A MODEL SUBSTANCE AND IMPROVED CONTROL OF HEATING FOR MOISTURE ANALYSIS OF CEREALS

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ABSTRACT   Cereal Chemistry 53(5): 725-732

Magnesium sulfate in a crystal size fraction 0.25 to 0.50 mm was found to be suitable for use as a model substance for the determination of moisture in cereal samples, its weight loss reflecting the usual variables in drying conditions. Heat transfer to the samples was found to be more critical to the accuracy of the determinations than the exact temperature during drying. Changes in the present definitions and control of drying time and temperature are suggested, as are possible applications of magnesium sulfate in the determination of moisture in foods other than cereals.

Despite the development of instrumental methods, the moisture content of foods is still in many cases most accurately determined by oven-drying methods. Drying to a constant weight is the goal often referred to, but seldom reached. As shown by Fisher (1), for cereal grains at each temperature level a prolonged drying time leads to continuous losses of weight. These are caused partly by the evaporation of volatile components other than water, and partly by the decomposition of organic matter. In other cases (Pulkki (2)) a minimum weight is reached, after which prolonged heating causes an increase in weight due mainly to oxidation reactions. The end point of the drying thus yields only an approximation of the water content. However, for commercial analyses it is important to define water content as reproducibly as practically possible.

Köster (3) lists the factors influencing drying as follows: time of drying, temperatures inside and outside the drying oven, relative humidities inside and outside the oven, pressure inside the oven, ventilation, layer thickness and particle size distribution, construction of the oven, and number and placement of the samples in the oven. Additional factors often referred to and/or standardized are the size, shape, and material of the drying dish.

Analyzing the above factors shows that the key factors in all the listed items are the heat and/or mass transfer. Since it is not possible to standardize adequately all the details listed, an internal standard controlling the variations in the remaining factors, indicating variations in heat or mass transfer conditions, would be desirable. The purpose of this study was to find a suitable model substance and to check the adequacy of the presently employed definitions and practices for controlling drying time and temperature.

MATERIALS AND METHODS

Drying Ovens

For the main part of the experiments, the following drying ovens were used: 1) circular, 500 mm in diameter (Heraeus GmbH, Hanau, W. Germany) with

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natural air convection; 2) cubical, edges 600 mm (Heraeus GmbH), with natural air convection; and 3) rectangular 670 by 700 mm (Horo, Stuttgart, W. Germany), forced air circulation.

Dishes
1) Aluminum, 42 mm ϕ by 35 mm, with covers
2) Glass, 49 mm ϕ by 30 mm, with covers
3) Stainless steel, 68 mm ϕ by 48 mm, with covers

Chemicals
All reagents tested for suitability as model substances were of analytical grade. The selection of the crystal sizes used in the experiments was done by sieving the commercial preparations.

Temperature Recording
For most experiments, the temperatures were recorded using the mercury thermometers of each oven and correcting their errors. Temperature distribution within the ovens and its variation during drying were recorded using copper-constantan thermocouples.

Preparation of the Cereal Samples
The samples were ground as described by the Nordic Committee on Food Analysis (4) or by Jacobsen (5).

Cooling and Weighing
After the drying treatments, the dishes were cooled for 2 hr in a desiccator containing silica gel, and weighed with an accuracy of $\pm$ 0.1 mg.

RESULTS AND DISCUSSION

Selection of the Model Substance
After a review of the literature of inorganic and organic compounds containing crystal water and their water vapor pressures at different temperatures, copper sulfate ($CuSO_4 \cdot 5 \ H_2O$), disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2 \ H_2O$), and magnesium sulfate ($MgSO_4 \cdot 7 \ H_2O$) were chosen for experimental study, due to their ready availability and the range of water vapor pressures of the various hydrates of these salts.

From copper sulfate, which is used by the European Brewery Convention (6) as a model substance for drying at $105° - 107°C$, a crystal size fraction of 3 to 10 mm was chosen. At temperatures near $130°C$, customarily used in the determination of moisture of cereal grains, the copper sulfate lost the main part of its crystal water remaining in the monohydrate stage within 0.5 to 1 hr. After this step, the losses of water were minimal, even during prolonged heating at this temperature. Although variations in the drying conditions were clearly reflected in the losses of weight after 0.5 hr, the variation between the replicates during this short heating time was too great to allow this substance to be reliably used for the purpose at this temperature range.

Disodium phosphate was tested both unfractioned and in fractions < 0.5 mm, $0.5 - 0.75$ mm, and $0.75 - 1.0$ mm. The weight loss of this salt correlated well with

the changes in drying conditions and with the weight loss of wheat. However, the finest fraction lost its crystal water almost completely within 30 min when dried at 130° C with natural air convection. The next size fraction after this treatment had less than 8% of its original crystal water. Using drying times shorter than 30 min or particle sizes greater than 0.75 mm caused too great a variation in weight loss between the replicates to allow this salt to be used successfully as a model substance. Due to its rapid complete drying, this salt was also unsuitable for revealing excessive heating during drying..

Magnesium sulfate loses its crystal water in several steps. The dihydrate at 30.7° C has a water vapor pressure of 0.00359 atm and the monohydrate has a corresponding pressure of 0.0013 atm at 25° C (7). These vapor pressures correspond to water activities of 0.086 and 0.042, respectively. After preliminary experiments, the crystal size fraction from 0.25 to 0.50 mm was selected for further trials. According to the specifications of the manufacturer (E. Merck, Darmstadt, W. Germany), the preparation used was calculated to contain 51.16% water. Determined according to the Karl Fischer method, the water content found in the original preparation was 51.1%, and in the chosen fraction after sieving it was 51.0%.

The weight loss of magnesium sulfate as a function of various factors, and compared to weight losses of ground wheat samples under the same conditions, is presented in Figs. 1−6. The weight loss of this salt follows the same pattern as that of drying wheat, and all the changes in conditions tested are reflected in the magnitude of weight loss. The differences due to varying conditions are greater with shorter drying times, but times of 30 min or less give too great a range of
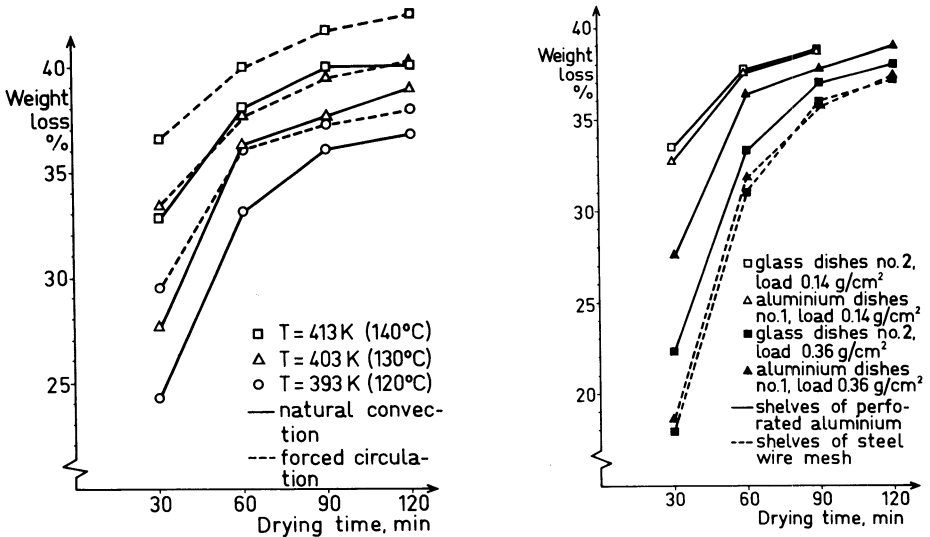

Fig. 1. Effect of temperature and ventilation on the weight loss of magnesium sulfate. Ovens 2 and 3, dish 1, load 0.36 g/cm². Fig. 2. Effect of loading and of material of dishes and shelves on the weight loss of magnesium sulfate. Oven 2. T = 130° C.
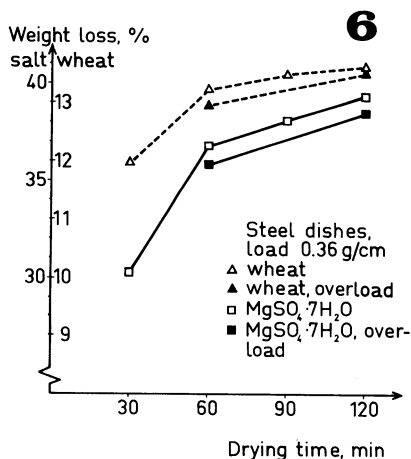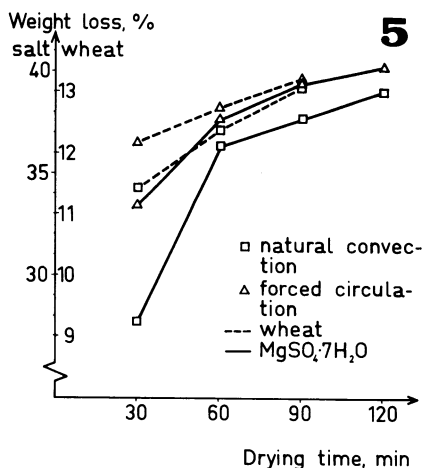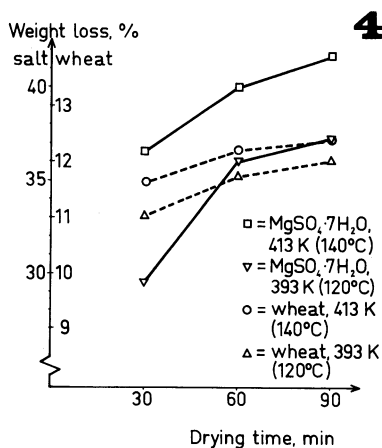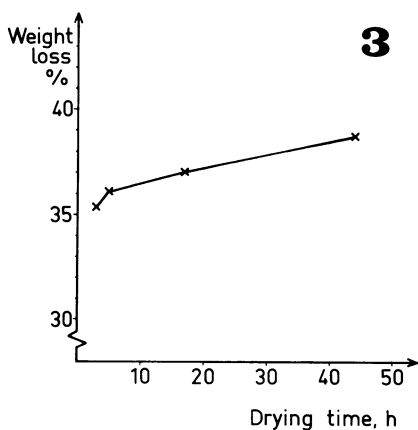
Fig. 3. Weight loss of magnesium sulfate in a vacuum oven (p < 3 kPa = 25 mm Hg; T = 98°−100°C. Fig. 4. Effect of drying temperature on the weight loss of wheat and magnesium sulfate. Oven 3 (forced circulation), dish 1, load 0.36 g/cm². Fig. 5. Effect of ventilation on the weight loss of wheat and magnesium sulfate. Ovens 2 and 3, dish 1, load 0.36 g/cm². T = 130°C. Fig. 6. Effect of overloading of the drying oven on the weight loss of wheat and magnesium sulfate. Oven 2. Normal load: 50−60 g of wheat + 35 g MgSO₄·7 H₂O. Overload: additional 70 g of MgSO₄·7 H₂O. T = 130°C.

variation and standard deviation to be useful for the purpose (Table I). The magnitude of the effect of some factors can be adjusted by changes in the surface load on the dishes, as shown for the effect of the material of the dishes in Fig. 2.

According to the results, a weight loss in magnesium sulfate of 36 to 39% corresponds to conditions in two usual types of moisture determinations for cereals, the air oven method (8; 9, Method 13.004; 10; 11; 12, Method 44-15), and the vacuum oven method (9, Methods 13.002 and 13.003; 12, Method 44-40). In these conditions, the standard deviation .between replicates is below 0.20%, assuming that the drying time has been more than 30 min (Table I). The standard deviation has a minimum in the range of 37.0 to 38.0% weight loss. This loss of weight is near the theoretical loss to the dihydrate stage, which would correspond to a 36.54% weight loss. The water activity of the dried salt, as measured by an Electric Hygrometer-Indicator (Hygrodynamics, Inc., Silver Spring, Md.), fell under the detection limit of the instrument ($a_w = 0.05$) after drying for more than 45 min at 130°C, thus giving smaller values than those calculated from the literature values referred to above.

Since water in foods can be bound in several ways, a complete correlation of drying of any food with the drying of an inorganic substance cannot be expected. For the cereal samples tested, the correlation seems to be close, a surface load of 0.36 g salt/cm² of dish giving higher response to variations in drying conditions than the corresponding load of drying of wheat. In prolonged drying, the weight loss of magnesium sulfate tends to continue more steeply than that of cereal samples. This, however, can also be regarded as an advantage in that it reveals excessive heating. Because of the continuous losses of weight under these conditions, no exact weight loss can be defined which would correspond to the end point of drying. Any point of reference is dependent on the macro conditions suitable for the grain or variety analyzed. The use of this substance as a model for drying foods other than cereals presupposes experiments on the drying conditions appropriate for the commodity in question, but the wide range of hydration levels of this salt indicates that it may also be applied to other conditions.

Recording the Drying Temperature and Time

In the present standard methods for moisture analysis, the temperature of the drying oven refers to that of air in the vicinity of samples (8; 12, Method 44-15), of air and shelves in the vicinity of the samples (10), or the point of control is not specified. Most standard methods use drying ovens with natural air convection.

TABLE I
Variation of the Weight Loss between Five Replicates

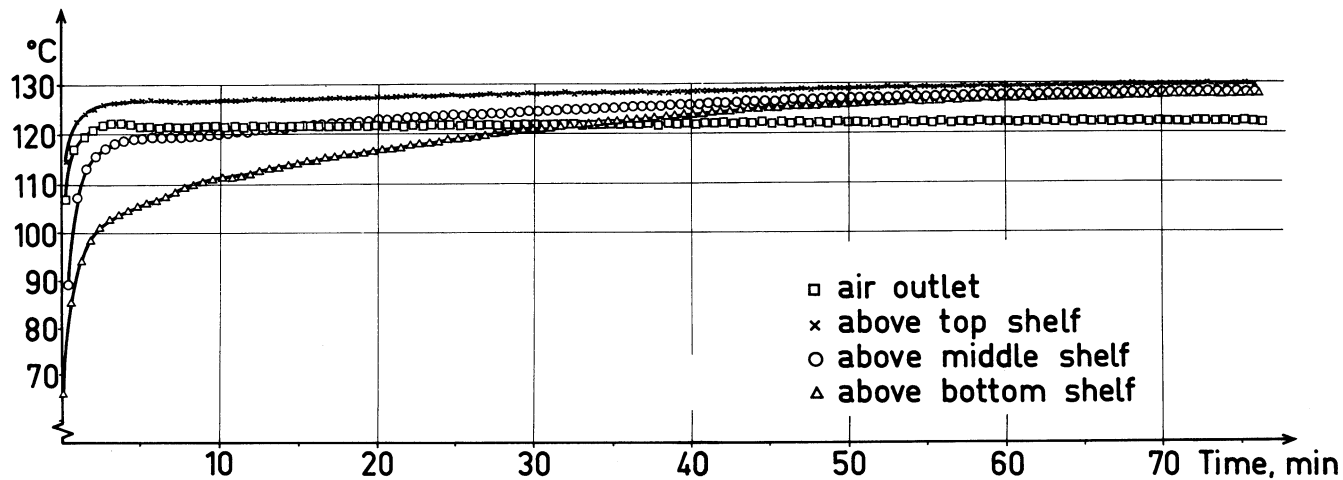| Time of Drying	Weight Loss Range	Standard Deviation % Units of Weight Loss		Number of Batches
		Range	Mean	
⩽ 30 min	15.5−36.4	0.78−4.07	1.17	17
⩾ 60 min	33.2−42.5	0.06−0.85	0.26	51
⩾ 60 min	36.0−39.0	0.06−0.62	0.19	31
⩾ 60 min	36.0−38.0	0.06−0.40	0.17	23
⩾ 60 min	37.0−38.0	0.06−0.24	0.16	13

Fig. 7. Temperature distribution in the course of drying cereal samples (*cf.* Table II). Oven 1, stabilized previously to 130°C.

Placement	Weight Loss, %		
	Wheat 1	Wheat 2	Rye
Top shelf	12.58	14.59	15.07
Middle shelf	12.63	14.65	15.03
Bottom shelf	12.64	14.61	15.01

[a]Oven No. 1, total load 15 dishes of No. 1, 5 g of sample in each.

Measurement of the drying time begins in most methods from the moment the temperature (as measured) has reached a certain limit after loading the oven.

When the temperature distribution in a drying oven with natural air convection was followed during the course of drying of cereal samples, a distinct layering of the temperature was observed (Fig. 7). The air temperature near the dishes remained considerably lower than the preset level until the main part of the moisture had evaporated. Despite the temperature layering, the cereal samples had weight losses close to each other on each of the three shelves (Table II). Evidently, the drying rate was mainly controlled by heat transfer from the shelves to the dishes as the comparison of two types of shelves in Fig. 2 shows for magnesium sulfate. The effective drying period thus begins from the moment the oven is loaded. Figure 7 also shows that the present practice of counting the drying time leads to great and unjustified differences in drying times depending on the placement of the thermometer. From this, it is concluded that measuring the drying time from the moment of loading will lead to more reproducible results than the present practices. A prerequisite for this approach is that the heat transfer capacity of the oven is not exceeded. This could be controlled by drying the reference substance, either by using it as an internal standard or by determining experimentally the drying times at each loading level required to give the same weight loss.

To ensure a reproducible heat transfer, the oven should be stabilized to the desired temperature well in advance, in our experience for more than 1 hr, and preferably for 2 hr or overnight. After this stabilization, the temperature differences in the ovens were within ± 1°C, and the exact point of temperature recording was not critical. Shorter stabilization times gave either lower or higher weight losses, depending on the system of temperature regulation in the oven, in spite of an even initial temperature.

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