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A DISK-CYLINDER METHOD FOR USING NMR
TO MEASURE MAGNETIC SUSCEPTIBILITY

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ABSTRACT

The sphere-cylinder method of using nuclear magnetic resonance (NMR) to measure the magnetic susceptibility of diamagnetic and paramagnetic materials has been generalized to the disk-cylinder method. A two-fold increase in sensitivity was obtained. Accuracies of 0.1% of the diamagnetism of water should be readily obtainable.

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INTRODUCTION

Magnetic susceptibility is an important property of materials. There are basically three types of magnetic character: ferromagnetism, paramagnetism, and diamagnetism. Ferromagnetism, of course, is the basis for common magnets. However, this paper will be limited to a discussion of paramagnetism and diamagnetism and their measurement. They provide insight into many fields of research, including the characterization of metal ions which have an unpaired electron in many inorganic and biological systems and the characterization of aromaticity in organic molecules.¹ The paramagnetism of O_2 provides the basis for many oxygen gas analyzers.

For gases and liquids composed of atoms and molecules with no unpaired electrons, the magnetic susceptibility is always diamagnetic. This means that the magnetic moment induced by a magnetic field will be anti-parallel to the field, and the energy (at constant temperature) of the sample will be higher than in the absence of the field. The "diamagnetic susceptibility" is actually a sum of nearly cancelling diamagnetic and paramagnetic contributions.²

If an unpaired electron is present, the magnetic susceptibility will be dominated by another paramagnetic contribution from the alignment of the magnetic moment due to electron spin. This contribution will be temperature dependent, and the theory describing this dependence is similar to that describing the properties of polar dielectrics.

The methods of measuring the magnetic susceptibility of weakly magnetic systems can be divided into three basic types. The first type measures the force exerted on the sample which is proportional to $F = H \cdot \partial H / \partial x$, where H is the magnetic field, $\partial H / \partial x$ is the field gradient, and χ is either the mass or volume susceptibility depending on the actual method. The Gouy and Faraday balances are of this type. The second type measures the response from a coil in the magnetic field when the sample is placed next to it. The sample may be stationary or oscillating and the field may be either constant or time dependent, depending on the method.

Several methods of each of the first two types have been developed which have an accuracy of 0.1 to 1% of the magnetic susceptibility of diamagnetic liquids and powders. The classical methods have been discussed by Selwood.³ Recent developments have been reviewed by Mulay and Mulay.⁴ However, all these methods suffer from the limitation that a special instrument, often quite complicated, is required.

For these reasons, the use of nuclear magnetic resonance (NMR) to measure magnetic susceptibility has been developed.⁵ This third type uses standard NMR spectrometers which are now available virtually everywhere. The method is based on the fact that the NMR resonance frequency of a nucleus (usually a proton) depends on the magnitude of the applied magnetic field and therefore on the magnetic susceptibility of the surrounding medium. This type, properly designed, can be as accurate as the best methods of the first two types.

Conceptually, the simplest method of the NMR type is the concentric cylinder method.⁶ A standard NMR tube is filled with the liquid of interest containing a small amount of dissolved reference material (e.g. $(\text{CH}_3)_4\text{Si}$ or $(\text{CH}_3)_3\text{COH}$). A small capillary containing the reference material is placed inside the NMR tube. The difference in the CH_3 resonance frequencies is related to the difference in χ_v between the two solutions.

Unfortunately, this method suffers from a neglect of solvent effects associated with chemical shift. Concentration effects related to the microscopic structure of the liquid can give contributions to the splitting as large as those from the bulk susceptibility.⁷ Furthermore, the method cannot be applied to powders.

For these reasons, the sphere-cylinder method⁸ has become the most popular method of the NMR type. It is based on the fact that the magnetic field in a magnetic medium depends on the shape of the medium. All microscopic contributions to the chemical shift cancel. The method can be applied to powders. Finally, commercially available sample tubes costing about \$10 can be used.

This report concerns an attempt to develop a method 2-3 times more sensitive than the sphere-cylinder method. Basically, it involves replacing the sphere-cylinder configuration with a disk-cylinder configuration. The equations describing this improvement are described below. The first attempt at fabricating and using this method are also described.

CALCULATION OF THE SPLITTING

As was mentioned in the introduction, the NMR resonance frequency is proportional to the magnetic field in the medium times a local field correction. In the derivation below, the local field correction is omitted because it produces only a multiplicative factor for the splittings which is essentially equal to one. The final result for the cylinder-disk configuration has been reported previously.⁹

The various magnetic fields involved in the disk-cylinder method are shown in Figure 1. All fields shown are equal to within a few parts per million. In practice, NMR spectra are obtained either by using a fixed radio frequency and varying the magnetic field slightly or vice versa. Chemical shifts are often measured in terms of ppm of applied magnetic field. Likewise, the observed splittings due to the slight difference in H_c and H_d will be on the order of a ppm.

The above discussion can be quantified by the following considerations. The general equation for relating the field, H_2 , along the i th axis of an ellipsoid of permeability μ_2 to the incident field, H_1 , in the surrounding medium of permeability μ_1 is given by

$$H_2 = \frac{\mu_1}{\mu_1 + (\mu_2 - \mu_1)S_i} H_1 \quad (1)$$

where the volume susceptibility is related to the permeability by

$$\chi_v = (\mu - 1) / 4\pi \quad (2)$$

and $S_{\perp}$ is the appropriate shape factor, commonly known as a demagnetizing factor.¹⁰ A few values for prolate and oblate ellipsoids are given in Table 1. The value of $S_{\perp}$ parallel and perpendicular to the symmetry axis is given by $S_{\parallel}$ and $S_{\perp}$, respectively.

The difference in the chemical shift, δ , between the reference material in the cylindrical and disk portion of the capillary is given by

$$\delta_c - \delta_d = \frac{H_c - H_d}{H_0} = \frac{H_1}{H_d} - \frac{H_1}{H_c} \quad (3)$$

where

$$H_c = \frac{2\mu_1}{\mu_1 + \mu_2} H_1 \quad (4)$$

and

$$H_d = \frac{\mu_1}{\mu_1 + (\mu_2 - \mu_1)S_d} H_1 \quad (5)$$

where S_d is $S_{\perp}$ for the oblate ellipsoid (disk).

Substituting Eqs. (4) and (5) into Eq. (3), we have

$$\delta_c - \delta_d = \frac{\mu_1 + \mu_2}{2\mu_1} - \frac{\mu_1 + (\mu_2 - \mu_1)S_d}{\mu_1} \quad (6a)$$

$$= (\mu_2 - \mu_1) (1 - 2S_d) / 2\mu_1 \quad (6b)$$

Now substituting Eq. (2) for the permeabilities,

$$\delta_c - \delta_d = 2\pi (\chi_2 - \chi_1) (1 - 2S_d), \quad (7)$$

where χ_2 and χ_1 are the volume susceptibilities of the material inside and outside the capillary tube. In the limiting case that the disk has a 1:1 axial ratio (i.e., a sphere), $S_d = 1/3$ and

$$\begin{aligned} \delta_c - \delta_s &= \frac{2\pi}{3} (\chi_2 - \chi_1) \\ &= 2.094 (\chi_2 - \chi_1) \end{aligned} \quad (8)$$

EXPERIMENTAL

Sample Tube

Several designs were considered to implement the configuration shown in Figure 1. It should first be noted that the outside material with susceptibility χ_1 need not be the unknown material. It could be part of the NMR tube or an insert made from some non-magnetic, chemically inert material. In this case, the chemical shift splitting could be measured using a resonance of the unknown material if one is available. This method could be implemented with less than 0.1 cm^3 of sample. However, it would not work for powders and possibly not for paramagnetic materials because of line broadening. It would be a useful design for studies at high pressure.

It was decided, therefore, to construct a capillary tube with the cylinder-disk shape. The tube eventually used in the measurements is shown in Figure 2. It was selected from six tubes made. The cylindrical region extends on both sides of the disk region for two reasons. In previous work, the volume of the sphere was much greater than the volume of the cylinder. It was difficult to align the tube so that both resonances were of reasonable intensity. It was thought that having the cylinder on both sides might help alleviate this problem. Moreover, it was thought that having the cylinder on both sides of the disk might make the tube easier to make.

The axial ratio of the disk was determined by measurements in Figure 2. The axial ratio obtained was $r_1/r_2 = 0.333$. This corresponds to $S_d = 0.182$. Substituting this value into Eq. (7), a prediction is obtained for the splitting:

$$\delta_c - \delta_d = 4.00 (x_2 - x_1) \quad (9)$$

For best results, however, the splitting should be calculated with substances of known susceptibility.

Measurements

A set of three liquids was chosen to obtain values of $x_2 - x_1$ spanning a large range. The capillary tube was filled with acetone and inserted into a teflon plug which fitted snugly into the NMR tube. The NMR tube was filled with either chloroform or benzene. All liquids were reagent or spectroscopic grade but were not degassed before use. The presence of dissolved oxygen could introduce errors of a percent or so. If air bubbles were trapped during the filling of the capillary, they could be removed by degassing.

The splittings were measured at room temperature in a 60 MHz spectrometer. The spectrometer was locked to either the chloroform or benzene signal. A sample of the observed spectrum of the acetone is shown in Figure 3. The observed splittings were very reproducible for a given tuning of the instrument. However, slight changes in the spectrum were observed upon retuning.

The spectrum shown was obtained after tuning on the acetone signal from one of the two cylindrical regions. Apparently, the field was quite inhomogenous in the other cylindrical region and it was severely broadened. Two distinct and sharp cylinder resonances split by about 5 Hz were observed once. In retrospect, probably the best procedure would be to tune the spectrometer on the signal from the disk region. If two cylinder resonances are obtained, the disk-cylinder splitting would be determined most accurately from the average of the two. The broadness of the disk signal probably was caused in part by a deviation of the disk from true ellipsoidal shape.

The splitting obtained for acetone surrounded by benzene and chloroform are shown in Figure 4. As predicted, the splitting for the disk-cylinder combination (solid line) is greater than for the sphere-cylinder combination (dashed line). Unfortunately, the scatter of the points from the line is somewhat greater than desired. This could be related to the tuning problems mentioned earlier.

DISCUSSION

The use of disk-cylinder combination in place of the sphere-cylinder configuration could result in a 2-3 fold increase in the sensitivity of the NMR method. The accuracy of the method could be improved by producing the capillary under more controlled conditions where a true ellipsoidal shape could be obtained.

It is doubtful that it is necessary or even desirable to have a cylindrical region on both sides of the disk. The relative intensity for the disk and one cylinder is adequate. The beneficial aspects of having two cylindrical regions may be overshadowed by the extra distortion resulting in the disk. Also, the distortion would be less severe if the diameter of the cylinder were half as large.

It appears that with a relatively small amount of development, the disk-cylinder method could easily attain an accuracy of 0.1% of the diamagnetism of water. At present, the limitation is due to imperfections in reference capillary shape. The method could be used on samples as small as 0.1 cm^3 . In addition, most commercial NMR spectrometers are fitted with temperature control equipment allowing measurements over a wide temperature range. The method also appears to be well suited for measurements at high pressure with a properly designed cell. Many other methods require a cell background correction which becomes dominant for large cell-small sample determinations.

There are several applications of this technique for projects currently in progress in the Chemical Engineering Division. Both oil shale and coal contain small amounts of iron. X-ray diffraction is not always sensitive to the state of the iron. Magnetic susceptibility would be sensitive to the bulk properties of iron, which undoubtedly provides a major contribution to the susceptibility. Magnetic susceptibility might also be useful in studying the chemistry of transition and inner-transition metals under extreme conditions of temperature and pressure relevant to geothermal energy and storage of nuclear wastes.

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Table 1. Values of $S_{\parallel}$ for various axial ratios.

$r_{\parallel}/r_{\perp}$	Shape	$S_{\parallel}$	$S_{\perp}$
0	plate	1.000	0.000
1/3		0.634	0.182
1/2	↑	0.528	0.236
2/3	oblate	0.446	0.277
1	sphere	0.333	0.333
3/2	prolate	0.232	0.384
2	↓	0.174	0.413
3		0.108	0.446
∞	cylinder	0.000	0.500

Figure 1. Experimental configuration for measuring magnetic susceptibility by NMR.

Figure 2. Capillary cell used in this study.

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Figure 3. Splitting of the acetone NMR signal into two peaks.

Fig. 4. Splitting of the disk and cylinder vs. the magnetic susceptibility of the liquid surrounding the capillary tube. The points correspond to acetone (●, δ assumed to be zero), benzene (■), and chloroform (▲). The solid line represents Eq. (9) and the dashed line represents Eq. (8).