Application Note 1096-306

VSM Sample Mounting Techniques

The techniques being illustrated will apply to the MPMS 3 (SQUID-VSM), PPMS-VSM and VersaLab cryogen-free VSM systems. Quantum Design provides the selected sample holders. The materials for securing the sample to the holders are not included with the installation. Due to high accelerations in VSM measurements, secure sample mounting is more challenging than in most other measurements. Loosely mounted samples will result in noise in the moment measurement, see app notes 1096-303 and 1500-009 on the Quantum Design website. Axial and radial sample positioning error introduces inaccuracy of the reported moment, see app note 1500-010. Also, the sample geometry influences accuracy of the reported moment, see app note 1500-015. Keep the sample length less than 5 mm to maintain the accuracy of the point source dipole approximation. Due to the need for better securing of samples, tape and glue are often used and these always carry with them some magnetic impurities (at least of the ~10^{-6} emu level). Please see the article by Garcia et al. (http://dx.doi.org/10.1063/1.3060808) which reviews common sources of such impurity contributions.

1. The **sample holders supplied by Quantum Design** are designed to fit on the mounting station. The total length of the holder and exact location of the sample are better defined by using the mounting station. While the fragile quartz paddle is designed for the lowest moment samples, a more robust brass half-tube provides versatility.

   A. The **quartz paddle** is redrawn from a 4 mm diameter rod. Elimination of surface microcracks improves mechanical strength of the quartz paddle. A nitric acid dip removes surface impurities. Smooth surface can make cleaning easy but reduces adhesion of glue. The adapter is made of glass-filled polycarbonate, which should never be exposed to organic solvents, especially acetone. The outer gluing surfaces of the quartz pieces are sanded to help bind with the epoxy. A complimentary shaped shim is added to the paddle and put inside the adapter containing epoxy resin. The epoxy is specially chosen to withstand both high temperatures (400 K) and cryogenic conditions. The assembly is cured straight in a custom fixture.

1. For mounting **thin films parallel to field** (see figure to the left), do not exceed the width of the paddle. Wider samples can be mechanically secured and better protected using the brass half-tube or aluminum frame techniques. Place the quartz holder in mounting station. Using a sharp wooden stick or other tool, place a small drop of glue on the paddle, set film on top and press to secure bond. Let it dry completely at ambient conditions. If the sample can handle the heat, increase temperature to 340 K and purge sample chamber. Return to 300 K, purge and seal, or lower temperature and follow centering routine. To remove sample, hold length of quartz paddle with no pressure on adapter junction. A thin wooden flat can transport solvent under the chip. Wait for solvent to penetrate. Free the sample with appropriate leverage.
2. For **single crystal** samples and low temperature analysis, put GE 7031 on crystal then secure to quartz. A small amount of **fine powder** can be mixed into a drop of varnish, although it is difficult to get a quantitative mass with this technique. If taken to 340 K to cure before completely dry, a large field like 5 Tesla should result in the alignment along a preferred crystallographic axis which is frozen in place by going cold. Kapton tape is also effective way to secure small amounts of material, but keep sample as point source and tape symmetrical along the axis of motion. The concern with tape is the random contamination from dust in a lab environment (see reference cited in introduction).
3. To **clean the quartz paddle** use a solvent specific to the glue. Cotton swabs help keep all solvents away from the polycarbonate adapter, especially acetone. Do not use sonicator, which could introduce cracks at the junction points. The common break point is at the adapter junction and caused by lateral force on the sample rod. Frequently, breakage occurs during the sample mounting and cleaning process.

B. The **brass half-tube** is made from cartridge brass tubing with a cobalt-hardened gold plating finish. The adapter is made of glass filled polycarbonate, which should never be exposed to organic solvents, especially acetone. After the assembly is fit together, the added epoxy is allowed to cure straight in a fixture. In the case of PPMS and VersaLab platforms, brass half-tube holders come in a small or large diameter which fit samples of diameter in the range of 4 or 6mm, respectively.

    1. The **palladium standard** (pictured) is mounted with GE-7031 varnish to help withstand thermal cycles during installation tests. The only function is calibration of magnetometer at 1 Tesla and 298 K. To get the expected moment, simply multiply the mass of palladium, the applied field and the susceptibility, which is 5.25×10^{-2} emu/gram-Tesla at 298 K. The expected moment at 1 Tesla for a 0.25 gram cylindrical shape is 0.01313 emu. While

magnetization versus temperature for palladium has characteristic features, it is not a suitable thermal reference standard. Consider temperature independent diamagnetic Quantalloy or the Curie-Weiss paramagnet dysprosium oxide pellet. Even at the lowest temperatures, the contribution from impurities in the varnish is below 0.1% of the large Pd moment.

2. For **films parallel to field**, the best technique for lowest background is to simply press fit with tension so the film acts as the point source dipole. Contamination of the inner walls of the half-tube is more likely through scratches. Adding glue or varnish should prevent the sample from becoming loose. A long (10 cm) Quantalloy support piece can be wedged into place and the films attached to this surface with glue. It is more easily cleaned, disposable and will not magnetically contaminate the brass half-tube. The short (4 mm tall) Quantalloy coupon is useful for sensitive oxygen leak tests near 50 K by providing a large surface area, point source dipole and diamagnetic signal at 1 Tesla. After the quartz sample holder breaks, the brass half-tube can be made to accommodate the inverted shape. The quartz provides a magnetically clean surface area.
3. For **films perpendicular to field**, an effective technique uses **quartz braces (4096-399)** that snap into the brass half-tube. In the case of SQUID and VSM large bore coil sets, straw sample mounting is available as well and is often preferable due to the low magnetic background signal from the straw. See Straw Adapter discussion below. When using quartz braces, the length of the brace will depend on the system, with the SQUID VSM needing the longest to minimize end effect issues. The braces must come into contact with both sides of the film to hold it securely. If contact with the surface is not allowed, glue sample to one end and put second quartz brace as close as possible to minimize gap signal. Matched sets of fixed angle quartz pieces with values such as 22.5, 30, 45 and 60 degrees can provide a useful data set for verification of rotator experiments. While the press fit of metal on quartz should be good over the range of 1.8 K to 400 K, it is prudent to secure ends of quartz pieces with glue. If the sample signal is comparable or smaller than the brass half-tube, one should use a quartz paddle. If the film is deposited on the silicon substrate (100), it is easy to cut a rectangular or square piece along (110) directions. Place two pieces of samples with a film side face to face and mount the pair vertically on the quartz paddle with an appropriate fixture using varnish or one of the glues. Two pieces of films increase the signal and help them stand perpendicular to the quartz paddle.
4. **VSM powder sample holder (4096-388)** is an injection molded polypropylene (Formolene 4100N) plastic part that snaps into the

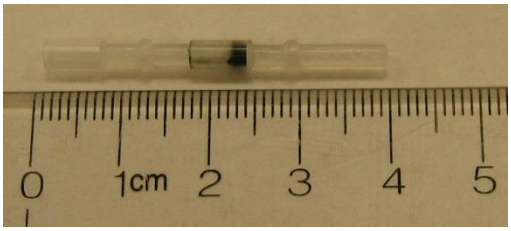
brass half-tube. The figure below shows the shapes of both parts are identical. Sample mass from 1 mg to 10 mg of powder is put into the opening. A second piece will compress the powder and seal the combination. The assembly snaps into the brass half-tube for a secure press fit. The material covers the entire temperature range from 1.8 K to 400 K. This powder holder is not recommended for liquid samples; Quantum Design does not currently have a recommendation for measuring liquids in VSM mode.

A guide to the complete experiment using the VSM powder holders is as follows:

- Inspect and clean the brass half-tube and both VSM powder holders.
- Snap rigidly into place within the brass half-tube. Allow for the appropriate sized gap as the 2 pieces are joined as will occur when the sample is later used. This is best done by measuring the overall length of the two holders, as mounted in the brass holder, using calipers. Measure the distance from end of brass half-tube to center of gap location using the mounting station. **IMPORTANT NOTE**: the measured background susceptibility of the VSM powder holders will be strongly dependent on the separation, and indeed can appear paramagnetic or diamagnetic due merely to the distribution of material along the vertical length. The polypropylene susceptibilty is diamagnetic and temperature independent, but can have positive M(H) curve if most of the material is in the negative portion of the coil response curve (see Fig. 4-3 in the VSM user manual).
- Insert sample holder and aligned rod into VSM at 300 K and nearest zero field. Use wizard to manually locate the sample position as previously measured.
- Run exact sequence to be performed when the sample is present. The sensitivity and precision of the VSM style lock-in technique allows accurate background determination, even though a center response function may not be obtainable.
- After sequence complete, remove parts from brass half-tube. Weigh both pieces, put powder inside the opening of one and securely close with the remaining piece. Weigh mass of assembly in addition to keeping track of mass change in source.
- Secure in brass half-tube and accurately measure location of gap using mounting station.
- At first, use wizard to manually locate sample position. Once field is applied, perform centering function. Repeat sequence run with the blank holder.
- The use of standard materials of similar dimensions and signal should be run for verification of the accuracy of the process. We have shown that remarkably sensitive measurements are easily obtained, especially for low field magnetization versus temperature analysis.

Three videos illustrating this process are available on the QuantumDesignUSA YouTube channel:

https://www.youtube.com/playlist?list=PLuI5kHh9kg1b2Xc1ZVB5Raq7C-NZYDEuc

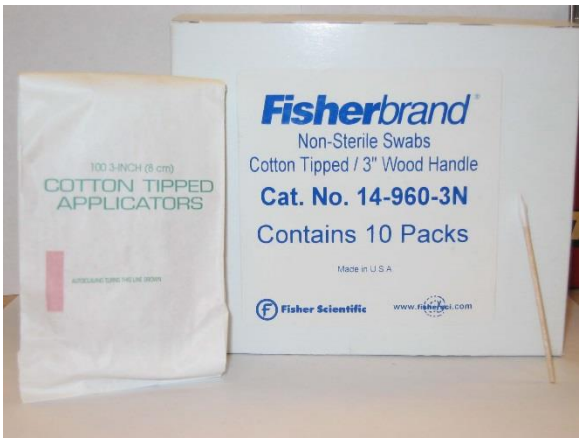


5. The **epoxy curing of powder into pellet** (pictured on left) is used for AC Susceptibility standard of Dysprosium Oxide (Dy_2O_3). Start by weighing sample mass and mixing both parts of the epoxy. Add smallest amount of thin epoxy to coat and bind the powder completely. Put in evacuation chamber to remove air pockets from mixture. Attempt quantitative transfer of mixture to Teflon mold of 4 mm diameter and 5 mm tall. The larger brass half-tube allows a diameter of 6 mm. Cure the epoxy in evacuation chamber. For some materials, placing the mold between the poles of a strong permanent magnet will preferentially align the material along a specific crystallographic axis. The epoxy pellet technique is very useful for air sensitive samples and preparation inside the glove box. Estimation of the diamagnetic contribution of the epoxy material can be obtained by preparing a sample of equivalent mass. The VSM image effect standard is a chip of pure nickel that is potted in an epoxy cylinder and is an example of a mounting technique for irregularly shaped samples. For low temperature operation, ensure sample does not slip by slightly compressing the brass half-tube before inserting the sample in it.
6. Air reactive and/or moisture sensitive samples can be stored in a sealed quartz tube that snaps into the brass half-tube. If a sample is a powder form, keep in mind that the sample might move inside the tube while vibrating.
7. The process of **cleaning brass half-tube** is best accomplished with organic solvent suitable for the dry glue. Even though the brass is gold plated, strong acidic washes should be avoided in case of scratches. While the junction is partly a press fit, the use of epoxy requires avoiding contact with cleaning solvents. Cotton swab soaked in appropriate solvent and let set against old glue until swab is dry. Apply a new soaked cotton swab to loosened glue and remove without risking the gold plating. Under the general principle of uniform mass of the holder for +/- 3 cm from the sample location, keeping a uniform gold coating is relevant to the background contribution.
8. For the VSM Large Bore option, a larger 5.5mm inner diameter **large bore brass half-tube holder (4096-630)** is provided, and can hold larger cylindrical samples.

C. **Straw Adapter (4084-814) and drinking straws (8000-001)** are for use with MPMS-3, ACMS-II, and VSM Large Bore coils only (not for use with VSM standard 6mm bore coils). For use on the PPMS-VSM, cut the straw to 83mm length, while on the MPMS-3 it should be 150mm long. The 2 part adapter works by pushing the straw over the barb of the main body (much like in older straw barb adapters from QD) and then screwing the collar down to retain the straw. Use straws for the following samples:

- Films perpendicular to field: diagonal size = 5.8mm (e.g., 4.1 x 4.1mm square film); this is best done by placing the film near the recommended sample offset (35mm for PPMS, 66mm MPMS-3) for and using two clean applicators from each end of straw to turn it sideways and jam it into the straw material so that it does not move.
- Films parallel to the field: width = 6mm; this width will ensure that the film does not slip, but note that if precise vertical alignment of the film is required, the quartz paddle may be preferred

For bulk samples or films that are slightly too small, consider the technique of slitting a ~80mm section of straw lengthwise so that it can be inserted in another straw, providing a smaller inner diameter for sample mounting. To immobilize the inner straw after it is inserted in the main straw, poke several holes with a pin near the bottom of the assembly so that the holes pass through both the outer and inner straws.



Pictures of cleaning supplies:

Specific cotton swab for brass half-tube iso-propanol (IPA), acetone, toluene, nitro-methane

1. Just a few of the **methods and materials for securing the sample** to the holder are presented. The primary goal is to keep the sample a point source dipole during the measurement. Since any glue or tape will introduce point source dipole contributions to the total magnetic moment, the material should be applied sparingly and symmetrically.

   A. The **press fit** into brass half-tube holder achieves all the ideal aspects of a secure sample mounting without the need for extra glue. One concern is a transfer of

material to the holder, but routine blank measurement checks will confirm the low-level background contribution. The technique is appropriate for samples directly in contact with the brass or through various support mechanisms.

B. The term **glue** is loosely applied to any material that will secure a sample to a support material. Generally the materials will harden over time, with the process aided by increasing temperature and keeping under vacuum. Pockets of trapped oxygen or adsorption to very high surface area materials will produce a magnetic signature around 50 K. Each material has a specific range of conditions for optimal usage; with varnish best at the lowest temperatures and Duco cement the most easily removed. Since the contents of each glue are not normally disclosed by manufacturers, it is hard to know magnetic properties. A general rule is that colorless materials are less magnetic than colored ones because dyes used in the materials tend to have magnetic signature. However, it is best for users to verify the magnetic property of the glue.

   1. The legendary **GE7031 varnish** is a vinyl phenolic adhesive (safety labeling H=1; F=4; R=3; PE=3). As the bulk material in container ages, it will become thicker. Adding iso-propanol (IPA) and/or toluene will thin solution. Cleaning is best aided with toluene. The aging and/or oxidation process will lead to a darker coloring of the solution. This tends to correlate with increased magnetic signature. The ideal solution is a light tan honey colored solution, freely flowing without addition of extra solvents.
   2. Easily obtained **Duco cement** is useful at room temperature and for securing materials of similar thermal properties, like quartz on quartz. Differing materials will force cracking in the brittle Duco cement upon cooling below 150 K. Duco may go on thick but it will dry or cure to a thin residue. A key reason for regular use is Duco solubility in acetone. Powders secured with Duco can be easily recovered by soaking in acetone.
   3. Easily obtained **Superglue** (cyanoacrylate) is a fast drying, very secure bonding method for room temperature measurements. The very thin nature allows low mass, low magnetic signature application. At the colder temperatures, it may not hold materials with different thermal properties. The solvent of choice is nitro-methane. Still readily available as a stock car fuel, it should be handled carefully. A cotton swab of nitro-methane with a thin stick to wedge the sample off the holder should work effectively. Please see MSDS for proper ventilation requirements when using these solvents.
   4. The **Zircar cement (ACA5)** is conveniently water based and supplied with the VSM-oven user kit. The primary purpose of application to over 1100 K has been verified. Used in conjunction with tight wrapping of copper foil provides a sufficiently robust design for VSM style measurements. The VSM oven sample holder is not specifically made for low temperature operation. While tests show no harm in thermal cycling to 2 K, there is always a risk of exposing a weakness in the wiring of the heater stick through this procedure. The mounting technique on a blank stick would hold to the lowest temperature. This Zircar cement is also a way to avoid using organic solvent-based materials. The water-based gradual drying process may be appropriate for incorporating powders from biological or other exotic systems. Removal of the sample usually involves a thinly wedged

stick providing lateral force on the sample. The cement cracks easily. While water or isopropanol (IPA) may aid in the removal of the excess, the main goal is to not hurt the laminate coating the patterned heater wires. No sharp metal objects, try disposable Teflon tweezers or thin flat wooden surfaces. Use a microscope to see detail of interface.

C. Tape is a simple and effective method for securing to the quartz rod. It will prevent the sample from being lost during the measurement. The background can be reasonably small if the mass is symmetrical about the sample. Keeping the tape clean from magnetic dust around the lab is the primary concern.

1. **Kapton tape** is commonly used at low temperatures and is available from Quantum Design. It retains properties over entire range of 1.8 K to 400 K. As a point source may show 10^{-6} emu ferro-magnetic signature at room temperature. Like with a straw, if the tape is evenly distributed in the background, there will be no contribution to the reported moment of the sample. To replace common drinking straws, Kapton tubing is available through the medical community and may provide flexibility in diameter selection with lowest level of impurities. Organic solvents like toluene or maybe iso-propanol (IPA) can help dissolve the glue remaining on the holder after tape is removed.
2. Thin Teflon tape can be wrapped around the quartz holder to secure the sample location without use of glue. However, the technique tends to produce a significant paramagnetic oxygen peak around 50 K. As a precaution, add a heat and purge step to the sequence. The Teflon tape can cover the full temperature range of the instrument, but 350 K is usually sufficient for this purpose. When Teflon becomes a point source dipole like when wrapping the sample, a more significant ferro-magnetic contribution is measured. Each batch should be tested for impurities.
3. The standard Parafilm roll and various wax materials can be used to secure the sample. Watch maximum exposure temperatures of the wax. These types of materials are typically low moment background and useful with air-sensitive samples or when recoverability is desired.

3. **Custom** mounting techniques for classes of samples:

Note that following techniques may not apply to all platforms.

A. The hydrostatic **pressure cells** by various vendors require securing the sample for the VSM style measurements. The GE7031 varnish has proven effective for room temperature analysis of dysprosium oxide pellet pieces.

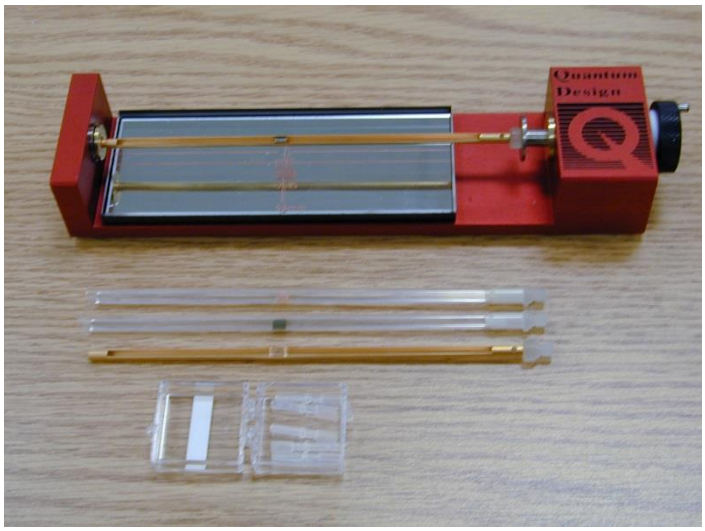
B. Components like **quartz braces** need to be longer for the SQUID-VSM as compared to the PPMS VSM due to the larger axial dimension of the second order gradiometer.

C. **Gelatin and polycarbonate capsules are not recommended in VSM measurements**. Due to challenge in securing both sides of the capsule and immobilizing the contents under the high accelerations of the VSM environment, we recommend using the powder sample holders (4096-388) instead.

D. The **quartz tube for MPMS-3 (4500-643)** is useful to mount a cylindrical sample as well as a bulk sample when the low background moment is important.

E. **Clear plastic materials** such as polycarbonate, polypropylene, Delrin (acetal copolymer), and Kel-F (PCTFE) are good candidates for low background moment holders due to their nonmagnetic material characteristics and cryogenic compatibility. Avoid using colored plastic materials, since the dyes used to color the plastics are generally magnetic. Specify "virgin" and/or "natural" to ensure this. Keep in mind that even though these plastic materials are good low moment candidates, manufacturing environment might introduce magnetic contaminants to these materials. Users should test these materials for the level of magnetic background.

Please e-mail requests and suggestions to apps@qdusa.com , and contact your local Quantum Design representative for sales inquiries.



Quantum Design supplied sample holders and MPMS 3 mounting station.

Quantum Design supplied sample holders and PPMS-VSM mounting station.

Securing agents from the left: 2-part epoxy; Duco cement; Zircar Cement; GE7031 Varnish; fast curing Superglue; slower curing Superglue; Kapton tape.

Information for ordering parts

part description	QD part number	
	PPMS	MPMS 3
quartz paddle sample holder	4096-392	4500-604
brass half-tube sample holder	4096-391	4500-608
quartz rod sample brace	4096-399	
powder sample holders (50 pairs)	4096-388	
VSM large bore brass half-tube	4096-630	
straw adapter	4084-814	
drinking straws (box of 500)	8000-001	
Zircar high temperature cement	ACA5	
Kapton tape: ¼" wide ½" wide	ATK1-025 ATK1-050	
MPMS 3 quartz tube sample holder		4500-643