Measurement of droplet size distribution in emulsions using benchtop NMR

Application Note

In many industries, there is a requirement to reliably and simply determine the droplet size distribution in the dispersed phase of an emulsion without disrupting the sample structure. The **MQR** time-domain Nuclear Magnetic Resonance (NMR) spectrometer fulfils this requirement with technology that provides a non-destructive method for measuring the distribution. Sample preparation is simple and results are fast and accurate. The use of the **MQR** allows more definitive and accurate formulation of new products, increased consistency in manufacturing operations, better process control and ultimately reduced costs.

Summary

MQR is a time-domain NMR spectrometer which addresses a range of industry specific quality control and research and development requirements using proven and reliable technology.

Advantages of the NMR technique for evaluation of droplet size distribution in emulsions include:

- One of the easiest and most reliable techniques available – suitable for unskilled personnel
- No hazardous solvents required; no hazardous waste produced
- Simple sample preparation minimising damage to the sample structure
- Measurements are made directly on the sample
- Uses standard approaches for data analysis
- Provides information about the dimensions of droplets, not droplet clusters
- Non-destructive, so the same sample may be measured several times
- Applicable to a wide variety of emulsions

Application

An emulsion is a mixture of two or more immiscible liquids which form a system of dispersed droplets *(dispersed phase)* separated by the *continuous phase matrix*. Spreads, margarine, mayonnaise, salad dressing, crude oil and paints are examples of emulsion products and materials. Emulsions remain stable and keep their structure (the droplets do not coalesce) for a period of time under certain conditions.

The *droplet size distribution (DSD)* is an important characteristic of emulsions. Droplet size analysis by NMR is used as an effective technique for the quality control of raw materials, characterisation of products at different stages of manufacturing and for monitoring properties of new products in research and development. Droplet size measurements help product developers and manufacturers achieve the required properties of emulsions and optimise production costs.

Advantages of NMR

The NMR method is applicable to a wide range of products and materials and in contrast to other techniques (e.g. optical microscopy and electric sensing) is much less destructive and can be quickly performed on a sample "as is". This means that sample structure distortion is minimised and the use of hazardous solvents, contrast agents or any other testing fluids is avoided, allowing multiple repeats of NMR measurements and further analysis of the same sample by other techniques. From a practical point of view, NMR measurements can be routinely performed by non-NMR experts using intuitive and user-friendly software which provides step-by-step instructions.

Method

The time-domain NMR method for analysing droplet size distributions is based on the phenomenon of *restricted diffusion,* where 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. This means that information about droplet size can be evaluated from NMR diffusometry measurements.

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The 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 improve the signal selection further, the sample temperature can be maintained at a certain value by using a *variable temperature NMR probe (VT probe)*. Under such conditions, the effective T_1 relaxation time of the continuous phase is much shorter than the relaxation time of the dispersed phase, and the efficiency of the T_1 filter becomes even better. This approach is used for the DSD analysis of dairy products (water-in-oil emulsions) where the samples are measured at a temperature of +5°C.

The measurement protocol consists of *four steps*:

Step 1: Adjusting the parameters of the T_1 filter to remove the continuous phase NMR signal.

Step 2: Collecting diffusion data for pure water to adjust the effective strength of the PFG.

Step 3: Collecting diffusion data for the pure dispersed phase to define the initial parameters for processing data.

Step 4: Collecting diffusion data for an emulsion sample (product). The data acquired during this step are used to obtain a droplet size distribution for the sample.

Steps 1-3 are the *calibration* steps and step 4 is the analysis step. The calibration steps may be skipped if the requirement is to measure several emulsion samples containing the same continuous and dispersed phases.

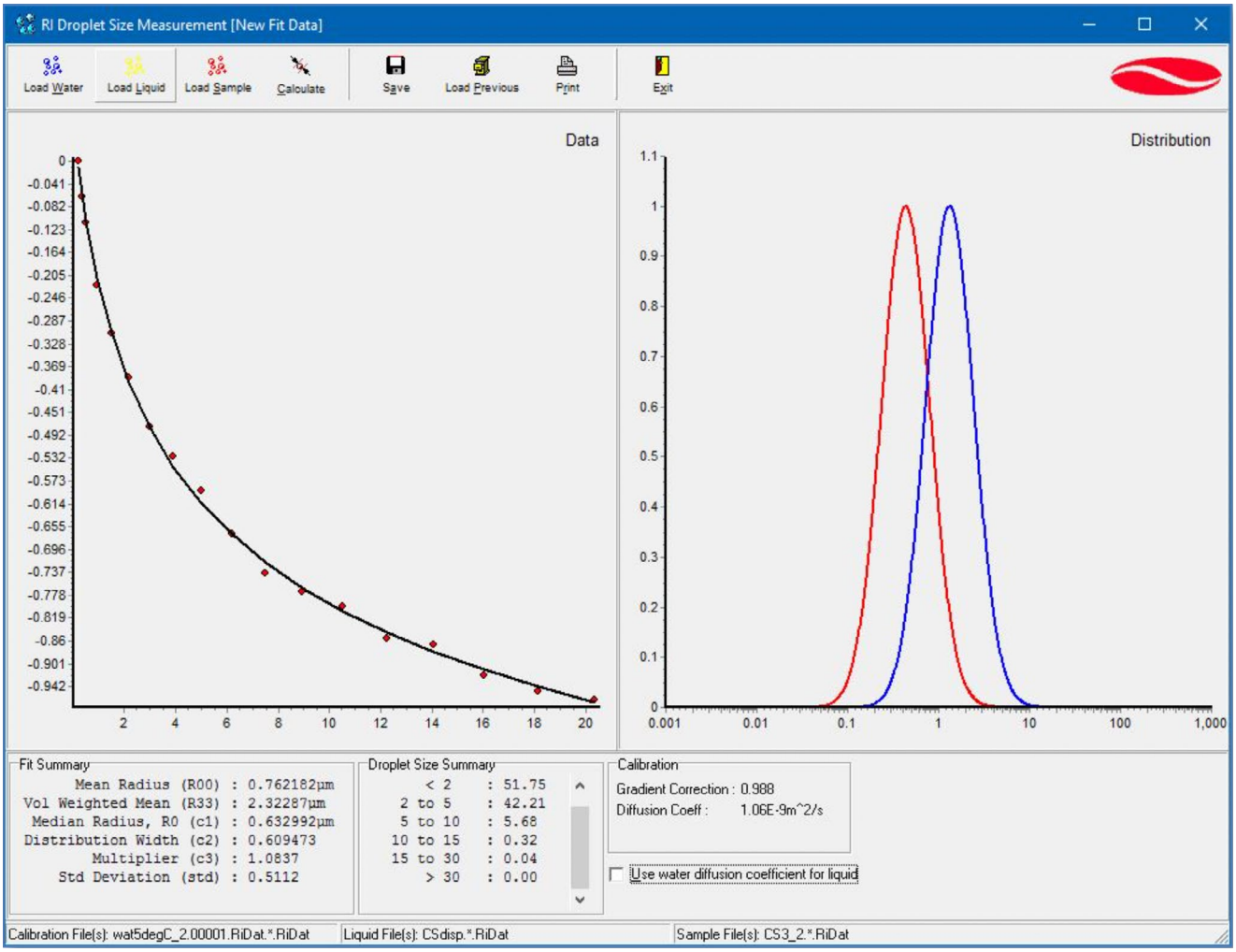


Figure 1: *The droplet size distribution results obtained after the fitting of NMR diffusometry data for a butter sample. The experimental diffusion decay (●, the red solid circles) and the log-normal fitting curve (—, the solid black line) are shown in the left-hand graph window. The volume-weighed 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 the data chart.*

The data analysis is carried out using a *log-normal distribution of diffusion coefficients* in a separate piece of provided software. The fitting results are reported as a graph of the distribution function and as a set of the distribution function parameters (see example in 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 with the size falling in the predefined radius ranges.* The radius ranges can be specified by users.

Sample Preparation

The NMR method for measuring droplet size distribution function requires four samples:

1) A sample of the pure continuous phase (for Step 1)
2) A sample of pure deionised water (for Step 2)
3) A sample of the pure dispersed phase (for Step 3)
4) An emulsion sample or a set of emulsion samples made of the continuous and dispersed phases mentioned in (1) and (3)

Samples (1) to (4) are transferred into suitable NMR tubes to the required sample height. The samples must be conditioned at the required temperature in a conditioning block or in the VT probe of the **MQR** analyser for a suitable period of time. The DSD software allows a time delay to be set to temper the sample prior to measurement.

NB:

- **Samples (1), (3) and (4) are required for each different formulation of emulsion.**
- **Information about the recommended sample sizes and conditioning time is provided in the respective Method Sheets for different probe sizes.**

Tables 1 and 2 show that NMR has good repeatability for the evaluation of the droplet size distributions.

Conclusion

The NMR technique is an accurate and repeatable method for defining droplet size distributions in a wide variety of emulsions.

Sample preparation for the NMR measurements is simple, does not distort the structure of emulsions and does not require hazardous solvents or contrast (testing) additives meaning that the emulsion is analysed "as is".

The NMR technique is non-destructive, so the same sample can be measured several times before being analysed by other techniques.

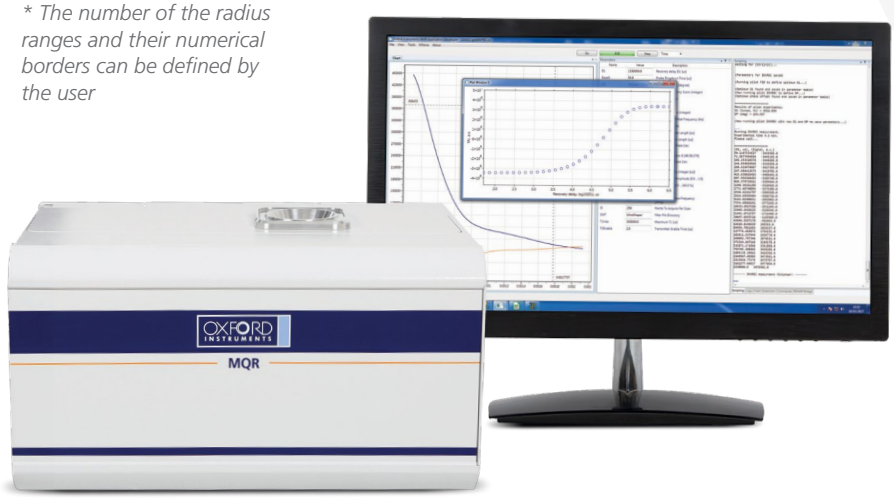
Table 1. Repeatability of NMR measurements for droplet size distribution parameters: Butter sample

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	0.76	0.70	0.75	0.74	0.03
Volume weighed mean, µm	2.32	2.41	2.32	2.35	0.05
Median radius, µm	0.63	0.57	0.62	0.61	0.04
Distribution width, µm	0.61	0.64	0.61	0.62	0.02

Table 2. Repeatability of NMR measurements for content of droplets with specific radius: Butter sample

Droplet radius ranges*	Percentage of droplets with radius within the respective range (%)			Average value for three repeats (%)	Standard deviation for three repeat measurements (%)
	Repeat 1	Repeat 2	Repeat 3		
smaller than 2 µm	51.75	50.74	51.96	51.48	0.65
from 2 to 5 µm	42.21	41.87	41.92	42.00	0.18
from 5 to 10 µm	5.68	6.81	5.74	6.08	0.64
from 10 to 15 µm	0.32	0.50	0.34	0.39	0.10
from 15 to 30 µm	0.04	0.08	0.04	0.05	0.02
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*



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