

# Karl Fischer Titration of Salami Products: Variation of the Water Content During Ripening and Kinetics of the KFT Process

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**Abstract:** The quality of meat products strongly depends on the water content. The study presents a Karl Fischer water titration (KFT) approach on salami products during the drying process. Two traditional salami products manufactured and commercialized in the West of Romania have been analyzed. The water content during the drying process as well as the kinetics of the KFT water reaction have been evaluated by using the volumetric bi-component technique. The total water content varies from 50-56% at the starting of drying to 26-27% after nine days of processing. The mean KFT water reaction rates corresponding to the "surface" water molecules decreases during drying from 5-6  $\text{mM}\cdot\text{s}^{-1}$  to 1-2  $\text{mM}\cdot\text{s}^{-1}$ . The "strongly-retained" water reaction rate had low variation in the range of 0.5-1  $\text{mM}\cdot\text{s}^{-1}$ . Consequently, the KFT method is an appropriate method for the quality evaluation of such non-homogenous and mostly hydrophobic food products by means of water content and behavior during KFT analysis.

**Keywords:** food quality, Karl Fischer water titration, salami, water kinetics

## 1. Introduction

Meat play a primordial role in the human nutrition. It is the main source of proteins. Many meat-based food products are manufactured and consumed all over the World, even at low or high processed level by using various methods, such as boiling and frying. Almost one-fifth of the World's meat is produced in Europe [1]. Among meat products, many types of salami or sausage products are produced [2]. Generally, they contain various grinded meat muscle or other organs, mixing with fat, salt, herbs and spices, including other additives [3]. The mixture is extruded in tube-like shapes by using natural or synthetic covering materials [4]. They can be provided as raw, pre-cooked, cooked, and smoked salami products. The "ripening" process, which often includes drying in the presence of starter cultures, is very important for the quality and stability of the final salami product [5-7]. Furthermore, the water content and its diffusion capability are strongly related to the quality of such products [8, 9].

Analysis of the water content of such complex and non-homogenous food products is difficult to perform due to many disadvantages such as the low stability of food components, which can be degraded at higher temperatures and release volatile compounds, and low solubility in water and other hydrophilic solvents if the analysis assumes the use of solvents. However, two groups of methods are used for water analysis [10-13]:

- Direct methods (distillation, quantitative chemical reactions evolving acetylene and hydrogen, drying methods, combined methods consist of drying and

electrical detection of water, drying under infrared radiation or microwaves, water titration etc.);

- Indirect methods (or secondary methods) that are based on the measuring of food properties depending on the water content (e.g. NMR, microwave spectroscopy, near infrared spectroscopy etc.).

Among these methods, Karl Fischer titration (KFT) is successfully applied for water analysis in various techniques. The bi-component technique assumes the specific reaction of methyl sulfite (resulted from methanol or other alcohol and sulfur dioxide in the presence of an organic base) from the "solvent" (component B) with water molecules from the food products and iodine from the "titrant" (component A) (Figure 1) [14-17]. The reaction is potentiometrically monitored and allows determining the water content of the food products according to the consumption of the iodine solution having known titer.

The KFT method is rapid and have accuracy and precision for the water content measurement. Furthermore, it works at moderate conditions and is selective to water. On the other hand, the amount of the sample depends on the approximate water content being higher for very low values of this parameter. In the case of salami products, the water content varies in a wide range and relatively small quantities of samples are sufficient for analysis.

In the present study, the variation of the "real" water content of salami products manufactured in the West of Romania was monitored during the ripening process by using Karl Fischer titration bi-component technique. The behavior of these food products during the KFT reaction was also determined by means of the "surface" and "strongly-retained" water kinetics.

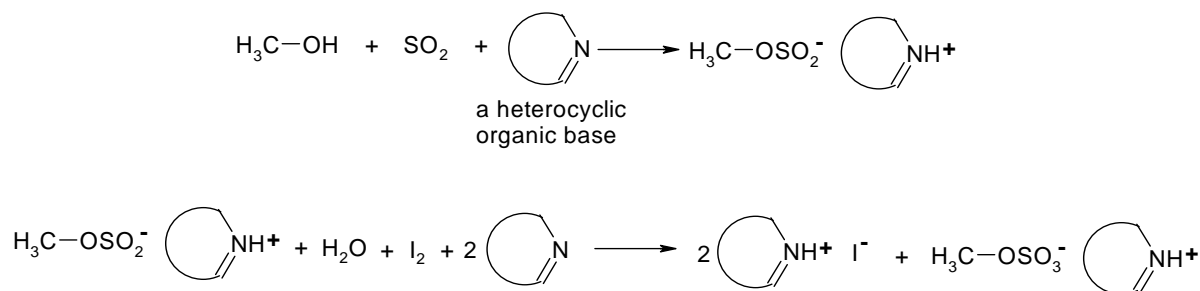


Figure 1. The Karl Fischer water reaction from the bi-component technique

## 2. Experimental

### 2.1. Materials

The salami-type food products have been selected from traditional products made in the West of Romania. Two types of salami named "Ardelenesc" (code "SA") and "Banatean" (code "SB") have been selected. During the ripening process performed in an industrial company, the water contents have been monitored for nine days. The sampling was made by classical statistical procedure after 2, 3, 4, 6, 8, and 9 days. All samples were obtained from the middle and the quarter distance from the end of the salami cylinder. The exterior up to 5 mm of the corresponding rolls have been removed and the selected parts were mixed and immediately analyzed. The KFT analysis of salami samples have been performed by bi-component technique. The component A was an iodine solution (Titrant 2 apura, Merck KGaA, Darmstadt, Germany) having a titer of  $2.3571 \pm 0.0663 \text{ mg H}_2\text{O} \cdot \text{mL}^{-1}$ . The titer was determined by means of Water standard 1% apura (Merck). Component B was a methanolic solution of sulfur dioxide and imidazole as organic base (Solvent apura, Merck). All determinations were made in duplicate.

### 2.2. Karl Fischer water titration of salami products

A Karl Fischer Titrand 701 (Metrohm, Herissau, Switzerland), connected to a Metrohm 10-mL dosing system and a Ti Stand 703 mixing system (Metrohm) have been used. The current was set up to  $50 \mu\text{A}$  and the endpoint voltage to 250 mV. The drift of the KFT process was  $15 \mu\text{L} \cdot \text{min}^{-1}$ . The extraction time was set to 900 s (it was presumed that all water is extracted during this time, but the titration can go further if the drift is not reached).

### 2.3. Statistical analysis

Classical ANOVA statistical analysis of the multiplicate data obtained for the total water content and water reaction kinetic parameters (mean water reaction rates corresponding to "surface" and "strongly-retained" water molecules) have been applied. Furthermore, the standard errors have been indicated for the graphical plots.

## 3. Results and Discussion

The KFT water titration process of the salami-type food products need longer analysis time due to the low solubility of the overall sample into the KF methanolic system. Generally, fifteen minutes is sufficient for completing the reaction, but some samples need longer time (probably due to the higher content of the lipid fraction). A logarithmic behavior of the titration process (expressed as the variation of the normalized titration volume in time) can be observed in the case of salami sample analysis (Figures 2 and 3).

The total water content of the raw salami products had no significant variation up to the first two days, most probably due to the fact that the sampling was performed starting from 5 mm of the exterior. The water content of the raw "Ardelenesc" and "Banatean" salami product was  $48.0 \pm 7.1 \%$  and  $56.0 \pm 8.7 \%$ , respectively. The standard deviation was higher at the beginning of the ripening process due to the low level of homogeneity. During the ripening, the water content rapidly decrease after approximately four to six days and became almost constant up to the end of the drying process. The final water concentration was  $25.7 \pm 1.2 \%$  for the "Ardelenesc" type salami and  $27.3 \pm 1.4 \%$  for the "Banatean" type salami (Figures 4 and 5).

Salami samples contain many ingredients that bind water molecules in various ways. Among these, carbohydrates and proteins play an important role in this context. On the other hand, sample particles are more or less soluble in the KFT solvent (methanol). Consequently, the reaction of water molecules strongly depends on the type of these molecules and the possibility to diffuse to the surface.

Three pseudolinear variations on the KFT titration curves were observed (examples for the titration behavior at the starting of ripening are presented in Figures 6 and 7). The first range, corresponding to the time interval of approximately 10-80 s is attributed to the titration of the "surface" water molecules (those water molecules that are even present in the methanolic solution, on the surface of the salami particles, or easier to diffuse to the surface). The second range is longer, from 80 s to ~240 s, and corresponds to the reaction of water molecules that diffuses slowly from inside of the particles. They are called "strongly-retained" water molecules. The last range corresponds to the "normal" drift of the KFT system.

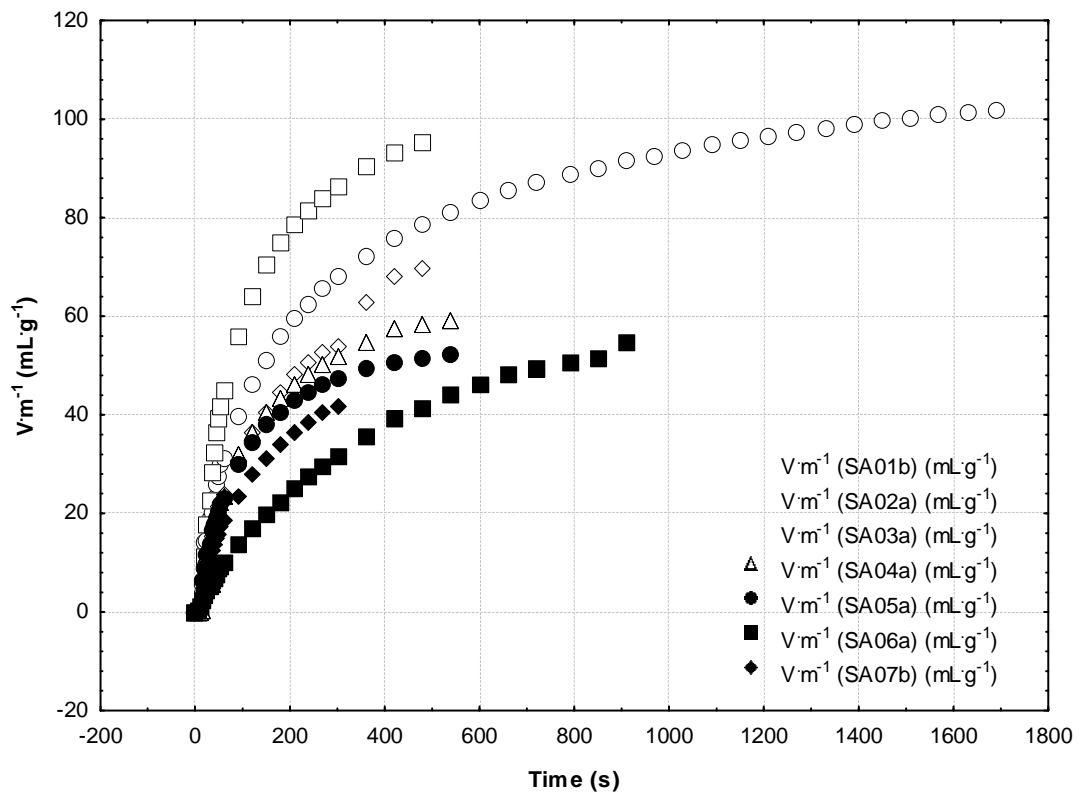


Figure 2. Titration volume / sample mass ( $V \cdot m^{-1}$ ) versus time from the KFT analysis of the "Ardelenesc" salami samples (codes "SA") (some samples needs longer time to reach the "normal" drift)

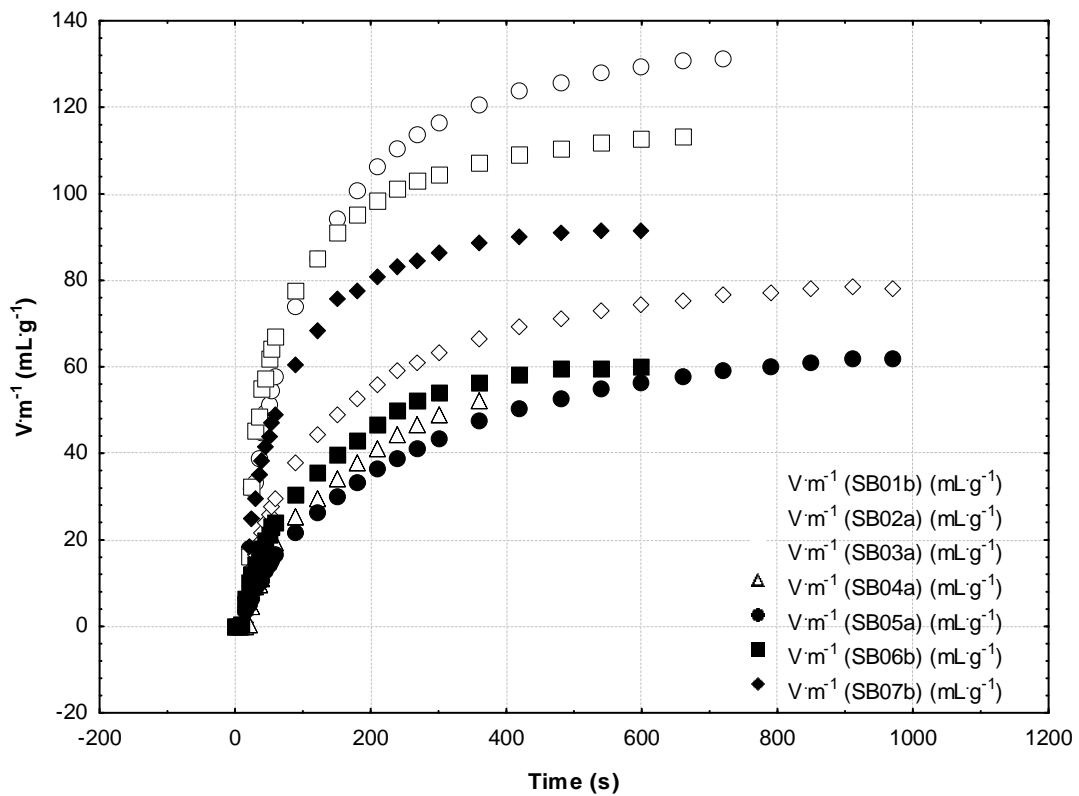


Figure 3. Titration volume / sample mass ( $V \cdot m^{-1}$ ) versus time from the KFT analysis of the "Banatean" salami samples (codes "SB") (some samples needs longer time to reach the "normal" drift)

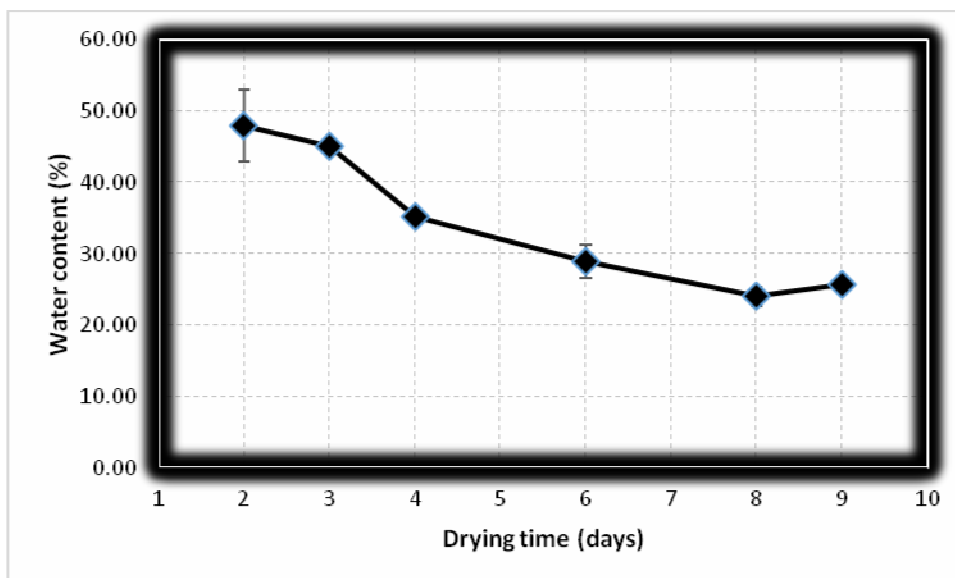


Figure 4. Variation of the total water content of "Ardelenesc" salami samples during ripening

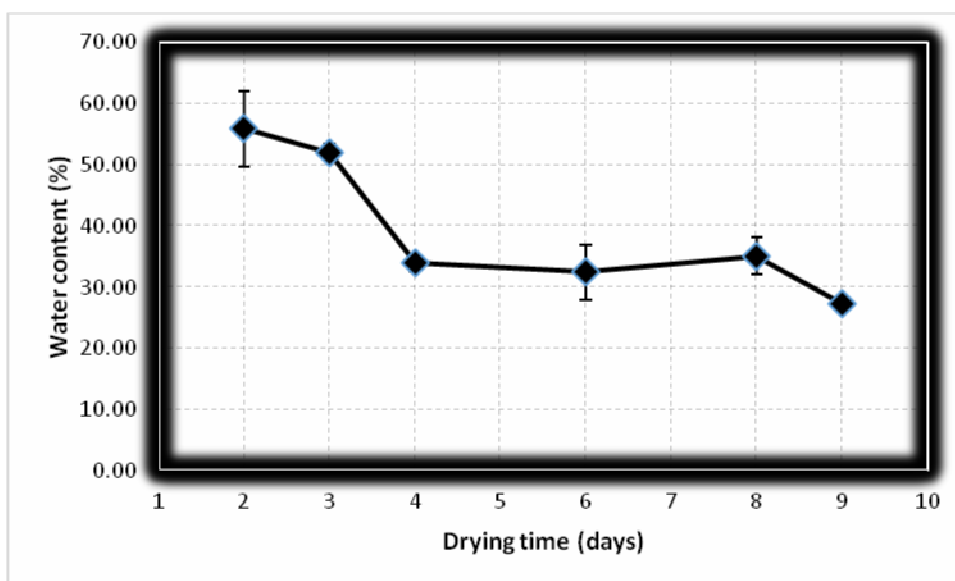


Figure 5. Variation of the total water content of "Banatean" salami samples during ripening

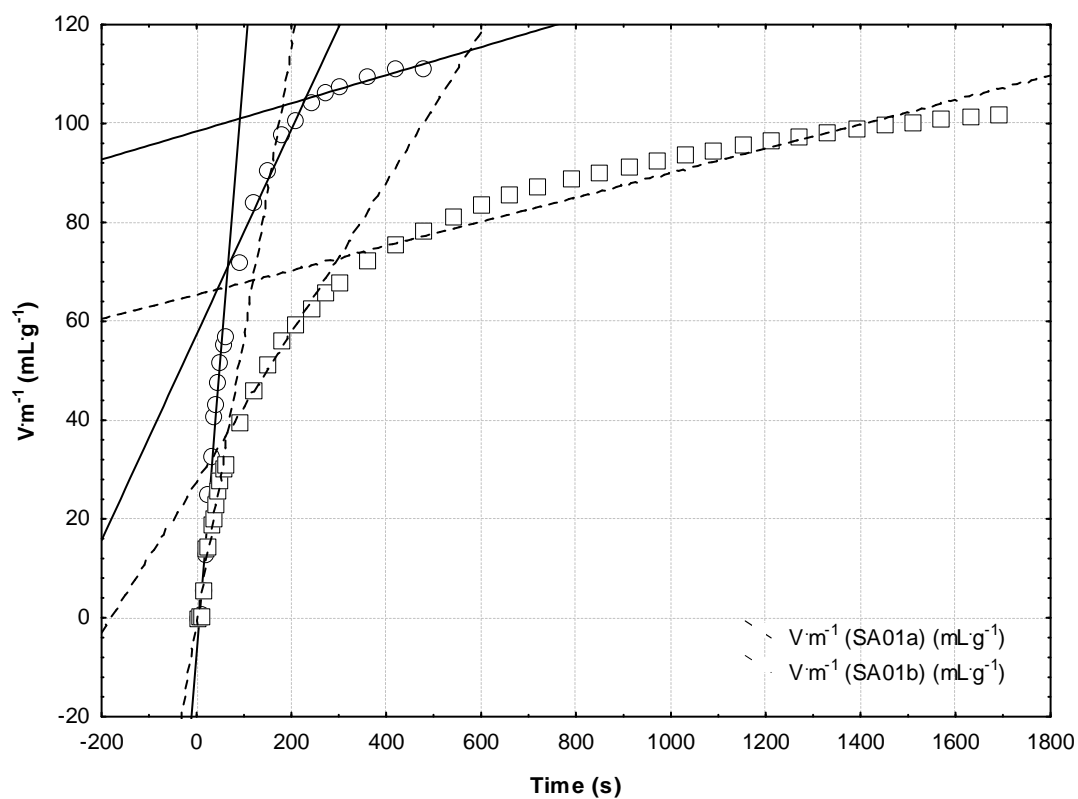


Figure 6. Evaluation of the “surface” (time interval of 10-80 s) and “strongly-retained” (time interval of 80-240 s) KFT water reaction rates for the “SA” samples (e.g., the first duplicate analysis is presented) (the last time interval corresponds to the “normal” drift)

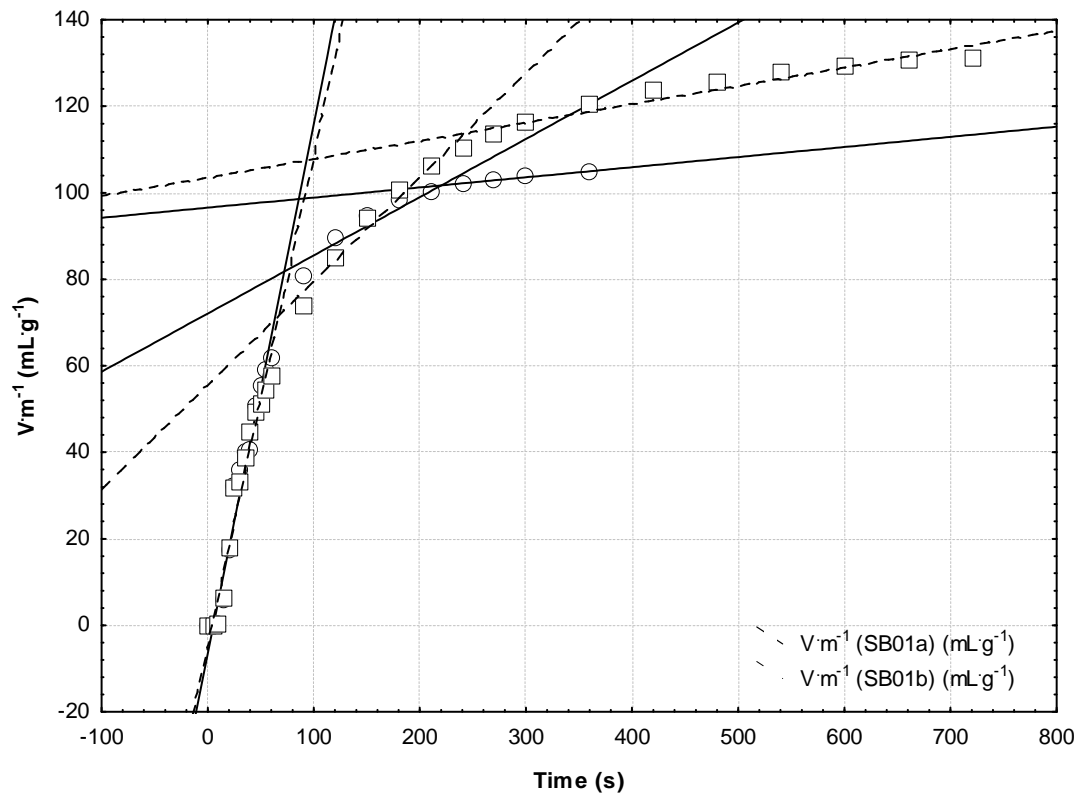


Figure 7. Evaluation of the “surface” (time interval of 10-80 s) and “strongly-retained” (time interval of 80-240 s) KFT water reaction rates for the “SB” samples (e.g., the first duplicate analysis is presented) (the last time interval corresponds to the “normal” drift)

The water reaction rate can indicate the proportion of such type of molecules, taking into account the known data for the determination. Thus, the variation of the KFT volume can be transformed in the variation of the iodine concentration (consumption) or the variation of water concentration by knowing the reaction volume (which varies during the KFT process) and the titer of the iodine solution. Furthermore, the mean water reaction rates,  $\bar{v}$  (expressed in millimole·L<sup>-1</sup>·s<sup>-1</sup> or mM·s<sup>-1</sup>), on the specified ranges can also be determined from the slopes of the pseudolinear KFT variations.

$$\bar{v} = -\frac{\Delta C_{H_2O}}{\Delta t} \text{ [mM}\cdot\text{s}^{-1}\text{]}$$

Two water reaction rates corresponding to “surface”,  $\bar{v}_1$  and “strongly-retained” water,  $\bar{v}_2$  can be determined for the salami type samples. The decreases of the water reaction rates corresponding to “surface” water is more evident for both salami types (Figures 8 and 9). These values decrease from 4.9-5.9 mM·s<sup>-1</sup> to 1.3 mM·s<sup>-1</sup> in the case of “Ardelenesc” salami and from 6.5 mM·s<sup>-1</sup> to 2-3 mM·s<sup>-1</sup> for “Banatean” salami samples. On the contrary, water reaction rate corresponding to “strongly-retained” water molecules had almost no variation for both cases. These values were in the range of 0.5-1 mM·s<sup>-1</sup> (see Figures 8 and 9, dashed lines). These observations suggest that almost all released water during the ripening process is “surface” water.

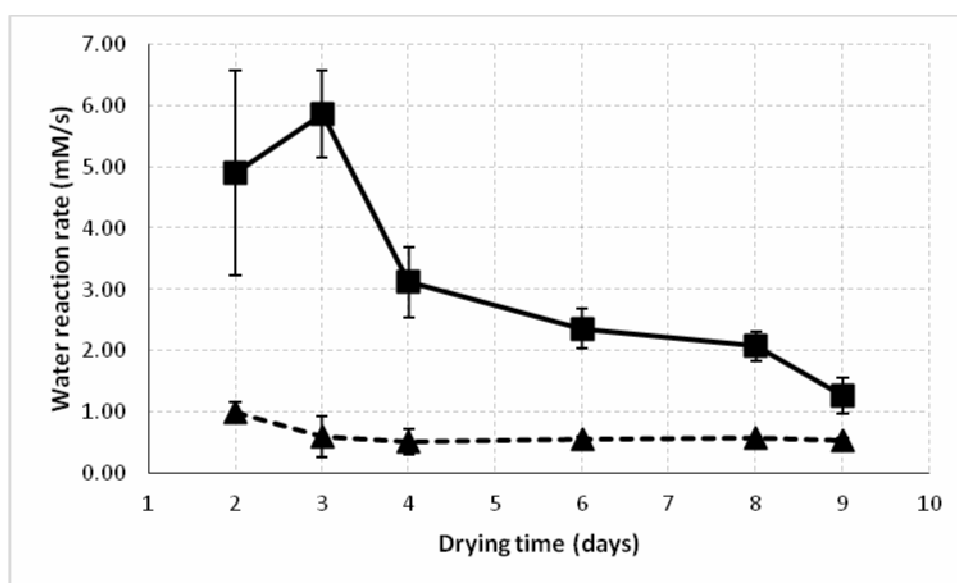


Figure 8. Variation of the “surface” (continuous line) and “strongly-retained” (dashed line) KFT water reaction rates during ripening of the “Ardelenesc” salami products

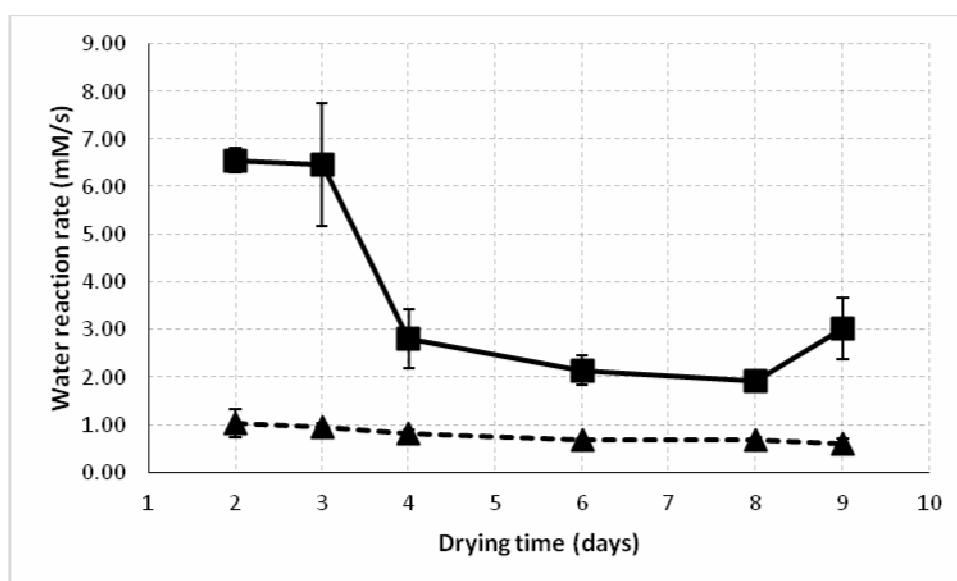


Figure 9. Variation of the “surface” (continuous line) and “strongly-retained” (dashed line) KFT water reaction rates during ripening of the “Banatean” salami products

#### 4. Conclusion

Karl Fischer water titration is an appropriate tool for evaluating the total and "real" water content of meat-based food products such as salami. The ripening process of Romanian traditional salami is completely finished after eight days, the faster drying being observed in the first four days. Furthermore, only a non-significant variation of the "strongly-retained" water reaction rate during ripening was observed. In comparison, the variation of the "surface" water reaction rate is more obvious and correlate with the total water content during the drying process. This observation demonstrates that almost only "surface" water is released during the ripening of salami-type products.

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