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NOTES

A Simple Multinuclear NMR Thermometer

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For many years we have been performing multinuclear kinetic NMR measurements and for the purpose of temperature measurement we currently utilize a simple, accurate Pt-resistance thermometer assembly. The method involves a substitution technique, possible nowadays because of the good stability of commercial NMR thermostating units.

The thermometer assembly is made of a temperature sensor contained in an NMR tube (Fig. 1) and connected to a readout device by an insulated cable. The temperature sensor consists of a 2-mm-diameter Pt 100-Ω resistor (J) at the end of an alumina rod (H). The sensor head (B) supports the connection plug (A) and can be fixed to tubes of either 5 or 10 mm external diameter by means of O-rings (C). The weight of the temperature sensor, 5 g only, permits rotation with the gas turbine. The resistance measurement is made with a digital ohmmeter (for example, Dana 4600 multimeter, 4½ digits). After subtraction of the small resistance of the connecting wire (typically 0.5 Ω), the resistance is converted to temperature by means of DIN 43760 tables. If one uses devices giving the temperature directly (for example, Hewlett-Packard 2802 A), account must be taken of the diversity of temperature coefficients of resistors of different origins.

To measure the temperature the sensor is placed in a tube of the same diameter as that of the sample. The liquid surrounding the sensor should have the same physical properties as those of the sample. The temperature measuring tube is placed in the probe head and is rotated if the following NMR measurement is to be done with rotation. After temperature equilibration (less than 3 min for 5-mm and 10 min for 10-mm tubes) the rotation, if used, is stopped, the sensor connected to the readout device, and the reading made within the 5 sec following the stoppage of rotation. The tube is replaced by the sample tube, the NMR measurement made, and the temperature rechecked at the end for higher accuracy.

No changes of the observed temperatures attributable to tube nonuniformity (Wilmad Glass Co.) have been detected (*1*, *2*). However, in nonspinning samples the temperature was found to depend (±1 K) on its angular position; this is attributed to poor axial symmetry of the tube and probe-head assembly. Rotation of the sample eliminates this problem and gives excellent reproducibility (±0.2 K).

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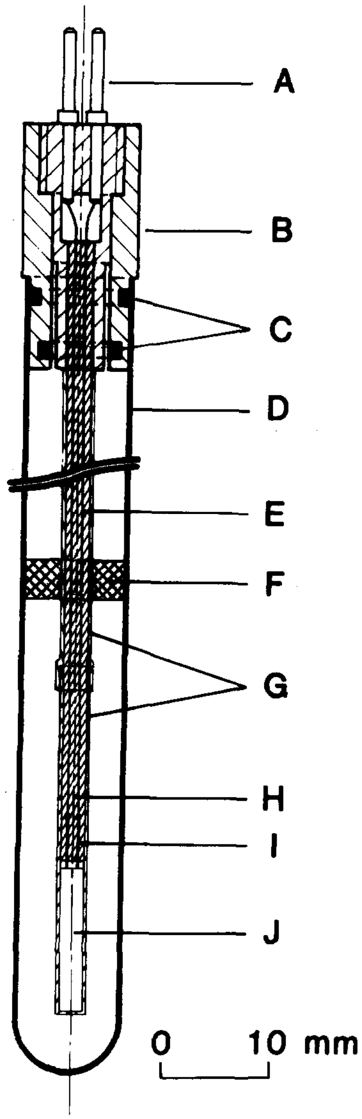

FIG. 1. Pt-resistor temperature sensor in a 10-mm-diameter NMR tube. (A) Connecting plug, (B) sensor head (Teflon), (C) O-rings, (D) 10-mm NMR tube, (E) Cu wires, (F) centering ring (Teflon), (G) thermoretractable protection sheath, (H) alumina rod with two holes, (I) connection wires, (J) Pt 100-Ω resistor (W 60150 Degussa Switzerland AG, Zurich).

It has been established that introduction of the sensor into the liquid of the temperature-measuring tube does not produce any detectable temperature changes in the liquid from, for example, modification of convection currents or loss of heat along the sensor length.

For the Bruker WP-60 spectrometer the difference between the temperature of a nonspinning sample and that of a spinning sample is at maximum 1 K from 150 to 460 K for 5-mm tubes, and from 150 to 370 K for 10-mm tubes. For the latter, above 370 K, the difference increases considerably to reach 5 K at 460 K. It is therefore recommended that the temperature-measuring tube be rotated before measurements. The rotation speed (15 to 60 Hz) does not affect the measured values. The magnitude of the vertical temperature gradients at the level of the NMR measuring coil depends on the difference between the experimental and ambient temperatures. In the 5-mm proton NMR probe head, the vertical gradients were ± 0.4 K cm^{-1} at 180 and 400 K.

In contrast to the magnetic field H_0 and the radiofrequency pulsed field H_1, the high-power radiofrequency decoupling field H_2 can cause large changes of the sample temperature, up to 50 K (*3*). Therefore, for measurements using H_2, it is essential that the liquid surrounding the temperature sensor be identical to the sample to be measured. Moreover H_2 must remain on during the thermostating of the temperature tube (like the sample tube) and turned off just before the reading so as not to perturb it.

In proton NMR the temperature is usually determined by means of two thermometric solutions: methanol and ethylene glycol. Numerous calibration equations have been proposed relating the chemical shift differences $\Delta\delta$ (ppm), and the temperature for these compounds (*4*). Our multinuclear thermometer yields the following equations:

$$T\ (\mathrm{K})\ (\mathrm{methanol}) = 409.0 - 36.54\ \Delta\delta - 21.85\ (\Delta\delta)^2, \quad \text{between 178 and 330 K,}$$

$$T\ (\mathrm{K})\ (\mathrm{ethylene\ glycol}) = 466.5 - 102.00\ \Delta\delta, \quad \text{between 273 and 416 K.}$$

These results agree to within ± 0.5 K with those obtained by Van Geet ((*5*); see also (*1*)).

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