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Berkeley, California

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ACCURATE NMR TEMPERATURE MEASUREMENTS

Richard Duerst and Andre Merbach

August, 1965

Accurate NMR Temperature Measurements

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In order to determine thermodynamic data by nuclear magnetic resonance it is highly desirable to measure the temperature of the sample to within a few tenths of a centigrade degree. A technique for this has been developed which gives consistent results to within ± 0.2 C°.

A capillary filled with a mixture of water, methanol,¹ and hydrochloric acid exhibits two sharp resonance signals. The chemical shift between these two signals is strongly, and approximately linearly dependent upon the temperature of the sample. It can therefore be used as an excellent indication of the sample temperature. In order to calibrate this chemical shift as a function of temperature, a capillary, one millimeter in diameter, was fastened to the inside of an NMR tube filled with toluene. In addition, a previously calibrated thermocouple in a second capillary was placed in the NMR tube. The capillary

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¹ A methanol sample is currently used to calibrate NMR variable temperature equipment to a precision of ± 1 °C (Varian A-60 Temperature Accessory Manual,

containing the thermocouple was supported at the top by a stationary arm, and hence did not rotate with the sample tube.

Large vertical temperature gradients inside the NMR tube often exist when the sample is being heated or cooled. In an A-60 variable temperature probe operating at 60°C this may be as much as 0.1°C per millimeter. Therefore it was of the utmost importance that the sample temperature be measured at the center of the receiver coil. This position was determined to within ± 0.25 millimeters by integrating spectra of a spherical water sample at various positions in the probe.

The chemical shifts between the two resonance signals in the mixture were determined by the standard sideband technique. As stated above, an approximately linear relationship was found to exist between the chemical shift and the temperature. For a mixture of 51.8% water, 48.1% methanol, and 0.1% hydrochloric acid by weight, the observed approximate relationship is:

$$T = 160.00 - 90.50 S \quad (1)$$

where T is given in degrees Centigrade, and S is given in ppm. In Fig. 1 the deviation between the observed temperature and the temperature calculated using equation 1 is plotted as a function of the observed chemical shift. The figure covers the range between -40°C and 80°C. As can be seen the scatter of points is less than $\pm 0.2^\circ\text{C}$.

Since the temperature dependence of the chemical shift is a sensitive function of the concentration of the sample, care must be taken during the sealing of the capillary to avoid alteration of the concentration. The reproducibility of the results from several capillaries made from a single solution was checked by measuring the NMR

signal from two capillaries enclosed in one sample tube. Line widths from such a sample were less than 0.3 cps which is similar to the line width of a single capillary, thus indicating that the sample concentrations were not substantially altered.

An accuracy limit is imposed on the calibration of the capillary solution by the broadening of the spectral lines caused by the introduction of the thermocouple in the region of the receiver coil. When a temperature calibrated capillary is in turn used for consequent temperature measurements, the precision is increased to $\pm 0.1^{\circ}\text{C}$ because of the improved line resolution. The method allows one to measure the sample temperature at that region in the sample which is being investigated by the NMR technique. It is also independent of the bulk susceptibility of the sample, of the spinning rate, and of the flow rate of the nitrogen used to control the sample temperature.

The above mentioned mixture gives satisfactory results over the range -25°C to 90°C . Below -25°C the lines become too broad for accurate shift measurements. However, mixtures could surely be found applicable to other temperature regions.

We are indebted to Dr. Otto Redlich and Dr. C. H. Sederholm for their interest in this problem. This research was supported by the U.S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

Figure Caption

Figure 1. Deviation between the observed temperature and the temperature T calculated as a function of the observed chemical shift S .

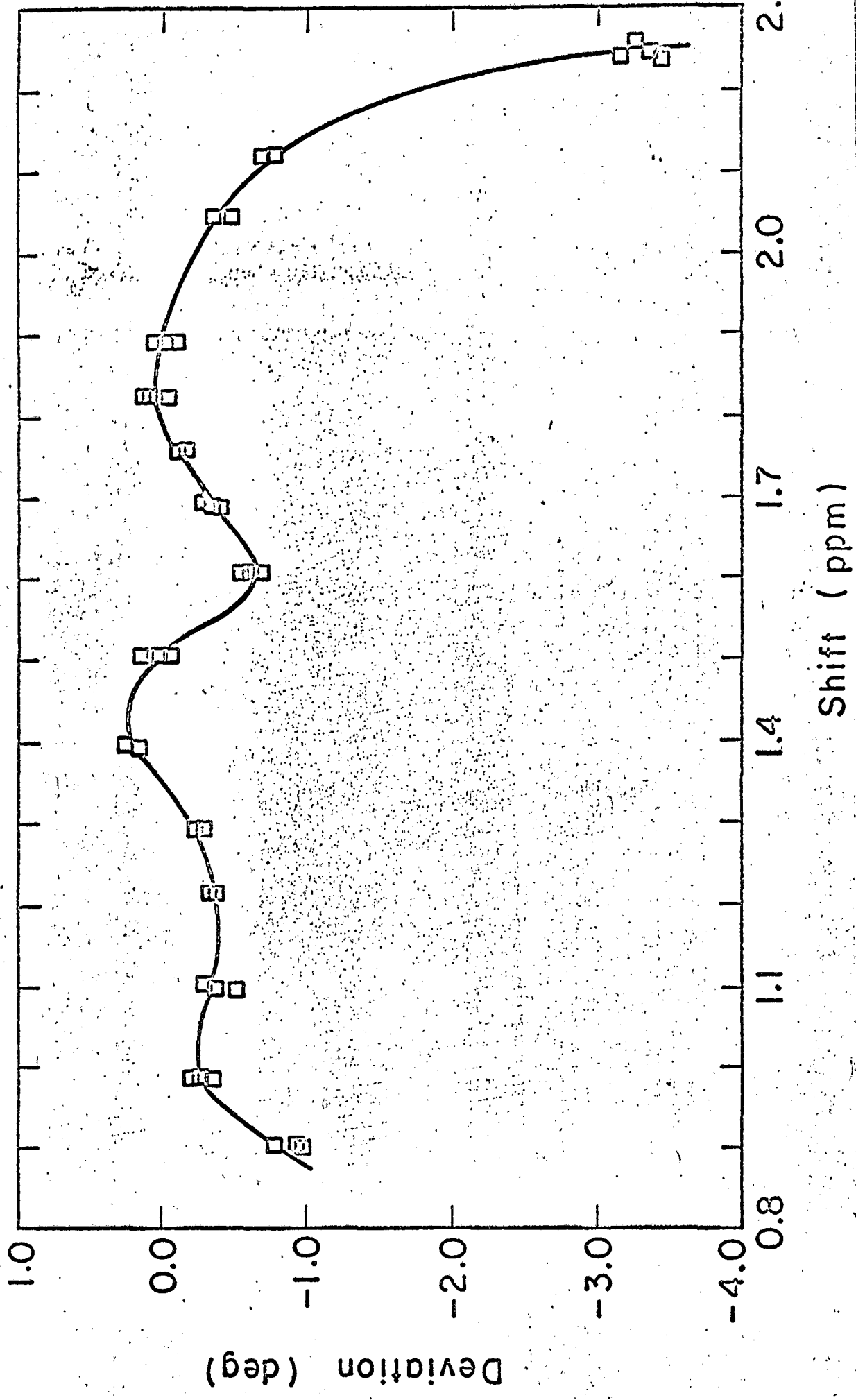


Fig. 1

