User's Guide

High Pressure NMR Cell

With High Pressure Tether

Bruker & Agilent Cells

Version 1.10

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WARNING: This device can be dangerous and potentially harmful to users and equipment. It is very important you read and understand these instructions before using this device. A certification sheet was included with your cell indicating the maximum pressure the cell should be used. Use of the cell above this pressure could result in NMR cell failure.

There are minor differences in the shape of the Agilent versus Bruker cell. The assembly and use instructions are the same.

GUIDELINES:

DO:

- Follow the maintenance schedule for the tube. See *Tube Maintenance*.

- Always align the tube serial number with the mark on the top surface of the base. This will assure consistent setup. Failure to do so could lead to tube failure.

- Exercise caution when pressurizing the tube. A suitable containment vessel such as a clear plastic box should be supplied to both hold the sample during preparation and for moving the NMR cell around the lab. This safety precaution is necessary to contain any fragments from a tube fracture.

- Apply **110-150 in.-lbs. (12.4 - 16.9 Nm)** of torque when assembling the cell to assure proper setting of the seal (See Cell Torque Settings).

- Wear proper safety equipment such as a face shield when transferring the NMR cell from the containment box to the NMR.

- Pretest the tube at the target pressure for at least 15 minutes outside the NMR to assure integrity of the cell setup.

- Check the axial alignment of the tube with the cell body, by inserting the unpressurized cell into the NMR. Once pressurized the tube cannot be adjusted to fit.

- Leave the high-pressure tubing tether attached to the cell between uses. Constant reseating of the fitting will reduce the seal integrity.

- Change the tube seal (TS01) after every use.

- Use care when inserting the cell into the magnet. Avoid hitting the pressurized tube against objects.

DON'T:

- Pressurize the tube above its rated limit. Remember the posted limit is the maximum pressure the cell should be used.

- Insert a fully pressurized tube into the magnet. It is preferable, especially when working near the posted maximum, to insert the tube first then take it to pressure. It is recommended the tube pressure be below 5,000 psi when inserting or removing the cell from the magnet.

- Over tighten the high-pressure tube fitting into the cell body. This can strip the threads or damage the seal surface and ruin the cell.

- Pressurize the tube while it is in the cell setup tool. The fit of the tube is very tight. If the setup is in some way improper, the tube may shift in the setup tool during pressurization. A slight shift could fracture the tube.

- Use metal needles to fill the tube. The tube is made from a hard ceramic that can scrape off metal into the sample.

VERSION SPECIFIC NOTE:

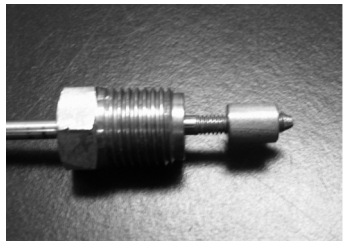
Previous versions used a TCSN or TCSN-M in the manifold base piece. Manifolds with serials numbers starting with four or higher do not have this component.

MATERIALS USED IN THE CELL:

The high magnetic field required for NMR demands that anything put into the magnet have no magnetic properties. Some stainless steels are considered non-magnetic, but at the high fields in use for NMR the slight magnetic properties are magnified to where stainless steel can only be used in small quantities.

These design requirements necessitate the high-pressure NMR cell be fabricated from materials such as aluminum, which is relatively soft. The high-pressure fittings used typically with this cell are made from stainless steel. Over tightening the fitting in the cell can strip the threads or deform the seal surface and ruin the cell. It is recommended that once the high-pressure tether line is attached it remain so. Constant reseating of the fitting will eventually degrade sealing performance.

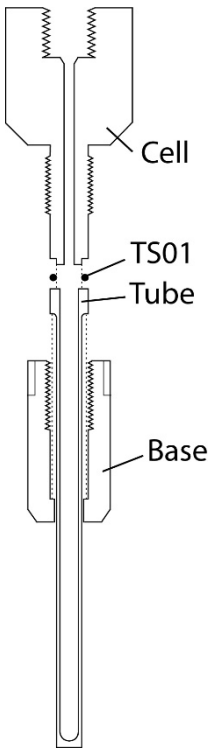
CELL SETUP:



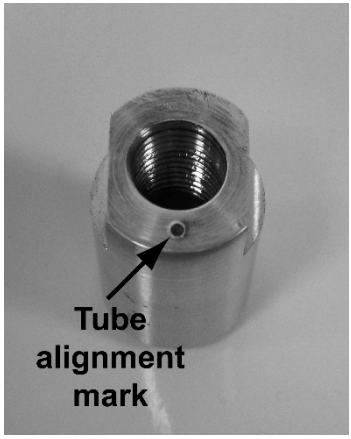
The high-pressure tether line should be attached prior to full assembly of the cell. The tubing used for this purpose is 1/8” O.D., with a high-pressure fitting with 1/2”-20 threads. A

collar is threaded onto the tubing as shown in the picture. The coned end of the tubing mates with the tapered hole in the cell. Therefore, be sure the collar is threaded far enough that these two surfaces will meet otherwise the seal integrity could be poor. Once attached this tether should not be removed between uses since repeated disassembly will likely lead to degradation in the sealing performance.

The cell was designed so that the tube can be easily removed and cleaned. As such the seal (TS01) is single use. Previous versions of the manifold included another component called the tube seat to act as a cushion between the tube and the metal manifold. Manifolds with a serial number starting with four or higher do not need this component. Instead there is a chamfer cut into the bottom of the base that accommodates the curvature of the tube such that the flat undersurface of the flange rests directly on the metal.



If the manifold being used has a serial number starting with three or lower, please obtain an earlier version of the manual for proper operation of the cell.



The base component of the cell has been marked with a punch. This mark was made during the certification process of the cell to reflect the alignment of the tube relative to the base. The center of the serial number on the tube should be aligned with this mark when assembling the cell. This will assure consistent setup.

Failure to align the tube properly in the base during assembly may result in a tube failure.

SAMPLE VOLUME:

A typical thin-walled NMR tube has an inner diameter of 4.2 mm. The NMR tube most commonly used with this manifold has an inner diameter of 3.0 mm. Thus, the sample volume used should be at least half what is typically used for an optimal sample in a thin-walled tube. Though water is typically considered incompressible in reality it does compress unless the sample has been thoroughly degassed. Therefore, it is good practice to include a little extra sample to accommodate the volume change and to account for the mixing interface between the sample and transducing fluid.

SAMPLE PREPARATION:

In most cases where this NMR cell is used the actual sample for study will only fill a small portion of the NMR tube volume. The remainder of the space will be taken up by a transducing fluid of some sort. Ideally this fluid would not mix or dilute the NMR sample during operation. For aqueous samples this generally means using an oil of some sort as the transducing fluid. However, it should be assumed that over prolonged experiment times that some mixing will inevitably occur between the sample and transducing fluid so using a slight excess sample volume will help minimize intrusion of signal into the NMR data.

There are a variety of methods in the literature for how this might be done. One common method is to use water as the transducing fluid with mineral oil forming a barrier between it and the sample. In this case the sample would be added to the tube first, mineral oil would then be layered on top of the sample to approximately 1 cm below the top of the tube, and finally a separate layer of water layered on top of that. The NMR cell is then assembled as usual. It is assumed that the high-pressure tubing tether and manifold have already been primed with water using some sort of pressure generator prior to the cell assembly to remove excess air.

The top-most water layer is present to keep oil off the sealing surface of the tube and also to minimize the possibility of oil leakage out of the NMR cell should a leak develop during operation.

When a sample is to be removed from the NMR tube the top water layer and a portion of the mineral oil is first removed. The remaining oil and NMR sample can then

be withdrawn in bulk and centrifuged to separate the two layers to recover the sample.

Other methods use paraffin oil or one of the Fluorinert™ compounds from 3M™ as the transducing fluid and bypass the need for a barrier layer.

Only glass or plastic, pipettes or tips should be used to add fluids to the NMR tube. No metal should ever be used inside the tube.

CELL ASSEMBLY:

For proper positioning of the tube the Cell Setup Tool should be used. This tool helps keep the tube axially aligned with the NMR cell. Improper positioning of the tube can prevent the cell from inserting into the NMR. To use the setup tool, first place the base with the tube already inserted. The fit is snug, so the tube may need to be pushed into position.

If desired, a single-turn of ¼" Teflon tape can be applied to the threads for optimal holding performance. This is not required as it does make the assembly more difficult due to the tape, but it may be necessary for long-term sealing performance. This step also reduces the amount of torque required to set the seal to 130 in.-lbs. for a 3 kbar NMR tube thus reducing the force on the tube.

The primary seal is provided by the part TS01. **The seal is single use only.** For setup it should be placed on the end of the cell section piece. It is press-fit and should remain in place. This assembly should then be threaded

into the base. Using a 7/8” wrench for the valve, and the 1/2” wrench (Bruker) or 5/8” wrench (Agilent) for the base, tighten to set the seal. **The recommended torque required for setting the seal without Teflon tape is 150 in.-lbs. (16.8 Nm). A torque wrench should be used for optimal setup.**

Do not exceed the maximum torque setting. This could damage the NMR cell or tube. See Cell Torque Settings section for more information.

Optimum tube alignment is achieved by iterative cycles of slight tightening followed by several full rotations of the cell setup tool while holding the cell static. This minimizes any tube misalignment attributable to the tool itself. During the first several cycles tighten by small increments, followed by several more cycles using larger increments. Finally, tighten to the proper torque setting.

Once the setup of the cell has been completed it should be checked for proper fit in the NMR before pressurizing the sample.

A pressurized tube cannot be readjusted without releasing the pressure first and potentially losing the sample so be certain to check the alignment before continuing.

INSERTING THE CELL INTO THE NMR:

The hig- pressure tether line is made of 316 stainless steel tubing. This rigid tether can sometimes make inserting the sample into the magnet a difficult process. For this reason it is strongly advised not to insert a tube pressurized over 5,000 psi. The tubes are themselves robust, but striking the tube against the magnet while pressurized near its maximum could potentially cause a tube failure.

To facilitate insertion, the high-pressure tether should be straightened for a length equivalent to the depth from the top of the bore to the probe head. The manifold itself has dimensions that should help minimize misalignment of the cell as it is inserted. Be sure to keep the pressurized cell inside a protective box when moving the cell. This keeps the user safe as well as minimizes the chance of hitting the tube against objects.

Once inserted the 1/8” high pressure tubing tether exiting the magnet should be secured to outside

structures to minimize movement during the experiment. It should be expected that metal tubing in motion outside the magnet will influence the quality of the data collected.

The cell can now be pressurized to the desired working pressure.

ADDITIONAL CELL INSERTION TIPS:

A long section of 1/8" high pressure tubing can be somewhat unwieldy. Sometimes too the clearance above the NMR is insufficient to allow for easy insertion of the cell into the magnet. One suggestion to overcome problems of this and of similar nature is to use a short section of tubing to connect to the NMR cell and then couple that to a longer section leading to the pressure generator. This section can be rather short especially for 500 and 600 MHz instruments. This approach may also aid in the assembly of the cell since it will no longer have the long tubing section creating a pull on it. High Pressure Equipment Company (www.highpressure.com) sells a variety of components useful for additional pressure setups. For the above example a right-angled elbow coupler with HM2 style fittings consistent with the manifold is P/N 60-22HF2.

The 1/8" tubing can be bent at right angles with a bend radius of 3/8". There are various vendors that sell tube benders for this purpose. Placing a right-angle bend close to where the tube exits the magnet may help by making it easier to keep a short section of tube straight as it is inserted.

An extreme approach would be to secure a section of small-bore plastic tubing that could form a sleeve around

the 1/8” tubing. If properly selected this could form a rigid setup to help insert the NMR cell.

CLEANING THE NMR TUBE:

For extensive cleaning the NMR tube can be exposed to detergents suitable for quartz cuvettes. If nitric acid is to be used it is recommended that only dilute solutions be used for short exposure times. Data from the literature indicates zirconia is non-reactive with nitric acid at room temperature, but the effect on performance due to prolonged exposure is not available.

The NMR tube can be autoclaved and subjected to temperatures up to 200°C.

CELL TORQUE SETTINGS:

To properly set the seal (TS01) the seal must be compressed a specific amount. To do this the cell must be assembled using sufficient torque. The recommended numbers are show below:

110 in.-lbs. (12.4 Nm)	*typical for 1.0 kbar*
130 in.-lbs. (14.7 Nm)	*typical for 2.5 kbar*
150 in.-lbs. (16.9 Nm)	*typical for 3.0 kbar*
130 in.-lbs. (14.7 Nm)	***typical for 3.0 kbar with Teflon tape***
170 in.-lbs. (18.1 Nm)	*maximum*

Using more torque does not assure a better seal and could cause damage to the cell or fracture of the tube. If the cell is leaking disassemble and try the following before applying additional torque:

1) Always make sure the sealing surfaces on the cell and tube are dry. Replace the seal.

2) Apply a single-turn of ¼" Teflon tape to the cell nipple threads.

3) A single drop of light machine oil can be placed on the threads to assist with threading and may improve the torque reading.

SPECIFICATIONS:

Wetted parts	Titanium, zirconia (NMR tube), Viton
Tube dimensions	**Tube section:** 5 mm O.D. x 2.8 mm I.D. x 87 mm length (3 kbar tube) **Head section:** 8 mm O.D. x 5 mm length
Tube volume	0.64 ml
Internal volume (manifold plus NMR tube)	**Bruker:** 0.81 ml **Agilent:** 0.76 ml
Temperature range	5°C - 100°C using standard seals
Pressure range	Indicated on certification sheet shipped with NMR tube
Manifold to tube seal	Viton seal standard; single-use Buna-N 3.0 kbar seals
Pressure connection	Manifold port is HiP HF2 (1/2"-20 UNF) for use with 1/8" tubing.
Allowed fluids	All fluids compatible with the wetted parts can be used in the cell. Examples are water, alcohols, alkanes, carbon dioxide, and xenon. Some solvents may cause buildup of aluminum oxide on the NMR manifold.
Cell assembly torque	110 in.-lbs. (12.4 Nm) *typical (1.0 kbar)* 130 in.-lbs. (14.7 Nm) *typical (2.5 kbar)* 150 in.-lbs. (16.9 Nm) *typical (3 kbar)* 170 in.-lbs. (18.1 Nm) *maximum*
HM2 gland into manifold torque	72 in.-lbs (8.1 Nm)

TUBE MAINTENANCE

Every tube that is shipped is exhaustively tested for 48 hours above the rated pressure of the tube. This testing has led to exceptional performance of in-the-field tubes. However, failure should not be considered impossible. There are a variety of factors that might influence the rating of the tube. A few examples:

1) Collisions of the tube with sharp edges or objects.
2) Unexpected lateral stress applied to the tube during insertion.
3) Significant thermal stresses applied to only a portion of the tube.

To further minimize the chances of failure it is recommended that after 100 hours of continuous use at 90% or more of the rated pressure that the tube be subjected to an overpressure condition of 100 bar (1,450 psi) above the rated pressure for 15 minutes outside the NMR instrument. The same procedure used to test each new assembly prior to insertion into the magnet can be followed.

This test should also be performed if there is cause to believe some action in the handling might have compromised the NMR tube.

It is expected that tubes will readily pass this test. They are quite robust. However, this will provide a measure of confidence that the tube in use is still performing properly.

FURTHER INFORMATION:

This document may be updated periodically to reflect questions from users. Please check back at www.daedalusinnovations.com in the support section for more recent versions of this document.

Technical support can also be obtained by emailing questions to support@daedalusinnovations.com, or contacting Daedalus directly at 610-358-4728.

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