Dynamic Fat Crystallization Based on the Indirect Solid Fat Content (SFC) Method

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The time domain nuclear magnetic resonance (TD-NMR) measurement of Solid Fat Content (SFC) in fats and fat compositions using the Direct and Indirect method are well established official standard methods (ISO, AOCS, IUPAC). While the measurement takes just 6 seconds ,the sample preparation (including melting the fat or fat mixture, filling the sample tube, tempering it at melting temperature, and crystallizing the fat sample in a certain polymorph plus the subsequent tempering at the measurement temperature) takes a lot of time. Especially for cocoa butter. When using cocoa butter equivalents and similar fats the whole sample preparation takes 44.5 hours. This is far too long to decide if the crystallization behavior of the fat or fat mixture matches the requirements of the product or not. At chocolate industry sites, shipments arrive with the fat composition and the decision has to be made within 2 hours to unload them or not. Moreover the end use of the fat in processing (filling, covering, etc.) has to be decided.

Based on these requirements Bruker developed the Dynamic Fat Crystallization application. It provides a crystallization pattern of fat on a timeline by measuring the solid fat content. This indirectly shows the initial crystallization, the main crystallization step and the final Solid Fat Content within 2 hours. Based on the speed of the crystallization and the final Solid Fat Content, QC managers at factories can decide if the delivered fat is acceptable and unloaded or rejected, or if fat or mixtures are used for filling or covering applications. A correlation between the measured fat crystallization pattern and product crystallization in the production helps to improve the product quality.

Features and Benefits

- Quality control of delivered fats and mixtures based on crystallization pattern
- Rapid dynamic fat crystallization analysis in a maximum of 2 hours including sample preparation
- Increased raw material quality leading to increased product quality
- Easy to use by NMR non-specialists
- Minimal requirements regarding site and infrastructure
- No chemical preparation needed

Method

The dynamic crystallization analysis is based on the Indirect method for SFC measurements in fats. Indirect means that the liquid fat content (LFC) is measured and the SFC value is calculated as 100 % minus the LFC. In the classical Indirect

measurement, an SFC sample is measured above the melting temperature at T_{liquid} to be sure that the fat is 100 % liquid. Afterwards the fat is crystallized according to the protocol given in the standard method and tempered at the temperature of interest $T_{int.}$. The percentage of liquid fat is calculated by the ratio of the amplitudes $A(T_{int.})/A(T_{liquid})$. Because the signal amplitude increases due to the Boltzmann effect when the sample is cooled down, the amplitude at $T_{int.}$ has to be corrected. For this purpose a reference oil sample is measured at both temperatures. As the oil is 100 % liquid at both temperatures, the ratio of the signal amplitudes $Aoil(T_{liquid})/Aoil(T_{int.})$ provides a correction factor f (corr. Tint.) that is used to correct the signal amplitude at the temperature of interest $A(corr.\ T_{int.}) = A(T_{int.})^*\ f(corr.\ T_{int.})$. Then subtracting the corrected liquid fat content from 100% leads to the current SFC value. The standard AOCS SFC method requires the measurement of the sample and the reference oil at T_{liquid} and $T_{int.}$. Therefore, for the four NMR measurements, crystallization and tempering steps, 44.5 hours are required. The advantage of the Dynamic Crystallization Analysis is the continuous recording of the SFC values during the crystallization process. The starting point is T_{liquid}. The temperature $T_{int.}$ at every measurement can either be calibrated or measured during the acquisition using a special thermometer. The SFC value is continuously recorded every minute in fats or blends being cooled down from e.g. 70 °C to 19 °C. The fat is pre-tempered above the melting temperature for 15 - 30 minutes depending on the starting temperature before the measurement is started. The monitored SFC values by the Dynamic Crystallization Analysis leads to a crystallization pattern which simulates the continuous cooling process in the cooling tunnel of such industries.

Application Fields

- Producers of cocoa butter, cocoa butter equivalents and similar fats
- Industries using the above mentioned fats and fat blends such as factories for chocolate, chocolate bars and filled chocolate (praline).

Boltzmann effect calibration

The Boltzmann effect can be compensated by tempering a sample at 4 different temperatures above the melting temperature (SFC value is 0), measuring the NMR amplitudes and correlating them with the 4 temperatures. This calibration is used to calculate a correction factor per degree Celsius (°C). The same can be done using an oil sample at temperatures between e. g. 70 and 19 °C. In both cases the correction factor can be entered and saved in the application program and it is used for every further measurement. Another option is the automatic measurement and calculation of the correction factor by the software during the dynamic SFC measurements if an optical temperature sensor is connected.

Measurement

The measurement procedure can be split in two phases:

1. The sample tube including sample and sensor block pre-tempered (e.g. 70 °C) are placed into the cooled probehead (e.g. 19 °C). Cooling curves are measured by recording the temperature inside the sample every

Hardware and Software

minispec mq20 NF series equipped with a VT probehead

Thermostat Cryostat Bath for the temperature control of the probehead

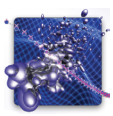
Block Thermostat to fully melt the sample

10 mm Glass Tubes

Digital Thermometer[1°] (Optional)

Optical Fiber Temperature Sensor[2*]

Spacer to position the sample into the center of the NMR coil



Bruker Dynamic Center software installed

Only one from both types of thermometer (1* or 2*) is needed by the application

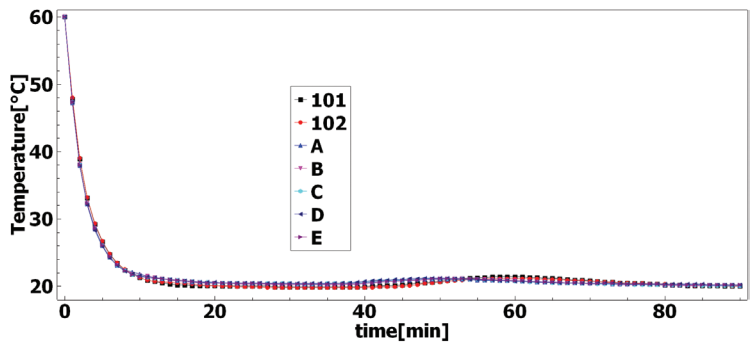
minute for 90 -105 minutes (See figure 1). As the thermal capacity of the fat and blend samples is almost the same the cooling curve can be calibrated and used for every further measurement. When using a previous calibration, measurements start with step 2 described in the following lines.

2. The second step consists of SFC measurements every minute for 90-105 minutes. Here, the sample without the sensor is placed into the probehead in a similar way as before. The ferromagnetic sensor is taken out to prevent disturbances of the NMR measurement.

With an optical temperature sensor connected, both steps can be run at the same time. In this case, the temperature curves do not need to be recorded beforehand and slightly different cooling behavior of the different samples are considered. Using an optical temperature sensor is highly recommended when various fats or blends are routinely measured. For facilities dealing only with one kind of fat, a common temperature sensor can be used to calibrate and save the cooling profile in a file being used in step 1 for all further measurements.

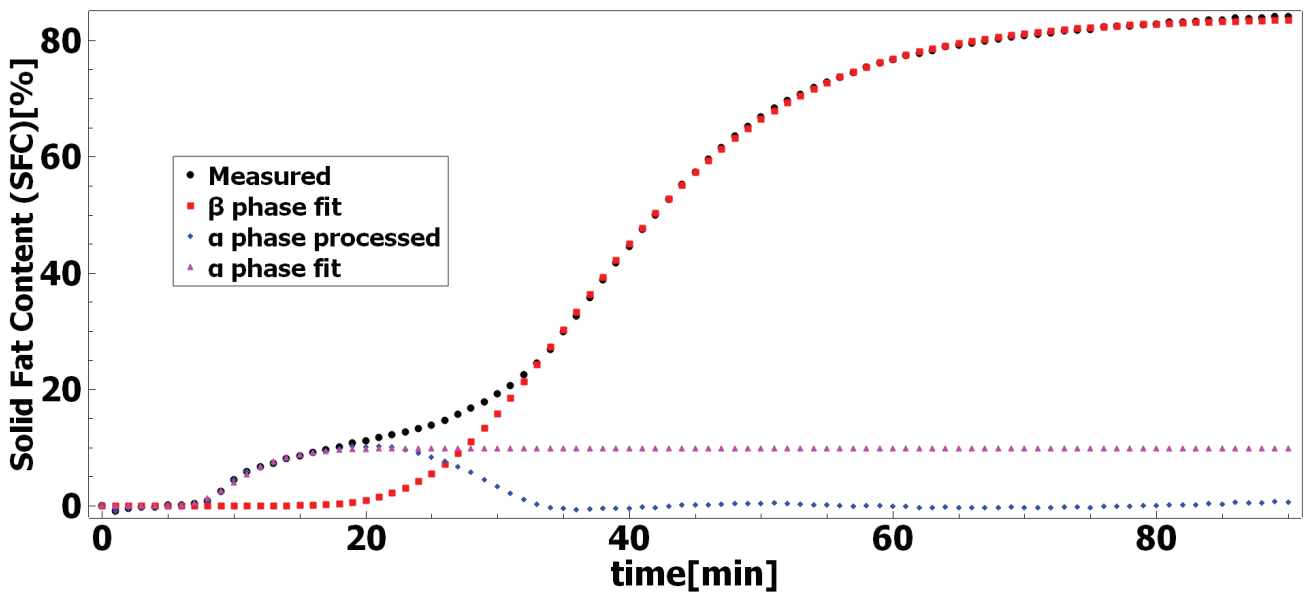
The resulting crystallization curve (see Figure 2) is then analyzed using a reparametrized Gompertz mathematical model (See figure 3) to interpret the physical properties of the fat. The process of applying the Boltzmann effect correction on the SFC values or fitting the data to the model is fully supported by the Dynamic Crystallization Analysis application package.

Figure 1



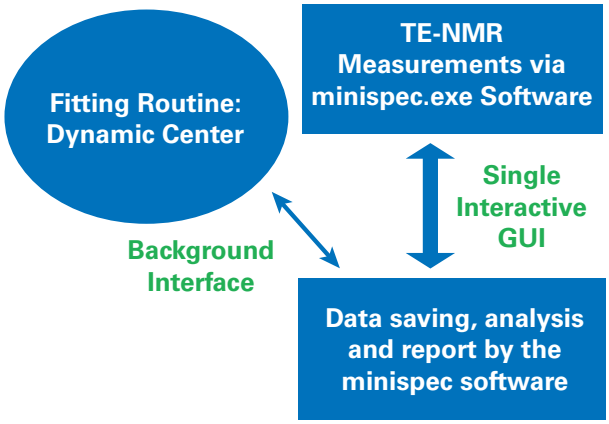
Cooling curves of various cocoa butter samples from 60°C to 19°C

Figure 2



: Dynamic Crystallization Analysis: Solid Fat Content versus time of a cocoa butter sample from 60 °C to 19 °C.

Dynamic Crystallization Chart



The result table reports:

- Maximum SFC
- Phase induction time
- Maximum phase forming rate

	Max. SFC(%)	Ind. time(min)	Max.Inc.(%SFC/min)	SFC offset(%)
Alpha phase:	29.100	3.76447	1.80288	-2.060
Beta phase:	79.710	14.59346	1.29113	22.870

Workflow

- Samples are prepared in standard 10 mm NMR glass tubes (details in the SOP).
- The user-friendly minispec.exe software is started and the dynamic crystallization application is loaded.
- The intuitive Dynamic Crystallization Analysis application is used to run the sample analysis interactively with the operator.
- At the end of the NMR measurement, the data are automatically processed in the background by Bruker's Dynamic Center software.
- The parameters for the alpha (crystallization initiation) and beta (main crystallization) phases are displayed in the GUI result box.
- When QA/QC mode is enabled, a prompted information box alerts the operator if a parameter is not in scope. Limits can be entered according to practical experience and adapted to the production process.
- The data can be reprocessed as many times as necessary with different boundary limits before closing the experiment.
- All data are saved with reference to name, date and time of the measurement.

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