

## Script for XIGO Intro Video Part 2

### **SLIDE 1: Exploring Surfaces: Part 2**

Welcome to the concluding second part of “Exploring Surfaces with the Acorn Area”.

### **SLIDE 2: NMR Measurements**

In Part 1, we introduced XiGo’s Acorn Area – a small and easy-to-use low field (13MHz) NMR device that utilizes NMR liquid relaxation to investigate and study the nature of particle suspensions. This new use of NMR relaxation for surface analysis was pioneered by XiGo and provides a paradigm shift compared with traditional particle characterization instrumentation.

In contrast to the well-known, large and expensive, analytical NMR instruments found in university and industrial analytical laboratories, the Acorn Area can be used in any laboratory from blue-sky, exploratory research and development, through quality control/quality assurance to process monitoring.

Also, although the relaxation times for bulk liquid measured using either a conventional analytical NMR instrument or the Acorn Area device are largely the same, surface liquid relaxation time are much shorter at the lower 13MHz frequency (see the paper by Claves). This results in superior relaxation time resolution when using the Acorn Area.

In future videos we will demonstrate that the Acorn Area is also a powerful new tool to aid in the formulation of not only suspensions but also semi-solids (for example, topical delivery systems) and emulsions. Indeed, it can even be used to fingerprint micro-emulsions for which very few techniques currently exist, especially for normal, routine laboratory analysis.

The Acorn Area can be used to solve dispersion problems in virtually all industrial applications from agricultural formulations to the emerging field of nanomedicine. Energy, electronics, pharma and pigments are but four industries investing heavily in development of formulations based on nanoparticles.

### **SLIDE 3: Agenda**

In this video we will continue to discuss NMR measurements. Our agenda will briefly reprise what is NMR relaxation time and rate and then focus on the two different ways – referred to as the  $T_1$  and  $T_2$  methods - in which relaxation can be measured, looking at typical data and then discuss the similarities and differences between the methods

and what useful practical advantages accrue to each. We will look at two examples of wetted surface analysis - that for porous and non-porous materials - and conclude with where NMR surface analysis measurements with the Acorn Area fit within the pantheon of traditional instrumentation for particle characterization.

#### **SLIDE 4: NMR Relaxation - Time and Rate**

In Part 1, we defined two liquid domains, liquid on the surface of a particle and bulk liquid far away from the particle surface. The liquid molecules far away from the particle (light blue) are much more mobile and relax slowly, on the order of 2-3 seconds; the relaxation time,  $T$ , is long and so the rate,  $R$  (the reciprocal) is small. However, liquid molecules on the particle surface (darker blue) are restricted and relax quickly, on the order of only 0.5-2 milliseconds; this results in a much shorter relaxation time,  $T$ , and a larger rate,  $R$ .

The relaxation *decreases* as the particle concentration and/or the wetted surface area *increases*.

A suspension of particles in a liquid with a large wetted surface area (for example, a nanoparticulate pigment) will have a smaller relaxation time than a suspension with a small wetted surface area sample because there will be more liquid molecules fluid associated with the particle surface.

In general, the higher the solids loading, the greater is the measurement precision. And, since a vast number of industrially usefully suspensions are manufactured, or used as concentrates, NMR measurements can prove very useful since they can be made using undiluted suspensions.

For any suspension, experimentally we measure the *difference* between bulk and surface relaxation times and then determine an average relaxation rate as given by the equation shown in the Slide.

Relaxation rates in each fluid domain are additive, weighted by the quantity of fluid present in each domain. In practice, we observe a single relaxation time that is an average of the relaxation rates of the surface liquid,  $R_s$ , and bulk liquid,  $R_b$ , weighted by their respective volume fraction.

Thus,  $p_s$  and  $p_b$  are the fractions of fluid present on the surface and in the bulk liquid, respectively, while  $R_s$  and  $R_b$  represent the relaxation rate of the fluid in each domain, surface and bulk, respectively.

For those familiar with NMR, we can utilize either the  $T_1$  (spin-lattice) or the  $T_2$  (spin-echo) measurement of relaxation time to determine an average relaxation rate constant.

### **SLIDE 5: NMR $T_1$ or $T_2$ values**

Liquid molecules rapidly switch between the surface and bulk domains (called fast exchange) and this is faster than the timescale of a single NMR experiment. That is why, in a measurement, we observe a single relaxation time. And, the principle of surface particle analysis via relaxation NMR is based on the fact that the liquid in contact with the particle surface relaxes much more rapidly.

Although both  $T_1$  and  $T_2$  depend on the rotation and translation motions of molecules, the magnitude of the shift may differ significantly because of the different way in which the two processes are linked to molecular motion. Experimentally, we typically observe a greater change in  $T_2$  compared with  $T_1$  for the same incremental change in concentration and/or surface area.

In general, when reagents - acids/bases to change the solution pH, or electrolytes to increase the solution conductivity - are introduced into the liquid phase it will have little or no impact on either  $T_1$  or  $T_2$  bulk liquid relaxation time, unless the species are ferro- or para-magnetic ions.

The same is true for surfactants, polyelectrolytes and polymers unless their concentration is high enough that they create a separate phase.

However, in this latter situation, the molecules can adsorb at the particle surface and, in so doing, will displace any surface liquid molecules. This will result in a change in both the  $T_1$  and  $T_2$  relaxation time of a suspension. This change can be used to study adsorption/desorption phenomena at interfaces and is the subject of a future video.

Either  $T_1$  or  $T_2$  relaxation can be used and the XiGo Acorn Area™ device provides both measurements.  $T_2$  is determined using what is termed a CPMG pulse sequence while  $T_1$  is determined using either an inversion recovery or a progressive saturation pulse sequence.

### **SLIDE 6: Typical $T_2$ and $T_1$ data**

Here we show typical  $T_2$  and  $T_1$  data, obtained on the same sample using the XiGo AreaQuant software. Note, that the value for  $T_2 < T_1$ .

So, the question is “Which method to use?”

### **SLIDE 7: T<sub>1</sub> or T<sub>2</sub> relaxation?**

First, it is important to note that both methods provide relevant data. However, each approach has advantages and disadvantages and part of robust method development is to decide which relaxation time, T<sub>1</sub> or T<sub>2</sub>, is more appropriate for a given application.

One analogy here would be measuring the particle size of suspensions using static- or dynamic-light scattering; another analogy would be measuring zeta potential by electrophoretic- or phase analysis-light scattering. Or, measuring surface area by static gas adsorption (BET) or by the Knudsen gas flow technique.

Both T<sub>1</sub> and T<sub>2</sub> are influenced by the molecular environment at the particle-liquid interface. Solution viscosity changes, surface polymer layers and microstructure as well as impurities all impact relaxation but to a different degree for T<sub>1</sub> and T<sub>2</sub>.

For example, T<sub>2</sub> can be more sensitive than T<sub>1</sub> to the presence of elemental impurities, especially ferromagnetic (e.g., Fe) and paramagnetic species (e.g., Al, Co, Cu, Mn).

T<sub>2</sub> is also more sensitive to changes in available and/or accessible surface area. T<sub>2</sub> values can become very small at very high concentrations (making it difficult to distinguish between samples) and so is better for more “dilute” suspensions. An ideal concentration would be in the range from about 10% to about 30%.

The T<sub>2</sub> measurement is technically more difficult but is faster than T<sub>1</sub> and so is better for samples in which the solid particles are sedimenting over time, or in emulsions where the droplets are creaming.

T<sub>1</sub> measurements work across the widest concentration range and is ideal for highly concentrated systems – solids of 60% or more and high internal phase emulsions (HIPEs) where the internal phase can exceed 90%.

### **SLIDE 8: T<sub>1</sub> or T<sub>2</sub>: Surface Chemistry**

The magnitude of the NMR signal depends very much upon the specific material under test.

Here we compare two samples of monodisperse, colloidal silica dispersions. One is a pure silicon dioxide, the other is an aluminum-modified silica. Both dispersions had been extensively dialyzed against distilled/de-ionized water. The final concentrations were similar (at 42wt% and 36wt%, respectively) and the particle sizes were the same (18 nm according to manufacturer’s literature).

$T_1$  and  $T_2$  measurements were made as a function of dilution of the suspensions but the data was plotted as relaxation rate,  $R$ .

First, the linearity in the plots confirms that the assumption regarding *fast exchange* between the surface and bulk water molecules applies and, also, that there are no concentration dependent secondary phenomena that would systematically alter the relaxation data - for example, particle aggregation.

Second, it is obvious that the  $T_1$  and  $T_2$  relaxation times for the pure silica are very similar; the slope of  $R_2$  is only a little greater than that for  $R_1$ .

A completely different picture emerges with the aluminum-modified silica. The presence of the aluminum on the silica surface has a dramatic effect. The  $T_2$  values are significantly smaller than the  $T_1$  values such that  $R_2$  is much greater than  $R_1$ .

Silicas are used extensively in a wide variety of applications and it is recognized that they can contain Fe and Al as impurities. The example given here demonstrates that NMR can readily reveal the presence of such impurities.

Natural alumino-silicate materials, such as clays, are also widely used. They have very diverse crystal chemistry that is critically dependent on the clays prehistory and it is recognized that care must be taken when comparing data on clays from different sources. It is clear that NMR can be used to compare and contrast such materials.

This topic will be dealt with in much more detail in a future video.

### **SLIDE 9: Wetted Surface Analysis: Nonporous Materials**

A prime use of NMR relaxation is to directly determine the wetted surface area of suspensions under relevant industrial conditions and concentrations.

The most common method of particle surface area determination is BET nitrogen ( $N_2$ ) gas adsorption. This technique requires the material under test to be a dry powder. However, drying wet suspensions inevitably results in unintentional (and unwanted) aggregates and agglomerates. As a consequence, the subsequent surface area results will be skewed. Indeed, it has long been accepted that any procedure which requires a dry sample (such as BET or Knudsen flow of a gas at low pressure) may give a surface area value which, for all its accuracy, has little relation to the effective area in solution. Thus, it is important to recognize that a *wetted* surface area values from NMR relaxation measurements can be quite

different from that obtained by N<sub>2</sub>/BET gas adsorption data but is the more appropriate metric for suspensions.

The Acorn Area<sup>+</sup> measures suspensions directly and requires no sample pretreatment. It is inherently a much simpler measurement technique; and as little as 0.1 mL of sample is needed.

The majority of commercial products involve suspensions of particulates in some liquid at some point in their manufacture and, typically, they are concentrates, especially nanoparticulate materials.

In Part 1 we discussed in detail why you need to measure suspensions as they are prepared and without dilution because, otherwise, it is possible to obtain a value that is not representative of the concentrated suspension and so may not translate into a useful performance metric.

In contrast to measurement of particle size by dynamic light scattering or light diffraction, where the raw scattered/diffracted intensity data has to be deconvoluted by means of complex algorithms (sums of exponentials or Bessel functions), the relation between NMR relaxation and wetted surface area is surprisingly simple; conversion of relaxation time to surface area is a straightforward calculation. As in the BET gas adsorption method, monolayer coverage of fluid onto the particle surface is assumed. Importantly, no assumptions are made as to the particle size (distribution) or particle shape.

This will be discussed further in a future video.

The schematic on the left hand side is the relaxation obtained for a 25% aqueous dispersion of a commercial polystyrene latex of nominal particle size 100 nm. The relaxation time was determined to be 40.2 ms which translates to an average suspension surface area of 59.1 m<sup>2</sup>g<sup>-1</sup>. Since the latex particles are spherical we can calculate a surface area based on the nominal particle size (of 100 nm) and this computes to 57.1 m<sup>2</sup>g<sup>-1</sup>. Although the results are in good agreement, the lower latter measured value arises because the suspension is not truly monodisperse and likely contains some aggregates and agglomerates.

The Table on the left shows data for a series of batches of commercial Bayhydrol polyurethane latexes. These materials are low volatile organic compounds used for coatings applications from automotive to medical usage. According to supplied Technical Literature, the solids concentration is 40% and the samples were each

measured as received. It can be seen that two of the batches are clearly different. Batch #694 has a lower surface area (at 30 m<sup>2</sup>/g) while Batch #888 has a larger surface area (at 36 m<sup>2</sup>/g); they could be, potentially, out-of-specification.

### **SLIDE 10: Wetted Surface Analysis: Porous Materials**

For porous solids, the total NMR signal is now proportional to the signals from both the total (internal) pore volume, the (external) volume of liquid on the material surface and the (external) volume of bulk liquid. Hence, the measured NMR relaxation time can differ depending upon the prevalent pore size and shape as well as particle surface chemistry.

The schematic shows the different signals. A double exponential is fitted to the total T<sub>2</sub> relaxation decay that results in two separate relaxation times – a short T<sub>2</sub> inside the pore and a long T<sub>2</sub> outside the pore.

### **SLIDE 11: Porous Graphene**

Porous graphene materials, including graphene nanomesh, crumpled graphene and graphene foam, have attracted tremendous attention and research interest, owing to their exceptional porous structure (high surface area, and high pore volume) in combination with the inherent properties of graphene. However, achieving complete wetting of many porous materials can be challenging. NMR relaxation measurements characterize any fraction of a particle surface that is wet by a liquid and so can be used to optimize the choice of liquid(s).

Here, on the left-hand side, we show T<sub>2</sub> relaxation data for two samples of the same porous graphene dispersed in water (using 1wt% surfactant) and ethanol, respectively, at 5wt%. The overall measurement reproducibility was excellent (the variation in NMR relaxation measurements was less than 1%).

However, in both cases, a single exponential fit (red dots) to the raw experimental data (black line) is particularly poor at high magnetization. Fitting, instead, with a double exponential (green dots) gives a significantly better agreement with the experimental data. From this we can extract two sets of data shown in the upper Table on the right-hand side. The T<sub>2</sub> (short) value was used to estimate the total surface area for each suspension (shown in the right-hand side lower Table). The values are large owing to the porosity of the graphene materials.

Both components (short and long T) of the double exponential fit to the dispersion in water have much longer decay times than the ethanol sample. This suggests an altogether much more mobile surface water bound layer and a stronger interaction

between the graphene surface and ethanol. Clearly, then, NMR relaxation can be used to interrogate the nature and wetting of porous materials.

**SLIDE 11: How the Acorn Area fits in...**

NMR surface analysis measurements provide *complementary* data to traditional particle analysis and characterization devices and can provide information that cannot readily be obtained with other using industrially relevant suspensions.

**SLIDE 12: Thank You**

Thank you very much for joining me in this conclusion to Exploring Surfaces with the Acorn Area.

I hope you will join me for future presentations. Please access the XiGo website for timings.