Application Note

Determining droplet size distribution in emulsions using MQC-R - a benchtop time domain NMR instrument

Droplet size distribution (DSD) is an important characteristic of emulsions. Its determination is crucial for quality control and assessment of products at various stages of processing, manufacturing, and production, and for evaluating properties of new formulations in research and development. In many industries, there is a requirement to determine the DSD of different emulsions simply, accurately and without disrupting the sample structure.

An emulsion is as a mixture of two or more immiscible liquids that form a system of dispersed droplets (dispersed phase) separated by the continuous phase matrix. Examples include margarines, butters, food dressings, paints and crude oil. Emulsions typically remain stable and keep their structure (i.e. the droplets do not coalesce) for a significant period of time and under certain conditions (e.g. temperature).

This application note demonstrates how **MQC-R**, a research focused time domain, nuclear magnetic resonance (NMR) spectrometer can be utilized to routinely determine the DSD in emulsions, in this case in a sample of margarine, and therefore may be employed in a quality control environment.

The time domain NMR approach

The time domain NMR method for analysing DSD is based on the phenomenon of restricted diffusion. The effective mobility of the dispersed phase molecules moving within the droplets is significantly lower, compared with that of the equivalent bulk liquid, due to interactions with the droplet walls. As such, information about droplet size can be obtained through NMR diffusometry measurements.

Raw data are acquired in the form of NMR signal diffusion decays. For an emulsion sample, where continuous and dispersed phases are present, both these components produce an NMR signal.

In order to collect NMR data only for the dispersed phase, the signal from the continuous phase is removed by

applying a suitable T_1 relaxation filter, followed by a pulsed-field gradient (PFG) diffusometry protocol. To further enhance the signal selection, the sample temperature is held constant using a variable temperature (VT) NMR sample probe. Under such conditions, the effective T_1 relaxation time of the continuous phase is much shorter than that for the dispersed phase, and therefore the efficiency of the T_1 filter is improved further.

Advantages of using **MQC-R** for droplet size distribution analysis:

- Easy and reliable technique
- Simple sample preparation
- Non-destructive: measure the same sample multiple times
- Delivers droplet dimension data, rather than droplet clusters
- No hazardous solvents or waste involved
- Direct measurement of a bulk sample
- Applicable to a wide range of emulsions
- Consistent results by fixing the sample temperature

Sample preparation

For each different emulsion formulation, three samples need to be prepared:

- A pure sample of the continuous phase
- A pure sample of the dispersed phase
- An emulsion sample, or set of emulsion samples made up of the continuous and dispersed phases

In addition, a sample of deionised water may be required for the calibration.

In this example application using margarine, we prepared the following three samples: (1) dispersed phase inside the droplets (water-based), (2) continuous phase (fat-based), and (3) emulsion - margarine. Once prepared, the samples were transferred into NMR tubes, and conditioned at +5°C, which is the typical temperature used when measuring the DSD of dairy products.

Calibration procedure

Calibration consists of three automated steps:

1) Adjusting the parameters of the T_1 filter to remove the continuous phase NMR signal
2) Collecting diffusion data for pure (deionised) water to adjust the effective strength of the PFG
3) Collecting diffusion data for the pure dispersed phase to define the initial parameters for data processing

Analysis procedure

Provided the instrument has been calibrated for samples containing the same continuous and dispersed phases, it may be used to routinely collect diffusion data, without further refinement, from emulsion samples equilibrated at the same temperature used for the calibration – this data is then used to determine the DSD results.

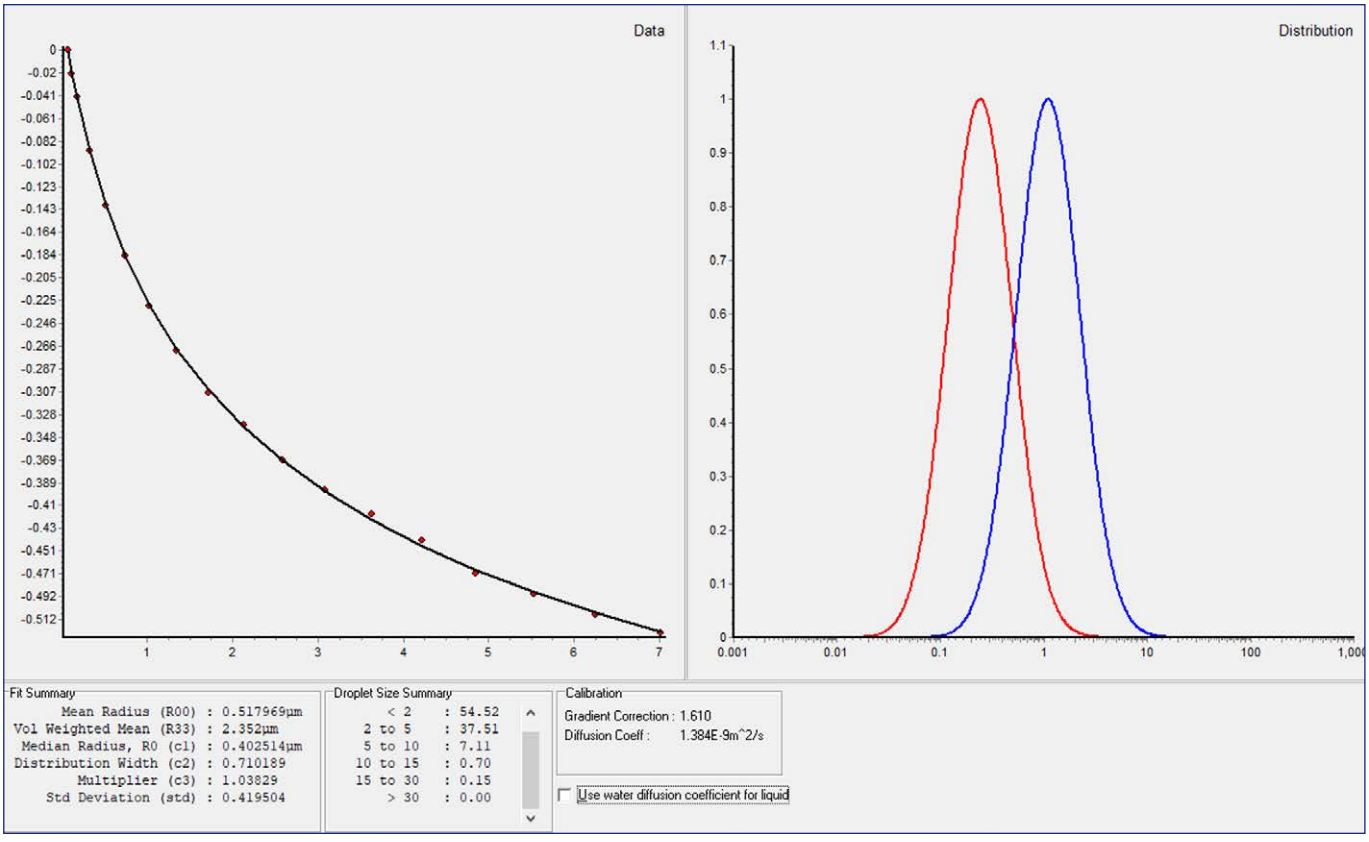

Figure 1. The DSD results obtained using the MQC-R after the fitting of NMR diffusometry data for a margarine sample. The experimental diffusion decay (●, the red solid circles) and the log-normal fitting curve (—, the solid black line) are shown in the left-hand graph window. The volume-weighed droplet size distribution (—, the blue curve) and the mean size distribution (—, the red curve) are plotted in the right-hand graph. The numerical parameters of the distribution are listed in the "Fit Summary" and "Droplet Size Summary" tables below.

Results

The data is processed using a log-normal distribution of diffusion coefficients. The fitting results are reported as a graph of the distribution function and as a set of the distribution function parameters (Figure. 1): the mean radius of droplets (R_{00}), the volume-mean radius (R_{33}), the median radius (R_0), the distribution width (σ), and the percentage of droplets falling within a user-specified, predefined radius range.

Tables 1 and 2 show the repeatability of the DSD measurements made with the **MQC-R**.

Table 1. Repeatability of DSD measurements obtained for the margarine sample using the **MQC-R**.

Droplet size distribution parameters	Repeat 1	Repeat 2	Repeat 3	Average value for three repeats (μm)	Standard deviation for three repeat measurements (μm)
Mean radius, (μm)	0.61	0.54	0.52	0.56	0.04
Volume weighed mean, (μm)	2.31	2.38	2.35	2.35	0.03
Median radius, (μm)	0.49	0.43	0.40	0.44	0.04
Distribution width, (μm)	0.67	0.70	0.71	0.69	0.02

Table 2. Repeatability of measurement of the content of droplets with a specific radius using the **MQC-R** for margarine.

Droplet radius ranges*	Percentage of droplets with radius within the respective range (%)			Average value for three repeats (μm)	Standard deviation for three repeat measurements (μm)
	Repeat 1	Repeat 2	Repeat 3		
Smaller than 2 μm	54.06	53.47	54.52	54.02	0.43
From 2 to 5 μm	39.04	38.40	37.51	38.32	0.63
From 5 to 10 μm	6.33	7.28	7.11	6.91	0.41
From 10 to 15 μm	0.49	0.70	0.70	0.63	0.10
From 15 to 30 μm	0.09	0.15	0.15	0.13	0.03
Larger than 30 μm	0.00	0.00	0.00	0.00	0.00

* The number of the radius ranges and their numerical borders can be defined by the user.

Conclusion

As demonstrated, **MQC-R** provides a non-destructive and reliable method for determining DSD in emulsions and enables the properties and consistency of products to be easily monitored. Sample preparation is straightforward, with no need for hazardous solvents or contrast additives. In addition, the sample is maintained at a constant temperature to preserve the emulsion structure during analysis. Furthermore, the NMR technique is non-destructive, so the same sample can be analysed multiple times before being used elsewhere.

Ultimately, **MQC-R** enables more definitive and accurate formulation of new emulsions, as well as increased consistency in manufacturing and better process control, leading to reduced costs.

If you have any questions about this application note, please contact our experts:
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