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 Haustrup

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

$$R_{n(av)} = p_s R_{ns} + p_b R_{nb}$$

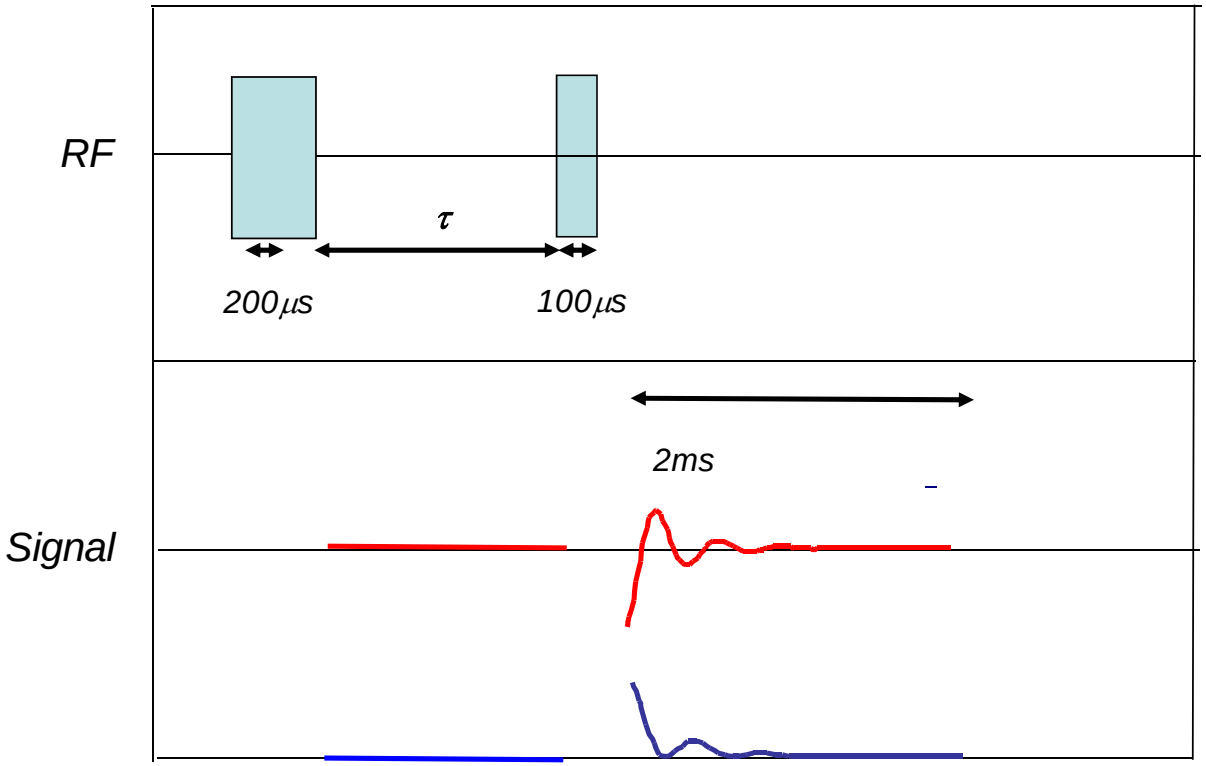
Where:

$R_{n(av)}$ is the average rate constant
n=1 for spin-lattice relaxation and n=2 for spin-spin relaxation
p_b is the fraction of solvent in the bulk phase
p_s is the fraction of solvent at the surface

Technique offers many advantages compared to traditional methods

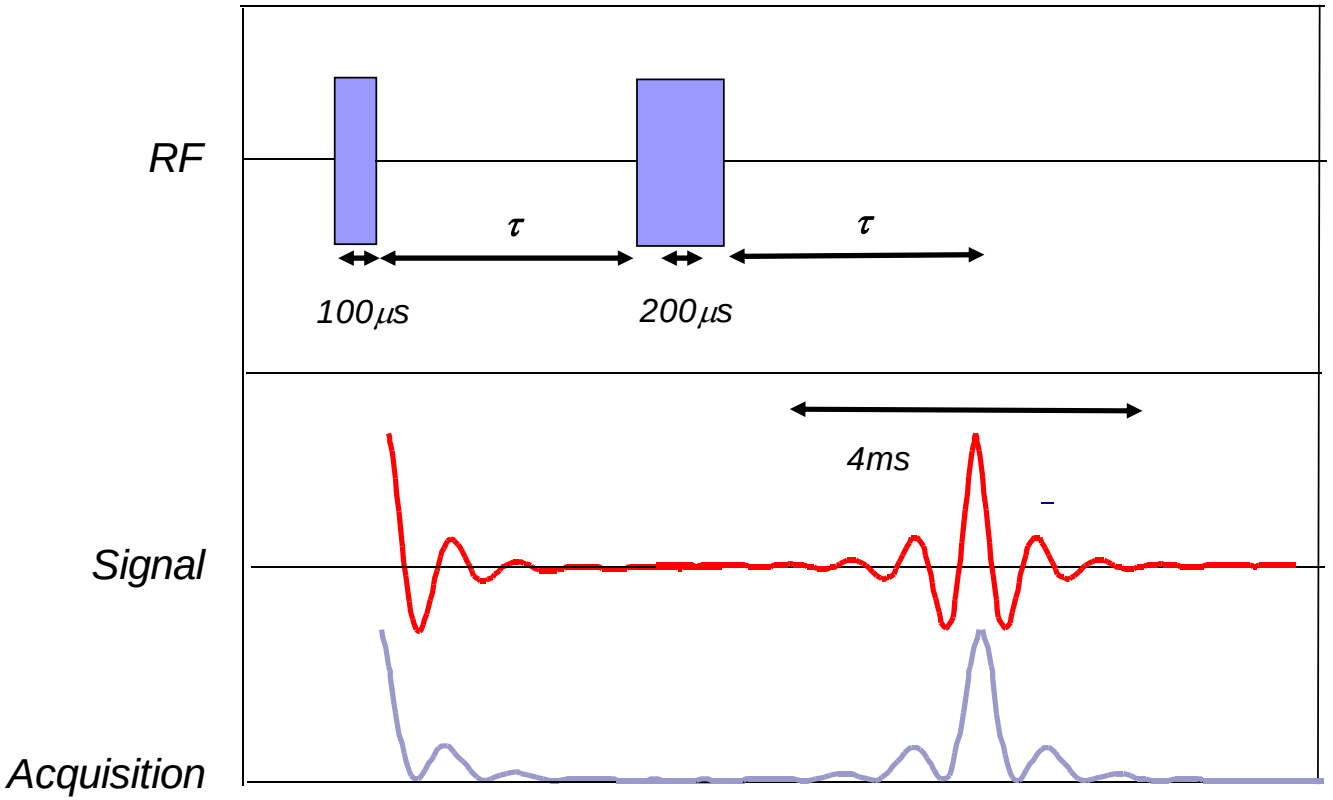
NMR Relaxation: T_1

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.

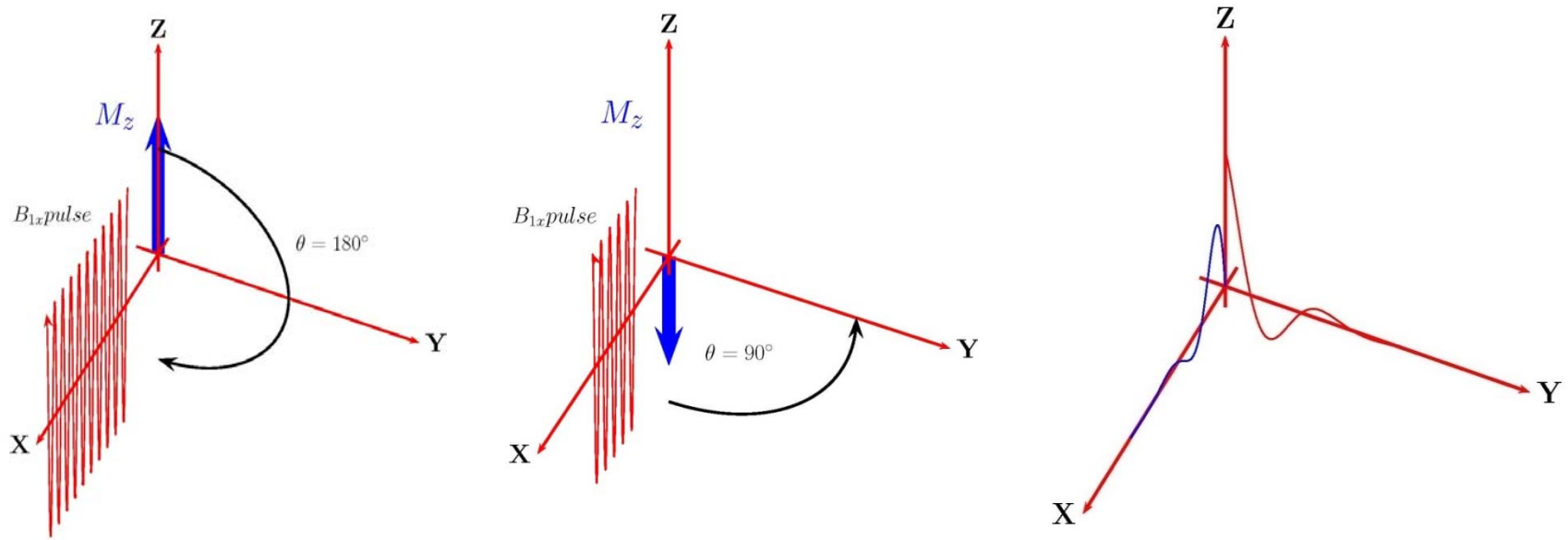


NMR Relaxation: T_2

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 singe scan (repeat second pulse n times at 2tau).



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:

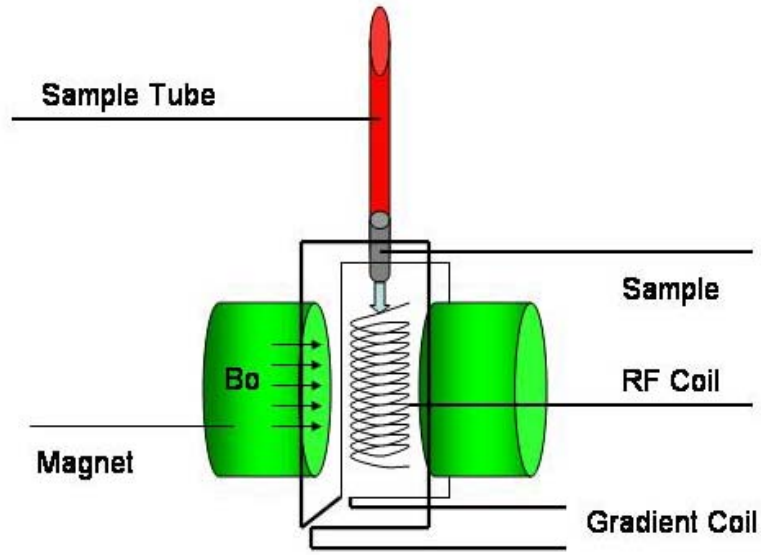
$$k_A = L \, \rho_p \, (R_s - R_b)$$

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

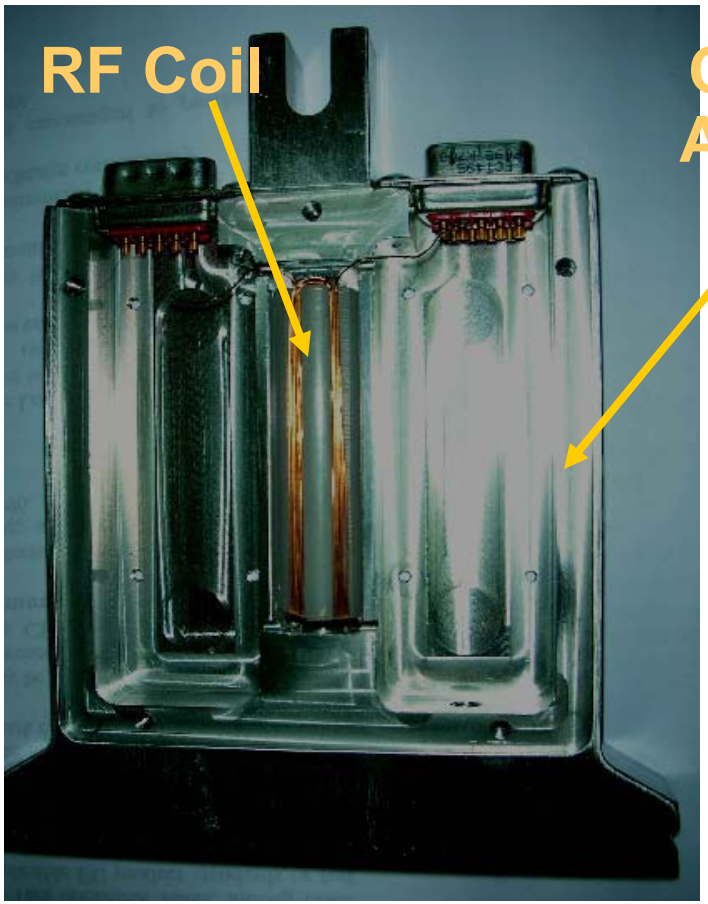
The Basic NMR Technique



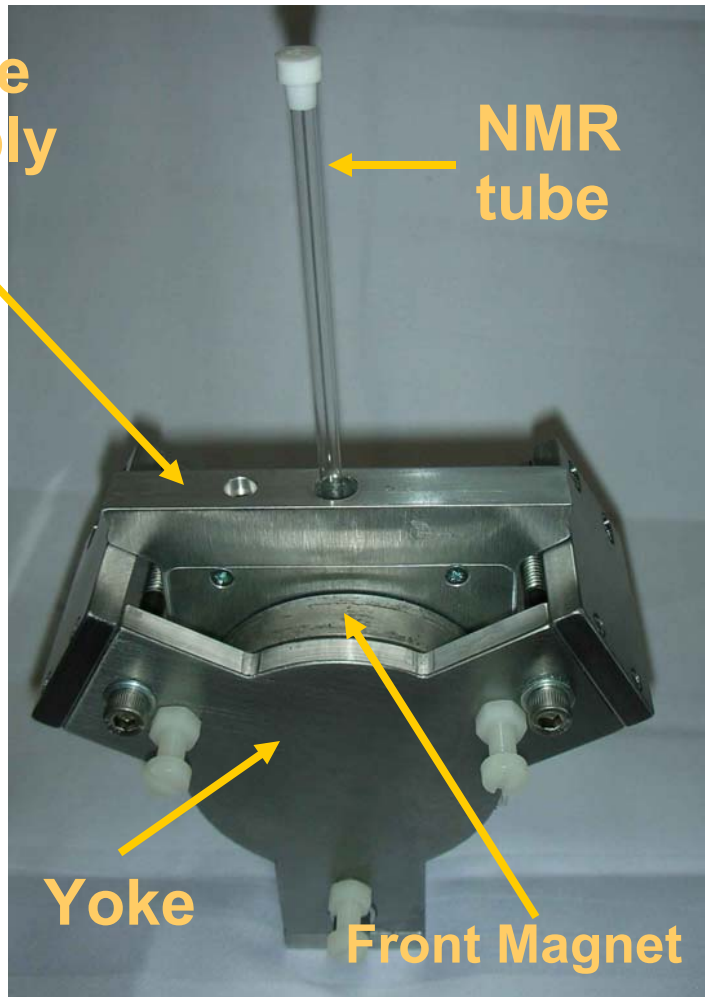
Sample placed in glass tube
→ inserted into cassette located between two magnets
Sample experiences static, uniform magnetic field
→ net magnetic moment of fluid aligned
RF pulse applied
→ temporary shift in magnetic orientation of sample
RF pulse removed
→ magnetic dipoles of fluid realign
Decaying 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



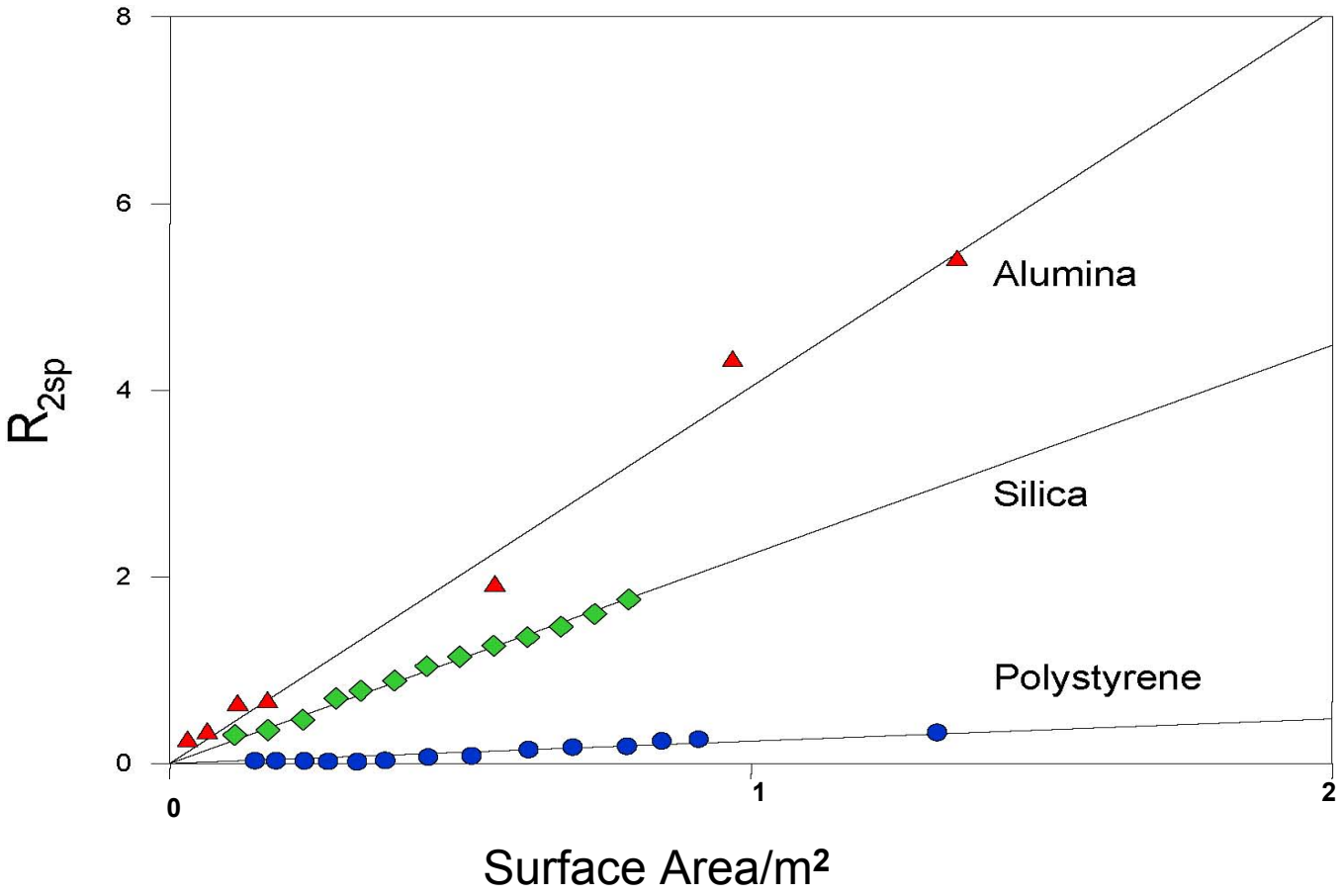
Validation of the NMR Technique

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

By Titration (Manufacturer)	Estimated from Particle Size (DLS)	Directly by Acorn™
120m^2/gm	123m^2/gm	121m^2/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)

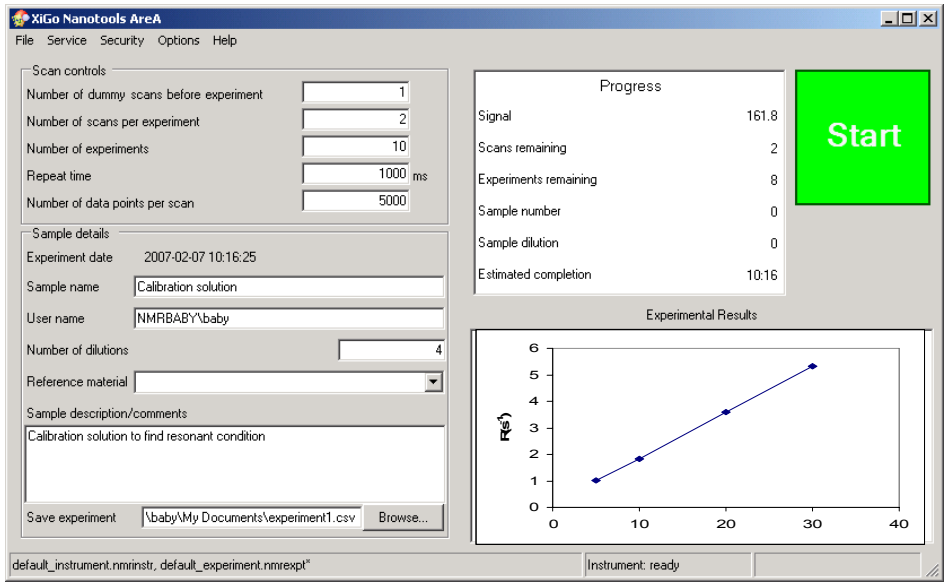
→ Single- and multi-point surface area, volume fraction, and time dependency

Advanced (R&D)

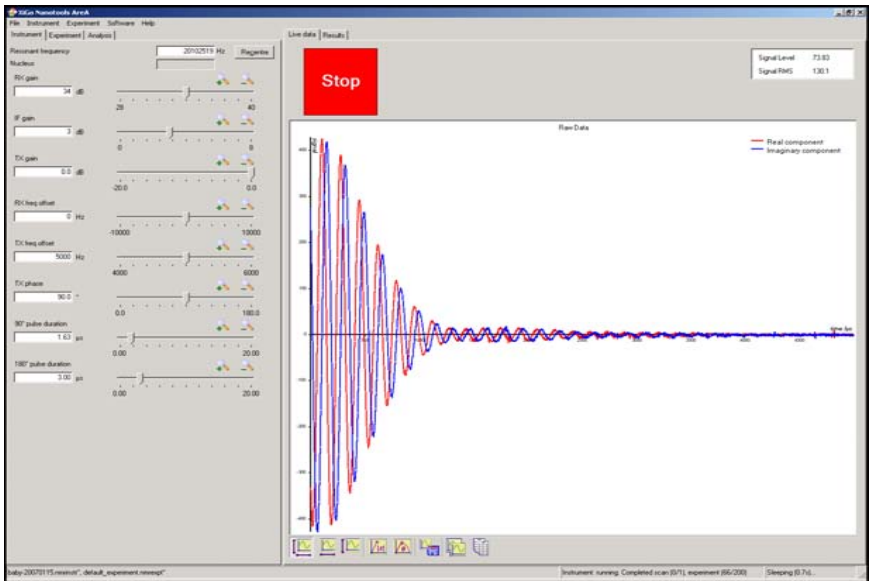
→ stand-alone, low resolution NMR instrument and teaching aid

acorn area

Software Interface
Standard (QC) Mode

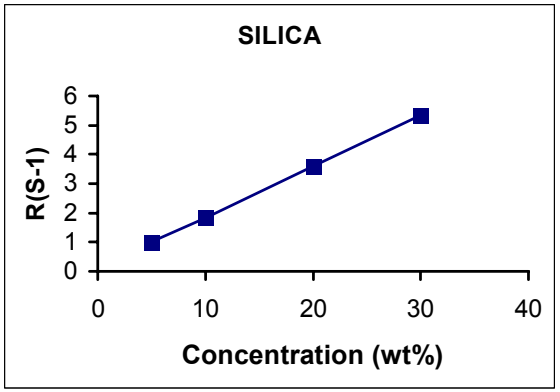


Software Interface
Advanced (R&D) Mode

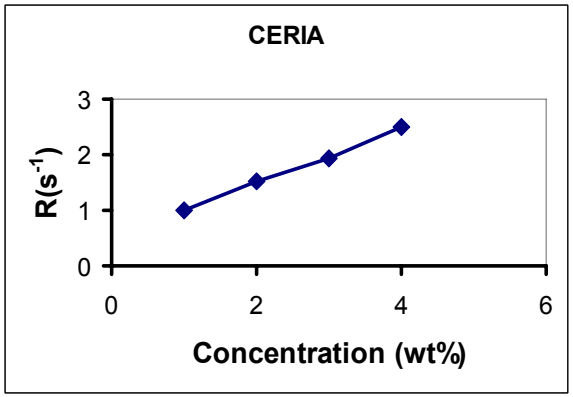


Measurement of Surface Area of various Oxide Suspensions

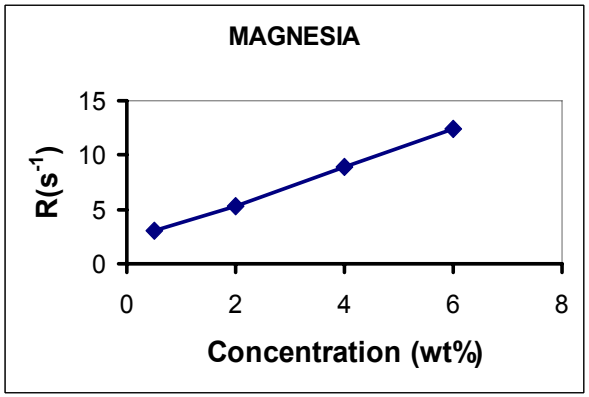
An industrial filler and thickener



A CMP agent



An OTC antacid and laxative material

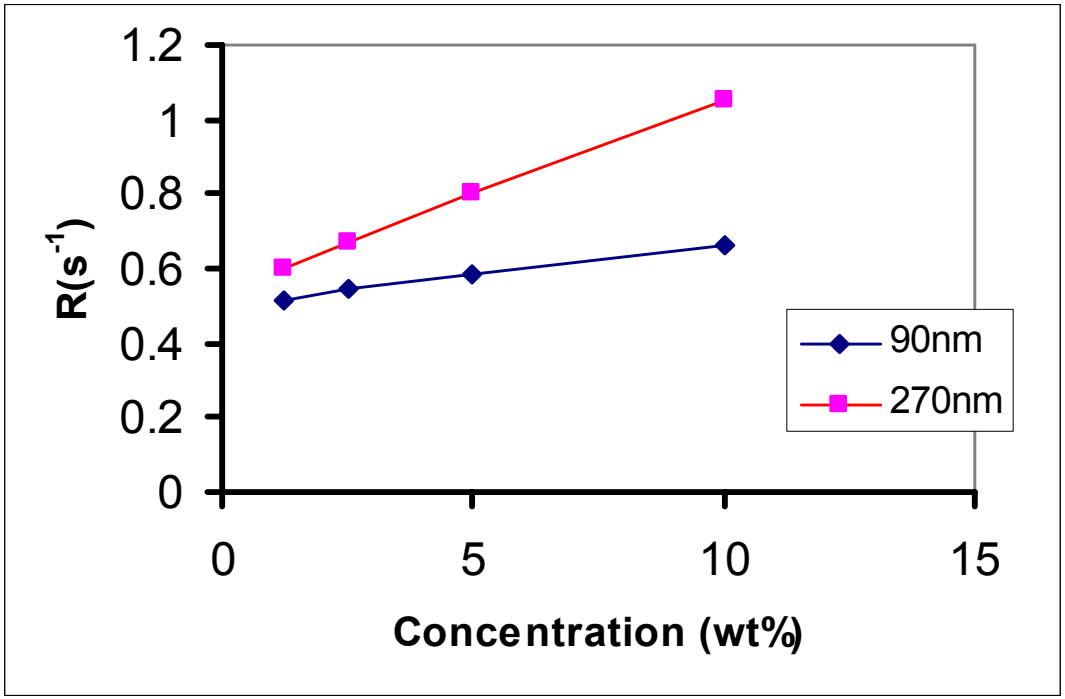


Measured Surface Area* (m^2g^{-1})

SiO_2	CeO_2	MgO
98	1340	2177

* Multi-point measurement

Comparison of two samples of commercial Titanium Dioxide

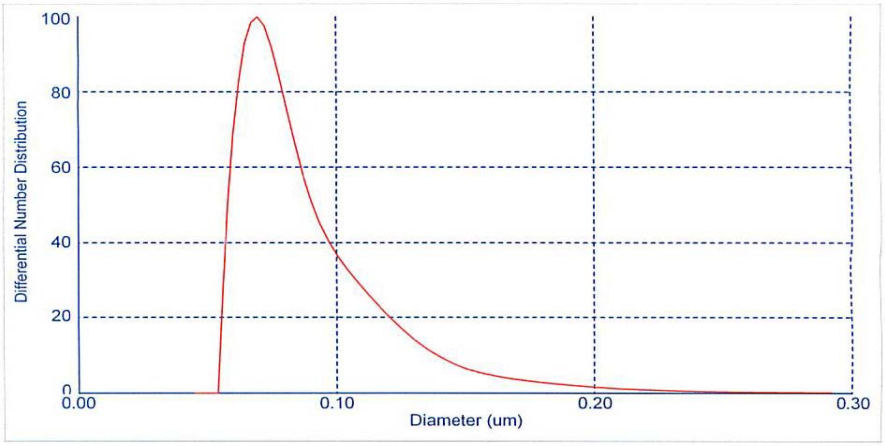


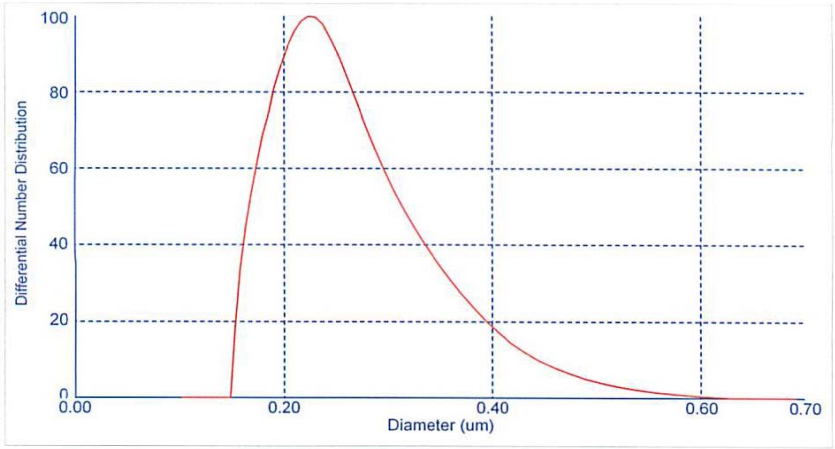
Nominal 90nm* TiO_2 sample: Microfine grade used in cosmetics and personal care as a "transparent" UV absorber (sunscreen agent)

Nominal 270nm* TiO_2 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	Industrial Grade
Mean	91nm	271nm
Mode	70nm	223nm
Median	82nm	254nm

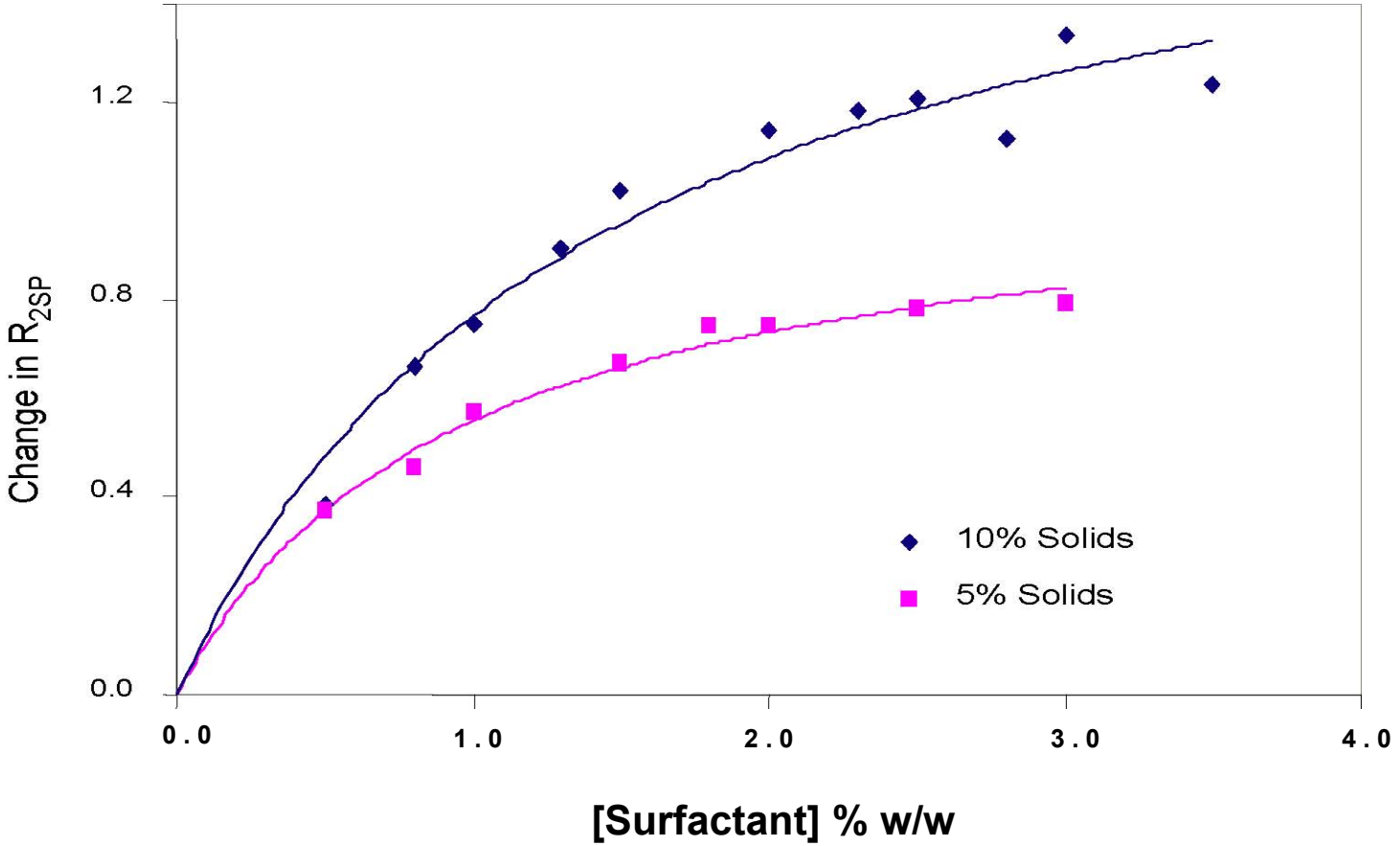
Surface Area of two samples of commercial Titanium Dioxide

	Nominal 90nm TiO_2	Nominal 270nm TiO_2
Estimation Based on XDC size*	20 m^2g^{-1}	5 m^2g^{-1}
Measured using N_2 (BET) gas adsorption**	38 m^2g^{-1}	11 m^2g^{-1}
Measured directly with Acorn Area*	170 m^2g^{-1}	50 m^2g^{-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.