

543.81 : 541.123.8/9

ENTRAINMENT DISTILLATION AS A REFERENCE
METHOD FOR THE DETERMINATION OF THE
WATER CONTENT OF FOODS.

I. Theoretical aspects of analytical dehydration with
special reference to entrainment desiccation.

BY

J. TH. G. OVERBEEK and D. A. A. MOSSEL *)

van 't Hoff Laboratory, University of Utrecht, Utrecht (The Netherlands).

1. Thermodynamic considerations indicate that in a *reference method for water determination* it is imperative to choose the water vapour pressure (p), prevailing during the analysis, very low (order: 1 mm Hg), to prevent a retention of water, which surpasses the precision of the method (order: 0.1 % abs.).

To reach the desiccation equilibrium in a reasonable time (≤ 8 h) an elevated temperature is necessary; the upper limit of temperature is determined by the thermostability of the least stable component of the actual substrate.

2. Out of the existing methods, *entrainment distillation with isooctane* (bpt 99° C) was chosen, since in a comparison, incorporating thermodynamic, kinetic, chemical and experimental aspects, it showed the highest overall suitability.
3. For this technique p was found to be directly proportional to the solubility of water in the entrainer at the temperature of the receiver. For isooctane as an entrainer, p was calculated from solubility data and found to be of the order of 1 or a few mm Hg, involving a total *retention* of water equalling 10—30 mg for an intake of 10—20 grams. The retention of water by the boiling entrainer was calculated and turned out to be negligible; the amount of water *dissolved* by the entrainer in the receiver was calculated and found not to surpass 10 mg.
4. Kinetic considerations revealed that under "*ideal*" conditions dehydration of the normal intake in entrainment distillation can be completed in about $\frac{1}{2}$ hour.
The additional time of operation (~ 5 h), noticed in practice, must be attributed to slow sedimentation and collection of small water droplets and to internal transport phenomena in the substrate.

*) Present address: Central Institute for Nutrition Research T.N.O., Utrecht, The Netherlands.

1. General aspects of dehydration.

The determination of the water content of a food is an intricate operation, since the term "food" comprises a great variety of chemical compounds, which may present specific difficulties on dehydration. The choice of a universal *reference method* for water determination in foods therefore makes it imperative to consider first of all the various aspects of dehydration.

1.1. Thermodynamics of dehydration.

Dehydration of a system only occurs as long as its equilibrium water vapour pressure (π) exceeds the water vapour pressure of the medium to which it is subjected (p). Generally π depends on the water content (W) and the temperature (T) of the system. The relation between π and W at a constant temperature is called the water sorption isotherm.

For a system, wherein crystalline hydrates may occur, this isotherm is a discontinuous step-function, the number of steps depending on the number of hydrates. Complete dehydration is achieved at any water vapour pressure p between zero and the decomposition pressure of the lowest hydrate.

On the contrary the water sorption isotherm for a system, containing a macromolecular component (e.g. a protein or a polymeric carbohydrate) and water, is continuous. This implies that at *any* finite external pressure p these systems contain a finite amount of water. Since practically any food contains one or more of the biocolloids mentioned, as a rule a food will not be completely dehydrated, but show a certain water *retention* r , unless $p = 0$.

If therefore a method for water determination in foods is intended to be used as a *reference method*, i.e. must show a high reproducibility and must be applicable to any substratum, it is inevitable to operate at a very low water vapour pressure p_0 , which involves a negligible retention.

One might be inclined to accept also a method, operating at an external water vapour pressure which is not equal to zero, but kept constant within narrow limits. Since, however, the retention $r(p)$ even at low values of p depends on the chemical composition of the dry substance¹⁾, this technique would not satisfy the second requirement of a reference method, and hence cannot be accepted as such. Of course this need not reduce the value of such a method for special purposes.

¹⁾ D. A. A. Mossel, Water bonding and water determinations in foods. Thesis Utrecht, 1949.

1.2. Kinetics of dehydration.

In current methods for the determination of the water content of foods the water vapour expelled from the substrate is removed by diffusion and similar transport phenomena. In order to achieve a rapid desiccation it is necessary to work at an elevated temperature (T), since with increasing temperature both the diffusion constant (D) and the diffusion gradient increase, the latter due to the circumstance that $\frac{\partial \pi(W)}{\partial T}$ is positive. Further it is very important to grind the substrate as finely as possible, since a coarser grind involves a smaller total diffusing surface.

But even an elevated temperature and a high degree of dispersion are no security against the highly unwanted "lingering", often noticed in the course of a dehydration. The cause of this effect is twofold. Generally, the diffusion "constant" in the material to be desiccated, depends upon the water content and in many cases shows a sharp decline at low water contents^{2) 3) 4)}.

Moreover in many foods *special* retarding factors may occur.

In the course of dehydration, liquid foods as sirups and extracts show considerable increases in viscosity which reduce D ; moreover with decreasing water content one or more solutes may crystallize and thus form strongly isolating crusts.

In solid substrates protein coagulation often gives rise to abnormally low diffusion rates and lipids may further interfere in this respect.

1.3. Chemical complications of dehydration.

Application of the elevated temperatures, necessary in the light of the preceding section, involves the risk of introducing changes in the chemical composition of the dry substance of the food.

As long as free water is present, *hydrolysis* may occur in salts⁵⁾, in disaccharides⁶⁾ and in starch^{7) 8)}. Further the expulsion of water during this phase of desiccation involves the entrainment of a significant part of the *volatile* components (essential oils, free fatty acids, nitrogen bases) present in many native food materials.

When once the free water has been expelled, other reactions inter-

²⁾ E. A. Fisher, *Cereal Chem.* **4**, 184—206 (1927).

³⁾ P. H. Hermans and D. Vermaas, *J. Polymer Sci.* **1**, 149—155 (1946).

⁴⁾ J. J. Hermans, *J. Colloid Sci.* **2**, 387—398 (1947).

⁵⁾ E. A. Schmidt und R. Schmidt, *Z. ges. Getreidewesen* **29**, 70—73 (1942)

⁶⁾ A. Leonhard, *Z. Untersuch. Lebensm.* **60**, 185—195 (1930).

⁷⁾ E. Parow, *Z. Spiritusind.* **45**, 39—40 (1922).

⁸⁾ H. Snyder and B. Sullivan, *Ind. Eng. Chem.* **16**, 1163—1167 (1924).

fering with the non-water-fraction of the substrate may present themselves. The most important examples are: *autoxidation* of lipids and *condensation* reactions, e.g. (acid) condensation of sugars^{9) 10) 11)} and condensation of reducing compounds with aminoacid derivatives^{12) 13) 14) 15)}.

In the conventional water determination methods hydrolysis and autoxidation suggest a fictitious low water content, while volatilization and condensation give rise to an illusory high water content.

2. Comparison of techniques, used as reference methods for the determination of the water content of foods.

2.1. Review of some current techniques.

In the *classic* reference methods for water determination the water content is calculated from the loss of weight noticed during desiccation ("indirect" methods).

About 1900 a "direct" desiccation method was developed, starting from the following so-called *entrainment-distillation*-principle. If a mixture of water and an organic liquid immiscible with water is boiled, a vapour is formed wherein the components participate according to their volatility. By condensing the vapour formed and collecting it in a graduated receiver, the volume of the water, originally present, can be determined^{16) 17) 18)}.

The method was rendered more popular by the introduction of continuously operating apparatus^{19) 20)}. The standard outfit of this type, using entrainers lighter than water, is sketched in figure 1. In the still F the substance under investigation is boiled with the entrainer and the vapour, emerging from the still, is condensed in the receiver R.

⁹⁾ J. W. Evans and W. R. Fetzer, *Ind. Eng. Chem. Anal. Ed.* **13**, 855—857 (1941).

¹⁰⁾ H. Hadorn, *Mitt. Geb. Lebensm. Unters. Hyg.* **36**, 324—334 (1945).

¹¹⁾ V. M. Lewis, W. B. Esselen and C. R. Fellers, *Ind. Eng. Chem.* **41**, 2591—2594 (1949).

¹²⁾ L. C. Maillard, *Compt. Rend. Acad. Sci. Paris* **154**, 66—68 (1912).

¹³⁾ L. Sattler and F. W. Zerban, *Ind. Eng. Chem.* **37**, 1133—1142 (1945).

¹⁴⁾ H. M. Barnes and C. W. Kaufman, *Ind. Eng. Chem.* **39**, 1167—1170 (1947).

¹⁵⁾ W. G. Iles and C. F. Sharman, *J. Soc. Chem. Ind.* **68**, 174—175 (1949).

¹⁶⁾ J. F. Hoffmann, *Z. angew. Chem.* **15**, 1193—1195 (1902).

¹⁷⁾ J. Marcussen, *Mitt. Königl. Materialprüfungsamt zu Gross-Lichterfelde-West* **22**, 48—49 (1904).

¹⁸⁾ B. Sjollema, *Chem. Weekblad* **4**, 343—347; 385—387 (1907).

¹⁹⁾ E. W. Dean and D. D. Stark, *Ind. Eng. Chem.* **12**, 486—490 (1920).

²⁰⁾ G. L. Bidwell and W. F. Sterling, *Ind. Eng. Chem.* **17**, 147—149 (1925).

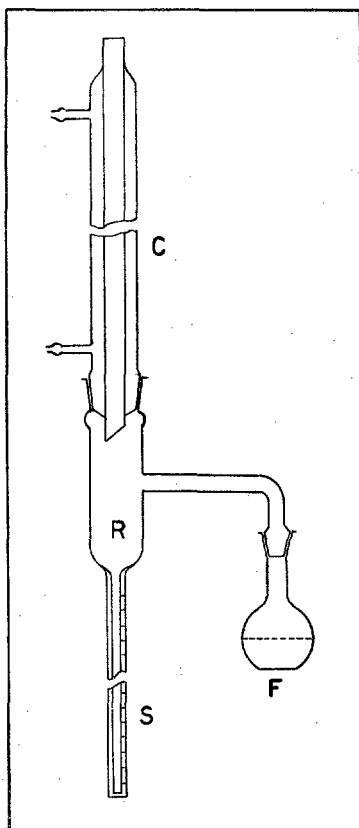


Fig. 1. Apparatus for water determination by entrainment distillation.

The water droplets collect in the lower part of the receiver, while the excess of entrainer flows back to the still. The total volume of the water after reaching a constant value, can be read from the graduated scale S.

A very recent principle of water determination is the *chemical* method originally introduced by *Fischer* and elaborated especially by *Mitchell* and co-workers²¹⁾. In this method the water is extracted from the substrate by elution with methanol, whereupon the methanolic water solution is titrated with a mixture of I, SO₂ and pyridine until no further iodine is reduced.

When we were faced with the problem of choosing a reference method for water determination in foods (January 1947) the *Fischer-*

²¹⁾ J. Mitchell and D. M. Smith, *Aquametry*, New York, 1948.

technique was in full development and therefore not suited to be incorporated in the comparative evaluation intended.

2.2. Comparison.

To arrive at an unbiased comparison of the merits of the other methods, one more aspect of analytical dehydration, i.e. the *operational factor*, must be considered. We divided this factor in 3 parts, i.e. availability of the apparatus and chemicals required; simplicity of the manual technique and possibility of rehydration in the course of the analysis. As a matter of fact most current methods of water determination are discontinuous, i.e. must be interrupted to determine the degree of dehydration at a certain moment. This interruption creates the possibility of rehydration, especially in the biocolloids, whose water content is a sensitive function of external water vapour pressure and temperature and hence will tend to rehydrate when unduly exposed to a lower temperature or higher water vapour pressure before being weighed.

The final appraisal has been attempted in table I. The favourable

Table I.
Appraisal of current reference methods for desiccational water determination

	Physical factors		Chemical factors			Operational factors			
	Thermod.	Kin.	Volat.	Autox.	Hydrol. condens. et al.	Avail.	Skill required	Rehydr. due to	
								ΔT	Δp
Open air oven (22)	—	±	—	—	±	+	+	—	+
Forced circulation oven (23, 24)	±	+	—	—	±	—	+	—	±
Pregl-technique (25, 26)	+	±	—	+	±	±	±	—	—
Vacuum-dessicator (27, 28, 1)	+	—	±	+	+	+	±	+	—
Entr. distillation	+	±	+	+	±	±	±	+	+

²²⁾ D. A. Mossel, Rec. trav. chim. 69, 932—934 (1950).

²³⁾ M. Sprockhoff, Z. Spiritusind. 52, 27 (1929).

²⁴⁾ F. A. Lee and J. C. Moyer, Foods Inds 15 (nr. 11) 64—77 (1943).

²⁵⁾ F. Pregl, Z. anal. Chem. 40, 781—785 (1901).

²⁶⁾ J. H. van de Kamer and N. F. Jansen, Anal. Chim. Acta 3, 397—404 (1949).

²⁷⁾ F. H. Campbell, J. Soc. Chem. Ind. 32, 67—70 (1913).

²⁸⁾ B. Makower, S. M. Chastain and E. Nielsen, Ind. Eng. Chem. 38, 725—731 (1946).

aspects of any method were rewarded by a mark +. Factors interfering with specificity, reproducibility or ease of operation were marked by —. If such an unfavourable extrinsic factor could be modified in the technique under investigation, or if it only exerted a small influence, it was marked by ±.

Some of the headings of table I have been printed in italics, i.e. those concerning the *essential* characteristics of a water determination. If one of these characteristics is scored as minus (—), the method is unsuitable as a reference method for the reasons outlined above.

It is evident that entrainment distillation is the most attractive of the methods reviewed. For this method no minus mark was awarded in any column and for most of the essential features full plusses were scored.

The vacuum desiccation at room temperature is not worse than entrainment desiccation as far as concerns the essential characteristics, but this method is a very lengthy one^{3) 28) 1)} and moreover involves rehydration chances. The other methods show essential disadvantages, which does not imply however, that they should not be useful for special purposes.

It was therefore decided to choose entrainment distillation as the reference method. Although this method has been adopted and advocated by workers in practically every field of analytical chemistry [cf. review by *Cleland* and *Fetzer*²⁹⁾] no systematic research on the theoretical and technical aspects has ever been carried out.

The results of a study of the *physico-chemical principles* of entrainment distillation will be reported in this paper. The development of the most convenient *technique* of entrainment desiccation and the *results* obtained, when applying this technique to current food substrates, will be the subject of two other papers of this series.

3. Theoretical aspects of entrainment desiccation.

For a fundamental treatment of entrainment desiccation the following subjects are to be considered.

1. *Thermodynamics* of the method, especially as regards the difference between the water originally present in the substrate and the water recovered in the calibrated part of the receiver. This difference arises from retention of water by the substrate, by the entrainer in the receiver and by the entrainer in the still.

2. *Kinetic factors*, i.e. the rate of desiccation as governed by the rate

²⁹⁾ J. E. Cleland and W. R. Fetzer, *Ind. Eng. Chem. Anal. Ed.* **14**, 124—129 (1942).

of distillation,³⁰ by the rate of liberation of water from the substrate and by practical limiting factors.

3.1. Thermodynamics; retention.

3.1.1 *Final situation in entrainment distillation.*

The final situation in entrainment distillation is not an equilibrium, but a steady state. We will consider first the distribution of the water in this steady state.

After prolonged distillation no net transport of water or entrainer occurs. In this situation water is transported:

1. by the vapour stream from the still to the receiver;
2. by the stream of liquid entrainer from the receiver to the still;
3. by diffusion from the receiver to the still, since the water vapour pressure in receiver and condenser is higher than that existing in the still.

The diffusion of water vapour from the laboratory atmosphere to the cool condenser will not be considered here, as in practice measures are taken to prevent this diffusion (cf. 2nd paper of this series).

We assume that in the stationary state the *liquid* stream shows a *constant* composition, characterized by a water content c_1 (grams/gram).

The *vapour* stream has a composition depending on the distance from the receiver or condenser. Calling the water content of the entrainer vapour at a certain place in the transport-path c_v (in grams/gram) and the distillation rate r (in grams per second) we find for the water transport by the vapour stream at that place:

$$t_1 = c_v r \quad \dots \quad (1)$$

Since in the stationary state the liquid entrainer flows back with the same rate r , analogously the transport t_2 is given by:

$$t_2 = c_1 r \quad \dots \quad (2)$$

The transport in the gas phase by diffusion (t_3) is given by *Fick's* first law³⁰) as:

$$t_3 = -D \frac{d(c_v/V)}{dx} \quad \dots \quad (3)$$

where D = diffusion constant of water vapour in the entrainer vapour;

³⁰) A. Fick, Ann. Phys. und Chem. 4, 59—86 (1855).

V = volume of one gram of entrainer vapour;

O = cross-section available for diffusion, which for simplicity is assumed to be constant (cf fig. 1);

x = coordinate perpendicular to this cross-section, which is zero in the receiver and condenser and increases in the direction of the still.

Since in the stationary state $t_1 = t_2 + t_3$,

$$\frac{d c_v}{dx} = -\frac{r V}{DO} (c_v - c_1) \dots \dots \dots (4)$$

Integration of this equation leads to:

$$c_v - c_1 = \{(c_v)_{x=0} - c_1\} \exp (-rVx/DO) \dots \dots (5)$$

In our standard apparatus, under normal working conditions O is about 1.5 cm^2 and r of the order of $10 \text{ g/min} = 0.2 \text{ g/sec}$. V calculated from the ideal gas laws for the entrainer used in this work, i.e. isooctane (C_8H_{18} , $M = 114$), is equal to:

$$V = 22400 \times \frac{372}{273} \times \frac{1}{114} \sim 270 \text{ cm}^3/\text{g}.$$

The diffusion constant of water vapour in isooctane is not known, but will certainly be smaller than that of water in air, which is about $0.25 \text{ cm}^2/\text{sec}$ [Guglielmo³¹]. Inserting these values in equation (5) we find:

$$c_v - c_1 = \{(c_v)_{x=0} - c_1\} \exp (-144 x) \dots \dots (6)$$

The high value of the coefficient of x in the exponential means that already at a very small distance from the condenser the difference between c_v and c_1 is negligible. Consequently the final water vapour pressure p_f in the still, where $x \sim 20 \text{ cm}$, is completely determined by the water content of the returning entrainer and thus can be calculated from the equation:

$$p_f = 760 \times \frac{114}{18} \times c_1 \sim 4800 c_1 \text{ (mm)} \dots \dots (7)$$

³¹) C. D. Hodgman, Handbook of Chemistry and Physics. 30th Ed. 1947, p. 1743.

This equation governs entrainment desiccation. It reveals that the most important parameter of such a method, i.e. the water vapour pressure prevailing in the still in the final stationary state, is directly proportional to the solubility of water in the liquid entrainer. Generally therefore paraffin hydrocarbons as entrainers are to be preferred above aromatics or chlorinated hydrocarbons.

3.1.2 Solubility of water in isooctane; calculation of final water vapour pressure.

For the standard working conditions it was deduced from numerous measurements of the temperature distribution in the receiver that the mean temperature is $\sim 60^\circ$ C. Unfortunately the solubility of water in isooctane at that temperature has not been determined. We were forced to make an approximation to this value from the following data.

a. *Berkengeim*³²⁾ determined the solubility (S) of water in isooctane in the range $10\text{--}40^\circ$ C, using the *Fischer-reagent-method*.

Extrapolating his values (plotted as a linear $\log S/\frac{1}{T_{\text{abs}}}$ — function) to 60° C we calculated $S_{60} = 0.015\%$.

In general, however, the values obtained by this author are too low. Taking the solubility of water in cyclohexane as an example, *Berkengeim* found values essentially below those of *Tarassenkov*³³⁾, the latter being satisfactorily duplicated recently by *Black et al.*³⁴⁾ using the tritium oxide-tracer method.

b. Unfortunately, *Black* and co-workers did not carry out measurements with isooctane themselves. Therefore we extrapolated their $\log S/\frac{1}{T}$ -line for heptane, which has its boiling point at exactly the same temperature as isooctane. Thus we found $S_{60} = 0.055\%$, a value which — referring to the circumstances outlined above — to our opinion will be closer to the real figure for isooctane than *Berkengeim's* value.

Hence we felt safe in taking for c_1 in the present case $0.05\% = 5 \times 10^{-4}$ g/g.

Thus according to eq. (7) the final vapour pressure is equal to:

$$p_f = 4800 \times 5 \times 10^{-4} = 2.4 \text{ mm}$$

³²⁾ T. I. *Berkengeim*, *Zavodskaya Lab.* **10**, 592—594 (1941).

³³⁾ D. N. *Tarassenkov* & E. N. *Polozhintzeva*, *Zhur. Obshchei Khim., Khim. Ser.* **1**, 71—79 (1931).

³⁴⁾ C. *Black*, G. G. *Joris* and H. S. *Taylor*, *J. Chem. Phys.* **16**, 537—543 (1948)

Due to the lack of knowledge of actual solubility data and the exact saturation conditions in the receiver, this "value" has only the significance of an order of magnitude. It can be safely stated however, that *the water vapour pressure — prevailing at the substrate — in an entrainment distillation, using isooctane, is of the order of 1 or a few mm.*

Therefore conditions in entrainment distillation are intermediate between the high water partial pressures in normal ovens²²⁾ and the low pressures, obtained when using chemical desiccants³⁵⁾.

3.1.3 Retention in crystal hydrates.

At water vapour pressures below the decomposition pressure of the lowest hydrate the retention in crystalline substances should be zero. Since, however, the equilibrium state may not be reached due to retarding effects as the occlusion of water within already dehydrated material, experiments were carried out with a sample of pure $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ in an air-oven at 100°C and a water vapour pressure of $p \sim 12 \text{ mm}$. A water retention of the order of 0.07 % abs. was found.

Since the vapour pressure of $\text{BaCl}_2 \cdot 1 \text{H}_2\text{O}$ at 100°C is much higher than 12 mm³⁶⁾ it may be assumed that the retention found is independent of the vapour pressure (at least at $p < 12 \text{ mm}$).

The intake of this hydrate, generally used in the distillation experiments, was 13 g; thus the retention can be expected to be slightly over 10 mg of H_2O , since the disturbance due to slow internal diffusion may be presumed to increase with increasing intake.

3.1.4 Retention in hydrophilic colloids.

One of us recently carried out measurements of the water retention in some representative foods in a well-ventilated air oven at about 100°C and $p = 10 \text{ mm}$ ²²⁾. A retention varying from 0.5—0.8 % was found. Since for low vapour pressures the adsorption of water by these materials is nearly proportional to the vapour pressure¹⁾ the retention at $p = 1—2.5 \text{ mm}$ may be estimated as 0.05—0.2 %. Hence, in a sample of about 15 g — the normal intake in distillation experiments — 7.5—30 mg of water will be retained.

It may thus be concluded that in the method under investigation the retention of water in the normal intake of foods and similar substances is of the order of 10—30 mg.

³⁵⁾ J. F. Reith, D. A. A. Mossel and J. H. van de Kamer, *Anal. Chim. Acta* 2, 359—369 (1948).

³⁶⁾ R. J. Meyer, *Gmelin's Handbuch der anorganischen Chemie*, 8^o Aufl., Syst. no. 30, p. 184—185.

3.1.5 Residual water in the entrainer condensed in the receiver.

The receiver contains about 20 ml = 14 g of isooctane. If it is assumed that the water in solution at the mean temperature of the receiver (60° C) does not separate or settle with measurable speed during the period of cooling preceding the final reading (cf. next paper in this series), a *maximum* loss of water of $14 \times c_1 = 14 \times 5 \times 10^{-4} \text{ g} = 7 \text{ mg}$ is found

3.1.6. Residual water in the boiling entrainer.

The boiling entrainer in the still is in equilibrium with a vapour containing 0.05 % of water (see 3.1.2). The composition of the liquid phase may be estimated from the phase diagram which is represented schematically in fig. 2.

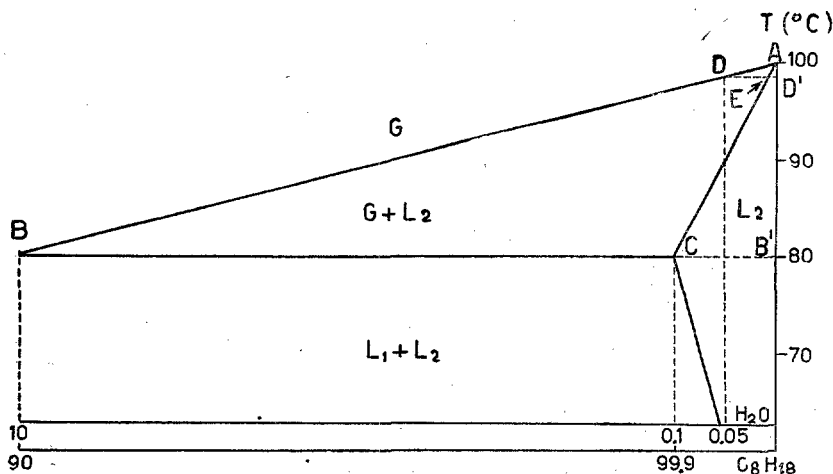


Fig. 2. Isooctane-part of the system water/isooctane.

The point B represents the vapour composition of the boiling two phase mixture of water and isooctane. In sect. 3.2.1 it will be shown that the isooctane concentration at B is about 90 %. The boiling point is 80° C.

C represents the saturated solution of water in isooctane at 80° C. By extrapolating *Black's* data (see 3.1.2) its water content can be estimated as 0.1 %.

Just to get an impression of the orders of magnitude concerned, the phase diagram may be completed by drawing straight lines, representing vapour and liquid compositions, from the points B and C to the boiling point (A) of pure isooctane ($\sim 100^\circ \text{C}$). It can be

seen then that the liquid in the still, E, in equilibrium with a vapour containing 0.05 % of water (D), contains only:

$$\frac{0.1}{10} \times 0.05 = 5 \times 10^{-4} \% \text{ water.}$$

Thus the 40 ml (30 g) of isooctane normally present in the still contain no more than about 0.15 mg of water, a quantity which may be neglected in our analysis.

3.2. Kinetic aspects of entrainment distillation.

3.2.1 Efficiency of an entrainer.

In analytical chemistry those methods are preferred, which yield the correct data in the shortest possible time. Hence in the present method an entrainer is "efficient", if it expels the water in a brief operation. This requires, that a vapour is formed which is rich in water.

The principle of entrainment distillation is, that "immiscible" liquid pairs, water (W)/organic solvent (O), produce a vapour, which in a good approximation at $T^{\circ}\text{C}$ exerts a pressure (π):

$$\pi_T = {}_W\pi_T + {}_O\pi_T \dots \dots \dots (8)$$

When two organic liquids with different boiling points are compared, the higher boiling liquid at any temperature (T) exerts a lower vapour pressure ${}_O\pi_T$ than the lower boiling one. Consequently the boiling point of the system, containing the higher boiling entrainer and water, will be higher than that of the other system. In the former case therefore, the water vapour pressure in the boiling system is higher than in the latter, showing that the efficiency of an entrainer increases with increasing boiling point.

In our experiments on water/isooctane the distillation temperature was 80°C at 767 mm; since ${}_W\pi_{80} = 355$ mm, ${}_O\pi_{80} = 412$ mm. Applying the ideal gas laws to this vapour mixture, the weight ratio of water and isooctane in the vapour is found as:

$$\frac{G_W}{G_O} = \frac{355}{412} \times \frac{18}{114} = 0.136.$$

Experimentally it was found that 100 ml of water/isooctane condensate contained 8 ml of water. Hence

$$\frac{G_W}{G_O} = \frac{8 \times 1}{92 \times 0.7} = 0.124,$$

which is in satisfactory agreement with the theoretical calculation.

From this value the time (t_c) necessary for complete expulsion of water, when pure water is subjected to entrainment distillation in our method, can be calculated.

The distillation capacity is about 10 g/min which corresponds to about 1 g of water per min. The quantity of water used in our experiments normally amounts to about 1.8 ml hence $t_0 \sim 2$ min.

In practice t_c -values of the order of 3 hours are found, however, although in the first 10 min over 90 % of the water is recovered. This demonstrates that other limiting factors govern the situation. *It is very likely that these "other factors" are: sticking of small droplets to the condenser and receiver walls and delayed sedimentation of these small droplets.*

3.2.2 Calculation of the time of distillation for a substrate.

For an actual biocolloidal substrate the theoretical time of distillation, t_0 , will be longer than that required for total entrainment of the free water, present in it, since in the course of the desiccation the water vapour pressure of the substrate decreases.

If complete absence of retarding factors is assumed, i.e. if the *water transport by the distillation process* is considered as the *limiting factor*, the course of the dehydration can be described by:

$$a dW = - E dt \quad \dots \quad (9)$$

where:

- a = intake of substrate (grams);
- W = water content of the substrate (grams/gram);
- E = intensity of entrainment (grams of water per hour);
- t = time (hours).

The correlation of E with the entrainment parameters *accidentally* is very simple.

Hydrocarbon entrainers of the aliphatic type and boiling range 90—100° C show heats of evaporation $\lambda \sim 95$ gcal/g, corresponding to molar heats of evaporation of about 10.000 gcal. Water possesses $\lambda = 540$ i.e. $\lambda_M = 9720$; thus: at a constant heat supply (as prevailing in an entrainment distillation) the molar distillation velocity v_M is practically independent of the water: entrainer-ratio.

As was outlined in 3.2.1 the molar proportion between water and water + entrainer in an entrainment distillation is:

$$\frac{\pi_W}{\pi_W + \pi_O} = \frac{\pi_w}{760}$$

Therefore a total molar distillation velocity v_M corresponds to a molar water distillation velocity $\frac{\pi_W}{760} \cdot v_M$ or a water distillation, expressed as

$$\text{g/h} : E = \frac{18\pi_W v_M}{760}$$

Now v_M in our technique — where abt. 10 g of entrainer are distilled per minute — amounts to $\frac{10}{114} \cdot 60$; hence $E = \frac{18 \cdot 600}{760 \cdot 114} \pi_w \sim 0.12 \pi_w$. Inserting this value in equation (9) and substituting for a : the current intake of abt. 20 g, we arrive at:

$$dW = -0.006 \pi_w dt \dots \dots \dots (10)$$

The total time of distillation, required for reducing the water content from e.g. 16 % = 0.16 to a low final value W_f , can now be found by an integration:

$$t_c = -\frac{1}{0.006} \int_{0.16}^{W_f} \frac{1}{\pi_w} dW \dots \dots \dots (11)$$

Morey and co-workers³⁷⁾ determined the water sorption isotherm of flour, which is a satisfactory representative of a biocolloid, at 95° C. From a plot of this isotherm¹⁾ we recalculated the data to a function $\frac{1}{\pi_w} = \varphi(W)$ in the columns 1—3 of table II. This φ -function was then graphically integrated and from the integral obtained finally t_c was calculated.

Table II
Calculation of t_c (flour) from Morey's data

W ($^{0}/_{10}$)	π (mm Hg)	$10^3 \cdot \varphi(W) = \frac{10^3}{\pi}$	$O = -10^3 \int_{0.16}^W \varphi(W) dW$	$t_c = \frac{10^{-3} O}{0.006} \times 60$ (min)
16	556	1.8	0	0
13	500	2.0	—	—
10	424	2.4	0.12	1.2
8	344	2.9	—	—
7	300	3.3	—	—
6	212	4.7	—	—
5	148	6.8	0.29	2.9
4	100	10.0	—	—
3	64	15.6	—	—
2	40	25.0	—	—
1	16	62.5	1.10	11
0.7	11.2	89.3	—	—
0.5	8.0	125.0	1.54	15
0.3	4.8	208.3	—	—
0.1	1.6	625.0	2.71	27

³⁷⁾ L. Morey, H. Kilmer and R. W. Selman, Cereal Chem. 24, 364—371 (1947).

It appears that in complete absence of retarding factors the water content of the substrate is reduced to 1 % in about 10 minutes and that after about $\frac{1}{2}$ h only 0.1 % of water is retained, being the highest degree of desiccation, which can be achieved in the present method, where $p_{\text{H}_2\text{O}} = 1-2$ mm.

In practice t_c -values from 5—7 h have been found. These values surpass significantly the times which, according to section 3.2.1, are required for completion of the water transport by the collection of the small droplets formed in the receiver and in the condenser. It is clear from these considerations that, unlike the supposition made at the beginning of this section, the limiting factor in entrainment distillation is the *internal diffusion* of water in the substrate subjected to desiccation, and not the water transport by the distillation process.

Referring to the results of these calculations, the entrainer velocity in the distillation method studied could have been reduced to 1/10 of the value adopted (10 g/min) without increasing the total time of desiccation.

By reducing the distillation velocity two advantages are obtained. In the first place the temperature of the receiver will be lower, which involves a lower water concentration in the returning liquid and hence a lower working water vapour pressure in the system. Further, for a lower distillation velocity a less intense heating of the still is sufficient, which eliminates the risk of local overheating.

On the other hand, a rapid distillation — according to indications found in the literature and our own experience — seems to eliminate small drops of water sticking to the condenser, which when undisturbed may seriously impair the results.

For a final choice between low or high rate of distillation new experiments are wanted.

Utrecht, May 1950.

(Received June 2nd 1950).