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Validation of the water content determination method using a moisture analyzer as an important factor in ensuring the quality of the measurement

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Słowa kluczowe: walidacja, przemysł spożywczy, waga, kwalifikacja, jakość, proces suszenia.

1. Introduction

Determining the water content in food products is performed in order to confirm product stability during storage period, to determine dry mass, nutritional value of the products [1], and to prove compliance of product quality parameters with specification provided by respective standards, especially when a new method is being introduced onto the market. Food product usage properties and quality mainly depend on water content of the finished goods [2]. Therefore, its amount is strictly controlled during the technological process as well as during a final laboratory inspection. Based on the information about the water content, the following can be defined: microbiological stability of the product, and, if applicable, whether it meets the legal requirements. Increased water content is a cause of hydrolytic and oxidative changes occurring in the product [3]. That is particularly important in case of those products that are acquired from oil crops, some authors consider them as unsuitable for use in the production process as they contain too much water [4]. Water content in product, when uncontrolled, dangerously affects the quality. Product's shelf-life shortens significantly, its sensory properties deteriorate. This type of product is considered to be less valuable and should not be put onto the market. Evaluation of water content in the product is performed in order to obtain true information reflecting real physical state of the product. Commonly used standard-specified methods [5] are characterized by a long-lasting test cycle, taking up to several hours. This process consist of following stages: sampling, sample preparing and sample drying carried out using respective methodology. This kind of practice allows to obtain repeatable and accurate results. The above described testing cycle is a time-consuming method unfortunately, and considering

in-process control the results should be available in the shortest possible time. Thus, alternative methods, which considerably reduce time of experiment, are being sought more often actually. Shorter time allows for both: quicker reaction of process engineers and effortless control of production process. Searching for alternative methods, such as drying in the moisture analyser can be an addition to standard-required methods. According to Journal of Laws of the Republic of Poland of 27th November 2015 [6], validation is an action aiming to confirm in a documented way, and in accordance with the rules of Good Manufacturing Practice, that procedures, processes, devices, materials, activities and systems lead to the assumed results. In this case the assumed result is the result obtained using the standard-specified method. Relations regarding validation of the drying process carried out using moisture analyser are presented in Figure 1.

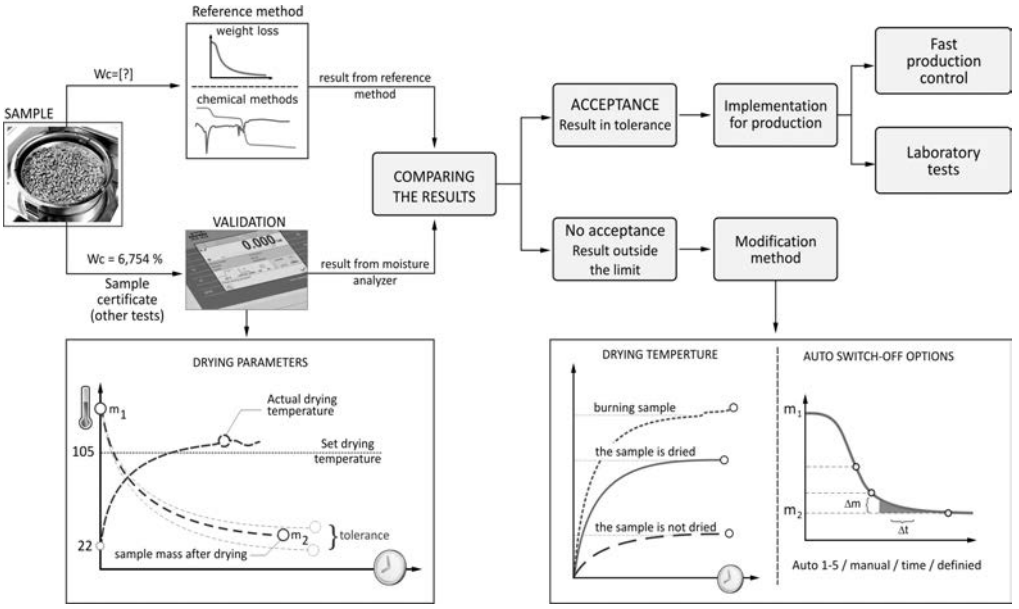


Fig. 1. Process of moisture analyser validation, corrective actions included
Rys. 1. Proces walidacji wagosuszarki z uwzględnieniem działań korygujących

Starting point in the validation process of drying methods is the water content result, obtained using standard-specified method. Next, the tests are carried out using moisture analyser and the obtained results via both methods are compared. If the results difference are within the assumed tolerance, the validation process is considered to be completed. However, such situation happens very rarely. While comparing the results obtained using two different methods it usually turns out that either the difference is too significant or drying time required by the moisture analyser is too long. This is a reason for method modification, i.e. modification of both drying parameters and sample preparation process (Figure 1).

Validation is precisely defined by Validation Policy, Documentation and Quali-fication process. Basic requirements with regard to the above are specified by res-pective legal acts [6]. Validation structure comprises various processes (qualifica-tions) which proves that the devices are properly installed, work properly and allow to obtain correct results. The following qualification types can be distinguished:

- Design Qualification (DQ),

- Installation Qualification (IQ),
- Operational Qualification (OQ),
- Process Qualification (PQ).

Design Qualification (DQ) is a verification determining whether the implemented device (moisture analyser) meets use-related requirements. In case of this study, the aim is to determine water content of the food products. More specifically, the intention is to show how precisely the water content (dry mass content) can be determined. Taking into account industrial scale it is usually some limit value, which is dictated by law, quality regulations and technological requirements. Each series of measurements is characterized with a certain variation of indications. Value of this parameter is as much significant as determination accuracy and it should always be given. Figure 2 presents significance of the variation of indications.

Installation Qualification (IQ) is a documented confirmation that the installed equipment complies with the design and the manufacturer's requirements. In case of weighing instruments such as moisture analyser, installation qualification concerns the workplace as well as health and safety requirements. Operational Qualification (OQ) is the key validation component. During this qualification process it is necessary to prove that the device operates as intended and expected. In practice, this type of qualification requires series of water content determinations, which should be carried out for the real product. As it was mentioned above, comparison of the results obtained via different methods should be performed and preferably the difference should be the lowest as possible.

To use the moisture analyser is a wise choice only when the analysis time is shorter than it is required by a valid standard-specified method. In case of some samples, compromise between accuracy of determination and test duration time has to be made. Due to this, information about tolerance value regarding the water content result is of a great importance. Thus, it is possible to optimize drying parameters (temperature, method), sample amount and preparation. Optimization of mentioned parameters is often neglected by the users mainly because of the extended effort. Sometimes, it is rather expected that some ready solutions regarding drying methods will be provided. Certain failures may occur when too high expectations, with respect to measurement repeatability, and as a result to drying process accuracy, are set up. Process Qualification (PQ) is a verification confirming that the weighing devices operate effectively and repetitively by means of periodical tests of the whole measuring system.

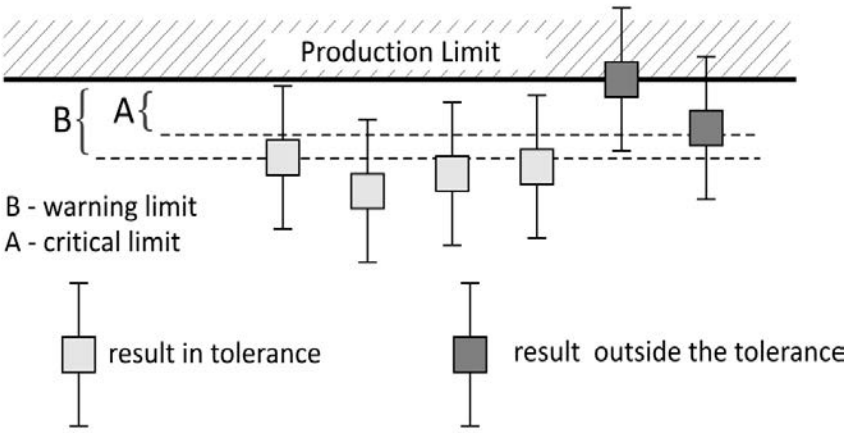


Fig. 2. Evaluation of measurement accuracy, variation of indications
Rys. 2. Ocena dokładności pomiaru z uwzględnieniem rozrzutu wskazań

Operational qualification of moisture analyser – mass measurement process

Operational qualification of the moisture analyser must be carried out with regard to mass measurement and drying process. Mass measurement proceeds similarly like in case of any electronic balance, force with which the sample is attracted by the Earth is measured using the following equation:

$$F = m \times g$$

where:

F – force,
m – sample mass,
g – gravitational acceleration.

In order to adjust moisture analyser, steel mass standards are used (with valid calibration certificate). Their mass *(m)* is constant regardless of the place of use. A result of the device transfer from one place of use to another results in a new value of a gravitational acceleration *(g)*. Therefore, readjustment is required for obtaining accurate results, using a mass standard of respective nominal value [7, 8]. Moreover, weighing range of moisture analysers is not wide, usually 50 g – 100 g. During the test, moisture analyser indications must be checked using mass standards in few selected measurement points (an example – Table 1).

Table 1. Assessment of errors of moisture analyser's indications within the weighing range
Tabela 1. Ocena błędów wskazań wagosuszarki w zakresie ważenia

Nominal mass	Mass standard's weight	Moisture analyser indication	Indication error
5 g	5.0010 g	4.999	-0.0020 g
10 g	9.9995 g	10.000	0.0005 g
20 g	20.0002 g	19.999	-0.0012 g
50 g	50.0001 g	50.002	0.0015 g

Indications error is calculated as a difference between indication of the weighing device and weight value of the mass standard [7, 9, 10]. Additionally, also repeatability should be checked. Determined repeatability value informs on the size of indications variation in the measuring series. Such test is carried out in one or two measurement points [11]. The procedure is based on the weighing of the same mass several number of times under the same conditions. An example of such test is presented in Table 2.

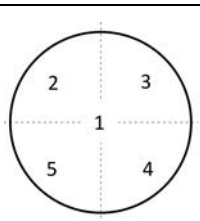
Table 2. Assessment of moisture analyser repeatability
Tabela 2. Ocena powtarzalności wagosuszarki

No.	Mass standard's nominal mass	Moisture analyser indication	Variation (Max – Min)
1	50 g	49,999	0,004 g
2	50 g	50,001	
3	50 g	50,000	
4	50 g	50,002	
5	50 g	49,998	

When it comes to mass measurement qualification, also deviation of eccentricity needs to be checked. The samples must be placed in the very centre of the weighing pan, which reduces potential indication error. During this test, a difference between indication of the device for

mass standard placed in the centre of the weighing pan and out of the centre is calculated [12]. Mass standard weight value should be 1/3 of maximum capacity. Assessment of eccentricity error of the moisture analyser is presented in Table 3.

Table 3. Assessment of eccentricity error of the moisture analyser (20 g mass standard)
Tabela 3. Ocena błędu centryczności wagosuszarki (wzorzec o masie 20 g)

Measurement point	Moisture analyser indication	Differential error of eccentricity	Weighing pan – top view
1	20.000 g	x	
2	20.001 g	+ 0.001 g	
3	19.999 g	- 0.001 g	
4	20.002 g	+ 0.002 g	
5	20.001 g	+ 0.001 g	

Control of parameters related to mass measurements is necessary when moisture analyser is used for precise mass measurement. The control process can be carried out either individually or via an Accredited Laboratory, as a part of the measuring equipment supervision. However, this type of control is required when quality management systems are implemented [13].

Operational qualification of moisture analyser – drying process

Moisture analyser is a weighing device performing two functions, mass measurement and drying. Range of qualification depends on the usage, in case of only drying function it is reasonable and acceptable to carry out qualification only for this one process. Qualification of the drying process is based on the measurement of real temperature inside the balance during drying operation at selected representative measurement points. Thermometer must be placed inside the drying chamber and indications are observed over a specified time intervals. Prior the test, tolerance for the measured value should be stated, in this case helpful can be reference standard's guidelines, according to them the drying temperature is given with tolerance of 2–3^{o}C.

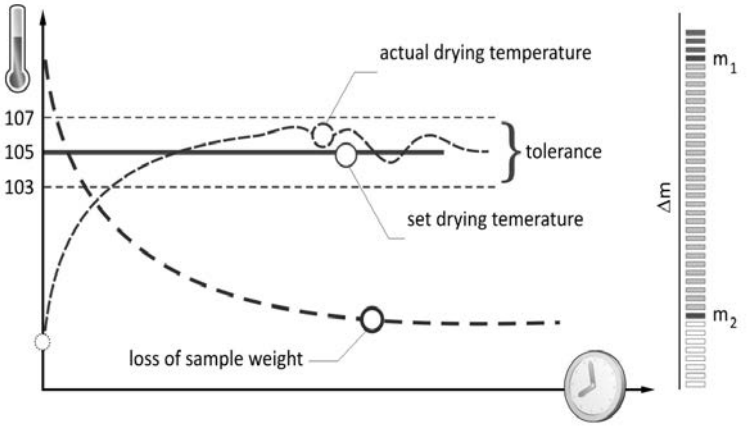


Fig. 4. Drying temperature – pre-set tolerance value
Rys. 4. Temperatura suszenia – tolerancja wartości zadanej

This determination allows to assess moisture analyser's accuracy and drying temperature stability. The test is carried out without use of real sample (Figure 5). The second part of this OQ concerns drying parameters optimisation. When the reference value of the water content (dry mass content) is known for the tested sample, the drying method must be designed in a way enabling to obtain such a result that is comparable to the reference one.

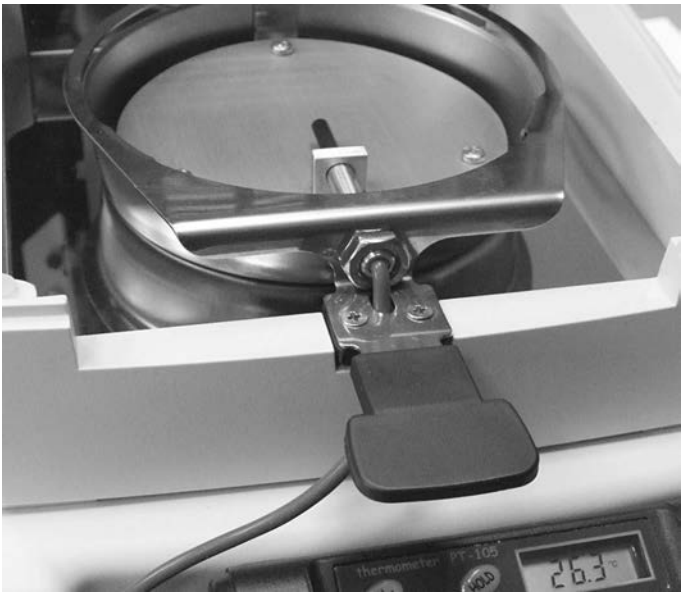


Fig. 5. Control thermometer placed in the moisture analyser's drying chamber
Rys. 5. Termometr kontrolny w komorze suszenia wagosuszarki

2. Experimental

2.1. Material

For the test purposes the following substances were used:

- Pomade for cakes (Arcots Creme manufacturer),
- wheat flour, type 750 1 kg, manufacturer: Polskie Młyny.

2.2. Methods

2.2.1. Moisture Content Determination Performed Using Standard-Specified Test Method

Cakes' pomade manufacturer provided information stating that the minimum dry mass content is 86 %. Presently there are no standard regulations regarding this type of product, therefore in order to verify manufacturer-provided information, respective tests were carried out. The drying process was performed at temperature of 105°C during 3 hours. The sample was mixed with silica sand before drying, this allowed to increase the active drying surface simultaneously preventing formation of crust on the sample surface. Dry mass content was determined using the following equation:

$$D_m = \frac{(m_2 - m_0)}{(m_1 - m_0)}\, x\, 100\ \%$$

where:

D_m – sample's dry mass content, expressed as mass fraction in percent,
m_0 – mass of the container, given in gram,
m_1 – mass of the analysed sample and container prior drying, given in gram,
m_2 – mass of the analysed sample and container after completed drying, given in gram.

For flour the test was carried out in accordance with ISO 712 'Cereals and Cereal Products, Determination of Moisture Content, Reference Method'. Humidity expressed in percent by product mass, was calculated using the following equation:

$$w = (1 - \frac{m_1}{m_0})\ x\ 100\ \%$$

where:

w – humidity expressed in percent by product mass,
m_0 – mass of the analysed sample, given in gram,
m1 – mass of the analysed sample after completed drying, given in gram.

2.2.2. Moisture Content Determination Performed Using Moisture Analyser

Moisture analyser of MAR 50.R series (Radwag Wagi Elektroniczne, Radom, Poland) was used. Drying temperature ranged between 40°C – 160°C with 1°C intervals. Sample mass was registered permanently during the test which allowed to assess drying process dynamics.

The flour was dried directly on the weighing pan, temperature 120°C was applied, mass of the sample was within the range of 3 g – 5.5 g. Difference of 1 mg over 25 second was adopted as criterion for assessment of sample mass stability.

The pomade was dried using Whatman paper filters with 90 mm diameter. The filters were dried, prior to the test. In order to prevent formation of an impermeable layer on the sample's surface, the pomade was placed between two filters. The test was carried out at 120°C using Auto 2 finish mode set. The water or dry mass content result was calculated using the following formula:

$$\%M = \frac{m_1 - m_2}{m_1} \cdot 100\ \%$$

where:

%M – content of water in the sample
m_1 – mass of the sample before drying
m_2 – mass of the sample after drying

$$\%D = \frac{m_2}{m_1} \cdot 100\ \%$$

where:

%D – dry mass content
m_1 – mass of the sample before drying
m_2 – mass of the sample after drying

3. Results and Discussion

Pomade for cakes

In the study two methods were used: standard-specified method and moisture analyser method. In case of the second method pomade sample was heated using IR waves emitter (MW). This kind of waves emission is optimal for many food products [15]. Authors [14] claim that drying process efficiency is influenced mainly by the way of heat is provided and by the temperature level. The results obtained during the pomade examination are presented in Tables 4 and 5.

Table 4. Pomade – results of dry mass content results and drying times
Tabela 4. Pomada – wyniki zawartości masy suchej oraz czasów suszenia

Pomade	Reference method	MA 50.R moisture analyzer
Dry mass content [%]	88	87.87
Drying time	3 hours	about 14 minutes

Table 5. Pomade – relation of the drying time and analysed sample mass
Tabela 5. Pomada – zależność czasu suszenia względem użytej masy próbki analitycznej

Sample mass	Dry mass content	Drying time
1,4 g	88,58 %	10:25 min
1,8 g	88,96 %	13:03 min
2,6 g	88,07 %	19:04 min

It was observed during the determination that important factor influencing variations of obtained results was the samples homogeneity. Despite thick consistency, it was noticed that the top layer of the sample demonstrated different water content than the lower layer. This observation could be a reason why results did not correspond to the manufacturer's quality criteria. In adopted drying methodology it was assumed that the analysed sample should be mixed each time before being analysed. The shortest drying time was obtained for the sample amount of 1.5 – 2 g. A relation between the drying time and the analysed sample amount has been determined (Table 5).

It has been observed that increase of the analysed sample amount of about 85 %, increase the drying time of about 80%. It is a crucial factor for an in-operational assessment of pomade quality, where accuracy, speed and precision are required. Placing the sample between filters allowed volume drying of the sample. The sample is heated from the top and the bottom. It has been noted that such practice ensures short analysis time and acceptable measurement repeatability. Figures 6a and 6b present the pomade sample before and after the drying process. The test showed that temperature increase resulted in sample caramelization. This process however does not affect either accuracy or duration of the analysis.

Proposed method of pomade drying, using two paper filters, results in increase of unit cost of the dry mass determination. Price per packaging of 100 filters is about 15 Euro. For the purposes of single determination, usage of 2 filters is required. Cost of single determination is about 0.3 Euro (about 1.2 PLN).

a. Sample before drying b. Sample after drying

Fig. 6. Pomade – sample placed on the filter
Rys. 6. Widok pomady do ciast – próbka umieszczona na filtrze

Wheat Flour

Drying flour with use of standard-specified method, resulted in moisture content value of 11.31 %. Moisture analyser determinations, required adjustment of the drying parameters (validation) so that similar value could have been obtained. For the series of 10 measurements, average moisture content value was 11.35 %, with the standard deviation of 0.03 % (Table 6).

Table 6. Flour – results of dry mass content and drying times
Tabela 6. Mąka – wyniki zawartości masy suchej oraz czasy suszenia

Flour	Standard-specified method	MA 50.R moisture analyser
Moisture content [%]	11.31 %	11.35 %
Drying time	3 hours	about 8 minutes
Standard deviation	0.05 %	0.03 %

A conclusion has been stated that flour is a substance susceptible to increase of temperature. It was observed during the determination that the top layer of the flour samples in the moisture analyser were burning. The change of the top surface layer colour was noted from white to yellow at the temperature above 130^{o}C. This means that it is possible to obtain moisture content results above the limit values. Due to this, validation of the testing method was necessary. Upon completed and successful validation, the obtained results were comparable to those that had been achieved by means of standard-specified method.

Figure 7 presents series of 10 measurements of moisture content performed for flour samples. Dashed line illustrates average value of humidity obtained with standard-specified method. Solid line illustrates average value of moisture content obtained with moisture analyser method. The difference between these values is marked as δ_{wc},, which specifies accuracy of moisture content determination by means of moisture analyser method. Obtained value was 0.04 % and it informs of correctness of the performed validation (sample preparation, drying temperature and selected control criterion for completion of the drying process).

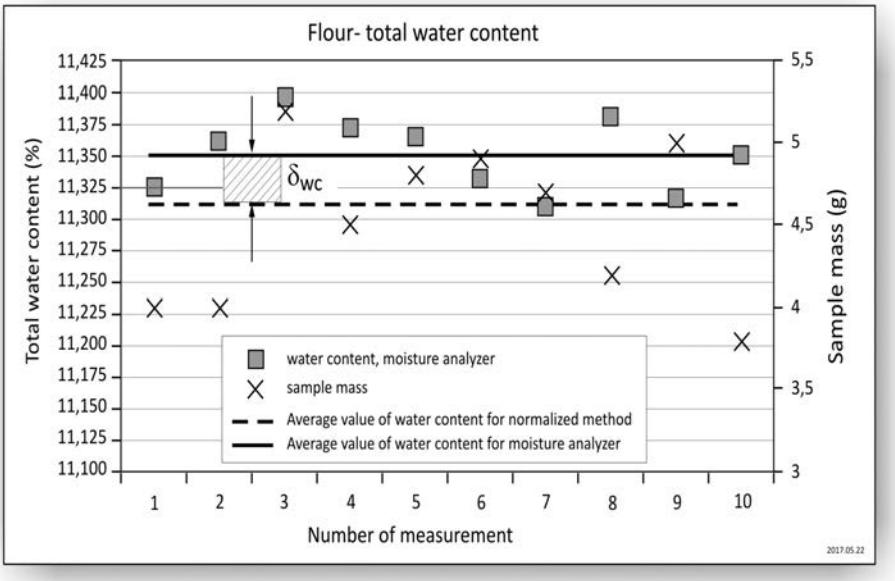


Fig. 7. Results of moisture content of flour in relation to standard-specified value
Rys. 7. Wyniki zawartości wilgotności w mące w odniesieniu do wartości znormalizowanej

Figure 7 presents also masses of analysed samples. It has been noted that variation of mass within 3.8 g – 5.2 g range does not influence the drying process accuracy. For the tested samples, average drying time was 7 minutes and 30 seconds. In the processes of assessment of flour quality, the analysis duration may be a key component deciding about usefulness of the moisture analyzer method. Thus, relation between the drying time and initial mass of the analysed sample has been determined (Figure 8). In the presented study, the samples were heated using IR emitter. This method ensures absorption of heat not only by external (surface) layers but also the penetrates sample's inside [16]. According to authors [17], the penetration depth is up to several millimetres (from 2 mm to 4 mm). It depends on radiation wave length and sample's structure (absorption and reflection).

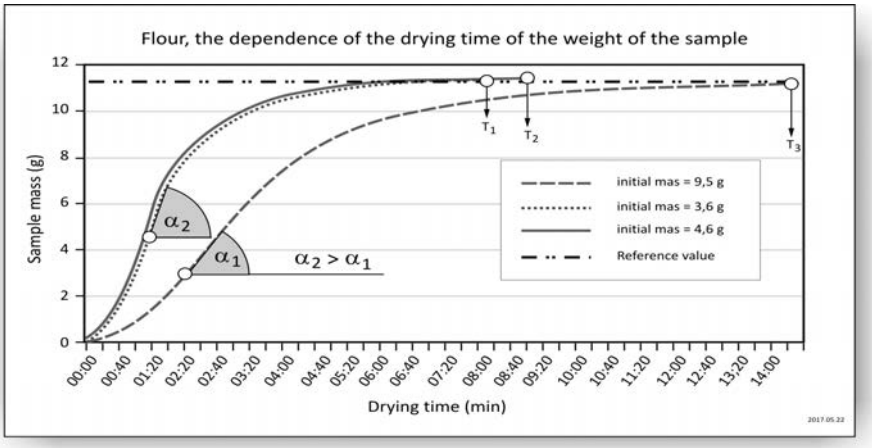


Fig. 8. Relation between drying time and initial mass of the analysed sample
Rys. 8. Zależność czasu suszenia względem wielkości masy początkowej próbki analitycznej

The following samples were tested: m_1 = 3.6 g; m_2 = 4.6 g; m_3 = 9.5 g. Drying curves for these samples have been marked in Figure 8. Each sample was dried in the same environmental conditions: drying temperature = 120^{o}C, control of end mass = variation of 1 mg within 25 seconds. It has been observed that for 3.6 g and 4.6 g samples, the dynamics of drying is greater than for 9.5 g sample. Difference of humidity evaporation rate was visualised by inclination angle of the drying curve, marked as α_1 and α_2. It has been noted that for 9.5 g sample, drying last 14 minutes, which was twice longer than in case of 3.6 g sample.
In figure 8 by means of dashed line reference value of moisture content of the flour sample was presented. It can be concluded that regardless of analysed sample mass, the obtained moisture content result was comparable to the reference value.

4. Conclusions

Before bringing the moisture analyser into routine use, it is required to check correctness of its operation. Two functions must be tested, mass measurement and accuracy of temperature adjustment. Although moisture analyser is a dual-function device, it is mostly used to determine moisture content. It is claimed that control of the drying temperature is a key issue. However, positive results of this control do not stand for accuracy of carried out test. Determinations obtained using pomade for cakes and flour's samples used in this work, confirmed that it is necessary to validate a test method. In authors opinion, such approach is an absolute necessity for not only single product but also for a group of products. It guarantees obtaining precise, repeatable and correct results, which can be related to the quality of each product. It was confirmed that taking into account the time of determination, the moisture analyser can complete standard-specified methods, especially in those cases where fast control is required.

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Summary

In some food processing one of the key parameters affecting the quality of the products is the water content in the final product. The work presents the importance of the validation process in the context of determining water content in food products. Legal issues concerning validation and its basic elements, which should be used in the food industry, have been discussed. Special attention was paid to the pro-quality aspect of every action.

Based on the measurements performed for an exemplary products, some crucial areas of increased risk were identified. This paper discusses specific requirements regarding usage of the moisture analyser, and the methodology of sample preparation and drying.

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WALIDACJA OZNACZANIA ZAWARTOŚCI WODY ZA POMOCĄ WAGOSUSZARKI JAKO ISTOTNY CZYNNIK W ZAPEWNIENIU JAKOŚCI POMIARU

Streszczenie

W niektórych procesach przetwórstwa spożywczego jednym z kluczowych parametrów mających wpływ na jakość produktów jest zawartość wody w końcowym produkcie. W pracy przedstawiono znaczenie procesu walidacji w kontekście procesów oznaczania zawartości wody w produktach spożywczych. Omówiono zagadnienia prawne związane z walidacją oraz jej zasadnicze elementy, jakie powinny być stosowane w przemyśle spożywczym. Zwrócono szczególną uwagę na aspekt projakościowy wszystkich działań.

Na podstawie pomiarów dla przykładowego produktu wskazano newralgiczne obszary zwiększonego ryzyka. W pracy uwzględniono specyficzne wymagania związane z użytkowaniem wagosuszarki, w tym metodykę postępowania związaną z przygotowaniem próbki oraz procesem suszenia.

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