



NMR as a tool to directly measure the surface area of particulate dispersions

David Fairhurst, PhD.

XiGo Nanotools, LLC., Morganville, NJ 07751 USA
and

Terence Cosgrove, DSc.

University of Bristol, Bristol, BS8 1TS, UK

**81st ACS Colloid and Surface
Science Symposium**
Univ. Delaware, June 26th 2007

Acknowledgements

Bristol

Michael Brozel

Stuart Prescott

Youssef Espidel

Natalie Hastrup

XiGo

Sean Race

Limitations of Current Surface Area Techniques

Need to determine surface area well established

→ Influences many aspects of product performance

Most widely employed technique is Gas Adsorption (BET)

- gravimetric and volumetric analysis: time consuming sample preparation

→ only useful for **dry powders**

Majority of manufactured products involve suspensions of particulates in some fluid

Gas adsorption not useful → significant overestimation of (dry) area compared with that for well dispersed (wet) suspension
→ significant underestimation of (dry) area after drying and aggregation of (wet) suspension

Wet techniques include:

Titration: non routine, requires specific adsorbates, time consuming

Estimation from particle size analysis: only useful for spherical particles

Surface Area Measurement by NMR

NMR solvent relaxation times are sensitive to the available surface area of suspensions of particles

→ Molecule adsorbed at an interface has a much shorter relaxation time compared with one in the bulk fluid: difference can be orders of magnitude

Spin relaxation rate constant, R_n is the reciprocal of spin relaxation time, T_n

$$R_{n(av)} = \rho_s R_{ns} + \rho_b R_{nb}$$

Where:

$R_{n(av)}$ is the average rate constant

$n=1$ for spin-lattice relaxation and $n=2$ for spin-spin relaxation

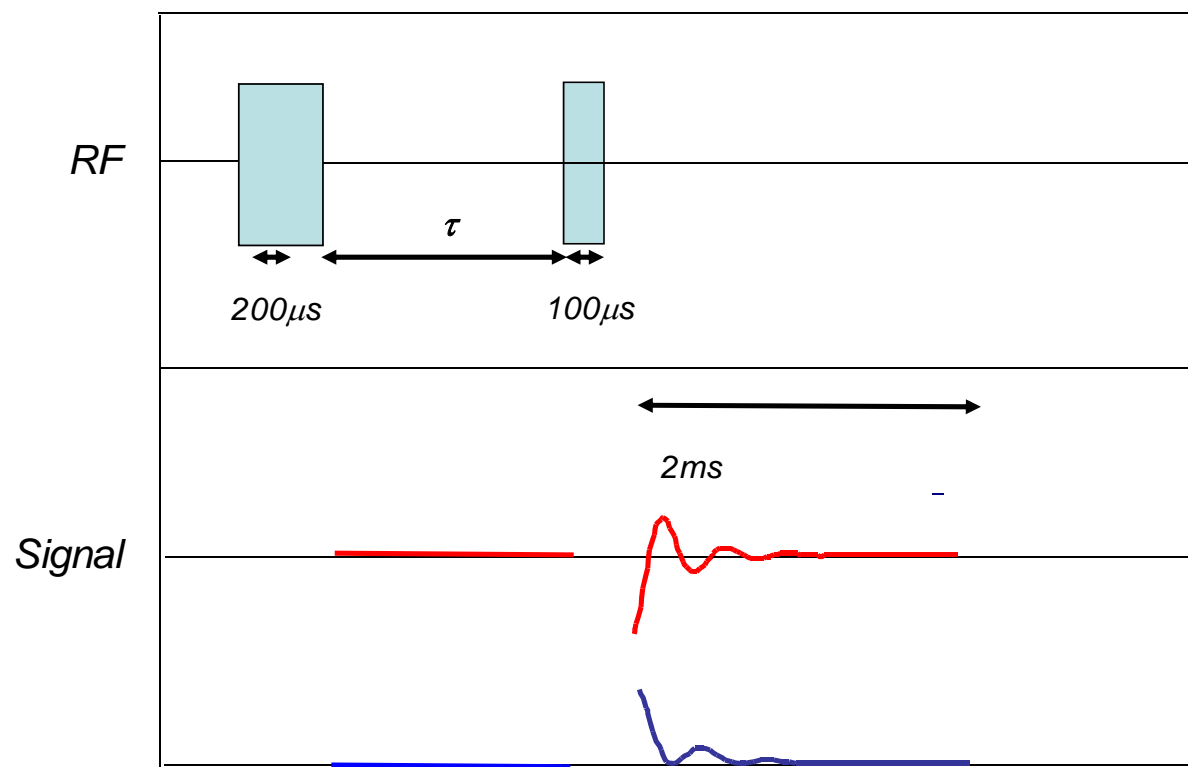
ρ_b is the fraction of solvent in the bulk phase

ρ_s is the fraction of solvent at the surface

Technique offers many advantages compared to traditional methods

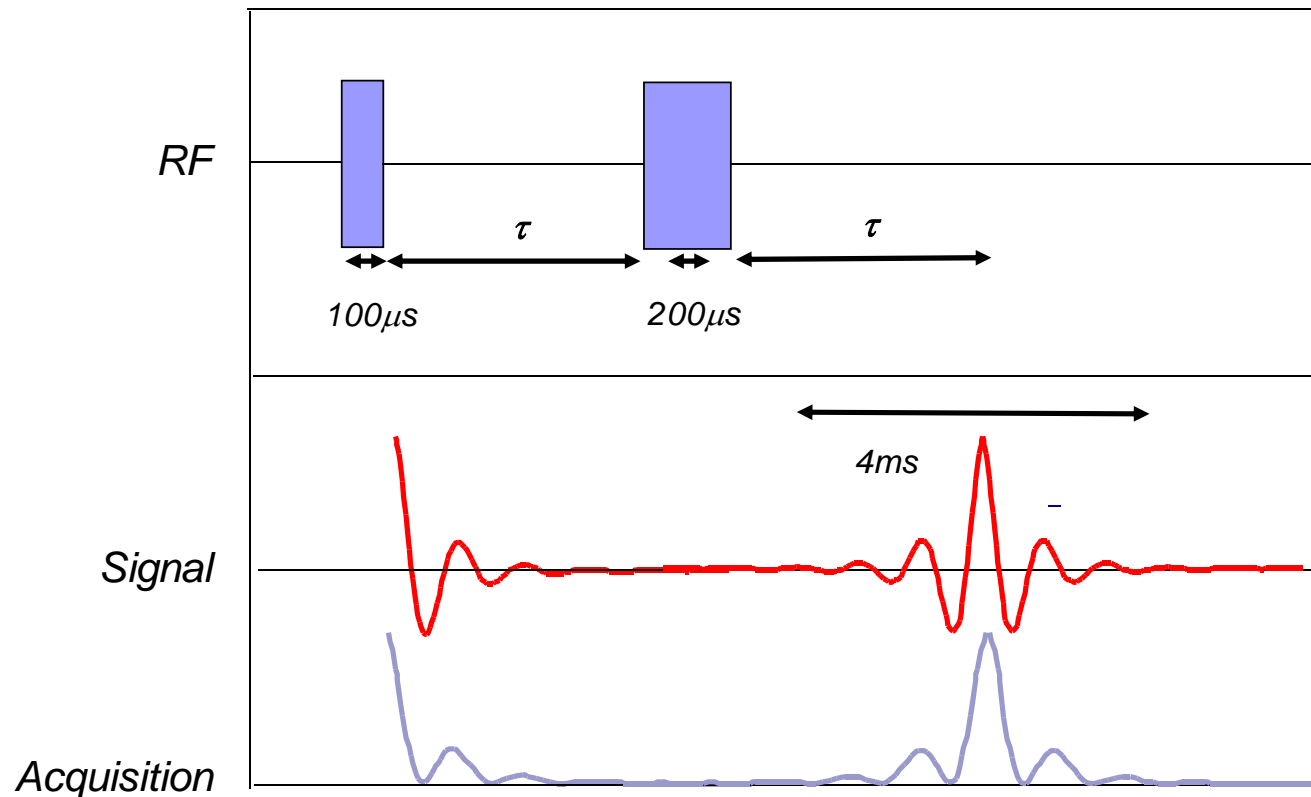
NMR Relaxation: T_1

T_1 can be measured by various pulse sequences, but the inversion recovery is the most straightforward. The disadvantage is that the experiment has to be repeated for several values of tau.

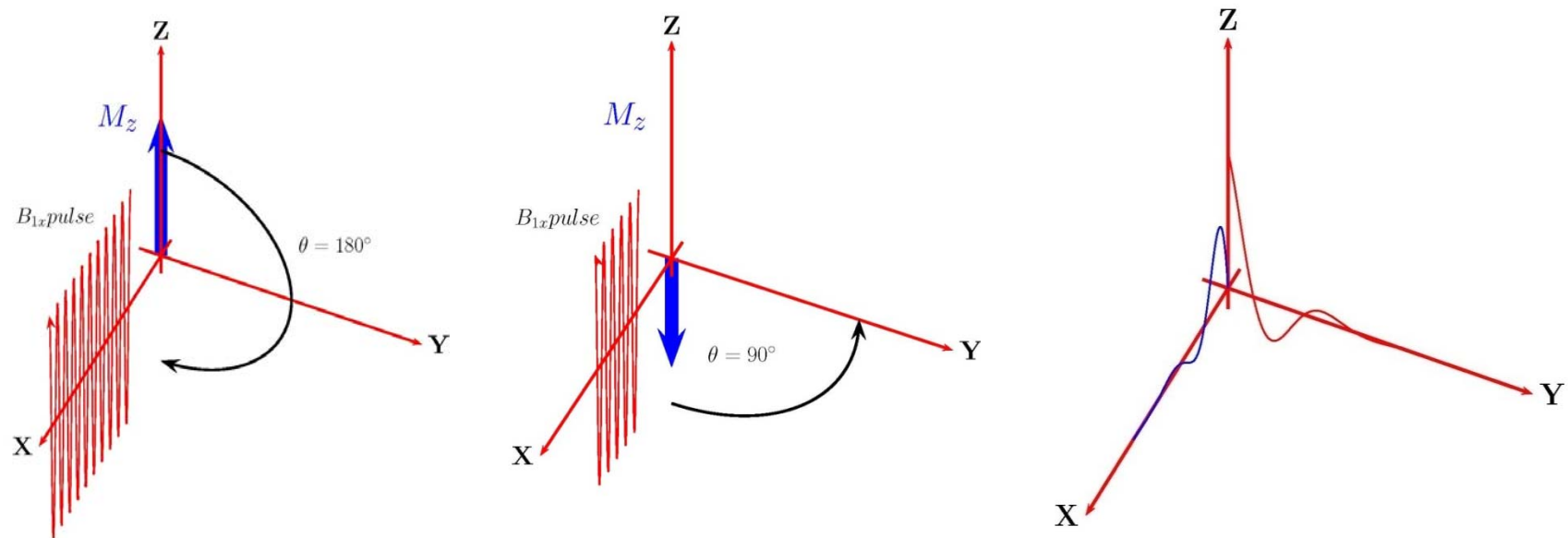


NMR Relaxation: T_2

T_2 is measured by the spin-echo method but there can be problems with field inhomogeneity and diffusion. The CPMG method overcomes these problems and data is obtained in a single scan (repeat second pulse n times at 2τ).



NMR Relaxation



In the T_1 experiment a 180° pulse (B_{1x}) first rotates the magnetization through 180° about the y axis.

After a time, t , the signal relaxes and the signal is sampled by a -90° degree pulse along the x axis and the resultant signal is measured along x and y.

Determination of Surface Area: Basic Equation

$$R_{av} = \psi_p \mathbf{S} L \rho_p (R_s - R_b) + R_b$$

Where:

R_{av} is the average spin relaxation rate constant

ψ_p is the particle volume to liquid volume ratio

S is the surface area per unit weight

L is the surface layer thickness of fluid (solvent)

ρ_p is the bulk particle density

R_s is relaxation rate constant for the bound solvent

R_b is the relaxation rate for the free or bulk solvent

All parameters are known or can be independently measured or calculated

If a suitable reference sample is available we can define a constant:

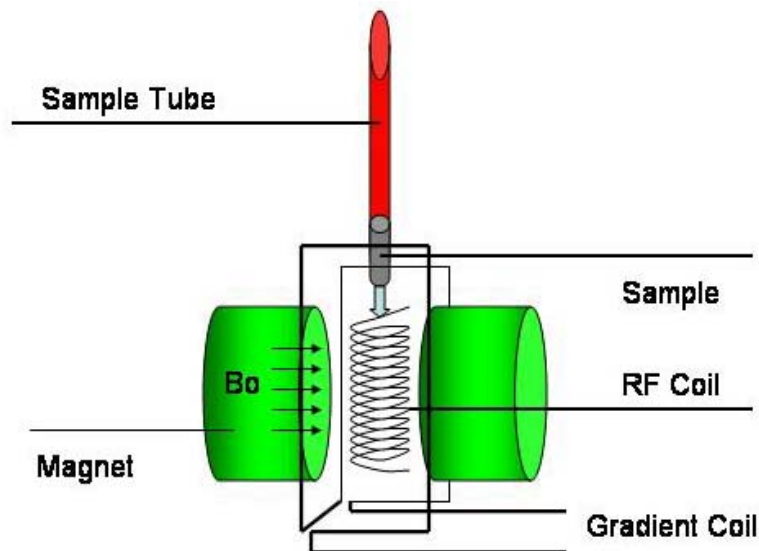
$$k_A = L \rho_p (R_s - R_b)$$

Then,

$$R_{av} = k_A \mathbf{S} \psi_p + R_b$$

After determination of k_A with a known sample, R_{av} can be used to find the surface area of an unknown sample of the same material

The Basic NMR Technique



Sample placed in glass tube

→ inserted into cassette located between two magnets

Sample experiences static, uniform magnetic field

→ net magnetic moment of fluid aligned

RF pulse applied

→ temporary shift in magnetic orientation of sample

RF pulse removed

→ magnetic dipoles of fluid realign

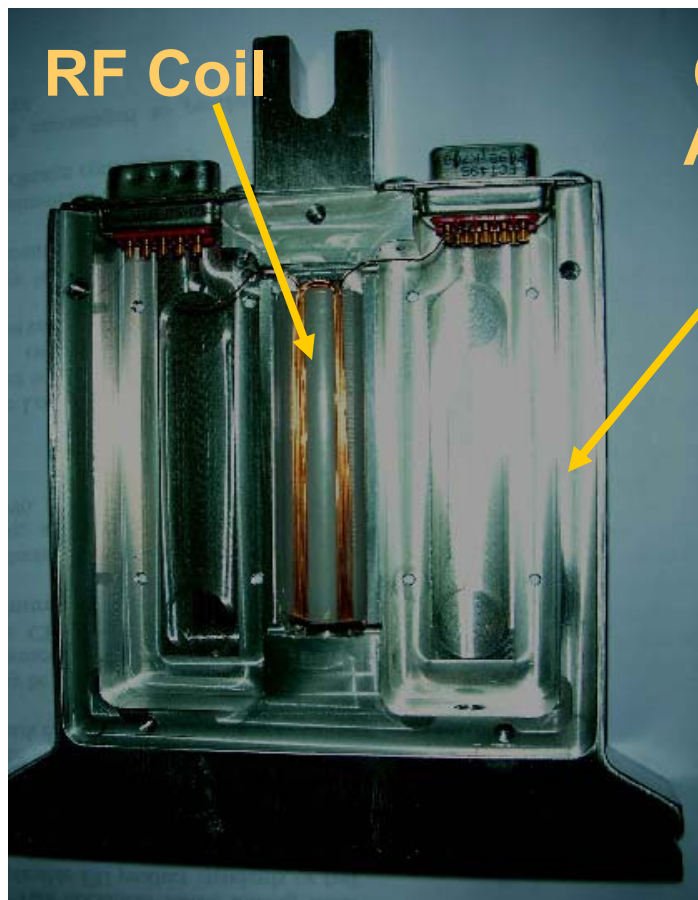
Decaying voltage induced in RF coil

→ free induction decay measured

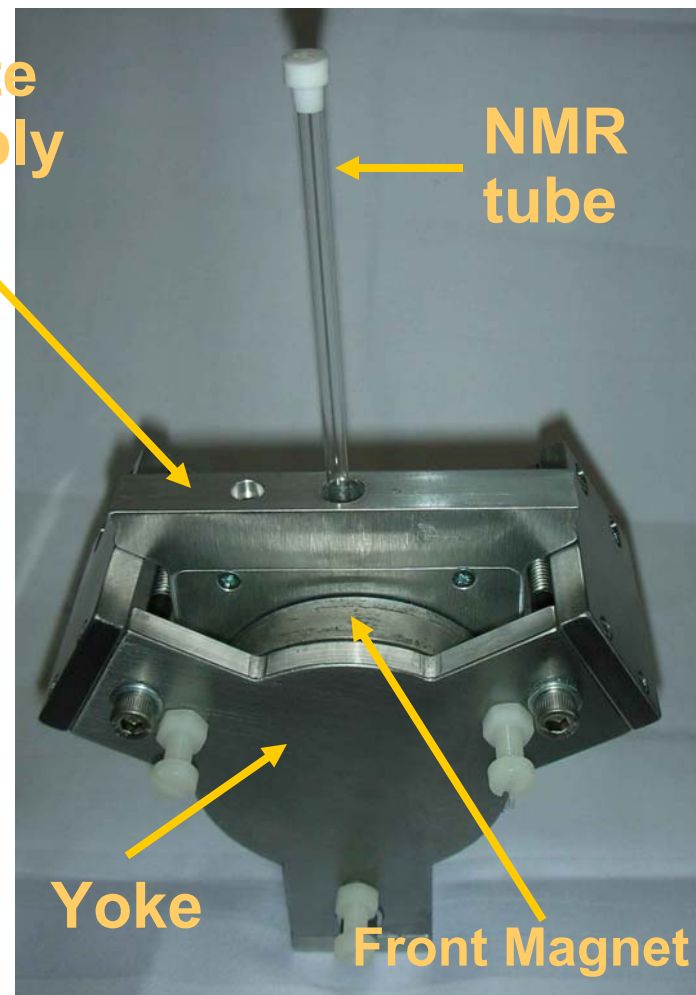
→ surface area calculated

Total time for measurement < 5min

The NMR Instrument: Yoke, Magnets and Cassette



Cassette Assembly
showing RF Coil



Yoke

Front Magnet

Validation of the NMR Technique

Comparison of measured surface area of sample of Klebosol™ - monodisperse, colloidal spherical silica suspension(30wt%)

By Titration
(Manufacturer)

120m²/gm

Estimated from
Particle Size (DLS)

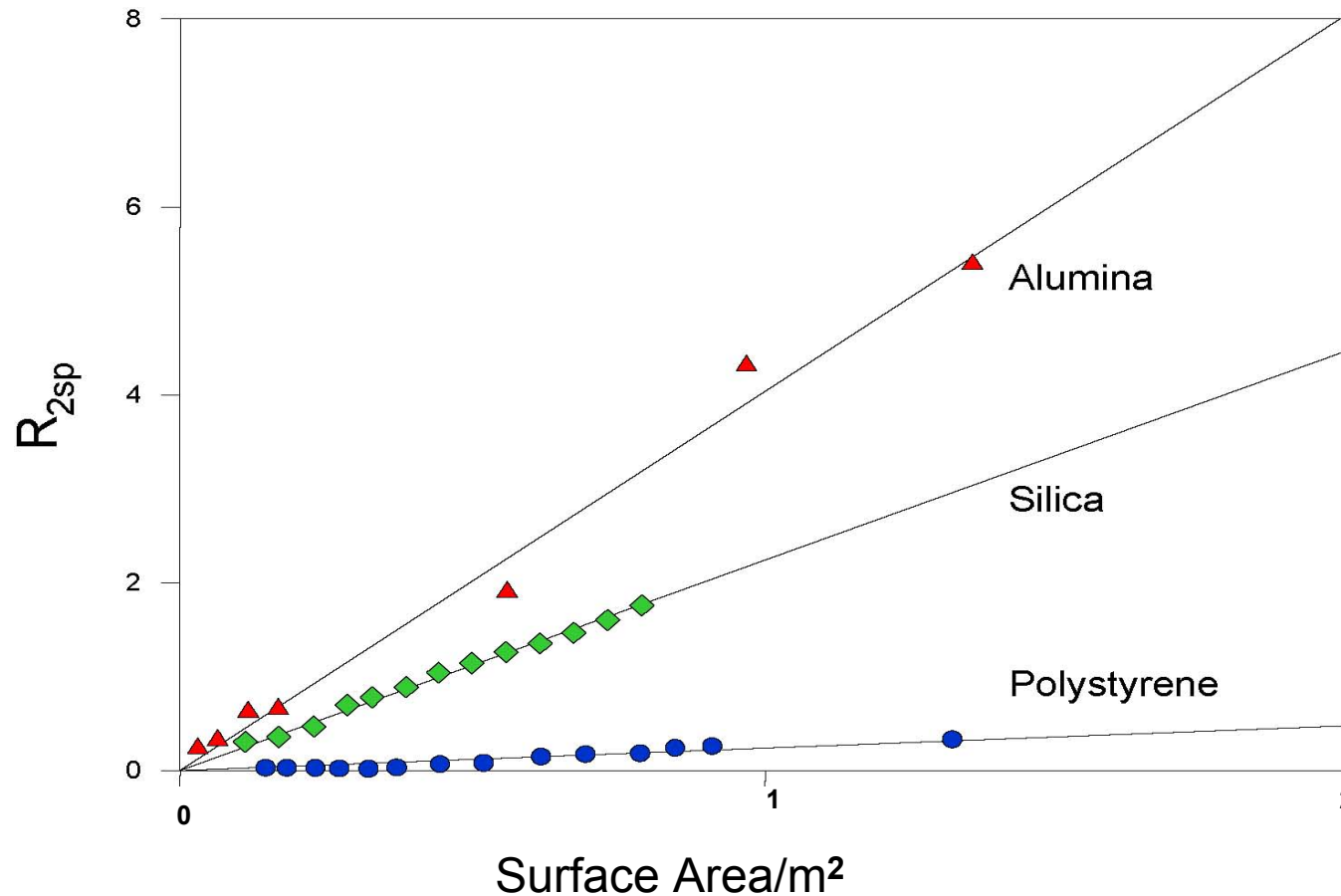
123m²/gm

Directly by
Acorn™

121m²/gm

Excellent Agreement between the three techniques

Measurement of the Surface Area of Colloidal Dispersions



Degree of Particle Hydrophobicity: Polystyrene > Silica > Alumina

The NMR Instrument:

acorn area

Data Analysis

Proprietary software: AreaQuant™

- automatically determines all measurement parameters
- FID function analyzed
- determines relative portion of bound and free liquid and corresponding surface area
- no assumptions needed regarding particle size or shape
- automatically determines volume fraction of solids in the dispersion

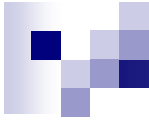
Operational Modes

Standard (QC)

- Single- and multi-point surface area, volume fraction, and time dependency

Advanced (R&D)

- stand-alone, low resolution NMR instrument and teaching aid



acorn area

Software Interface Standard (QC) Mode

Software Interface Advanced (R&D) Mode

The screenshot shows the 'Xigo Nanotools Area' window in Standard (QC) Mode. The interface is divided into several sections:

- Scan controls:** Includes input fields for 'Number of dummy scans before experiment' (1), 'Number of scans per experiment' (2), 'Number of experiments' (10), 'Repeat time' (1000 ms), and 'Number of data points per scan' (5000).
- Sample details:** Includes 'Experiment date' (2007-02-07 10:16:25), 'Sample name' (Calibration solution), 'User name' (NMRBABY\baby), 'Number of dilutions' (4), and a 'Reference material' dropdown menu.
- Progress:** A central panel showing 'Signal' (161.8), 'Scans remaining' (2), 'Experiments remaining' (8), 'Sample number' (0), 'Sample dilution' (0), and 'Estimated completion' (10:16). A large green 'Start' button is visible.
- Experimental Results:** A line graph showing 'Re²' on the y-axis (0 to 6) versus an unlabeled x-axis (0 to 40). The graph shows a linear increase from approximately (5, 1) to (30, 5.5).
- Footer:** Shows 'default_instrument.nminstr; default_experiment.nmrexp1' and 'Instrument ready'.

The screenshot shows the 'Xigo Nanotools Area' window in Advanced (R&D) Mode. The interface is more complex, featuring:

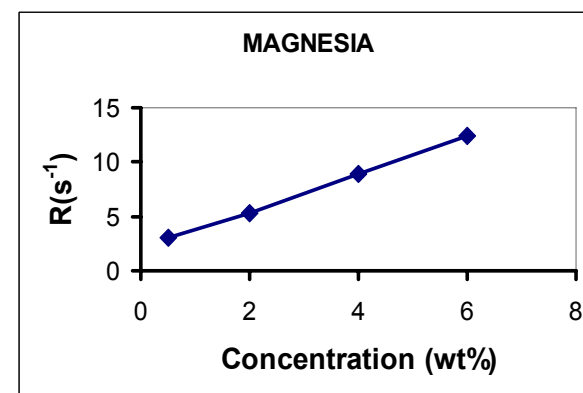
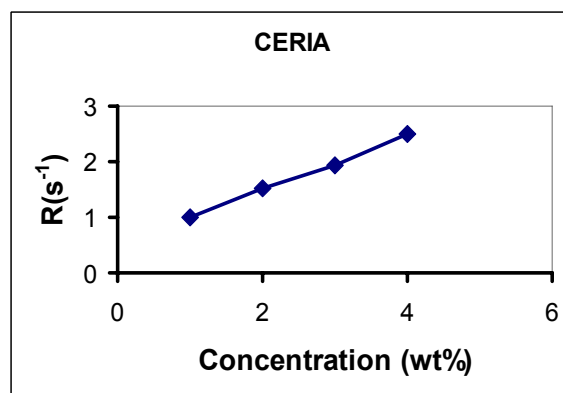
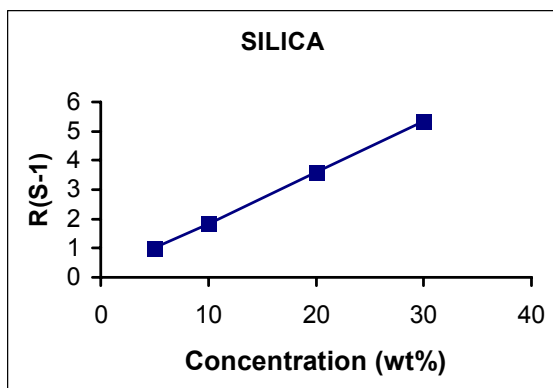
- Parameters:** A list of adjustable parameters on the left, including 'Resonant frequency' (2010211 Hz), 'RF gain' (34 dB), 'IF gain' (25 dB), 'TX gain' (0.7 dB), 'RF loop offset' (0 Hz), 'TX loop offset' (-10000 Hz), 'TX phase' (90.0°), '90° pulse duration' (1.03 µs), and '180° pulse duration' (3.00 µs).
- Live data:** A large plot area on the right showing 'Raw Data' with a red 'Stop' button. The plot displays two traces: 'Real component' (red) and 'Imaginary component' (blue), showing a decaying oscillation over time.
- Footer:** Shows 'baby\20070115\resonant; default_experiment.nmrexp1' and 'Instrument running. Completed scan (5/7), experiment (55/200). Sleeping (0.7s)'.

Measurement of Surface Area of various Oxide Suspensions

An industrial filler and thickener

A CMP agent

An OTC antacid and laxative material



Measured Surface Area* (m²g⁻¹)

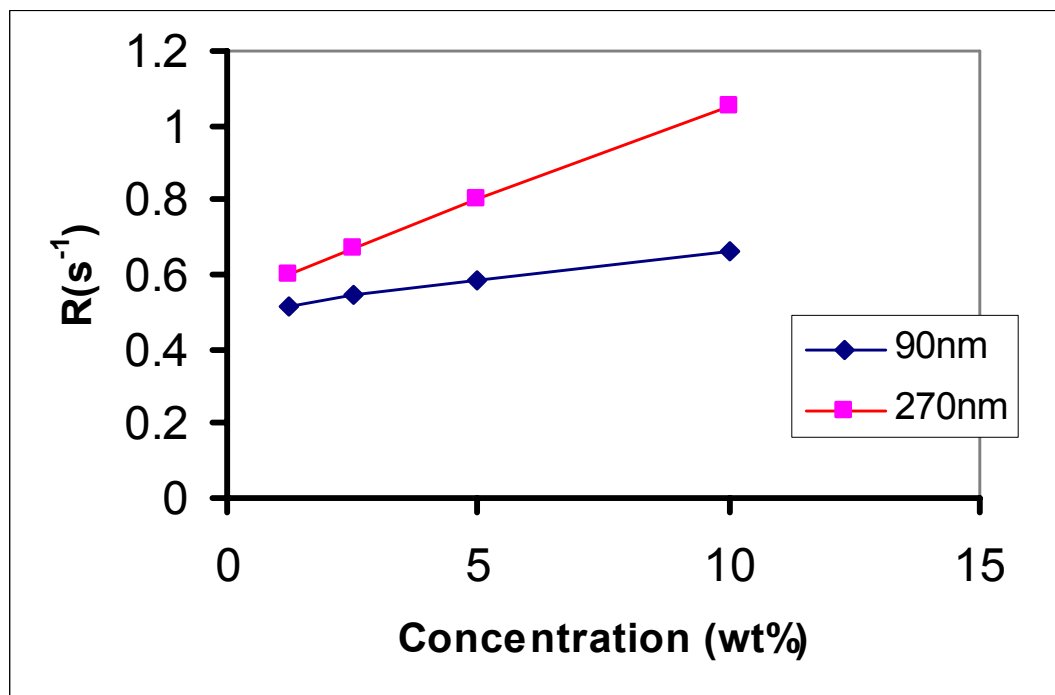
SiO₂
98

CeO₂
1340

MgO
2177

* Multi-point measurement

Comparison of two samples of commercial Titanium Dioxide

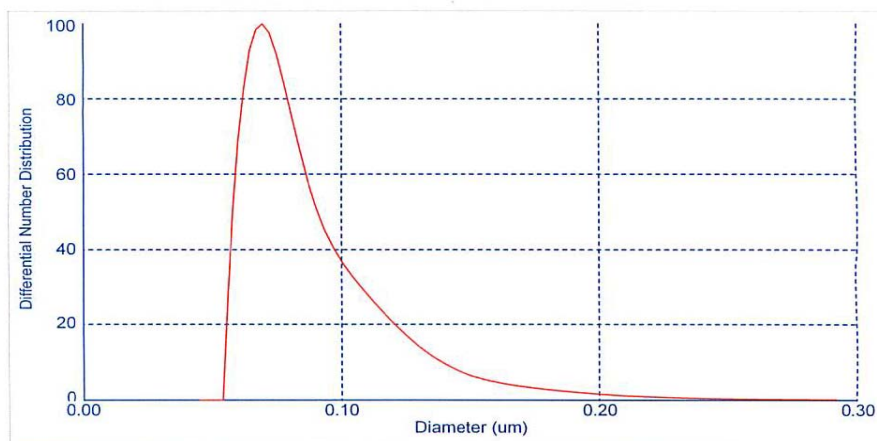


Nominal 90nm* TiO₂ sample:
Microfine grade used in cosmetics and personal care as a “transparent” UV absorber (sunscreen agent)

Nominal 270nm* TiO₂ sample:
Industrial grade material used in paints and plastics as an opacifier and whitening agent

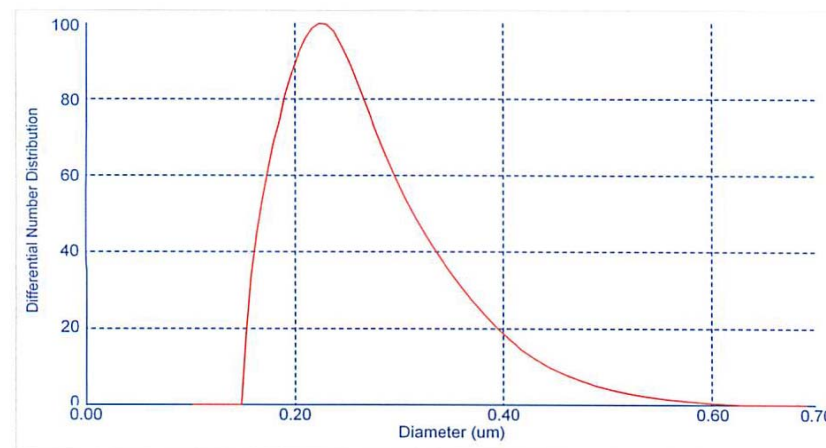
* Average (D_n) size of 2vol% suspension in 0.1% TSPP (aq) measured using X-ray Disc Centrifugation

PSD (D_n) of Two TiO_2 Dispersions



Microfine Grade

Mean **91nm**
Mode **70nm**
Median **82nm**



Industrial Grade

271nm
223nm
254nm

Surface Area of two samples of commercial Titanium Dioxide

Nominal 90nm TiO₂

Nominal 270nm TiO₂

Estimation
Based on
XDC size*

20m²g⁻¹

5m²g⁻¹

Measured
using N₂ (BET)
gas adsorption**

38m²g⁻¹

11m²g⁻¹

Measured
directly with
Acorn Area*

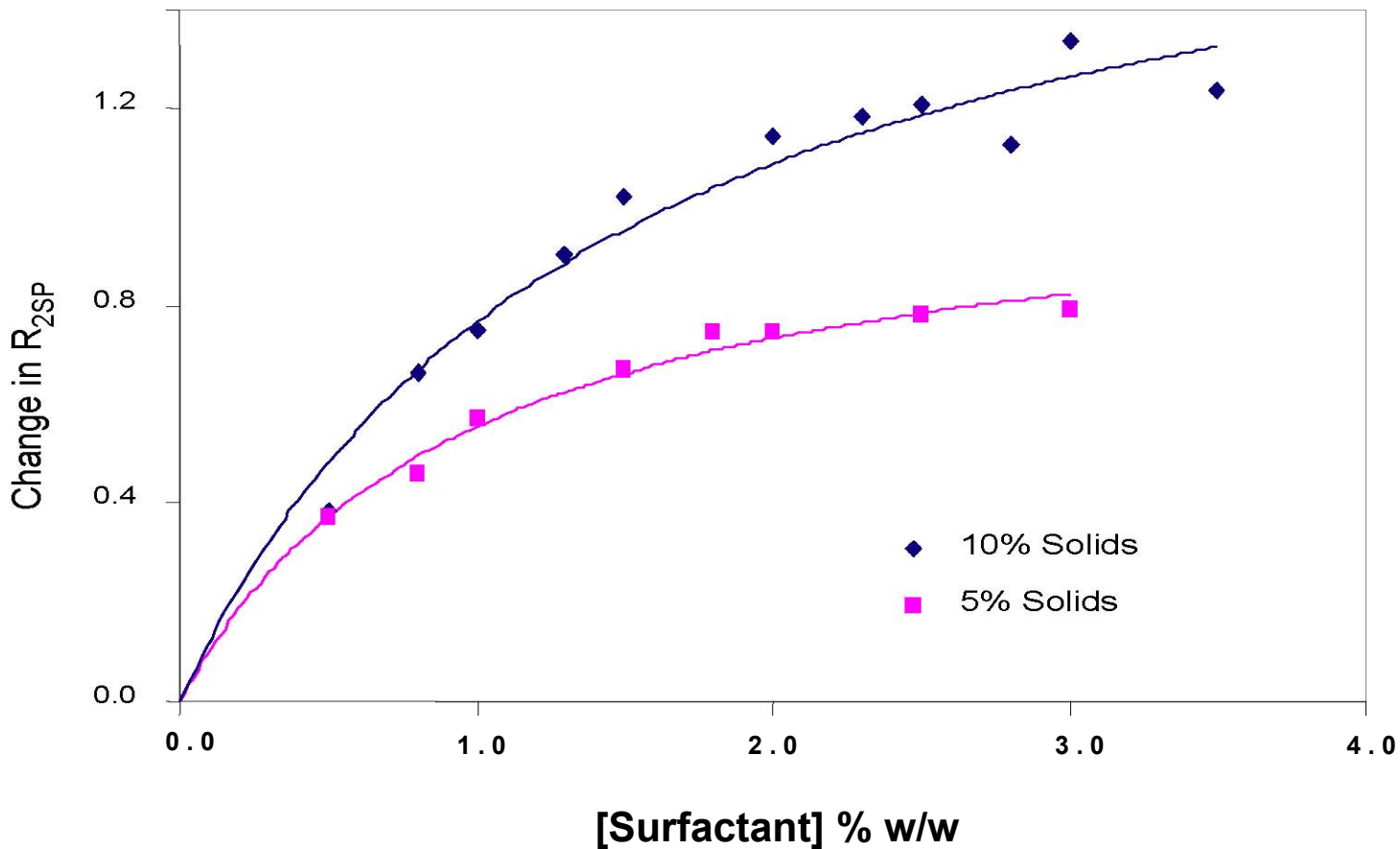
170m²g⁻¹

50m²g⁻¹

NMR surface area is independent of any PS or shape

* 2vol% aqueous suspension ** Dry powder before dispersion

In-situ Measurement of the Adsorption of a Surfactant onto Silica



acorn area



- Measures without dilution:
Surface Area and Volume Fraction
- Any particle in any fluid
- Any particle size or shape
- No sample preparation
- No clean-up
- Small footprint
- Portable
- Robust
- No moving parts
- Simple to use
- Results in less than 5 min.