

# Preliminary experiments on apparatus for *in situ* studies of microwave-driven reactions by small angle neutron scattering

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(Received 31 January 2000; accepted for publication 16 October 2000)

In this article we describe apparatus for the study of the microwave-driven growth of particles in solution by *in situ* small angle neutron scattering (SANS). This apparatus has enabled the first preliminary experiments using microwave-activated *in situ* diffraction. We take iron oxide as the prototype system, but the technique may be extended to a wide variety of chemical reactions that deposit solids from solution. The key features of the apparatus are a microwave cavity with a modular construction that may be adapted to the geometric constraints of the diffractometer, and a computer-controlled microwave generator that may be set to maintain either constant pressure or temperature in the reaction vessel. In this particular piece of equipment the reaction vessel is adapted so that part of the sample fills a cell of identical construction to those commonly used in SANS measurements for optimal transmission of the neutron beam. © 2001 American Institute of Physics. [DOI: 10.1063/1.1332112]

## I. INTRODUCTION

Over the past decade, microwaves have been increasingly employed by chemists to enhance the selectivity or speed of chemical reactions.<sup>1</sup> In the majority of cases many of the claimed “microwave-specific” effects have been rationalized by allowing for solvent superheating effects.<sup>2</sup> In a number of cases, however, the use of microwaves has led to new and unexpected products, or to reaction enhancements which cannot be attributed to superheating.<sup>3</sup> Indeed, their use has occasionally resulted in the formation of unexpected products which cannot be synthesized by analogous conventional routes.<sup>4</sup> Whatever the underlying cause of the reaction enhancements in particular cases, microwave-induced reactions often offer significant benefits over classical methods, and are being increasingly employed as a routine method by chemists. However, despite widespread activity in this field, there has been remarkably little work to determine whether the path taken by a microwave-driven reaction differs from that followed during conventional heating. In this article we describe apparatus that has been designed to monitor the progress of a microwave-driven reaction in terms of colloidal particle formation, using small angle neutron scattering (SANS) as the probe. In future articles we will describe apparatus for complementary wide-angle x-ray scattering studies of microwave-induced reactions.

Neutron diffraction is now a well-established technique for studying the structure of materials<sup>5</sup>, offering several advantages over x-ray methods. In this work we exploit the fact that neutrons are adsorbed only weakly by most dense materials (some exceptions being B, Gd, and Cd), so they may

penetrate deeply into a sample, and this makes it much easier to build equipment to control the sample environment. For example, furnaces and cryostats may be built using dense materials optimized for their thermal or mechanical properties while similar equipment for x-ray scattering generally requires a compromise to allow a significant x-ray flux in and out of the sample. For this reason we decided to construct apparatus for *in situ* diffraction with neutrons rather than x rays as the structural probe.

The chemical system we wished to study was the growth of iron oxide and oxyhydroxide particles by microwave-induced hydrolysis of ferric solutions, a process that is of primary importance in the production of pigments, catalysts, and magnetic recording media.<sup>6</sup> A central question in this process is the rate at which particles grow, depending on temperature and the concentration and nature of the reagents. In spite of the importance of this synthetic route, few, if any previous investigations aimed at its understanding have involved *in situ* studies. Studies to date have involved sampling the solutions and performing a *post mortem* on any solid deposits isolated. The process of isolating such materials could easily change their character so it is preferable to monitor growth *in situ*. Small-angle scattering provides a direct probe of the species in solution in real time, with a resolution ranging from seconds to minutes, depending on the sample and the diffractometer. In particular, this technique provides a measure of the size, and in favorable cases the shape, of particles whose diameter  $D$  is of the order of 10–1000 Å, depending on the particular instrument used. In this case we employed the LOQ diffractometer at the ISIS Facility<sup>7</sup> which has a range of  $Q=(4\pi/\lambda)\sin(\theta/2)=2\pi/D$  of 0.008–1.6 Å<sup>-1</sup>, where  $\theta$  is the diffraction angle. The ISIS

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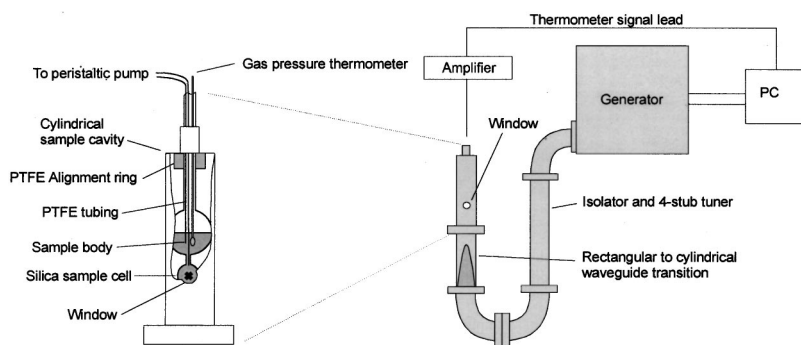


FIG. 1. Apparatus for the *in situ* study of a microwave-driven reaction by small angle neutron scattering.

Facility is a spallation neutron source in which a 50 Hz pulsed proton beam impinges on a tantalum target to produce short pulses of neutrons which are then slowed by moderators to the desired energy range. The arrival time of neutrons at a detector 10–15 m from the moderator establishes their wavelengths  $\lambda$ . By using wavelengths of 2.2–10 Å simultaneously, a wider range of  $Q$  or  $D$  is accessed than on a conventional fixed wavelength instrument.

This article describes the construction and application of apparatus for *in situ* SANS from colloidal particles formed during microwave-driven hydrolysis of aqueous ferric solutions, but could be extended to any microwave-driven reaction in which small particles are formed.

## II. APPARATUS

The majority of microwave chemical studies have been performed using multimode  $Q$  cavities similar to those in domestic ovens, despite the fact that greater flexibility and control are possible using guided wave applicators. Because these applicators rely heavily upon the principle used in radar, telecommunications, and other microwave technologies, it is possible to create bespoke microwave heating apparatus with commercially available microwave components using highly developed and well-understood principles.<sup>8</sup> The microwave applicator described here was constructed so that it allowed presentation of the sample to the SANS instrument in the correct orientation.

Although the existing SANS instrument sample position is designed to be as flexible as possible, this remained somewhat limiting in terms of the size of our apparatus. The need for reliable sample temperature control meant that the modified domestic oven which had previously been used for these reactions, while of suitable size, was inadequate as a microwave source. In our working design, a commercial 0–1 kW variable power microwave source (Microwave Heating Type GU14) was used to generate microwaves at 2.45 GHz which were delivered to the sample space through a compact wave guide arrangement using wave guide 9a (312) components (Fig. 1).

In order to accommodate the required wave guide components within the available space, the microwaves are immediately turned vertically through a 90°  $E$  bend into an isolator and four-stub tuner. While it is not desirable to have wave guide transitions between the source and the isolator, space considerations make it unavoidable. After the four-stub tuner, the waves are turned back through a 180°  $E$  bend

so as to allow an upright position for the rectangular to circular wave guide transition and cylindrical sample cavity. The design includes a cylindrical sample cavity because the axial symmetry enables development of the apparatus' capabilities for *in situ* high angle diffraction techniques without the need for significant modification. For the small angle neutron diffraction instrument, the relatively small angular range of the incident and diffracted beams allowed the use of two 17.5 mm diameter holes, placed with axial symmetry 17 cm from the wave guide termination, as neutron windows. These holes are sufficiently large both to accommodate the 12 mm diameter neutron beam without causing any unwanted scattering and also to ease the sample alignment procedures. The relatively small diameter also means that there is no requirement for chokes or vanadium windows to be included in order to maintain microwave leakage within legal safety limits. On the other hand, the port for the reflux attachment includes a 6 cm choke to reduce leakage resulting from the presence of a glass/water dielectric core.

The 100 cm<sup>3</sup> glass round-bottomed reaction vessel holds the bulk of the 50 cm<sup>3</sup> sample centrally within the cylindrical cavity. This reservoir is then connected directly to a sample cell *via* a short 3 mm inner diameter (i.d.) tube. This enables more reliable temperature characteristics for the sample while retaining the optimum physical characteristics for the sample cell. In order to maintain a representative sample in the sample cell, the solution is circulated *via* 0.5 mm i.d. polytetrafluoroethylene (PTFE) tubing at a rate of approximately 1 cm<sup>3</sup> min<sup>-1</sup> using a peristaltic pump.

The reaction vessel is held vertical, with markers to ensure the correct axial orientation and positioning with respect to the beam, and is held central with microwave-transparent plastic spacers. The temperature is monitored using a calibrated gas pressure thermometer,<sup>9</sup> capable of an accuracy of better than 0.1 K. Software, written in VISUAL BASIC 5.0 specifically for this instrument, controls the microwave output power to hold the temperature of the sample to within  $\pm 0.5$  K for the period of the experiment. This is an important feature, since the interfaces of air or vapor bubbles and associated density fluctuations in a refluxing sample might also give rise to SANS signals.

The apparatus design includes a fused silica sample cell which is as close as possible in dimensions and transmission properties to those of the cells which are conventionally employed for SANS, with a 2 mm sample path length. Since the sample cell characteristics did not differ significantly from

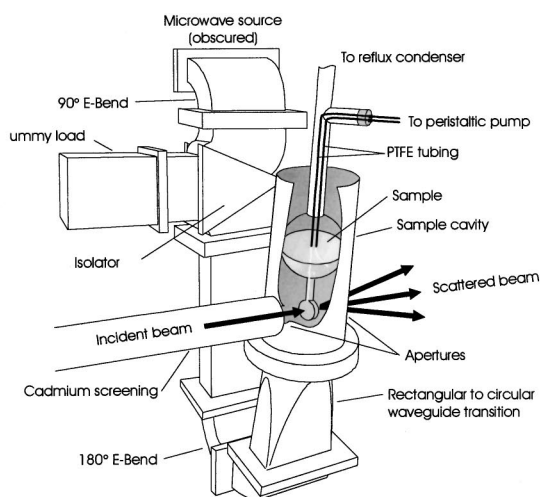
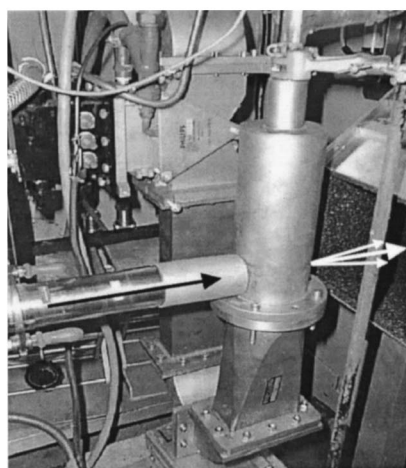


FIG. 2. Detail of the installed microwave applicator.

those of the conventional cells, compensation for background scattering during the data analysis was straightforward.

### III. EXPERIMENT

#### A. Background

Our efforts to synthesize a variety of iron oxide particles by heating aqueous solutions of iron ions with microwave radiation have produced materials that are not observed when heated conventionally.<sup>10</sup> In particular, when an aqueous solution of ferrous and ferric ions is heated at about 80 °C for several hours, we obtained acicular magnetite ( $\text{Fe}_3\text{O}_4$ ) rather than the expected product hematite ( $\gamma\text{-Fe}_2\text{O}_3$ ). Not only is this product different, but it is the first known direct synthesis of acicular magnetite from solution, other routes yielding either other oxides or magnetite with cubic or irregular morphology.<sup>6</sup> It has been postulated that particle formation may proceed *via* the needle-shaped material goethite [ $\beta\text{-FeO(OH)}$ ] followed by microwave-enhanced  $\text{Fe}^{3+}$  diffusion into the oxyhydroxide lattice to yield  $\text{Fe}_3\text{O}_4$  needles. In order to understand the precise mechanism, and because the reaction proceeds even at room temperatures, it is necessary to be able to follow the reaction in real time and SANS appears to provide a suitable probe. Not only should it be possible to construct a suitable reaction vessel that the neutrons can penetrate, but the dependence of neutron scattering strength on the atomic number  $Z$  of the various elements involved allows us to select a reaction medium that has a good contrast with the growing particles. The elements H and D have scattering lengths of opposite sign so by altering the ratio  $\text{D}_2\text{O}/\text{H}_2\text{O}$  in the solvent it is possible to produce an aqueous medium that has a very different scattering strength from anything suspended in that medium. However, there are problems associated with performing a SANS experiment on a reaction mixture that represents a typical growth medium: reagents and products for the growth of well-defined particles are generally of low concentration, which limits the rate at which data may be collected. This is offset by the timescales involved in the growth process which are relatively long (of the order of hours—and typically 18–24 h for completion) so a low rate of data collection

need not be a problem. The need to keep the sample free from gas or vapor bubbles also added to the reaction time since this can only be accomplished by holding the reaction below the solvent's boiling point.

#### B. Experimental procedure

The precise sample positioning, and the overall size of the apparatus, required piecemeal construction of the waveguide components around the neutron beam at the start of the experiment. Markers on the vessel and the use of microwave-transparent PTFE spacers enabled repeatable alignment of the apparatus on all subsequent measurements. The fully assembled applicator is shown in Fig. 2.

The peripheral instrumentation (pump, signal amplifiers, etc.) was assembled in the remaining available space. Other peripherals such as the controlling computer were located outside the sample enclosure, so allowing remote control of the reaction.

Once assembled, the reaction components (50 cm<sup>3</sup> of 0.03 M  $\text{FeCl}_3$  in  $\text{D}_2\text{O}$ ) were added to the sample vessel, and pumping started to clear air pockets from the measurement cell. The sample was heated at 95 °C ( $\pm 0.5$  °C) for 8 h and scattering data collected in consecutive 30 min runs.

#### C. Preliminary results

Standard SANS data corrections,<sup>7</sup> for the wavelength dependencies of the incident spectrum, sample transmission and detector efficiencies, were made to combine the SANS patterns from the different wavelengths recorded by time of flight. This gives the differential scattering cross section,  $(d\Sigma/d\Omega)(Q)$ , which for a dilute system of particles of size  $R$  and volume  $V_p$  is  $d\Sigma/d\Omega(Q) = N_p V_p^2 (\Delta\rho)^2 P(Q,R) + B(\lambda)$ , where  $N_p$  is the number concentration,  $\Delta\rho$  is the neutron scattering length density difference between the particles and solvent, and  $B(\lambda)$  is the wavelength-dependent background signal. The particle form factor,  $P(Q,R)$  describes interference between radiation scattered by different parts of the same particle and is sensitive to the *shape* of the particle.

Model fits to the SANS signal may incorporate an integration over a suitable particle size distribution function

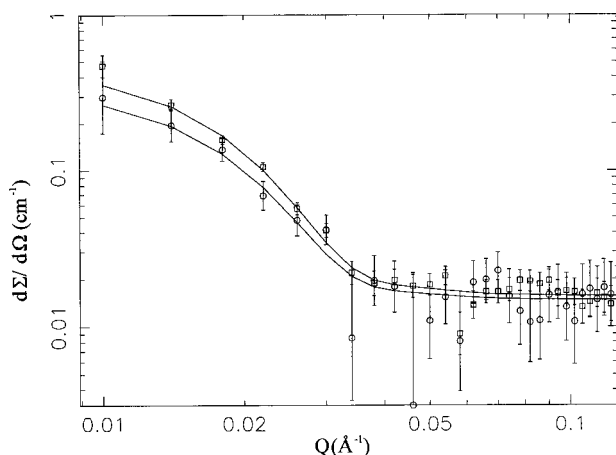


FIG. 3. SANS data for microwave-driven hydrolysis of  $\text{FeCl}_3$  and  $\text{D}_2\text{O}$  with fits to polydispersed spheres (see the text) for the first 30 min of reaction (upper line), average from 30 to 150 min (lower line).

$N_p(R)$ . Though a variety of particle shapes were tried the data obtained here was best represented as polydisperse spheres, for which was used a Schultz polydispersity function (similar to a log normal)

$$N_p(R) = [(Z+1)/R]^{Z+1} R^Z \exp\{- (Z+1)r/\bar{R}\} / \Gamma(Z+1),$$

where  $\bar{R}$  is the average particle radius, the polydispersity index,  $\sigma/\bar{R} = (Z+1)^{-1/2}$ , is a measure of the width of the distribution, and  $\Gamma$  is the Gamma function. Least squares fits<sup>11</sup> to the data are illustrated in Fig. 3.

Data obtained from heating the sample of  $\text{FeCl}_3$  in  $\text{D}_2\text{O}$  at 95 °C indicated that particle formation had already begun within the first 30 min time frame. The SANS signal was also lower than expected, possibly indicating that the scattering particles were rather diffuse. Small angle x-ray scattering (SAXS) measurements on this system under conventional heating are consistent with these observations,<sup>12</sup> and suggest that rapid initial particle growth to sizes of approximately 100 Å takes place, which subsequently agglomerate to produce macroscopic particles. The intensity of the scattered beam in the SANS experiment displays some variation during the early stages of the reaction, and complementary experimental data will be required for a fuller understanding of the mechanism of particle formation. However, the SAXS data suggest that, as the changes in intensity are wholly due to very low angle scattering, the SANS data may be explained by the growth and decay of very low angle scattering peaks during the course of a complex growth process. It is suggested that this process involves particles that are too large to be seen using the  $Q$  range available in this experiment.

For the first time, however, *in situ* SANS measurements on the hydrothermal preparation of iron oxide particles have

been carried out, and these preliminary data have yielded new and interesting information. The principal limitation of the apparatus described here is the timescale of the measurement required for reasonable signal to noise ratio in the data, and confines the systems that may be studied to those that generate particles over relatively long periods. This problem may be circumvented in the future with the advent of new, higher flux instruments, or brighter neutron sources. The apparatus may also be adapted for wide-angle diffraction measurements to probe structure on atomic length scales and determine the chemical character of the species that are formed. This would also require much higher flux, or far more concentrated samples than were used in the experiments described here.

The basic principles that have been employed in the design of this apparatus also lend themselves to other *in situ* measurements on chemical systems. In particular, we are currently planning complementary experiments using a microwave applicator, which has been designed for use with synchrotron radiation sources. Once again, more rapid data collection and the possibility of *in situ* WAXS and extended x-ray absorption fine structure measurements to complement the existing data make such apparatus an attractive and worthwhile goal.

## ACKNOWLEDGMENTS

The authors would like to thank S. Mains, D. Paden, J. Ashfield, K. Anderson, and S. Johnson of the University of Edinburgh for their efforts in fabricating the various components of this apparatus. They also thank the EPSRC who support our work on microwave chemistry (Grant No. GR/L53601).

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