

Design and performance of a high pressure insert for use in a standard magic angle spinning NMR probe

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Abstract

In this paper we describe the construction and performance of high pressure magic angle inserts made from the polymer PEEK. The inserts were designed to fit inside standard commercial 7 mm magic angle spinning rotors and spin at the maximum frequency of the probe. The sample volume of the inserts was 100 μ L. A gas loading chamber that operates at room temperature is described. The performance of the inserts is discussed for a number of gases in terms of resolution as a function of spinning speed and leakage of the gas due to permeation through the polymer. Finally, some preliminary results are shown in relation to complex food materials. © 2006 Elsevier Inc. All rights reserved.

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1. Introduction

Magic angle spinning is a standard technique used in solid state NMR to average anisotropic interactions in solid materials to obtain high resolution spectra [1–3]. There are very few reports where this technique has been used with gases under moderately high pressures. Previously, high pressure magic angle spinning has been performed using thick walled flame sealed glass ampules where the maximum pressure attained was 70 bar (7 MPa) [4]. Recently, accounts of high pressure NMR sample devices made from the polymer PEEK (polyether ether ketone) have been reported for static samples using normal liquid NMR probes [5–7]. This work makes use of the fittings found in HPLC instruments to seal the high pressure sample tube. With such devices, maximum experimental pressures of 200 bar have been attained and have been applied for use in supercritical fluid work [5]. This idea of using a high performance polymer as the material for the

high pressure sample holder has been taken up by Yonker and co-workers [8] for use in magic angle spinning NMR experiments. They have reported the use of an 11 mm outer and 3.3 mm inner diameter MAS high pressure sample vessel made from the polymer Delrin (polyoxymethylene) which fits into a 13 mm outer diameter ceramic rotor. The maximum working pressure for this system was 350 bar the rotor was usually spun at frequencies of 1.5–2.0 kHz.

In this work we have concerned ourselves with building a high pressure MAS insert that could fit inside a commercially available standard 7 mm outer diameter ceramic rotor, where the maximum spinning frequency is 5 kHz. The main interest for our research is in the use of aerated food materials and to understand more completely the factors that influence their industrial manufacture. One of the main difficulties with working with food materials is that they are normally not at thermodynamic equilibrium. One is usually confronted with materials whose properties are more or less a function of their process history. Therefore, it is important to perform NMR studies on such materials without further processing, in particular, changes

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in temperature or water content. This has ruled out the routine use of high pressure inserts made from glass since this usually requires solidifying the gas with liquid nitrogen prior to flame-sealing the sample. This procedure would leave the food material in an unknown state in terms of thermal history and water content.

2. Experimental

2.1. Solid state NMR

All NMR experiments were performed on a Bruker AVANCE DSX wide-bore NMR spectrometer operating at a ^1H Larmor frequency of 400.13 MHz (9.4 T). A Bruker 7 mm MAS double tuned multinuclear probe was used in all experiments. In order to observe ^{14}N spectra the probe was modified by the addition of fixed capacitor of 60 pF across the variable tuning capacitor of the probe. The capacitor was mounted with screws and was removed from the probe for observing other nuclei such as carbon-13 and xenon-129. The $\pi/2$ pulse width for the ^{14}N nucleus was 11 μs . The ^{14}N chemical shift was calibrated using an external sample of saturated ammonium nitrate in water and the $^{14}\text{NO}_3$ signal was set to -4 ppm [9].

2.2. Sample preparation

Small cylindrical samples of 2 mm diameter and length 6–7 mm were cut out from commercial chocolate bars and placed in the high pressure insert. The cap of the insert was loosely screwed onto the high pressure insert so that gas could still enter the insert. The insert was then placed

into the gas loading chamber and evacuated for up to an hour. The chamber was then pressurized with N_2O gas at 40 bar for a further hour. The high pressure insert was then sealed by screwing the cap down and the gas was released from the chamber prior to removing the sample from the chamber. The mass of the high pressure insert was weighed before and after the addition of the chocolate sample and gas in order to know the amounts present. The high pressure insert was then placed in a Bruker 7 mm outer diameter silicon nitride MAS rotor and then the rotor drive cap was placed firmly on the rotor.

3. Results and discussion

3.1. Design of high pressure inserts

The high pressure inserts were machined from the polymer PEEK (Ketron PEEK 1000). They comprised two parts: a screw on cap and a hollowed cylinder to hold the sample. Fig. 1 shows a schematic of the final design of the high pressure insert with some of the main dimensions. The overall length of the insert was 15.3 mm so that it could fit tightly into the MAS rotor. The top of the cap had a diameter of 4.0 mm, smaller than the overall diameter of the insert so that the spinning tip of the rotor would fit around when it was pressed tight to the rotor. For NMR MAS rotors to spin correctly there must be no gap between the ceramic rotor and the drive tip. The outside diameter of the insert was 5.5 mm and the wall thickness of the insert was 0.925 mm to give an inner diameter of 3.65 mm. Both the bottom and cap were machined so that they would fit into a hexagonal bolt for closing and opening the insert.

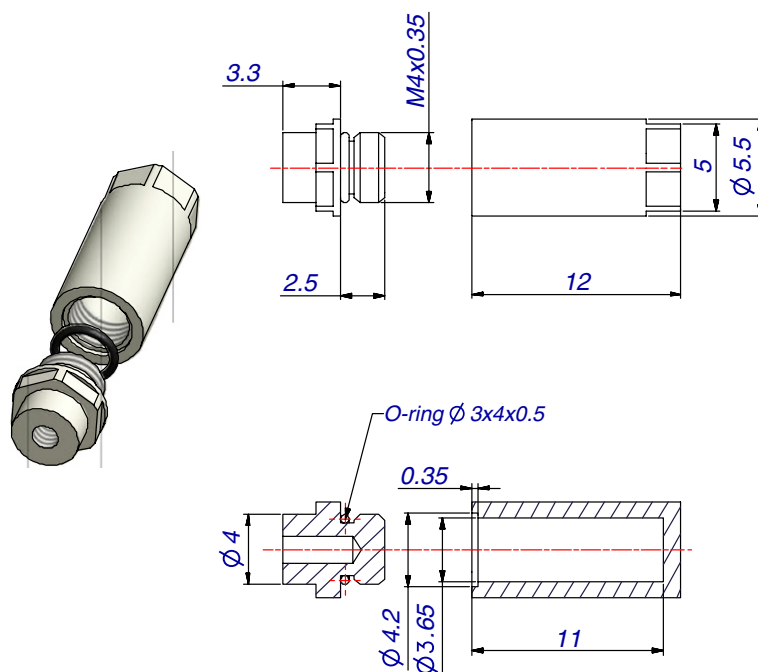


Fig. 1. Schematic of high pressure insert machined from PEEK with dimensions in millimetres.

At the top of the insert a groove was cut into the rim to a depth of 0.35 mm and a diameter of 4.2 mm so that an o-ring could make an air tight seal between the cap and the bottom half of the insert. When PEEK is used in high performance liquid chromatography instruments to make air tight connections between the instrument and the tubing, no o-rings are required due to the design of the ferrules and the fittings. We experimented without using o-rings and had some success but finally chose to incorporate an o-ring into the high pressure insert design. The cap is designed to be closed by simply screwing it into the bottom of the insert. A 2.5-mm length thread was used with a pitch of 0.35 mm and diameter 4.0 mm. The length of the thread and pitch determines to some extent the pressure that can be held by the insert. In order to have a reasonable sample volume a compromise must be made between the maximum pressure the insert can hold and the volume left for the sample. In this design the volume left for the sample was approximately 100 μL . With the final design of the thread length and pitch, we have estimated that the maximum pressure the insert can withstand is approximately 100 bar. In the design of the cap a threaded hole is machined into the top of it so that a screw can be inserted which is used to pull the insert out of the rotor, as the fit between the rotor and insert is very close. This is necessary so that the MAS rotor with the high pressure insert is well balanced, and then it is easy to spin the rotor up to its maximum speed.

3.2. Design of high pressure gas loading device

The high pressure loading chamber was constructed from a hollowed stainless steel block with two observation windows of polycarbonate, each 10 mm thick, at the front and rear. The windows were held in place by stainless steel plates using six bolts (ISO 4017-M6x60). The overall outside dimensions of the chamber were 70 mm high, 70 mm wide and 53 mm deep. The inner volume of the chamber was 26 mL. In the bottom of the chamber a circular hole of diameter 16 mm was cut for access of the samples. This was plugged with stopper made from stainless steel that was designed to hold the high pressure insert. The stopper was made air-tight with an o-ring and kept in place when the chamber was under pressure using a metal latch that swung into place below the stopper.

When a high pressure insert is placed in the chamber its cap mates with a six-sided nut that is attached to a rod that feeds through the top of the chamber where it can be turned by hand using a large knob. An air tight seal was maintained between the rod and the chamber (Lubroseal L4990P, part number: 11.5990.0015, Angst + Pfister AG) of diameter 15 mm. This joint is rated to 50-bar. The whole cap closing assembly is polished and turns on a roller bearing (part number: AXK 0515TN, Technomag SA) so that it can be turned without too much torque and wear from friction is minimized. The high pressure insert cannot be over tightened as the bottom holding device is designed

to turn. Once the cap has been screwed down and mates with the bottom half of the insert any further turning will just cause the whole high pressure insert to turn. A schematic of the high pressure loading chamber is shown in Fig. 2. The chamber has one inlet for the gas and was designed to be heated electrically but this has yet to be implemented.

3.3. Performance of high pressure insert

The performance of the high pressure inserts can be seen from the experiments performed with N_2O gas. In Fig. 3 one can see the signal obtained from an insert loaded only with N_2O gas at 40 bar. In the top spectrum the sample is static and the line-widths measured at half height are around 14 and 16 Hz for the resonances at -146 and -234 ppm, respectively. The splitting of the resonances due to homonuclear J -coupling between the two nitrogen atoms is only slightly apparent. The effects of spinning the sample at a frequency of 4 kHz is shown in the bottom half of the figure. Although the overall line-widths of the two resonances have not been significantly reduced, the tails of the peaks at the base-line are much narrower and the splitting from the J -coupling is now clearly distinguishable. The line-shape of the signals is very good, which shows that the high pressure inserts do not introduce any problems in terms of shimming the magnetic field. Each

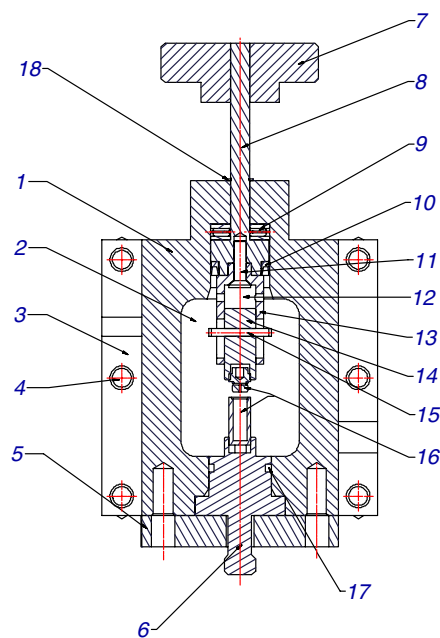


Fig. 2. Schematic of high pressure loading chamber. (1) Stainless-steel chamber, (2) ten millimetres thick polycarbonate windows, (3) stainless steel brackets to hold windows in place, (4) six ISO-4017 M6x60 bolts, (5) hinged closing bracket, (6) bottom stopper to hold insert, (7) knob, (8) rod, (9) high pressure bearings, (10) high pressure air tight seal, (11) holding screw, (12) spring, (13) joint, (14) insert cap holder, (15) holding pin, (16) high pressure PEEK insert, (17) o-ring 13 mm diameter and (18) clamp.

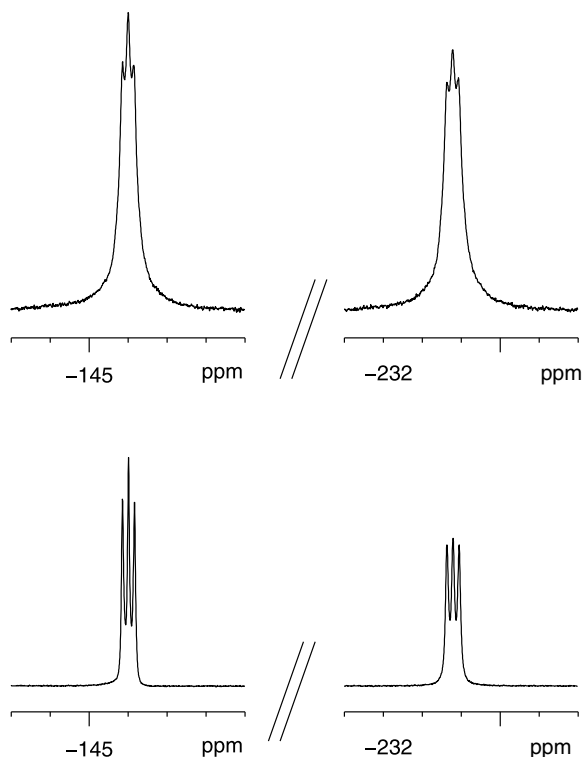


Fig. 3. ^{14}N NMR spectra of N_2O gas at a pressure of 40 bar. (Top) Static spectrum. (Bottom) Spinning spectrum, rotor frequency 4 kHz. Each small division represents 1 ppm. Number of acquisitions 256. Exponential line-broadening of 0.2 Hz. Recycle delay 4 s. Spectral width 180 ppm. Number of data points in FID 16 K.

resonance is split into three peaks to give a J -coupling value of 4.53 Hz.

In Fig. 4 the ^{14}N spectra of N_2O at 40 bar in the presence of a commercial milk chocolate are shown under static (top) and spinning (bottom) conditions. A mass of approximately 65 mg of chocolate in the shape of a cylinder was placed in the high pressure insert. The sample was evacuated for an hour and then N_2O gas was introduced at a pressure of 40 bar. The high pressure insert was left in the loading chamber for one hour before the cap was closed and the pressure in the chamber released. The volume of the chocolate sample is approximately 50 μL since the density of chocolate is around 1.3 g/cm^3 , therefore there will be N_2O gas around the chocolate after the high pressure insert is sealed.

The static spectrum in Fig. 4 shows the resonance for the N_2O outside the chocolate at the same chemical shift for the spectrum corresponding to gas alone. It also shows two broad resonances both spanning a chemical shift of approximately 7 ppm at the foot of the peaks due to the gas surrounding the chocolate. Upon spinning the sample (Fig. 4, bottom) at 4 kHz the broad resonances narrow considerably to give signals appearing at chemical shifts of -145.5 and -230.2 ppm. It is assumed that these two peaks arise from N_2O dissolved in the chocolate. This narrowing occurs at much lower spinning frequencies also (1 kHz), therefore it is likely that the line width of the

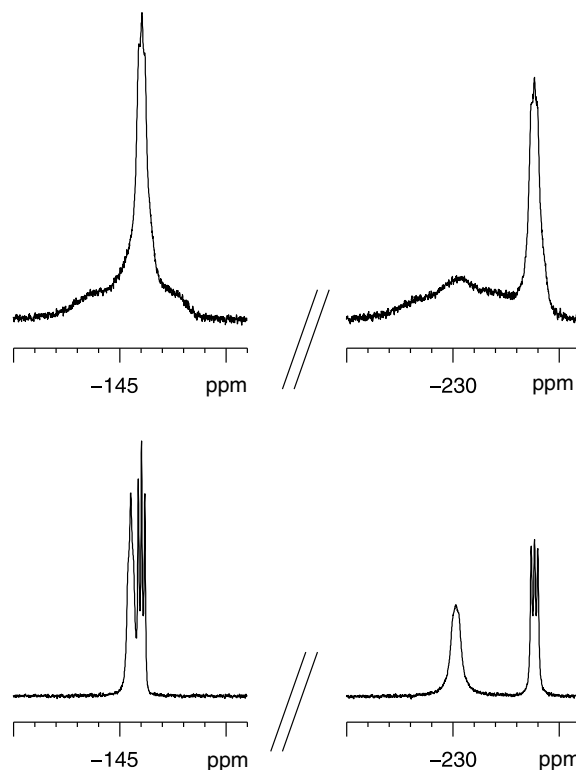


Fig. 4. ^{14}N NMR spectra of N_2O gas at a pressure of 40 bar in the presence of a commercial milk chocolate. (Top) Static spectrum. (Bottom) Spinning spectrum, rotor frequency 4 kHz. Number of acquisitions 256. Each small division represents 1 ppm. Exponential line-broadening of 0.2 Hz. Recycle delay 4 s. Spectral width 180 ppm. Number of data points in FID 16 K.

dissolved gas in the static experiments is probably due to susceptibility broadening. On the resonance at -145.5 ppm, under spinning conditions, there is still evidence of splitting due to J -coupling.

The ^{14}N spectra of N_2O are quantitative, therefore an estimation of the solubility of the gas in the chocolate can be calculated. The ratio between the gas dissolved in the chocolate and the gas surrounding the chocolate is 1:0.87 calculated by area. The total amount of gas present in the high pressure insert was 9.8 mg. Therefore the amount of gas dissolved in the chocolate was 2.1 $\text{g}/\text{kg}/\text{bar}$ assuming Henry's Law applies.

3.4. Permeability of polymers to different gases

We have used the high pressure inserts with a number of gases, namely, nitrogen, nitrous oxide, carbon dioxide and xenon. It was noticed at the start of the study when different designs of the high pressure inserts were being tested that many suffered from leaks. However, it was realized that it only occurred for certain gases, in particular nitrous oxide and carbon dioxide. Nitrous oxide leaked particularly badly. It seems that this gas is highly soluble in many materials and the gas was permeating through the PEEK polymer. Fig. 5 shows the signal intensity for nitrogen

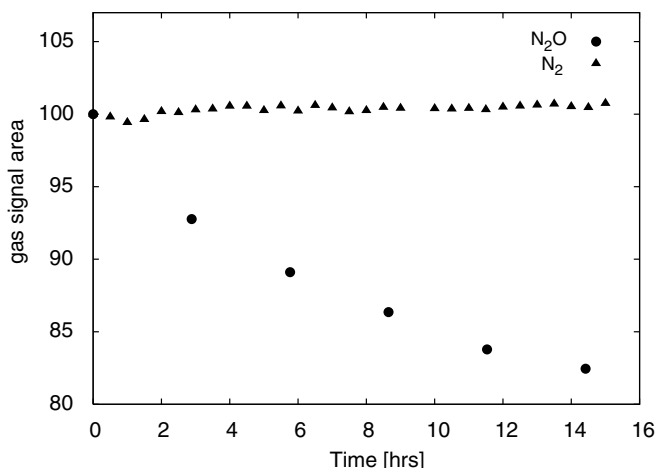


Fig. 5. Gas loss over time for N₂ and N₂O for an initial pressure of 40 bar.

and nitrous oxide over a 15 h period. The nitrogen signal is almost constant, whereas the nitrous oxide signal decreases constantly over time until, at the end of the time period of the experiment only 82 % of the signal is still present. Carbon dioxide showed similar results to nitrous oxide, however no mention of this problem had been reported in earlier work using static high pressure NMR vessels constructed from PEEK [5].

4. Conclusions

We have successfully designed and built high pressure MAS inserts and an associated gas loading chamber. The high pressure inserts can be easily loaded with a gas and then be placed into commercial spinning rotors to perform MAS experiments. The commercial MAS rotors, when loaded with a high pressure insert, can be spun to their

maximum designed frequency of 5 kHz. By constructing the inserts out of a polymer we have avoided many of the problems associated with glass inserts such as flame-sealing, freezing to trap the gas prior to sealing and poorly balanced so difficult to spin. The inner sample volume of 100 μ L is perfectly adequate for obtaining NMR data with good signal to noise in a reasonable time. The permeability of the gases through the PEEK polymer is a drawback to this approach, but maybe reduced by using different polymers with lower permeability but still retaining the same suitable physical properties of good machinability and rigidity.

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