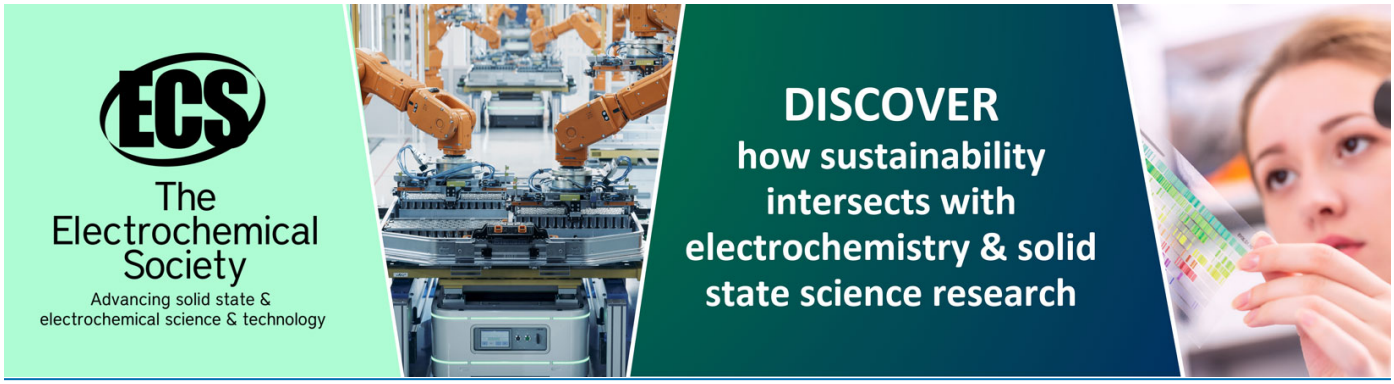
# Using synchronous thermal analysis instrument to identify number of cycles of fish refrigeration





# Using synchronous thermal analysis instrument to identify number of cycles of fish refrigeration

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**Abstract.** The aim of the work is to develop a technique for Express determination of trout falsification by the method of heat treatment by differentiating its thermal state: "chilled" – "frozen" with the use of a synchronous thermal analysis device. The device of the synchronous thermal analysis STA 449 F3, Jupiter, made by NETZSCH was used for experiments. The trout samples were examined in a copper furnace with the connection of a Dewar’s vessel in oxidized aluminum crucibles in helium atmosphere, while simultaneously fixing differential scanning calorimetry (DSC) curves and and the weight loss (WL) curves. The developed methodology includes recommendations for the selection of a trout sample for analysis; the DSC temperature program for monitoring fish processing and storage, the conditions for obtaining a DSC curve for the reference sample; a criterion for the thermal state of the experimental sample of trout. The DSC temperature program provides for sequential two-fold freezing operations - heating of a sample of trout muscle tissue from its spine mass of 24 mg in the temperature range from 25 to minus 30 ° C by cooling with nitrogen at a speed of 5 K / min. The exothermic effect of the second freezing for the reference sample serves as a criterion for the thermal state of the experimental trout sample.

## 1. Introduction

The problem of developing a methodology for instrumental rapid identification of the number of cycles of fish refrigeration is relevant for two reasons at least. First, as noted by the authors [1], illegal, undeclared and unregulated fishing, dishonesty or fraud in the supply chain of fresh and chilled fish products to the consumer is a multifaceted problem. In order to solve it, it is necessary to fully equip the quality control laboratories of these products. To ensure effective traceability of fish products, modern means and methods of instrumental control are needed along with a set of measures to organize a chain of traceability in relation to products of processing of farm animals and poultry [2-5].

Secondly, the development of technological processes of fish processing [6-7], which are the factors that form the quality of food products, dictates new requirements for the formation of the regulatory and legislative framework in the field of fish processing in Russia. For example, the analysis of the fish production scheme makes it necessary to distinguish the concepts of "chilled fish" and "thawed fish" [8]. Hence, it is necessary to equip quality control laboratories of fish products with

a technique for instrumental identification of the thermal condition of fish in order to distinguish "thawed" products from "chilled" products under the same temperature storage conditions [8, 9].

The aim of the work is to develop a technique for Express determination of trout falsification by the method of heat treatment by differentiating its thermal state: "chilled" – "frozen" with the use of a synchronous thermal analysis device.

## 2. Materials and methods

The rainbow trout (Oncorhynchus mykiss) of the genus Oncorhynchus of salmon family (Salmonidae) was used as an object of the study. The trout was grown in the aquaculture of the trout farm "Rosa" (v. Trudovoe, Voronezh Region, Private Enterprise Head of Farm I.A. Alimenko). Private Enterprise Head of Farm I.A. Alimenko implements the Management System that conforms to the requirements of the standard EN ISO 9001:2008 for the following scope: growing and sale of fish.

For the analysis, a sample of muscle tissue was selected from the spinal part of the trout weighing 24 mg. The thermal analysis was started in 1 hour after catch.

To perform thermal analysis of fish in the heating-cooling process, synchronous thermal analysis instrument STA 449 F3, Jupter, made by NETZSCH, was used. The device simultaneously captures the differential scanning calorimetry (DSC) curves and the weight loss (WL). The analysis of the fish sample was carried out in a copper furnace with the connection of Dewar’s vessel in oxidized aluminum crucibles in helium atmosphere. The accuracy of the temperature measurement was ± 0.3 ° C.

**Table 1.** Temperature program of the research in closed crucible

| Test procedure number | Process | Initial temperature of the process, $^0$C | Final temperature of the process, $^0$C |
|---|---|---|---|
| 1 | Freezing of fresh fish | 25 | -30 |
| 2 | Thawing | -30 | 25 |
| 3 | Freezing | 25 | -30 |
| 4 | Thawing | -30 | 25 |
| 5 | Freezing | 25 | -30 |
| 6 | Heating | -30 | 250 |

## 3. Results and Discussion

The choice of trout as the object of study is justified by the fact that it is characterized by the largest content of nutrients and the smallest water content, respectively it has the largest food density in comparison with other types of commercial fish such as sea perch, spotted catfish, sea flounder, Atlantic cod [10].

The main indicators in determining the freshness of fat and fat-containing products are acid and the peroxide number, so the physico-chemical parameters affecting the nutritional value of the product are estimated by the degree of fat decomposition [11]. Multiple repeated thawing and freezing lead to disruption of cell integrity or denaturation of the protein, which is accompanied by a change in the relationship between the forms of moisture binding to the product, the study of which makes it possible to determine whether the fish has thawed and how many times.

Figure 1 and Table 2 show the results of the DSC study of the single trout sample after a three-time freezing and thawing. The DSC curve show a minimum corresponding to the endothermic thawing of the sample. When conducting studies on the temperature program presented in Table 1, it was established that as the number of freeze-thaw cycles increases, the DSC curve peak area decreases monotonously, directly proportional to the change in the enthalpy of the process, which is associated with a decrease of the amount of free water in the sample [12].

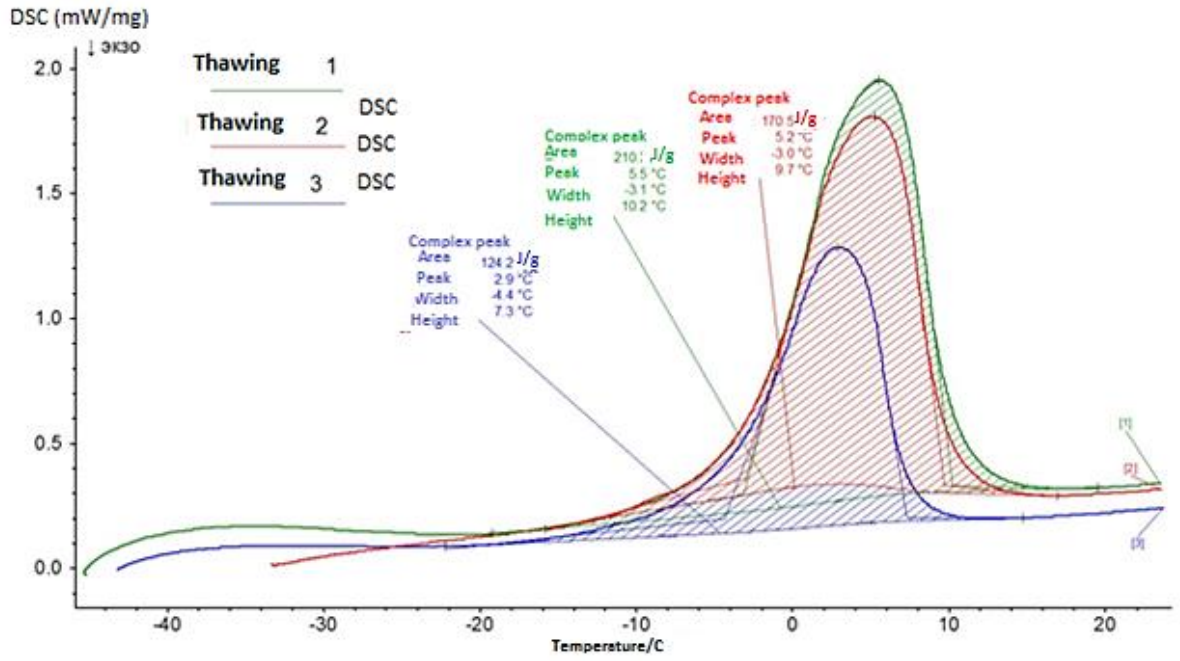


**Figure 1.** Thermoanalytical DSC curves: 1 - first thawing; 2 – second thawing; 3 - third thawing

**Table 2.** Parameters of DSC curves during thawing of a trout sample

| Test procedure, process number according to table 1 | The peak temperature of the melting, °C | The temperature interval of melting, °C | Area of peak of DSC curves, J / g |
|---|---|---|---|
| Melting after the first freezing (№. 2) | 5.55 | -2.8….-10.20 | 195.9 |
| Melting after the second freezing (№ 4) | 5.12 | -3.40….-9.76 | 176.8 |
| Melting after the third freezing (№ 6) | 2.87 | -4.42….-7.26 | 118.6 |

According to Raoult's laws, the freezing point of the solution is always below the freezing point of the pure solvent, and since in fish, during the freezing, the tissue juice containing a certain amount of dissolved substances crystallizes; the temperature of water crystallization in the fish is below the freezing point of pure water.

It should be noted that with a monotonic increase in the enthalpy, there is no regularity in the change of water crystallization temperature in the product. Since the difference between the crystallization temperatures of the first and second, second and third does not exceed freezing of 1°C (Table 1), the absence of regularity is insignificant. In this case, the magnitude of enthalpy change is more important for determining the quality of fish.

When the sample is heated from negative temperature (Test 6, Table 1), the possibility of water mass loss is excluded, the peaks are separated; it is easier to identify them, determine the beginning and end of the endothermic dehydration effect (Figure 2, Table 3). The first endothermic effect on the DSC curve (Figure 2) corresponds to the melting of ice, the second effect to the evaporation of water. In the process of dehydration, the mass, detected by the WL curve (Figure 2), falls by 76.53%, which coincides with the data in [10] on the moisture content in trout (76-82%). In the process of dehydration, 754.2 kJ / mol of heat is absorbed.

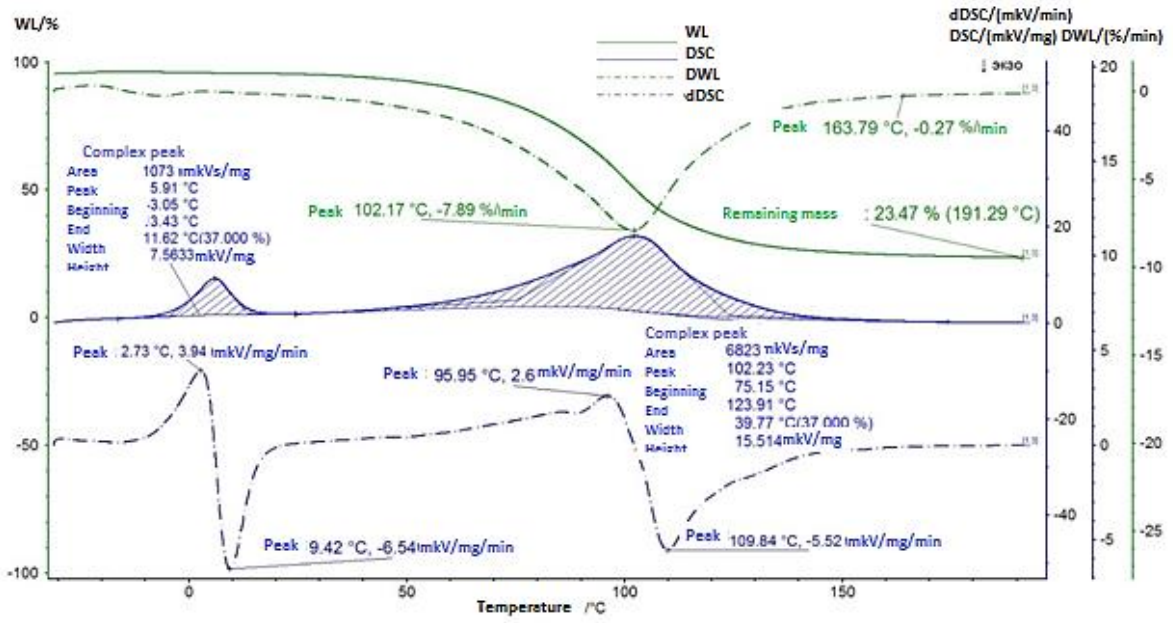


**Figure 2.** Thermoanalytical curves of a fish sample when heated from minus 30 to 250 ºC (Test 6, Table 1)

**Table 3.** Parameters of thermal effects when heating trout from -30 ºC to + 250 ºC

| | Thermal effect | Enthalpy, kJ / mol | Initial temperature of the effect, ºC | Peak temperature, ºC | End tem-perature, ºC | Mass loss, % | Event |
|---|---|---|---|---|---|---|---|
| **Frozen trout** | 1. Endothermic | 118.6 | -3.05 | 5.91 | 13.43 | - | Ice melting |
| | 2. Endothermic | 754.2 | 75.15 | 102.2 | 123.9 | 76.53 | Dehydration |

The established endothermic effects characterizing the processes of melting ice and dehydration of frozen trout when studied by the DSC method in accordance with the developed temperature program were used in the development of the procedure for differentiating the "freeze-thaw" cycles of fish.

The developed methodology includes recommendations for the selection of a trout sample for analysis; the DSC temperature program for monitoring fish processing and storage, the conditions for obtaining a DSC curve for the reference sample; a criterion for the thermal state of the experimental sample of trout. The DSC temperature program provides for sequential two-fold freezing operations - heating of a sample of trout muscle tissue from its spine mass of 24 mg in the temperature range from 25 to minus 30 ° C by cooling with nitrogen at a speed of 5 K / min. The exothermic effect of the second freezing for the reference sample serves as a criterion for the thermal state of the experimental trout sample.

In this case, the discrepancy between the values of the criterion for the test and the reference samples over the error of the device (±5 %) indicates a preliminary freezing of the trout sample.

## 4. Conclusion

For fish-processing enterprises and trade enterprises, an actual problem is the objective evaluation and classification of fish and fish products on the base of the thermal state and the types of refrigeration

processed by the fish in accordance with the scheme of technological processing and logistics. The expediency has been proved and the technique of using the synchronous thermal analysis instrument for monitoring the storage, processing, transportation of fresh and chilled fish has been developed and the facts of fish falsification in the thermal state in the conditions of analytical laboratories have been revealed.

The developed method does not require complicated sample preparation, it is suitable for online or at-line processing control, it ensures the objectivity and reliability of the measurement results, since it allows identifying fish changes not in the scales or surface layer, but in the muscle tissue.

## 5. Acknowledgments

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