressure of pure water (saturation pressure) at the same temperature. The $a_w$ level is therefore dimensionless; pure water has a level of 1.0, and a completely water-free substance has a level of 0.0. The relationship between the equilibrium relative humidity (ERH) in a food and the water activity is

$$a_w \times 100 = ERH$$

The $a_w$ level is expressed as a fraction of 1, the equilibrium relative humidity as a percentage.

## 16.2 Significance of water activity

### 16.2.1 Effect of water activity on food quality

For foods with a high level of water activity, the shelf life is limited mainly by microbiological activity. Products with $a_w$ levels below about 0.70 may well be stable microbiologically and consequently have a longer shelf life, but now the slower, enzyme-related breakdown processes come to the fore. It is mainly chemical reactions that determine the quality and stability of these foods. Figure 16.1 clarifies the mechanisms of food deterioration as a function of water activity (Heiss and Eichner 1971; Labuza *et al.* 1972b). As shown in the figure, the shelf life of products with very low water activity is limited primarily by a marked fat oxidation (Maloney *et al.* 1966), whereas non-enzymic browning (Maillard reaction) is dominant, with a pronounced maximum in the range of intermediate water activities. Labuza *et al.* (1972b) also observed a further increase in fat

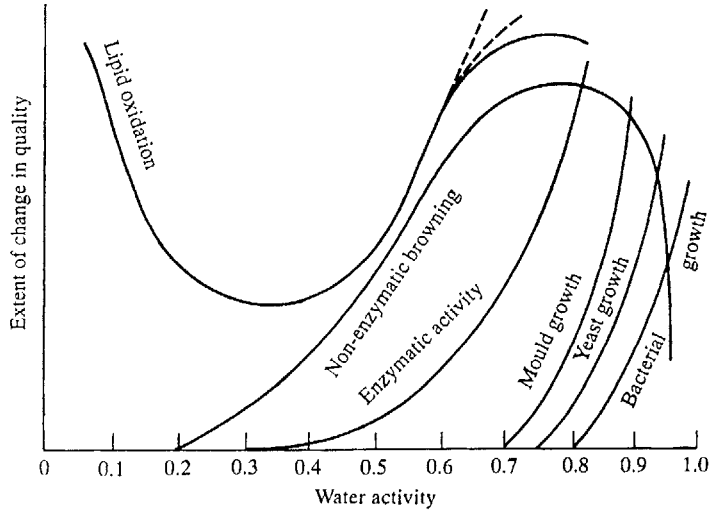


**Fig. 16.1** Extent of change in quality as a function of water activity (from Heiss and Eichner 1971; Labuza *et al*. 1972b). The figure represents bacteria, yeasts and moulds of average tolerance. Individual strains can have exceptional $a_w$ tolerance (see Table 16.1).

oxidation in certain cases within this intermediate range. In foods with even higher $a_w$ levels, the rate of reaction of enzyme-catalysed oxidation and hydrolysis also increases (Hunter *et al.* 1951; Acker 1962; Acker and Huber 1970), as there is now enough water available to transport the substrate to the enzyme. For water activities over 0.70, changes in the food are mainly caused by the growth of micro-organisms (bacteria, yeasts and moulds).

### 16.2.2 Effect of water activity on food stability

*Water activity tolerance of bacteria, yeasts and moulds*

Micro-organisms, like people, contain over 70 per cent water. A very important function of water is maintaining osmotic pressure within the cell of the micro-organism and transporting nutrients. This transport mechanism works principally because the necessary osmotic forces required for osmosis between the inside of the cell and its surroundings are present. In this environment, the endogenous and exogenous enzymes produced by the micro-organisms can play their role in the microbial metabolism. By means of exogenous enzymes, larger molecules, which may not pass through the cell membrane of the micro-organism, may be split up into smaller fragments, which can then diffuse inside the cell through the osmotic barriers, aided by active transport mechanisms. Once here, the fragments are then either further oxidised directly by endogenous enzymes or prepared for oxidation in several stages. If this ordered, highly complicated cooperation between different enzyme systems in the living cell is disturbed, for example by a reduction in the water activity, the reproduction, metabolic activity, resistance and survival of the micro-organisms in the food are affected.

As shown in Fig. 16.2, many traditional food preservation processes, such as salting, sugaring, drying and freezing, alter the concentration of the particles dissolved in the water of the product and thus its $a_w$ level (Rödel *et al.* 1979). The transport of nutrients into the cell interior of the micro-organism is affected by the reduction in water activity, since the osmotic pressure in the cell or its water activity can be changed and adapted to environmental conditions only within a limited individual range. The result is retarded growth of the micro-organism, or its death, thus producing a stabilising or preserving effect on the food.

Micro-organisms occurring in food are frequently responsible for spoilage, and under certain conditions also for food-induced infections or food poisoning. They may, however, be desirable, for example to preserve and add flavour to meat products (raw sausage and raw ham) or to dairy products by fermentation. All these desirable and undesirable microbial activities take place only if the water activity of the product permits multiplication of the appropriate micro-organisms. Table 16.1 gives the minimum $a_w$ levels for the growth of various species of bacteria, yeasts and moulds. This table was compiled by Leistner *et al.* (1981) from data by various authors.

As can be seen from the table, bacteria in general require higher water activity in the substrate than yeasts, and yeasts higher levels than moulds. The micro-organisms under discussion are no longer capable of reproduction below these $a_w$ levels. The test results of the cited authors do not always agree on the $a_w$ level limits for individual strains, partly because of the different experimental conditions. Therefore, the values in Table 16.1 must be seen as something of a compromise. As Table 16.1 shows, reproduction of most of the Gram-negative rods is inhibited in foods with an $a_w$ level lower than 0.95, and this is also the case for most bacilli and clostridia and for germination of their spores. Neither can *Shigella*, *Salmonella*, *Escherichia coli* or most *Vibriona* multiply, so the most

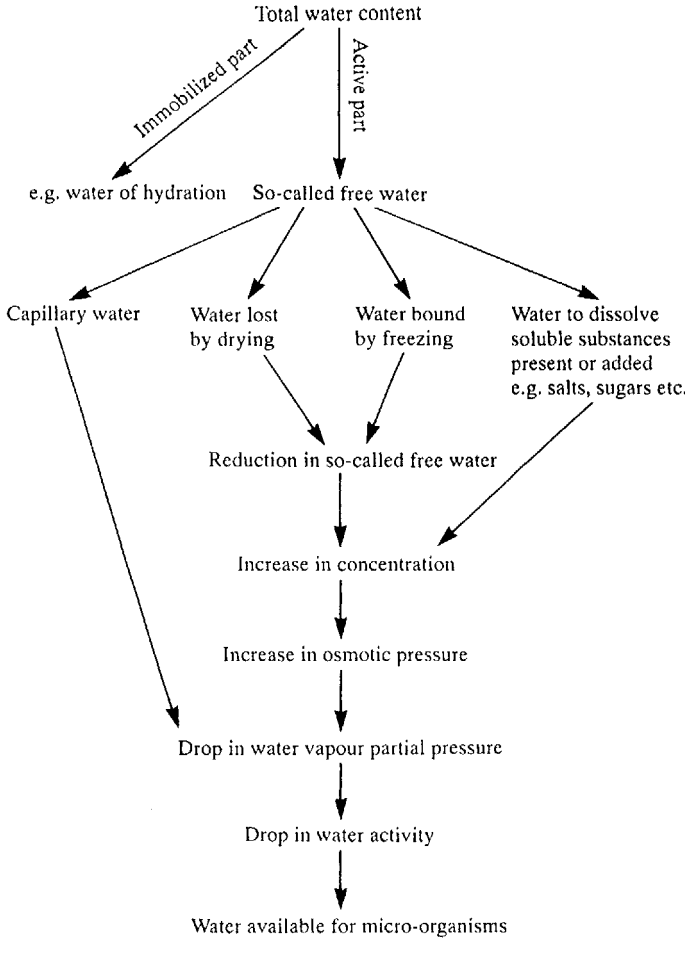


**Fig. 16.2** Comparison between the water available to micro-organisms and the total water content of foods.

common causes of spoilage by microbial activity are eliminated, together with food-related infections and food poisoning. *Staphylococcus aureus*, also a food-poisoning organism, can tolerate $a_w$ levels as low as 0.86, but under conditions of reduced oxygen this type of cell is inhibited at a level of 0.91.

If water activity in the substrate is adjusted not with NaCl or sugar but with glycerol, then different micro-organisms, such as *Clostridium botulinum* types A, B and E (Baird-Parker and Freame 1967), *Clostridium perfringens* (Kang *et al.* 1969), *Bacillus cereus* (Jakobsen *et al.* 1972; Jakobsen and Murrell 1977), *Salmonella oranienburg* (Christian 1955b; Marshall *et al.* 1971; Rödel and Lücke 1983) and *Vibrio parahaemolyticus* (Beuchat 1974), grow if water activity is lower. This is worth mentioning because glycerol is frequently used in place of NaCl or sugar to reduce $a_w$ in products of intermediate moisture content.

The tolerance of individual micro-organisms to water activity is in general lower if other factors in the foodstuff such as temperature, pH value, redox potential, oxygen and carbon dioxide concentration deviate from the optimum, or if the product has been treated with preservatives. This 'hurdle effect' (Leistner and Rödel 1976a; Leistner 1977; 1978)

**Table 16.1** Minimum water activity ($a_w$) for multiplication of micro-organisms associated with foods (Leistner *et al*. 1981)

| $a_w$ | Bacteria | Yeasts | Moulds |
|---|---|---|---|
| 0.98 | *Clostridium*[b], *Pseudomonas*[a] | — | — |
| 0.97 | *Clostridium*[c], *Pseudomonas*[a] | — | — |
| 0.96 | *Flavobacterium, Klebsiella, Lactobacillus, Proteus*[a], *Pseudomonas*[a], *Shigella* | — | — |
| 0.95 | *Alcaligenes, Bacillus, Citrobacter, Clostridium*[d], *Enterobacter, Escherichia, Propionibacterium, Proteus, Pseudomonas, Salmonella, Serratia, Vibrio* | — | — |
| 0.94 | *Bacillus*[a], *Clostridium*[e], *Lactobacillus, Microbacterium, Pediococcus, Vibrio Streptococcus*[a] | — | *Stachybotrys* |
| 0.93 | *Bacillus*[f], *Micrococcus*[a] | | *Botrytis, Mucor* |
| | *Lactobacillus*[a], *Streptococcus* | — | *Rhizopus* |
| 0.92 | — | *Pichia Rhodotorula, Saccharomyces*[a] | — |
| 0.91 | *Corynebacterium, Streptococcus* | — | — |
| 0.90 | *Bacillus*[g], *Lactobacillus*[a] *Micrococcus, Staphyloccus*[h], *Vibrio*[a] | *Hansenula, Saccharomyces* | — |
| 0.88 | — | *Candida, Debaryomyces, Hanseniaspora* | *Cladsosporium* |
| 0.87 | — | *Debaryomyces*[a] | — |
| 0.86 | *Micrococcus*[a], *Staphylococcus*[i], *Vibrio*[j] | — | — |
| 0.84 | — | — | *Alternaria, Aspergillus*[a], *Paecilomyces* |
| 0.83 | *Staphylococcus* | *Debaryomyces*[a] | *Penicillium*[a] |
| 0.81 | — | *Saccharomyces*[a] | *Penicillium* |
| 0.79 | — | — | *Penicillium*[a] |
| 0.78 | — | — | *Aspergillus, Emericella* |
| 0.75 | *Halobacterium, Halococcus* | — | *Aspergillus*[a], *Wallemia* |
| 0.70 | — | — | *Aspergillus*[a], *Chrysosporium* |
| 0.62 | — | *Saccharomyces*[a] | *Eurotium*[a] |
| 0.61 | — | — | *Monascus* |

[a] Some isolates. [b] *Clostridium botulinum* type C. [c] *C. botulinum* type E, and some isolates of *C. perfringens*. [d] *C. botulinum* type A and B, and *C. perfringens*. [e] Some isolates of *C. botulinum* type B. [g] Some isolates of *Bacillus stearothermophilus*. [g] *B. subtilis* under certain conditions. [h] *Staphylococcus aureus* anaerobic. [i] *S. aureus* aerobic. [j] Some isolates of *Vibro costicolus*.

*Sources*: Stille 1948; Snow 1949; Burcik 1950; Bullock and Tallentire 1952; Christian and Scott 1953; Scott 1953; 1957; Williams and Purnall 1953; Christian 1955a; Wodjinski and Frazier 1960; 1961; Christian and Waltho 1962; 1964; Lanigan 1963; Riemann 1963; Blanche Koelensmid and van Rhee 1964; Gough and Alford 1965; Hobbs 1965; Matz 1965; Brownlie 1966; Limsong and Frazier 1966; Segner *et al*. 1966; 1971; Baird-Parker and Freame 1967; Ohye and Christian 1967; Ohye *et al*. 1967; Kushner 1968; McLean *et al*. 1968; Pitt and Christian 1968; Pivnick and Thatcher 1968; Emodi amd Lechowich 1969 1969; Kang *et al*. 1969; Mossel 1969; Bem and Leistner 1970; Strong *et al*. 1970; Troller 1971; 1972; Jakobsen *et al*. 1972; Rödel *et al*. 1973; Tomcov *et al*. 1974; Beuchat 1974; Pitt 1975; Leistner and Rödel 1975; 1976a; 1976b; Jakobsen and Murrell 1977; Troller and Christian 1978; Christian 1981; Rüegg and Blanc 1981.

is of fundamental importance for food preservation because it may be used to prevent food-related infections, food poisoning and deterioration due to microbes, and the fermentation of food can be controlled more easily.

The water activity of food influences the toxin-forming ability of micro-organisms as well as their growth. According to Leistner *et al.* (1981) the limits for producing toxins by *Clostridium botulinum*, *Staphylococcus aureus* and toxinogenic moulds are as presented in Table 16.2. *Clostridium botulinum* types A, B, and E tolerate $a_w$ levels of 0.95, 0.94 and 0.97; type C tolerates 0.98. The limit for the formation of enterotoxin C by *Staphylococcus aureus* is 0.94, whilst for enterotoxin B it is as low as 0.90. The staphylococci that cause most food poisoning are represented by type A, which only loses its toxin-forming ability at water activities below 0.87.

**Table 16.2** Minimum water activity for toxin production by micro-organisms

| Micro-organism | Minimum $a_w$ | Source |
|---|---|---|
| *Clostridium botulinum* | | |
| Type C | 0.98 | a |
| Type E | 0.97 | b |
| Type A | 0.95 | b |
| Type B | 0.94 | b |
| *Staphylococcus aureus* | | |
| Enterotoxin C | 0.94 | c |
| Enterotoxin B | 0.90 | d,e,f,g |
| Enterotoxin A | 0.87 | h |
| *Mycotoxins* | | |
| Penitrem A | 0.94 | i,j |
| Citrinin | 0.90 | i,j |
| PR-toxin | 0.90 | i |
| Patulin | 0.88 | i |
| Cyclopiazonic acid | 0.87 | i,j |
| Roquefortine | 0.87 | i,j |
| Citreoviridin | 0.86 | j |
| Ochratoxin A | 0.85 | k,m |
| Griseofulvin | 0.85 | j |
| Verrucosidin | 0.84 | j |
| Aflatoxins | 0.83 | l |
| Ochratoxin A | 0.83 | n |
| Ochratoxin B | 0.81 | n |
| Penicillic acid | 0.80 | j,k |

[a]Segner *et al*. 1971
[b]Ohye and Christian 1967
[c]Genigeorgis *et al*. 1971
[d]Genigeorgis and Sadler 1966
[e]McLean *et al*. 1968
[f]Genigeorgis *et al*. 1969
[g]Troller 1971
[h]Lotter and Leistner 1978
[i]Beuchat 1983
[j]Lötzsch and Trapper 1979
[k]Bacon *et al*. 1973
[l]Northolt *et al*. 1977
[m]Harwig and Chen 1974
[n]Gareis and Rödel 2000

**Table 16.3** Expected inactivation time of bovine bladderworm (with and without bladder) by different NaCl concentrations (Schmidt and Rödel 1987)

| NaCl (%) | With bladder (hours) | Without bladder (hours) |
|---|---|---|
| 1.72 ($a_w$ 0.990) | 96 | 72 |
| 3.19 ($a_w$ 0.981) | 15 | 10 |
| 4.90 ($a_w$ 0.972) | 3 | 1 |

*Water activity tolerance of trichinae and bovine bladderworms*

The sensitivity of trichinae to reduced $a_w$ levels should also be mentioned. In model tests on sausage artificially infected with trichinae, Lötzsch and Rödel (1974) found that there were no further invasive trichinae when, by curing and drying the sausages, $a_w$ levels fell below 0.93. In further tests Lötzsch and Leistner (1977) proposed $a_w$ limits of 0.90 for sausage and 0.87 for ham as a protection against the possibility of trichinae in meat products.

A human parasite found worldwide is the beef tapeworm *Taenia saginata*. It is estimated that 40 million people are carriers of this intestinal parasite. In the (former) Federal Republic of Germany, on average 1 per cent of slaughtered cattle are infected with *Cysticercus bovis* or bladderworm, the larval stage of the beef tapeworm (Krauss and Weber 1986). This cysticercus is the sexless immature stage of the tapeworm, and lives in the muscles of cattle, its intermediate host. About 1 per cent of the population of the (former) Federal Republic of Germany are estimated to be tapeworm carriers (Grossklaus 1977). If any bladderworms are overlooked during the legally prescribed meat inspection then, despite all the care taken, if this meat is consumed raw – for example, in the form of steak tartare, rare steak or pink roast beef – the bladderworms grow into tapeworms in the human intestine. With this in mind, Schmidt and Rödel (1987) carried out tests to find out the $a_w$ levels needed to destroy *Cysticercus bovis*. The results are given in Table 16.3. The high NaCl sensitivity of the beef bladderworm, observed in the table, also permits statements on the possible risk of invasion through raw sausage. In NaCl concentrations of about 3 per cent bladderworms will not survive after 24 hours, and even in NaCl concentrations of 2.5 per cent they will most probably die after two days at the most. Human ingestion of viable bladderworms through eating sausage is almost totally avoided by a curing period of at least seven days, which is allowed even for quick-cured raw sausage products. For other meat products such as, for example, raw ham with the usual common salt content, it can also be concluded that any potential bladderworm will die after two days at the most and there will be no danger to the consumer.

### 16.2.3 Legal requirements

The importance attached to water activity as one of the few parameters easily measurable in food, for assessing chemical and microbiological stability, is underlined in many countries by legal specifications. These regulations contain limits for water activity alone as well as in combination with the pH value. These two parameters are then used to designate product stability. In Canada, meat products may be stored at room temperature if the $a_w$ level is less than or equal to 0.90 and the pH value less than or equal to 5.4 (*Meat Hygiene Manual*, Meat Hygiene Division, Agriculture Canada, 1987). In Japan, dried or salted, smoked and dried meat products must have $a_w$ levels less than 0.86 to be stored

above 10ºC, or lower than 0.94 to be stored below 10ºC (*Food Sanitation Law*, Ministry of Health and Welfare). Limits for food in the USA, which refer only to the water activity, stipulate an $a_w$ of less than 0.85, with no pH requirement (Johnston and Lin 1987; FDA 1979; 1985). These few examples show clearly how important it is to control the water activity of foodstuffs; and, particularly where sausage and ham are being produced for export into the above-mentioned countries, it is absolutely essential to control the water activity of these products. Compliance with the required limits is often strictly and severely enforced by the importing countries.

## 16.3 Water activity levels in food and their control

The water activity levels of fruits, vegetables, milk products and meat, measured by various authors in separate studies, have been published in the comprehensive work of Chirife and Ferro Fontan (1982). Alzamora and Chirife (1983) published water activity levels of different types of canned food such as fruits, vegetables and meat products. Detailed information on $a_w$ levels in German meat products has been published by Rödel (1975).

### 16.3.1 Water activity levels in food of animal origin

The water activity of meat and meat products is at the top of the $a_w$ scale because of their high water content. Fresh meat has the highest water activity level, but this declines to a greater or lesser extent during processing into meat products. In this process, the $a_w$ level is characterised particularly by the content of common salt in the aqueous phase of the product. The water activity of salted and dried meat products, such as raw sausage and ham, is therefore correspondingly lower. The levels for different meat products can be found in Table 16.4 (Leistner *et al.* 1981).

Fresh meat comes top of the list, with an $a_w$ of 0.99 in the lean part. This level is not affected by the type of animal, muscle group, or water-holding capacity. Meat products

**Table 16.4** Water activity range of fresh meat and some representative meat products (Leistner *et al.* 1981)

| Product | Minimum | Maximum | Average |
|---|---|---|---|
| Fresh meat | 0.98 | 0.99 | 0.99 |
| Bologna sausage | 0.87[a] | 0.98 | 0.97 |
| Liver sausage | 0.95 | 0.97 | 0.96 |
| Blood sausage | 0.86[b] | 0.97 | 0.96 |
| Raw ham | 0.80[c] | 0.96 | 0.92 |
| Dried beef[d] | 0.80 | 0.94 | 0.90 |
| Fermented sausage | 0.65[e] | 0.96[f] | 0.91 |

[a] Tiroler.
[b] Speckwurst.
[c] Country cured ham.
[d] Bündener Fleisch.
[e] Hard Sausage.
[f] Fresh Mettwurst.

**Table 16.5** Water activity of porcine and bovine fat (Rödel *et al*. 1980)

| Species and location | Treatment | $a_w$ | $H_2O$ (%) | NaCl (%) |
|---|---|---|---|---|
| Pork, back fat | Fresh | 0.991 | 9.6 | 0.1 |
| | Chilled | 0.982 | 6.5 | 0.1 |
| | Salted and smoked | 0.724 | 2.4 | 1.2 |
| Beef, tallow | Fresh | 0.993 | 13.6 | 0.2 |
| | Chilled | 0.984 | 4.2 | 0.2 |

have a lower water activity than fresh meat and therefore in general a longer shelf life. Measures such as, for example, adding common salt, extracting water or adding fat have the greatest effect in reducing the $a_w$ level of meat products. The addition of fat indirectly influences the $a_w$ level of meat products, since fat contains very little water in comparison with lean meat, as shown in Table 16.5. Meat products that are very rich in fat therefore contain relatively little water, so that the same amount of salt added to these products produces a sharper decrease in the $a_w$ level than in products with a greater lean portion (Rödel *et al.* 1980). Meats with a relatively high $a_w$ level, and therefore short shelf life, are frankfurter-type products; this is attributed to a large and variable excess of water, according to recipe, which is a processing requirement for this product group. Meat products produced without heating, and so consumed raw, must have lower water activities to guarantee the required stability towards microbial spoilage of the product, and to ensure safety by avoiding any threat to the health of the consumer. Allowance is made for this demand in the traditional production processes for sausage and ham and similar products by expensive drying processes, for example. The water activity of raw ham and bacon comes within the wide range of 0.88 to 0.96. This variation is principally due to the difference in the degree of drying. There is less variation with dried beef. The $a_w$ range for sausages is also quite wide. Hungarian and Italian salamis have the lowest $a_w$ levels, and the shelf life for these products is limited only by chemical changes, such as rancidity.

Bone (1973) and Karmas and Chen (1975) demonstrated in their work that low-molecular-weight soluble compounds in food, in contrast to high-molecular-weight compounds, have a considerable effect on the water activity. The number of dissolved particles is critical for the $a_w$. It is not only in meat products but also in cheese that proteins of high molecular weight are found alongside compounds of low molecular weight. Some of these, according to Rüegg and Blanc (1977), develop in cheese during the maturing process; others are added during production, for example sodium chloride. Table 16.6 gives the $a_w$ levels of different cheeses. Detailed assay data on different types of European cheese were published by Rüegg and Blanc (1977; 1981) and by Marcos *et al.* (1981).

### 16.3.2 Water activity levels in food of vegetable origin

Most bakery products have water activities that do not allow bacteria or yeasts to grow. Moulds, on the other hand, may still develop. Individual types of mould again require different minimum $a_w$ levels for growth in bakery products. The kinds of *Penicillium* forming a velour-type cushion may still develop well on bread and brioches, for example, whereas they are no longer able to multiply on cake because of the lower water activity.

**Table 16.6** Water activity of various European cheeses (Rüegg and Blanc 1981)

| Type | $a_w$ (25ºC) | Standard deviation |
|---|---|---|
| Appenzeller | 0.962 | 0.011 |
| Brie | 0.980 | 0.006 |
| Camembert | 0.982 | 0.008 |
| Cheddar | 0.950 | 0.010 |
| Cottage cheese | 0.988 | 0.006 |
| Edam | 0.960 | 0.008 |
| Emmentaler[a] | 0.972 | 0.007 |
| Fontal | 0.962 | 0.010 |
| Gorgonzola | 0.970 | 0.017 |
| Gouda | 0.950 | 0.009 |
| Gruyère[a] | 0.948 | 0.012 |
| Limburger | 0.974 | 0.015 |
| Münster | 0.977 | 0.011 |
| St Paulin | 0.968 | 0.007 |
| Parmesan | 0.917 | 0.012 |
| Quarg | 0.990 | 0.005 |
| Sbrinz[a] | 0.940 | 0.011 |
| Tilsiter | 0.962 | 0.014 |
| Processed cheese | 0.975 | 0.010 |

[a] Values for Emmentaler, Gruyère and Sbrinz were measured after ripening periods of 4–5, 6–5 and 10–11 months, respectively. The other values were determined using commercially available samples.

**Table 16.7** Water activity and water content of some breads and pastries (Flückiger and Cleven 1978)

| Product | $a_w$ | $H_2O$ (%) |
|---|---|---|
| White bread | 0.92 | 40 |
| Plundergebäck[a] | 0.86 | 26 |
| Cake | 0.83 | 26 |
| High-ratio cake | 0.76 | 26 |
| Gingerbread | 0.63 | 16 |
| Rusk | 0.38 | 6 |
| Waffles | 0.30 | 5 |

[a] Danish pastry.

However, cake might still be affected by types of *Aspergillus*, which impart the appearance of a spider's web. It is possible to influence the water activity of bakery products principally by means of sugar (sucrose), invert sugar, fructose, glucose, sorbitol and salt, as well as by reducing the overall water content (Flückiger and Cleven 1978; Brack and Röcken 1997). Table 16.7 presents a general survey of the $a_w$ levels of different bakery products. Chirife and Ferro Fontan (1982) give an overview of the water activity levels of produce in a paper in which the $a_w$ levels of over 80 fruit and vegetable products are listed.

### 16.3.3 Control of the water activity level

The modification of the water activity in foods is not only limited by flavour considerations, but also restricted more or less rigidly by the legal regulations in

individual countries. However, numerous publications have described technologies for new types of foods termed 'intermediate-moisture foods' (Heiss and Eichner 1971; Labuza *et al.* 1972a; 1972b; Bone 1973; Ross 1975; Davies *et al.* 1976; Simatos and Multon 1985). These products, in which mostly glycerol is used to retain moisture, have achieved great significance in a similar form in animal feeds. The moisture retainers or humectants, such as glycerol or propylene glycol, used in these products combine with or replace part of the water in the product and therefore reduce the $a_w$ level without the product losing its tenderness. These products can be stored for a long period even without refrigeration if a fungal growth inhibitor is applied. For traditional meat products, the water activity can be reduced mainly by salting, adding fat and drying. For Asian products the water activity is also in many cases reduced additionally by large quantities of sugar.

According to Flückiger and Cleven (1978) there are two ways of reducing the water activity of bakery products to below the critical limit of 0.75 for these products (lower limit for mould growth). During bakery production the water content of the product can be greatly reduced either through the choice of recipe and the process, or by the addition of sugar or sugar substitutes. In Great Britain and the USA the latter option is used for so-called high-ratio cakes. When special flours (cake flour) are used, sugar may be added at levels up to 160 per cent in proportion to the flour. The $a_w$ level of these very moist cakes lies in the range between 0.70 and 0.76. Unopened, these products are protected from mould growth even after prolonged storage. The fact that cakes containing raisins or candied fruit are hardly affected by mould is likewise due to a reduction in the water activity brought about by the soluble sugars present in the fruits.

### 16.3.4 Example: regulating raw sausage ripening by controlling the water activity level

It is not only from a microbiological point of view that water activity in food is of interest. This parameter may also be used to optimise products and to save energy in the processing steps involved in the fermentation of raw sausages such as salami. Conventional sausage ripening is currently based mainly on empirical principles. Thus, established processing conditions are regarded as optimal if there are no significant losses in the form of faulty products, for example with overdried edge zones or with tears. The ripening conditions (that is, temperature, humidity, air flow rate and time) are still altered mainly on the basis of sensory impressions, for example elasticity and dampness of the skin, external colour, etc. As a safeguard, a spot check is sometimes made on weight loss, pH value or water activity. Only in conditioned curing rooms in larger plants are continuous records of temperature and humidity standard practice. The character of modern curing plants has, however, changed with the increased use of microprocessors. In these new-generation microprocessor-controlled air-conditioned curing chambers, particularly those used in the production of raw slicing sausage, it is necessary to replace the older 'time control' of the curing chamber with process control, involving continuous assessment of selected fermentation parameters to allow continuous feedback to the curing process. It is then possible to react to desired – or particularly to undesired – changes and processes in the sausage during the long fermentation process by regulating the curing plant. The measurements necessary for this are supplied to the microprocessor by sensors (Rödel and Stiebing 1987; Stiebing and Rödel 1989).

## 16.4 Measuring water activity level

### 16.4.1 Background

The following methods for measuring water activity in foods, with the exception of the freezing point technique, operate by determining the equilibrium moisture content. In this context, equilibrium means that equality has been reached between the water activity of the food and the relative humidity of the air enclosed in a measuring chamber impermeable to water vapour. The following conditions are therefore essential for accurate practical measurement of $a_w$. The measuring chamber must be sealed to prevent the effects of humidity in the external air on the equilibrium humidity in the chamber, and to prevent water vapour losses from the chamber. The water content of the samples should be practically identical before and after achieving equilibrium in the measuring chamber, which presupposes that the volume of air enclosed with the food in the measuring chamber is small. The rate of equilibration (determining the measuring period) is also increased for small volumes of air.

### 16.4.2 Water activity as a function of temperature

The water activity of foods decreases as the temperature drops (Ross 1975; Van den Berg 1975; Fennema 1978). Research carried out by Krispien and Rödel (1976) and Rödel and Krispien (1977) on meat and meat products has shown that if these products are cooled from 25ºC down to the chilled and frozen range, there is a reduction in the $a_w$ level. At temperatures above the onset of freezing the decrease in $a_w$ level is insignificant (~0.00015 per K), whereas below this point the decrease is considerable (~0.008 per K). Below the freezing point of meat and meat products, the $a_w$ level equals the $a_w$ level of ice at the particular freezing temperature (Table 16.8). The $a_w$ level of foods at freezing temperatures can be read from this table. Table 16.9 illustrates the processes at decreasing temperatures for meat and meat products. All frozen foods, including frozen water, have the same $a_w$ level at the same temperature.

The temperature above freezing point at which the $a_w$ is measured therefore makes no difference, as the effect of temperature on the vapour pressure ratios is very slight. It is only necessary to ensure that calibration and sample measurement take place at the same temperatures. A measurement temperature of 25ºC has proved practical, as there is a great deal of information in the literature on calibration references at this temperature. Particular attention must be paid to the constancy of temperature while the $a_w$ is being measured. Any difference in temperature between measuring chamber, sensor and food may cause gross errors in the measurement. The higher the $a_w$ level of the sample, the greater the error.

### 16.4.3 Influence of equilibration periods and sample properties

It is not only the humidity equilibrium that can be adversely affected by variations in temperature during measurement; most electronic $a_w$ sensors also have a typical temperature response. Thus all water activity measurements must be taken at ambient temperatures that are as constant as possible (maximum ±0.2K fluctuation), which requires the use of temperature-controlled cabinets or Peltier-cooled boxes. The accuracy and in particular the reproducibility of many methods are adversely affected by inadequate measuring periods. If the $a_w$ level of the sample is determined by the process of equilibration, the measuring period for foods is generally about 2 to 4 hours. For better

**Table 16.8** Water activity of meat at freezing temperatures (calculated data from Moran 1936; Storey and Stainsby 1970; Fennema and Berny 1974)

| Temp (ºC) | $a_w$ |
|---|---|
| −1 | 0.990 |
| −2 | 0.981 |
| −3 | 0.971 |
| −4 | 0.962 |
| −5 | 0.953 |
| −6 | 0.943 |
| −7 | 0.934 |
| −8 | 0.925 |
| −9 | 0.916 |
| −10 | 0.907 |
| −11 | 0.899 |
| −12 | 0.889 |
| −13 | 0.881 |
| −14 | 0.873 |
| −15 | 0.864 |
| −16 | 0.856 |
| −17 | 0.847 |
| −18 | 0.839 |
| −19 | 0.831 |
| −20 | 0.823 |
| −21 | 0.815 |
| −22 | 0.807 |
| −23 | 0.799 |
| −24 | 0.792 |
| −25 | 0.784 |
| −26 | 0.776 |
| −27 | 0.769 |
| −28 | 0.761 |
| −29 | 0.754 |
| −30 | 0.746 |

control during measurement, the equilibration should be checked with a recorder. If, however, the $a_w$ level of a sample is established by determining the freezing point, then about 8 to 30 minutes will be necessary, depending on the level of water activity.

In the measurement of water activity by certain techniques, reactions may occur at the sensor due to various chemical compounds introduced with the sample, and these reactions can then compromise the results (Rödel *et al.* 1979; Pollio *et al.* 1986); glycerol, propylene glycol and similar compounds are principally responsible for such reactions. Sample inhomogeneity can also influence the result, particularly for air-dried sausages or hams. For such products, the average water activity is of little significance. To determine the storage stability, the sample portion with the highest $a_w$ (namely the sample core) needs to be tested. The $a_w$ profile can assist in studying the drying technology employed.

### 16.4.4 Instrument calibration

Both saturated and unsaturated solutions of various salts are suitable as standards for testing or calibrating a measurement technique. For calibration, Stoloff (1978) recommends saturated salt solutions in the form of salt slurries (Table 16.10). Tables of $a_w$ levels (percentage relative humidity) of saturated salt solutions at different

**Table 16.9** Water activity of meat and meat products at freezing temperatures (Rödel and Krispien 1977)

| | $a_w$ of product examples | | | |
|---|---|---|---|---|
| Temperature (°C) | Fresh Meat | Bologna sausage | Liver sausage | Fermented sausage |
| 25 | 0.993 | 0.980 | 0.970 | 0.870 |
| 5 | essentially ↓ unchanged | essentially ↓ unchanged | essentially ↓ unchanged | essentially ↓ unchanged |
| 0 | | | | |
| −1 | | | | |
| −2 | 0.981 | | | |
| −3 | 0.971 | 0.971 | | |
| −4 | 0.962 | 0.962 | 0.962 | |
| −5 | 0.953 | 0.953 | 0.953 | |
| −10 | 0.907 | 0.907 | 0.907 | |
| −15 | 0.864 | 0.864 | 0.864 | 0.864 |
| −20 | 0.823 | 0.823 | 0.823 | 0.823 |

temperatures can be found in Greenspan (1977), Resnik *et al.* (1984), Kitic *et al.* (1986) and Pollio *et al.* (1987). Unsaturated NaCl solutions varying in concentration are particularly suitable for calibrating instruments in the $a_w$ range from 0.75 to 0.99, critical for the microbial stability of foods. These solutions are easily made up and are relatively unaffected by temperature over a wide range (Chirife and Resnik 1984). The $a_w$ levels of NaCl solutions of differing molality and differing percentage levels (according to Robinson and Stokes 1965; Krispien and Rödel 1976) are brought together in Table 16.11. Saguy and Drew (1987) report on the adequate statistical evaluation of calibration data determined by different techniques for $a_w$ measurements.

## 16.5 Measurement techniques

### 16.5.1 Manometric method

Numerous methods of measuring water activity have been treated in detail in review articles (Troller and Christian 1978; Prior 1979; Rödel *et al.* 1979; Troller 1983a; Wolf 1984; Weisser *et al.* 1985). A special measuring technique, the direct manometric measurement of vapour pressure, has been described by Legault *et al.* (1948), Taylor

**Table 16.10** Water activity of salt slurries at 25°C (Stoloff 1978)

| Salt | $a_w$ | Salt | $a_w$ |
|---|---|---|---|
| $MgCl_2$ | 0.328 | KBr | 0.809 |
| $K_2CO_3$ | 0.432 | $(NH_4)_2SO_4$ | 0.810 |
| $MgNO_3$ | 0.529 | KCl | 0.843 |
| NaBr | 0.576 | $Sr(NO_3)_2$ | 0.851 |
| $CoCl_2$ | 0.649 | $BaCl_2$ | 0.902 |
| $SrCl_2$ | 0.709 | $KNO_3$ | 0.936 |
| $NaNO_3$ | 0.743 | $K_2SO_4$ | 0.973 |
| NaCl | 0.753 | | |

**Table 16.11** Water activity of NaCl solutions with various molalities at 25ºC (from Robinson and Stokes 1965)

| Molality | NaCl (% w/w) | $a_w$ |
|---|---|---|
| 0.1 | 0.58 | 0.996 |
| 0.2 | 1.15 | 0.993 |
| 0.3 | 1.72 | 0.990 |
| 0.4 | 2.28 | 0.986 |
| 0.5 | 2.84 | 0.983 |
| 0.6 | 3.39 | 0.980 |
| 0.7 | 3.93 | 0.976 |
| 0.8 | 4.47 | 0.973 |
| 0.9 | 5.00 | 0.970 |
| 1.0 | 5.52 | 0.966 |
| 1.2 | 6.55 | 0.960 |
| 1.4 | 7.56 | 0.953 |
| 1.6 | 8.55 | 0.946 |
| 1.8 | 9.52 | 0.938 |
| 2.0 | 10.46 | 0.931 |
| 2.2 | 11.39 | 0.924 |
| 2.4 | 12.30 | 0.916 |
| 2.6 | 13.19 | 0.908 |
| 2.8 | 14.06 | 0.901 |
| 3.0 | 14.92 | 0.893 |
| 3.2 | 15.75 | 0.885 |
| 3.4 | 16.58 | 0.876 |
| 3.6 | 17.38 | 0.868 |
| 3.8 | 18.17 | 0.860 |
| 4.0 | 18.95 | 0.851 |
| 5.0 | 22.62 | 0.807 |
| 6.0 | 25.97 | 0.760 |

(1961), Sood and Heldman (1974), Lewicki *et al.* (1978), Troller (1983b), Nunes *et al.* (1985), Benado and Rizvi (1987), Saguy and Drew (1987) and Zazoni *et al.* (1999). For this method, the comminuted sample is evacuated in a desiccator for several minutes, and after 1 hour the water vapour pressure in equilibrium with the sample is measured by means of an oil or capacitance manometer. This method requires very accurate temperature control. Sample volatiles other than water, if present, will influence the measurement.

### 16.5.2 Gravimetric method

In the isopiestic method, one determines the water activity of foods from the sorption isotherms of suitable materials (Landrock and Proctor 1951; Smith 1965; Gur-Arieh *et al.* 1965). In the so-called Fett-Vos method, the water activity of food is determined by means of dried reference materials (proteins, microcrystalline cellulose) (Fett 1973; Vos and Labuza 1974; Vansteenkiste and van Hoof 1982). The dried reference material is equilibrated with the sample in an evacuated desiccator, and any weight alteration in the reference substance is then recorded. The water activity in the sample is calculated from the change in weight and the known sorption isotherms of the reference substances. In a comparable method, Steele (1987) used polyols as references, determining the change in water content refractometrically rather than

gravimetrically. These methods are relatively easy to perform. If equilibration is carried out in a static atmosphere they are not, however, suitable for measuring perishable foods because of the long adjustment period of more than 24 hours. But if the work is carried out in a dynamic, conditioned air stream, this period is substantially reduced (Multon *et al.* 1980). Lang *et al.* (1981), McCune *et al.* (1981), Lenart and Flink (1983), Palacha and Flink (1987) and Marcos-Esteban (1997) describe a proximity equilibration cell (PEC) method, which is not very expensive and makes use of the change in weight of filter paper to determine the $a_w$ level of the sample.

### 16.5.3 Psychrometric method

Sharpe *et al.* (1991) outline a psychrometric technique for foods (Water Activity meter, Model aw-10, Ottawa Instrumentation Ltd., 169 Fifth Avenue, Ottawa, Ontario K12 2M8 CA). The instrument is valuable for the measurement of $a_w$ in cheeses, meats, preserves, butter, and canned vegetables. The principle of the method is to use a miniature hygrometer probe which contains both 'dry' reference and a 'wet' sensor. The latter is exposed to the atmosphere above the food sample after equilibration. The resulting temperature change is a very linear function. Measurement may be made with respect to pure water reference ($a_w = 1.00$) or a suitable sodium chloride reference ($a_w$ from 0.78 to 1.00). The measurement time is largely constrained by the time taken to achieve temperature stability. Five minutes are allowed for equilibration, and the measurement of $a_w$ takes a further 30 seconds. The total time per sample is normally well under ten minutes. The instrument is calibrated by measuring the response to a pure water sample and then one of 0.80 $a_w$ units. The $a_w$ resolution is ±0.01 units.

### 16.5.4 Hygrometric methods

*Salt method*

The $a_w$ level may be determined relatively cheaply using apparatus with the salt/filter-paper method of Kvaale and Dalhoff (1963), as modified by Northolt and Heuvelman (1982) and Hilsheimer and Hauschild (1985). The method is based on the fact that dried salt adhering to filter paper is dissolved if the humidity of the surrounding air has reached a point equal to the saturation humidity of the salt. If salts of different saturation humidities are used, the $a_w$ level of a sample may be estimated.

*Thread hygrometers*

This method is based on the hygroscopicity of the polyamide thread, which reacts to an increase in moisture by elongating noticeably. The instrument shown in Fig. 16.3 for measuring $a_w$ ($a_w$ level meter 5803, made by G. Lufft Mess- und Regeltechnik GmbH, Gutenbergstrasse 20, D-70736 Fellbach, Germany) consists of a sample-scale pan and an attachment that is connected from the pan to a measuring unit by means of a lever system. The polyamide thread is inside the attachment. The change in thread length is converted to a scale on an indicator by means of an axle and lever mechanism.

Measuring water activity with this instrument (which takes about 3–4 hours) requires constant temperature. This method has been extensively tested and described by Rödel and Leistner (1971), Rödel *et al.* (1975), Labuza *et al.* (1977), Bousquet-Ricard *et al.* (1980), Jakobsen (1983), Gerschenson *et al.* (1984) and Stroup *et al.* (1987). The accuracy of the instrument is 0.01 $a_w$ and the reproducibility is also 0.01 $a_w$ (Rödel *et al.* 1975; Bousquet-Ricard *et al.* 1980; Jakobsen 1983) at a constant temperature of 25ºC,

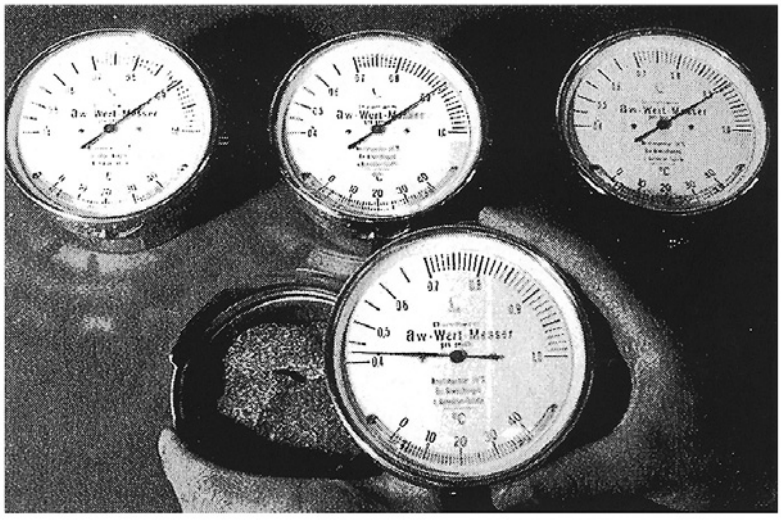


**Fig. 16.3** Thread hygrometer $a_w$-Wert-Messer Lufft, model 5803.00.

with a sufficient equilibration period and using an adsorptive procedure. Foods that contain glycerine or similar volatile organic compounds cannot be measured using this equipment.

*Electric hygrometers*

There are a relatively large number of different electric hygrometers on the market for measuring the water activity of foods. Since they cannot all be mentioned here, details will be given only of those employed in our own measurements on foods. The electric or electronic hygrometers fall into the category of capacitive hygrometers, conductivity hygrometers and dewpoint hygrometers according to the principle on which they function.

Capacitive hygrometers

In capacitive hygrometers the capacitance of a polymer capacitor in a measuring chamber changes as a function of humidity. The instrument shown in Fig. 16.4 (Hygrocontrol Labo 47, made by Hygrocontrol GmbH, Hospitalstraße 26, D-63450 Hanau, Germany) works on this principle to determine $a_w$. The equipment consists of a display unit connected to a measuring chamber. It may be used to take reliable $a_w$ measurements for foods in the range 0 to 1.00, with the aid of microprocessor-controlled linearisation of the calibration curve linked to temperature compensation of both sensor and electronics, and a provision for calibration storage. The instrument has digital data output (serial interface RS 232-V24), enabling further computerised data processing.

The measuring principle is based on a capacitor of very low mass (rapid temperature adjustment) acting as a humidity sensor. The dielectric is a hygroscopic polymer, which has a thin permeable sputtered layer of metal on both sides. Any alteration in relative humidity triggers a very rapid proportional change in capacitance. The adjustment period for equilibrium humidity in the measuring chamber is optimised by means of an integral fan, the period being about 2.5 hours for foods. The measuring head with the capacitance-measuring cell is pressed by a compression system against the surface of the sample dish so that it is water-vapour tight. Potentiometer adjustments are not necessary because of


**Fig. 16.4** Capacitive humidity meter Hygrocontrol Labo 47 and a probe type 4703 for water activity measurement.

software-controlled equipment calibration. Calibration points for $a_w$ from 0.00 to 0.95 are programmed into the digital electronics of the instrument. The accuracy of the system over this range of measurements is better than ±0.015 $a_w$ and there is good reproducibility in the 0.95 $a_w$ range under investigation (standard deviation 0.001, $CV = 0.11$ per cent for $n = 6$) (Rödel 1989, unpublished data).

The $a_w$ measuring equipment DK 1010, made by Driesen + Kern GmbH, Am Hasselt 25, D-24576 Bad Bramstedt, Germany also works on the principle of capacitance measurement. The system consists of the digital humidity/dewpoint/temperature display attached to the special sorption probe. A miniature fan is fitted to this probe to reduce the equilibration time. The head, with its capacitance-measuring cell and complete probe electronics, is simply laid on to the surface of a sample dish. Similar equipment is built by Rotronic AG (Grindelstraße 6, CH-8303 Bassersdorf, Switzerland) and consists of a $a_w$-station $A_w$VC and the instrument BT-RS1.

Conductivity hygrometers

With conductivity hygrometers, the measurement of electric impedance of a liquid hygroscopic substance is used for direct reading of the relative humidity or water activity in foods. The liquid hygroscopic materials include salt solutions or mixtures of various salt solutions, depending on the make. These sensors are thus also called electrolytic cells. The principle on which these cells are based relies (with only minor variations between individual makes) on a very precisely defined tiny quantity of the hygroscopic material sandwiched between a pair of electrodes mounted on a support plate. This substance tends towards equilibrium with the ambient humidity. The electrolyte produces a defined water vapour pressure at its surface, depending on its temperature and water content. If there are differences between this water vapour pressure and that in a test chamber, there is a water vapour exchange until the two pressures are identical. The water content of the electrolyte thus changes, depending on the temperature and water vapour pressure in the monitored surroundings, that is as a function of the relative humidity of the air or, in equilibrium, of the $a_w$ level of a food. The impedance of the system, measured by an electronic bridge with a high-frequency signal, is proportional to the water content. The effects of temperature on the hygroscopic material are largely corrected by electronic compensation, which is built directly into the cell. The

electrolytic measuring cells are calibrated against salt solutions with known $a_w$ levels and provide a signal that is directly dependent on the measured $a_w$ level.

When this type of $a_w$ measurement system is used, in addition to the upper temperature limit, the following conditions should generally be observed. Direct contact of the test cells with water or salt solutions should be avoided under all circumstances. This means that the $a_w$ level of calibration liquids and of foods may be measured only in the air space above their surfaces. Measuring chambers for samples are designed accordingly for different systems. The electrolytic cells must not be subjected to any heavy shock condensation such as may occur with larger swings from low to high temperatures. Heavy mechanical impacts when measuring above $a_w$ 0.80 must be avoided.

Electrolytic measuring cells, in common with capacitance cells, may react to volatile inorganic and organic substances by changing their characteristics, and these changes can be difficult to interpret. Low concentrations (~ 100 ppm) are normally tolerated, with the operating range for temperature and humidity also having an influence. To protect the measuring cell, some manufacturers offer special filters (active carbon filters) which are particularly recommended for use when measuring the $a_w$ of petfoods, as these animal foods are frequently produced with a propylene glycol additive (Pollio *et al.* 1986). If filters are not used, high concentrations of organic vapours may dissolve in the hygroscopic material and its characteristics may change. Some chemicals have only a temporary effect on the cell (that is the measuring cell regenerates when they evaporate from the electrolyte), but others have an irreversible effect on the electrolyte, destroying the measuring cell. Oil and fat volatiles are also harmful to the cell as these materials can condense in the sensor and prevent it from functioning.

Figure 16.5 illustrates the BT-RS1 electrolytic $a_w$ measuring system with the WA-40 and AwD measuring stations (made by Rotronic AG, Grindelstraße 6, CH-8303 Bassersdorf, Switzerland, and Rotronic Instrument Corp., 160, East Main Street, Huntington, N.Y. 11743, USA). This system is particularly suitable for measuring water activity of foods over an $a_w$ range of 0 to 1.0. Because the chamber is of solid metal construction, temperature differences within it are eliminated and rapid changes in temperature are compensated. The chamber WA-40 is well sealed (leakage rate lower than 0.005 $a_w$ per 24 h), permitting exact measurements of foods even with very long equilibration periods. The test cell is calibrated against reference salt solutions under the same conditions as the actual $a_w$ measurement.

The samples to be measured are placed in small polystyrene dishes in the bottom half of the measuring station. The top part of the chamber WA-40 contains the measuring head and is locked from above with a lever compression system to seal the measuring station against a neoprene O-ring. The lever system allows rapid opening and closing of the chamber. The WA-40 or AwD measuring stations, together with the BT-RS1, gives very accurate $a_w$ measurements of foods because of the high stability and very good linearity of the instrument. However, one requirement is that the temperature must be kept very constant, which is only possible in precision heating/cooling cabinets. Temperature and $a_w$ levels are indicated simultaneously on the instrument. The serial RS232 interface and the Windows®-software allow continuous signal recording and documentation.

An older but very similar measurement system was investigated in detail under practical conditions by Rödel *et al.* (1979), Vansteenkiste and van Hoof (1982), Stamp *et al.* (1984), Saguy and Drew (1987) and Stroup *et al.* (1987). With regard to the influence of volatiles, Yamada *et al.* (1984) did not note any effect of ethanol on the measuring cell.

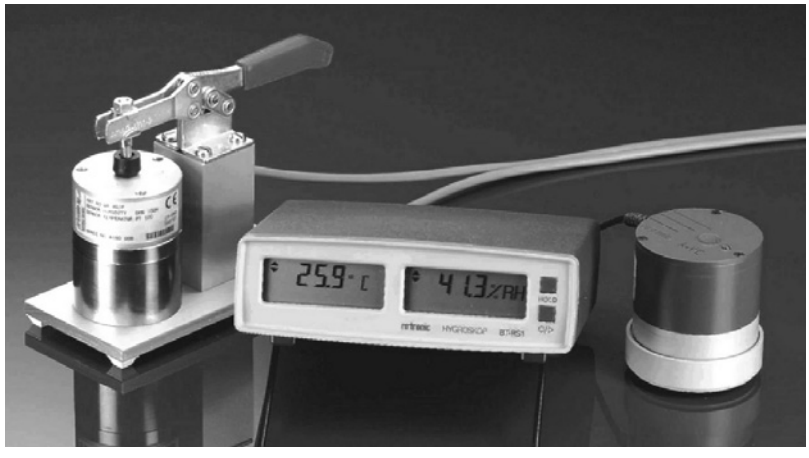


**Fig. 16.5** Conductivity humidity meter Rotronic BT-RS1 with special probes WA-40 and AwVD (right).

In comparing experiments, Rödel *et al.* (1990) were able to record good reproducibility of the resulting measurements (eleven measurements each for NaCl solutions with $a_w$ levels 0.90 and 0.95). The standard deviations were 0.0004 $a_w$ (CV 0.04 per cent) or 0.0007 $a_w$ (CV 0.07 per cent).

The electrolytic $a_w$ measuring system made by Novasina (Talstraße 35-37, CH-8808 Pfäffikon, Switzerland) works on a very similar principle. Figure 16.6 shows the Novasina AW SPRINT TH 500. Water activity of food in the range 0.10 to 1.00 may be measured thermostatically in this AW SPRINT. This measuring system comprises the $a_w$ sensor and the thermostatic device. The thermostatic device is a well-insulated metal box


**Fig. 16.6** Conductivity humidity meter Novasina Aw SPRINT TH 500 for measuring water activity.

in which an air-cooled Peltier system thermostatically controls the interior, and thus the sensor and the sample, with great precision. This measuring system is independent of the ambient temperature at the measurement location because of the thermostat, which is electronically controlled. The serial interface (RS232) and a PC software Novalog allows the connection to a computer for signal monitoring and documentation of the $a_w$-values. As tests on this system have shown, $a_w$ levels of foods may be determined with high reproducibility (±0.002 $a_w$).

Dew-point hygrometer
Decagon Devices, Inc. (P.O. Box 835, Pullman, Washington 99163, USA) offers a dew-point hygrometer for determining the water activity of various foods (Aqualab, Model CX-3). The CX-3 determines the water activity of a 7-ml food sample by measuring the sample temperature and the dew point temperature of air in equilibrium with the sample. The water activity is computed as the ratio of saturation vapour pressure at dewpoint temperature to saturation vapour pressure at sample temperature. Both temperatures must be precisely measured in order to obtain an accurate water activity measurement. Since this method of determining water activity goes back to basic principles, no calibration of the CX-3 should be necessary. The sample temperature is measured with a small thermopile sensor. A filter over the sensor limits the spectral response to the 8 to 14 $\mu$m waveband. All samples tend to have very high absorptivities and emissivities in this waveband, so the calibration of the infrared sensor should be almost independent of type or visible colour of the sample. The resolution is ±0.001 and the accuracy is ±0.003 $a_w$ (Richard and Labuza 1990; Roa and Tapia de Daza 1991, Voysey 1993; Harris 1995/96).

### 16.5.5 Thermometric technique

The freezing point of a food is closely linked in a physical/chemical sense with the water activity of the product, this being shown diagrammatically for meat products in Fig. 16.7. All those processes in a product that reduce the water activity also lower the freezing point of the food. The point at which foods begin to freeze can be measured and from this the $a_w$ level at 25ºC can be calculated. The $a_w$ Kryometer AWK-20, made by Nagy Messsysteme GmbH (Siedlerstrasse 34, D-71126 Gäufelden-Nebringen, Germany) works on this principle. With this instrument water activity, particularly for meat products, can be determined thermometrically. The measuring system includes an electronic indicator module with a microprocessor, a cylindrical sample chamber and a Peltier-cooling box at a temperature of approximately −50ºC. The measuring period for this cryoscopic $a_w$ test on meat products depends on the $a_w$ level. The higher the water activity of the sample, the shorter the measuring period. It is between about 8 and 30 minutes with an $a_w$ range from 0.999 to 0.80.

Because the freezing point of a sample is identified without operator intervention, the equipment automatically finishes the measuring procedure after calculating and displaying the water activity level, and it is then ready to commence a new measurement. Sample-specific effects, for example from humectants such as glycerol or similar materials, do not pose any problem with thermometric $a_w$ measurement, and the method has very good reproducibility. When salt solutions with $a_w$ levels of 0.90 and 0.95 were used, the standard deviation on eleven measurements was 0.0002 (CV 0.03 per cent) and 0.0001 (CV 0.01 per cent), respectively (Rödel *et al.* 1990; Thumel 1993).

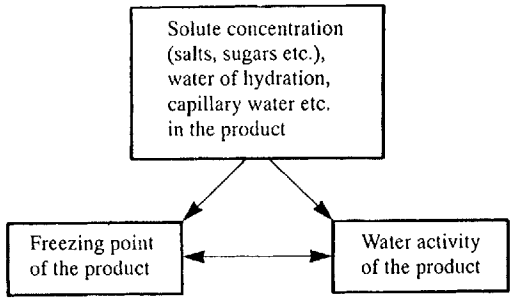


**Fig. 16.7** Relation between freezing point and water activity of meat products.

## 16.6 Conclusions

In this chapter, an attempt has been made to present a general survey of water activity in food to the student of food sciences, the engineer in the food industry, and also to manufacturers of measuring equipment. The significance of water activity for the quality and stability of food has been outlined, and a description and a discussion of the current possibilities provided by modern instrumentation for determining the water activity of foods have been given. From the many methods of $a_w$ measurement cited in the literature, those that are suitable for practical applications and which have already been proven in science and industry have been chosen for detailed discussion. There is no intention of discounting other methods that are not mentioned in this survey, some of which may well be better for an intended application.

The cost of the individual $a_w$ measurement methods varies greatly. The gravimetric methods in particular are less expensive, but cannot all be used for perishable foods because of the relatively long measuring period involved. The acquisition of electronic instruments to determine the water activity of foods means higher costs, but they generally produce good reproducibility. These instruments are therefore suitable for scientific and industrial applications.

## 16.7 References

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