DETERMINATION OF THE WATER CONTENT OF FOODS

I. INDIRECT DETERMINATION OF THE WATER CONTENT

by

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INTRODUCTION

The water content of foodstuffs is of greater importance than might at first be supposed. It is a decisive factor for the keeping quality of numerous edible products, e.g., cereals and dried vegetables. In the food trade it is necessary that the water content of the foodstuffs should be known very accurately. From the analytical point of view the determination of the water content of natural products is of special importance. The determination of every other component must be carried out in conjunction with the determination of the water content of the same specimen, only in that case can the content of any other component be expressed as a percentage of the theoretical anhydrous product, i.e., on "water free" basis. The "air-dried" product however is a bad basis, the water content of this substrate depends upon the humidity of the atmosphere during desiccation.

In course of time numerous determinations of the water content in foodstuffs have been carried out at the Central Institute for Nutrition Research. We hope to record the main facts of our experience in some future articles, but before doing so we consider it desirable to give a general survey of the methods known for the *indirect* determination of the water content.

The indirect determination of water can be carried out according to many principles of which we mention: desiccation; calculation from specific gravity or index of refraction (syrups, juices et al); deduction from conductivity or dielectric constant values. We shall only discuss here the methods deriving from the first principle, which may be classified as follows:

By means of a drying agent	room temperature	normal pressure · .	ordinary desiccator.
		in vacuo·	vacuum desiccator.
	raised temperature	normal pressure: .	MEIHUIZEN's apparatus.
		in vacuo:	PREGL's apparatus.
Without a drying agent	room temperature	normal pressure: .	unsuitable for analysis.
		in vacuo:	unsuitable for analysis.
	raised temperature	normal pressure: .	drying oven.
		in vacuo:	vacuum drying oven.

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The advantages and disadvantages of these methods will be discussed from the following points of view:

A. the absolute vapour pressure of the water in the substances to be dried;
B. the absolute vapour pressure of the water in the surrounding air;
C. the behaviour of the other components of the substance to be dried;
D. special causes of errors;
E. the rate of the drying process; requirements of practice.

A. ABSOLUTE VAPOUR PRESSURE OF THE WATER IN THE SUBSTANCE TO BE DRIED

Free water is met with in foodstuffs as a component of solutions, as water of crystallisation in hydrates and as "adsorptive water". We will consider the water in hydrophilic macromolecular substances as a special case.

Solutions in water are of very different nature; they may contain salts, proteins, sugars, and many other substances. The vapour pressure of these saturated or unsaturated solutions is of such an order of magnitude that the water can escape during the drying processes. The vapour pressure of unsaturated solutions increases rapidly with the temperature. The vapour pressure of saturated solutions also increases with the temperature (at least in the temperature range in which water determinations are usually effected) notwithstanding the fact that the solubility in water of most solids increases with the temperature.

If the drying of a *hydrate* proceeds in stages, one of the lower hydrates, in equilibrium with a next one ($+ H_2O$) at the temperature of desiccation may have a vapour pressure of the same order of magnitude as that of atmospheric moisture.

In this case even small changes in the relative humidity of the atmosphere may essentially change the final state of dehydration and thus considerably influence the results of the water determination.

By *"adsorptive water"* we mean the thin layer of water molecules adhering to the surface of all solids in a water-containing atmosphere. The thickness of this layer depends on the nature of the surface and decreases with decreasing atmospheric water vapour pressure and increasing temperature. STRÖMBERG (1928) determined the thickness of this "water film" at $25°$ C and relative humidities from 0.20 to 0.80. He found that the film on cleaned glass was 150–350, on quartz 16–65, on platinum 18–140 and on gold 3–23 Å.

The calculated surface area of 1 gram of powder with a sp. gr. of 1, consisting of globules of 0.1 mm radius, is about 3 sq. decimetre. A water film with a thickness of 100 Å over an area of 1 sq. dm weighs 0.1 mg. Thus it is obvious that the quantity of adsorptive water in powders is not always negligible. More complete data and a relevant bibliography are given by STRÖMBERG, *l.c.*

Macromolecular substances such as starch, protein, cellulose and pectic substances contain considerable quantities of water when in hygroscopic equilibrium with the atmosphere. At $25°$ C in equilibrium with air in which the water vapour

pressure is 14 mm Hg, starch contains 17%, protein 15% and cellulose (filter paper) 7% water. Due to the mechanism of water retention in this kind of substances, which will be fully discussed elsewhere (MOSSEL, Thesis Utrecht, in preparation), the water vapour pressure of these systems varies continuously with its water content.

Inversely at any different external water vapour pressure such substances show a different water content, as is shown in the typical S-curves of Fig. 1.
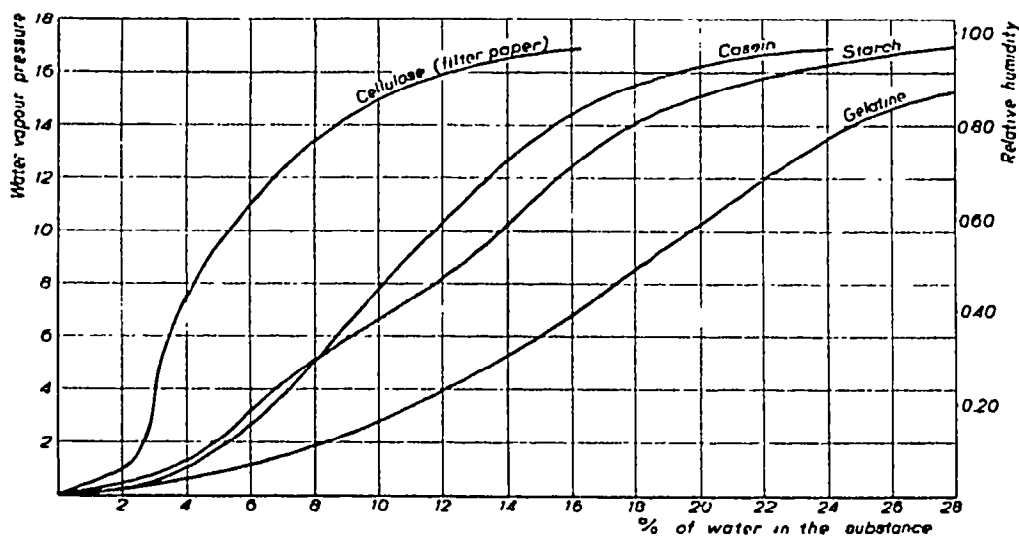

Fig. 1. Relation between water vapour pressure in the air and water content of macromolecular substances (according to KATZ's data)

It is evident from the S-form of the curves that even at a very low water vapour pressure in the surrounding air a significant quantity of water is retained.

As regards the *temperature* dependency we remark that even at a comparatively high water content the vapour pressure rises rapidly with the temperature. Thus it was found that potato starch containing 16% of water shows a water vapour pressure of 12 mm at 25° C and of 539 mm at 92° C. In the case of a low water content, i.e. in the region in which drying problems occur, the water vapour pressure shows a still greater temperature dependency; although here the absolute water content is so much smaller, this effect can be traced analytically. In cereals LEAVITT (1910) found considerable differences in loss of water when the temperature of the drying oven deviated 1° C from its standard temperature of 100° C; such differences were also observed by SCHERINGA (1920).

MAKOWER et al. (1946) when determining water in vegetables at 70° C, found differences of 0.1% absolute per degree of difference in temperature of the drying oven.

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With increasing temperature the first part of the S-curve invariably shifts towards the pressure-axis (PAP, 1934; GANE, 1943). This means that the change in water content, caused by a given change in relative humidity, decreases with increasing temperature. The analytical consequence of this effect is, that changes in the water vapour pressure of the air at high drying temperatures cause negligible differences in the results of the water determination, whereas the same changes at a lower drying temperature may cause marked differences in the water content found (VOGELENZANG, 1922).

B. ABSOLUTE VAPOUR PRESSURE OF THE WATER IN THE SURROUNDING AIR

The absolute water vapour pressure of the air in our laboratories may vary considerably, as a rule between 6 and 20 mm Hg. Therefore the results of water determinations in a drying oven at low temperatures depend considerably on prevailing humidity conditions of the atmosphere. The absolute water vapour pressure does not vary when the air is heated; therefore in a heated oven affording fair ventilation the same water vapour pressure prevails as in the laboratory.

In a vacuum oven, however, the absolute water vapour pressure is lowered considerably (see Table I).

TABLE I
WATER VAPOUR PRESSURE IN A VACUUM OVEN, THE WATER VAPOUR PRESSURE IN THE LABORATORY BEING 6 AND 20 mm Hg RESPECTIVELY

Air pressure in vacuum oven		Water vapour pressure in mm Hg	
		In lab. = 6, in vacuum oven	In lab. = 20; in vacuum oven
According to A.O.A.C standards	100 down to 25 mm Hg . .	0.79 down to 0.20	2.63 down to 0 66
According to practical standards	5 down to 1 mm Hg . .	0.04 down to 0.008	0.13 down to 0.026

TABLE II
WATER VAPOUR PRESSURE OVER CHEMICAL DRYING AGENTS

Drying agent	Temp. ° C	Water vap. pressure mm Hg	Reference
P_2O_5	20	10^{-8}	HUTTIG AND TOISCHER
P_2O_5	room temp.	< 0 00003	MORLEY
$Mg(ClO_4)_2$	room temp.	< 0 00003	SMITH
BaO	20	10^{-16}	HUTTIG AND TOISCHER
BaO	30	< 0.00065	BOWER
CaO	20	10^{-9}	HUTTIG AND TOISCHER
CaO	30	< 0 003	BOWER
H_2SO_4 97.5%	15	0 001	HUTTIG AND TOISCHER
H_2SO_4 95%	20	0.005	HUTTIG AND TOISCHER
$CaCl_2$	20	0.1	HUTTIG AND TOISCHER

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Chemical drying agents (DOVER AND MARDEN, 1917) are more effective in reducing water vapour pressures. The figures shown in Table II, however, are for various reasons (HUTTIG AND TOISCHER, 1930) highly uncertain.

According to American data the most effective drying agent is $Mg(ClO_4)_2$; it can be regenerated by SMITH's method.

Sometimes it is recommended to combine two principles, *i.e.*: passing predesiccated air instead of ordinary air through an evacuated vacuum oven. MAKOWER *et al.* (1946) however, applying this method to vegetables (70° C, 1–5 mm Hg), found no greater water content than when drying without the passage of dry air. Presumably at water vapour pressures between 0.01 and 0.13 mm in the vacuum oven the amount of residual water in the material is so small that it can not be determined analytically.

<center>

C. BEHAVIOUR OF THE NON-WATER COMPONENTS OF THE

SUBSTANCES TO BE DRIED

</center>

If components with a non-negligible vapour pressure, *e.g.*, essential oils or volatile fatty acids, are present, they interfere with the indirect water determination. Sometimes the error may be restricted by carrying out the determination in a small space by means of a desiccant.

Various chemical reactions may also interfere, especially with thermal methods. For instance, too small a quantity of water may be found due to chemical bonding of a part of the water, e.g. in dextrination of starch, inversion of saccharose and hydrolysis of protein. Erratic low results may further be caused by oxydative changes in the non-water components, especially in fats. On the other hand the results are too high if thermal destruction of unstable compounds — forming water or other volatile substances — takes place during the drying process. The labile compounds are mostly organic substances, but inorganic compounds e.g. acid salts (hydrocarbonates) may also decompose. A well investigated example of these numerous decomposition processes is the caramelisation of lactose unter the influence of phosphates (SCHOORL AND GERRITZEN, 1921).

For many substances it is possible to indicate a critical temperature below which decomposition may arbitrarily be considered to be negligible. Every substratum has its own critical temperature; for potato starch this temperature was found by PORTER AND WILLITS (1944) to be 145° C. For vegetables the following losses in weight per hour, due to decomposition in the vacuum oven were established by MAKOWER *et al.* (1946). At 60° C: cabbage and onions 0.002%; at 70° C: onions 0.019%, cabbage 0.026%, carrots 0.003%, potatoes of low sugar content: immeasurably slight, potatoes of high sugar content 0.005%.

In some cases the interference caused by volatile substances or by decomposition

can be calculated by making use of the reversibility method of SAIR AND FETZER (1942), a variant of which is the rehydration method of MAKOWER (1946). We can merely draw attention to these methods here.

D. SPECIAL CAUSES OF ERROR

Even if a method for determining the water content is selected in accordance with the general directions discussed here, several errors may still creep in as a result of the following causes.

1. Delay in the establishment of equilibrium

It is evident, that in the course of a desiccation, due to the decreasing water content of the substrate, its water vapour pressure decreases and therefore the velocity of desiccation. In some cases this phenomenon causes serious experimental difficulties.

At 105° C lactose hydrate has to be heated for no less than 200 hours before the water of hydration is removed, whereas at 130° C only 3 hours' heating is required (BLEYER AND BRAUN, 1931). Maltose hydrate loses its water of hydration at temperatures above 90° C, but a vacuum is necessary to attain a sufficient speed (CLELAND AND FETZER, 1942). According to the same authors glucose hydrate becomes anhydrous in 17 hours in vacuo at a temperature of only 60° C.

The final percentages of water in starch, proteins, cellulose, etc. also escape slowly during desiccation. Thus no true equilibrium is reached within reasonable times (HERMANS) and it may happen that a substance shows *apparent* equilibria at different water contents, though at the same water vapour pressure of the atmosphere (hysteresis; KATZ, 1917).

2. Retardation due to the structure of the substance to be dried   .

The drying of biological material proceeds essentially as follows. At first water escapes from the surface of the particles. Water then diffuses from the interior of the particles to the surface; the higher the temperature the more rapid the diffusion. This process is accelerated by the fact that evaporation of water causes the concentration of salts, sugars, etc. to be greater on the surface than in the centre. Further, the loss of water causes shrinkage of the cells and hence of the entire particle; as some cells offer more resistance than others to these changes, cracks and splits are produced which create new evaporation possibilities.

Towards the end of the drying process, however, retarding factors appear. The permeability of the cell walls probably diminishes and in addition the contents of the internal cells also become highly concentrated; due to this lower concentration-gradient the speed of diffusion diminishes. So the speed of desiccation, governed by the speed of diffusion of water from the interior of the particles to the surface, depends upon the shape and size of the particles, the nature of the cell walls and the substances dissolved in the cel sap.

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The difficulty with which water escapes from crystal vacuoles, well known for instance in the case of sodium chloride, may be ranked among these causes of retardation.

3. Crust formation

When biological material such as syrups, extracts, etc., are dried, saturated solutions may be formed which are covered with crusts. These crusts are also formed in cracks and splits and they retard or prevent further evaporation of water. In some methods crust formation is reduced by distributing the substance over a layer of sand or pumice-stone, while the substance is usually stirred during the initial stage of the drying process. Pumice-stone is less suitable for this purpose (SCHOORL, 1918); air-dried sand contains only 0.033% of water and air-dried pumice-stone 0.5%. Moreover, pumice-stone is far more hygroscopic than sand. Distribution of the material over a large area of filter paper was recommended by EVANS AND FETZER (1941) and by CLELAND AND FETZER (1941, 1942).

As a result of retardations (D 1 and D 2) and crust formation, there are many cases in which a constant weight cannot be obtained. In such cases a limit can be fixed, e.g., by stipulating that no more than 0.05% in weight may be lost during a further 2 hours period of desiccation (A.O.A.C. method for syrups).

4. Analytical errors

As a rule too little attention is paid to the extremely hygroscopic nature of desiccated material, the humidity of just opened desiccators and the formation of a water film on the outer wall and on the inside of the weighing bottle (SCHOORL, 1919), on the sand or on the pumice-stone. It should be noted that 60 ml of air, the contents of an ordinary weighing bottle, at a water vapour pressure of 14 mm Hg, contain 0.9 mg H_2O.

E. RATE OF DESICCATION. REFERENCE METHODS AND RAPID ROUTINE METHODS

The process of desiccation should not only be as complete as possible but should take place at a reasonable speed. As the rate of desiccation is dependent on the difference between the vapour pressures of the water in the surface of the substance and in the air layer adjoining it, it can be increased:

a. by ventilation; in some vacuum ovens and in BRABENDER ovens passage of (dry) air is effected. In MEIHUIZEN's apparatus the rate of desiccation increases considerably by ventilation;

b. by evacuation, causing the molecules to diffuse more rapidly towards the drying agent; especially a high vacuum is very effective (LINDSAY AND MANS-FIELD, 1944);

c. by shortening the distance which the water molecules have to travel in reaching the drying agent.

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We have already noticed that the rate of desiccation in most materials is dependent on the rate of diffusion of water through the particles; therefore the particle size is decisive (PERRY, 1944; MAKOWER et al., 1944; HERMANS, page 13).

No method for the indirect determination of water is a satisfactory *universal reference method*. For each material a reference method should be developed which has as good a theoretical basis as possible. Such a reference method will generally be time-consuming: e.g. desiccation in vacuo at room temperature (the reference method for many thermo-labile substances) may take 3 to 6 months.

For serial analysis rapid *routine methods* have therefore been developed in which the conditions have so been chosen that they give the same result as the reference method; this correct result is frequently obtained by compensation of small errors. Examples of such procedures are the BRABENDER oven and various electric methods.

INDIRECT DETERMINATION OF THE WATER CONTENT, VIEWED IN CONNECTION WITH RELATIVE HUMIDITY (RH)

In the foregoing chapters our considerations were based on the *absolute* water vapour pressure in the air. Most authors (KATZ, 1917; PAP, 1934; KÖSTER, 1936) base their work in the *relative humidity* (RH) of the air. Their line of thought is briefly as follows.

Every value of RH corresponds to a certain equilibrium water content W of the substance. If the RH is sufficiently lowered, the substance will lose practically its entire water content. How RH can be lowered follows from the definition:

$$RH = \frac{p}{E}, \text{ where p } = \text{ water vapour pressure at } t°, \text{ and}$$

$$E = \text{ maximum water vapour pressure at } t°.$$

By means of a drying agent or by evacuation p can be diminished; raising the temperature causes E to increase. If air is heated, for instance in a drying oven to a temperature of 100° C, the value of p will remain the same as it is outside the drying oven, but E, which at 25° C amounts to 24 mm Hg, will increase to 760 mm Hg. The RH in the drying oven will thus drop to $\frac{24}{760}$ of its initial value. If the water adsorption isotherm has been once determined (Fig. 1), the residual water content of the material in hygroscopic equilibrium with air of this low RH can then simply be read from this isotherm.

This line of reasoning has its advantages and disadvantages. The advantages are:

1. W/RH-curves show only a slight dependence on temperature in contrast to W/p-curves.

2. Some investigators consider it an advantage that the RH indicates how far

conditions are different from saturation; thus the RH gives an idea of the "humi-difying capacity".

3. The concept RH is used in the fairly extensive literature on the subject of indirect water determination.

The first argument can be opposed by realizing that the W/RH-curves apply only to the temperature at which the relationship was experimentally investigated. Change of temperature shifts the position of the curves; Fig. 2 shows this for four substances in the temperature range 0°–60° C and RH = 0.50. The water content of wood and silk at 50° C is about 75 and 82 % of the value at 25° C respectively.
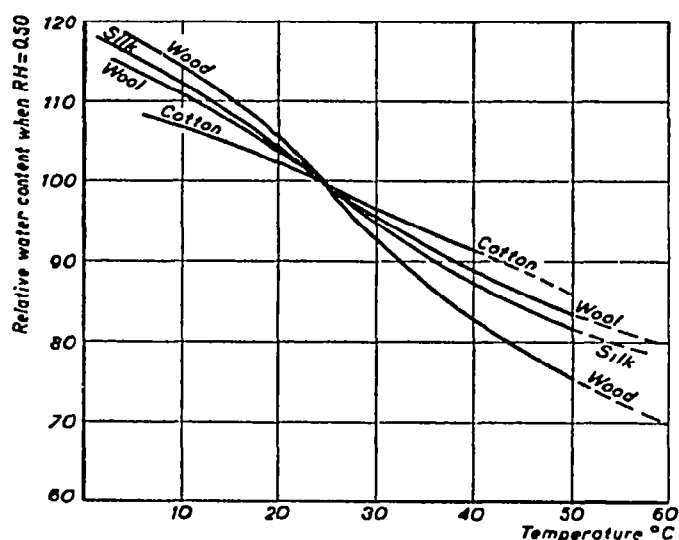

Fig. 2. Influence of temperature on the water content of some macromolecular substances at a constant RH (0.50) according to WILSON AND FUWA.

The usual temperatures prevailing during water determinations are within the range 70°–120° C, in which range the W/RH-curves of the substances under consideration have only been determined in a few instances (PAP, 1934; GANE, 1943; MOREY, 1947). Use is therefore made of curves established at lower tempe-ratures, a practice which, in view of the above, is quantitatively incorrect. This aspect should be considered all the more because the analytical difficulties arise chiefly on account of the residual traces of water in macromolecular substances. This water is adsorbed with great intensity and thus in this range the temperature dependency of the W/RH-curves is very pronounced.

A secondary argument against the use of the RH is that kinetic considerations must be based on the absolute vapour pressure p.

We are of opinion that from our treatise on the indirect determination of water content it is evident that all the factors involved can be freely discussed without introducing the concept of relative humidity.

SUMMARY

The indirect determination of the water content of foods is dealt with on the basis of the following general considerations:

A. The absolute vapour pressure of the water in the substance to be desiccated;
B. The absolute vapour pressure of the water in the surrounding air,
C. Behaviour of the non-water components of the substance to be desiccated,
D. Special causes of errors, viz.:
    1. Retardation in the establishment of equilibrium;
    2. Retardation due to the structure of the substance to be desiccated,
    3. Crust formation;
    4. Analytical errors.
E. Rate of desiccation: reference methods and rapid routine methods.

We prefer to consider the problems relating to the indirect determination of the water content on the basis of absolute water vapour pressures. The advantages and disadvantages of this method of treatment have been indicated.

RÉSUMÉ

Le dosage indirect de la teneur en eau dans les substances alimentaires est basé sur les considérations générales suivantes.

A. La tension de vapeur absolue de l'eau de la substance à sécher,
B. La tension de vapeur absolue de l'eau de l'air environnant;
C. Le comportement des composés anhydres de la substance à sécher;
D. Les causes d'erreur spéciales
    1. Retard dans l'établissement de l'équilibre;
    2. Retard dû à la structure de la substance à sécher;
    3. Formation d'une croûte;
    4. Erreurs analytiques,
E. Vitesse de dessication: méthodes de référence et méthodes rapides de routine.

Nous préférons considérer les problèmes relatifs au dosage indirect de la teneur en eau, comme basé sur la tension de vapeur d'eau absolue.
Les avantages et les désavantages de cette méthode sont indiqués.

ZUSAMMENFASSUNG

Die indirekte Wasserbestimmung in Nahrungsmitteln wird unter Bezugnahme auf den folgenden allgemeinen Betrachtungen behandelt:

A. Der absolute Dampfdruck des Wassers in der Substanz, die getrocknet werden soll;
B. Der absolute Dampfdruck des Wassers in der Umgebungsluft;
C. Das Verhalten der anderen Komponenten in der zu trocknenden Substanz;
D. Besondere Fehlerquellen, u.a.:
    1. Verzögerung in der Gleichgewichtseinstellung;
    2. Verzögerung infolge der Struktur der zu trocknenden Substanz;
    3. Krustenbildung;
    4. Analytische Fehler;
E. Trockengeschwindigkeit: Vergleichsmethoden und schnelle Routinemethoden.

Wir ziehen es vor, die Probleme, die mit der indirekten Bestimmung des Wassergehaltes zusammenhangen, auf der Basis der absoluten Wasserdampfdrucke zu untersuchen. Die Vor- und Nachteile dieser Behandlungsmethode werden angegeben.

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