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16. Abstract

This study involves the development of ^{13}C nuclear resonance as an on-line detector for liquid chromatography (LC-^{13}C NMR) for the chemical characterization of aviation fuels. The initial focus of this study was the development of a high sensitivity flow ^{13}C NMR probe. Since ^{13}C NMR sensitivity is of paramount concern, considerable effort during the first year was directed at new NMR probe designs. In particular, various toroid coil designs were examined. In addition, corresponding shim coils for correcting the main magnetic field (B_0) homogeneity were examined. Based on these initial probe design studies, an LC-^{13}C NMR probe was built and flow ^{13}C NMR data was obtained for a limited number of samples.

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SUMMARY

The first year of this study focused attention on ways of improving sensitivity in the LC-^{13}C NMR experiment. In particular, various studies explored the development of a toroid-shaped sample and coil system applicable to the LC-^{13}C NMR approach. Although the toroid cell provides a dramatic improvement in signal-to-noise (S/N) in comparison with the more common Helmholtz design, main magnetic field inhomogeneity (B_0) remains as a major problem in the use of this detector. Therefore, considerable effort was directed at developing shim coils which would correct this B_0 inhomogeneity problem. Although considerable improvements were obtained, a linewidth of only ~10 Hz was achieved for ^{1}H NMR at 200 MHz for a torus volume of (~0.25 ml). The corresponding linewidth for ^{13}C NMR would still be marginally acceptable (~3 Hz) for a 0.25 ml volume. However, a flow ^{13}C NMR probe was constructed using conventional probe technology (Helmholtz coil) in order to initiate flow ^{13}C NMR studies during the first phase of this study. Finally, flow ^{13}C NMR spectra were obtained on several typical fuel components utilizing this conventional probe design.

INTRODUCTION

In 1978, Watanabe reported results for direct coupling of high performance liquid chromatography to ^{1}H nuclear magnetic resonance utilizing a stop-flow mode[1]. The first continuous flow LC-^{1}H NMR experiments were reported in 1979[2]. In the last few years, several papers have been published which clearly indicate the evolution of a new analytical tool (LC-^{1}H NMR) for rapid structural elucidation of components present in complex mixtures[3-15]. Initial LC-^{1}H NMR studies were hampered by signal-to-noise (S/N) limitations of the electromagnetic based NMR systems. However, more recent studies employing high field superconducting NMR magnets (e.g., 4.7-9.4T) have amply demonstrated that sensitivity considerations are greatly alleviated with these new "state-of-the-art" NMR systems[9-15]. Presently, continuous flow detection limits for a single compound in a complex mixture is 10-20 μg for molecules having molecular weights of 100-300 daltons (200 MHz ^{1}H NMR). In addition, the superconducting NMR systems have dramatically increased the number of resolution elements in a given LC-NMR spectral profile. This is not only because of increased chemical shift dispersion (e.g., 100 MHz vs. 400 MHz ^{1}H NMR spectra), but better main magnetic field (B_0) homogeneity of the superconducting magnet and technical improvements in flow cell design.

A major problem originally envisioned for the LC-^{1}H NMR approach was the limited choices of chromatographically and/or NMR acceptable solvent systems which could be employed without extensive background signals in the ^{1}H NMR spectra. This problem has been largely overcome by: 1) the use of deuterated solvents, chlorinated and/or fluorinated solvents, and 2) the use of solvent suppression homodecoupling sequences for hydrogen containing solvents[11].

The progression to smaller analytical scale columns and lower injection volumes (i.e., 25-100 ml) has dramatically decreased the total solvent (~20-30 ml) necessary for a given LC-NMR experiment. This has helped alleviate costs when relatively expensive deuterated solvents must be employed. Demonstration of LC-^{1}H NMR as a quantitative analytical tool was first reported in 1982[10]. Methods for obtaining average molecular properties (e.g., average molecular weights) for a given liquid chromataographic fraction (e.g., monocyclic aromatic, dicyclic aromatics, etc.) of fuels was also reported in 1982[12]. These NMR derived molecular parameters are very useful for predicting and understanding physical properties (e.g., smoke points and frreezing points) of various fuels[13]. The results of the latter study were in excellent agreement with GC-MS data obtained in an independent laboratory.

All common liquid chromatographic separation modes including size-exclusion[9] and reversed-phase[11] have been demonstrated with the LC-^{1}H NMR technique. To date, applications of the LC-^{1}H NMR approach have been demonstrated for fuel samples[3,8,9,13], samples of biological interest[6,11], and organic chemistry reaction mixture analysis[14]. However, widespread application of this technique for characterization of complex mixtures has been limited by the expense of the instrumentation and access.

Development of ^{13}C NMR as a detector for liquid chromatography (LC-^{13}C NMR) has not been reported; however, flow ^{13}C NMR studies have recently been reported[15]. A major impediment in the use of the ^{13}C nuclide is the much lower sensitivity to NMR observation. This is because of the lower natural abundance of ^{13}C (1.11%) and lower nuclear moment in comparison with the ^{1}H nuclide. However, it should be noted that for studies of aviation fuels, sample size is not a limitation. Thus, the chromatographic column size and/or sample injection volume can be increased.

EXPERIMENTAL METHODS

The toroid coil has potential advantages for both static and flowing NMR studies in superconducting solenoids[16-20] . For example, we have reported data indicating the toroid coil has a (S/N) advantages of 4-6 in comparison with the more commonly employed Helmholtz coil[18]. Also NQR results reported by Zussman[19] suggested a factor of 2 improvement for the toroid in comparison with a solenoid configuration at 4.6 MHz. In addition, the more efficient and linear $(r)^{-1}$ dependence for the B_1 field generated in a toroid coil dramatically reduces 90° pulse lengths[17-19]. Unfortunately, the poor Bo homogeneity usually encountered for the torus region has limited the utility of this detector. Furthermore, most commercial shim coil systems are specifically designed for spherical or cylindrical sample volumes. For example, commercial shim systems provide an improvement of only 10-20% for typical toroid geometries[17]. To improve the Bo homogeneity specifically for a given torus region, we have constructed various experimental shim coil systems. An improved shim coil system for the toroid-shaped sample volumes is described (vide infra).

The present design is based on the classic Anderson shim coil approach[21]. Two types of the Anderson shims are appropriate for the toroid-shaped sample volume. One of them is the quadratic shim which consist of four loops above and below the toroid sample.

$$\frac{\alpha^2 B_z}{\alpha z^2} = - \frac{2 \alpha^2 B_z}{\alpha x^2} = - \frac{2 \alpha^2 B_z}{\alpha y^2} \tag{1}$$

The configuration is sketched in Figure 1a. The quadratic gradient can be produced with current loops centered on the Z which we designate as a "C"
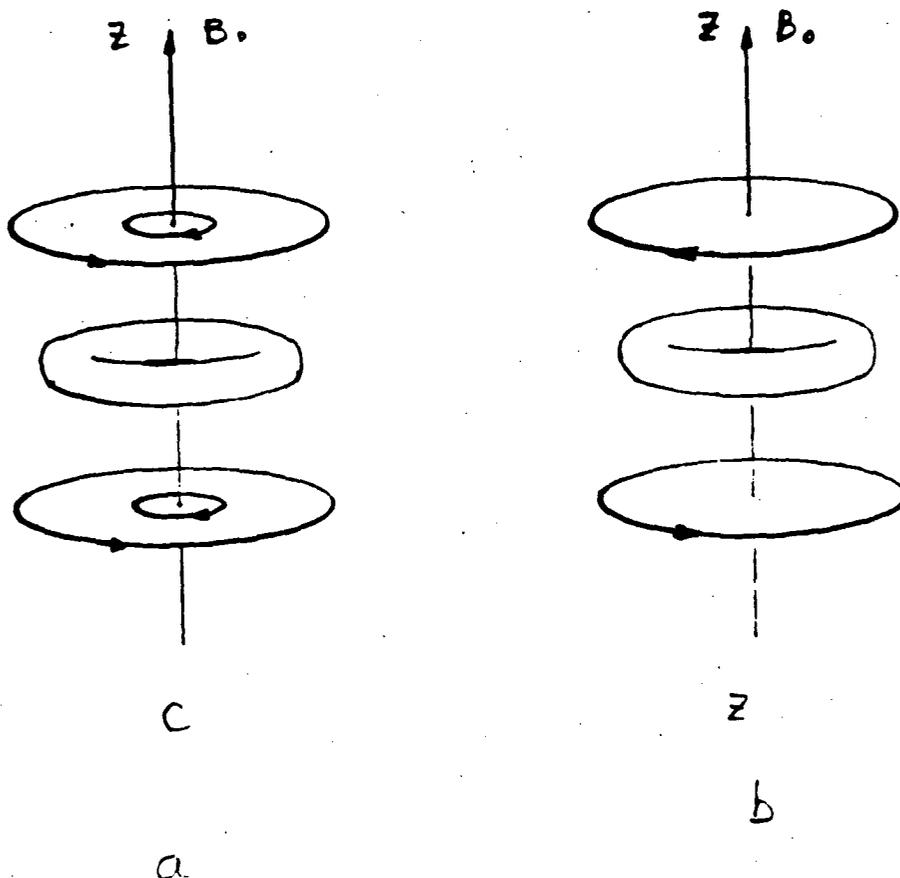
Figure 1. Sketch of four current loops for the gradient shim (1a) and opposed linear gradients (1b), respectively. The torus sample volume is also indicated for reference purposes.

shim. Another is the linear shim which consists of two opposed current loops. This configuration is sketched in Figure 1b. The linear field gradient is produced by these two current loops centered on the Z axis and is similar to a coil system reported by Cooper[20]. In this coil configuration (designated "Z"), there exists a region in the plane perpendicular to the axis between these opposed coils where the field is homogeneous[20].

The structure of the ^{1}H toroid probe (Probe A) with the toroid-shaped sample and shim systems is illustrated in Figure 2. There are three groups of shim "C" coils (C_1, C_2, and C_3) and two groups of shim "Z" coils. The group of C_1 shims, consist of four planar coils, however, the groups of shims C_2, C_3, Z_1 and Z_2 consist of cylindrical coils. The coils are mounted on an outer glass tube (~30 mm) and held in plane with "super glue." The homogeneity of the field within the toroid-shaped sample volume is improved by adjusting the current in these coils.

In an attempt to improve the homogeneity of the field within a specific portion of the toroid-shaped volume a point shim system was also utilized. The structure of this shims is illustrated in Figure 3. There are eight groups of shims P_1, P_2 .....P_8. Each group is a "Z" shim consisting of two coils placed above and below the probe.

The method for adjusting the position of this probe in the super-conducting solenoid is shown in Figure 4. The support C is made from plastic. The probe position can be changed (screws a and b) along two axes of freedom in the plane perpendicular to the Z axis. The photographs for the completed probe is shown in Figure 5.

A second ^{13}C/^{1}H probe (Probe B) was built using a conventional flow LC-^{1}H NMR probe design similar to a design previously published[8-9]. Pictures of this probe are presented in Figures 7 and 8. This probe consists of a tilted
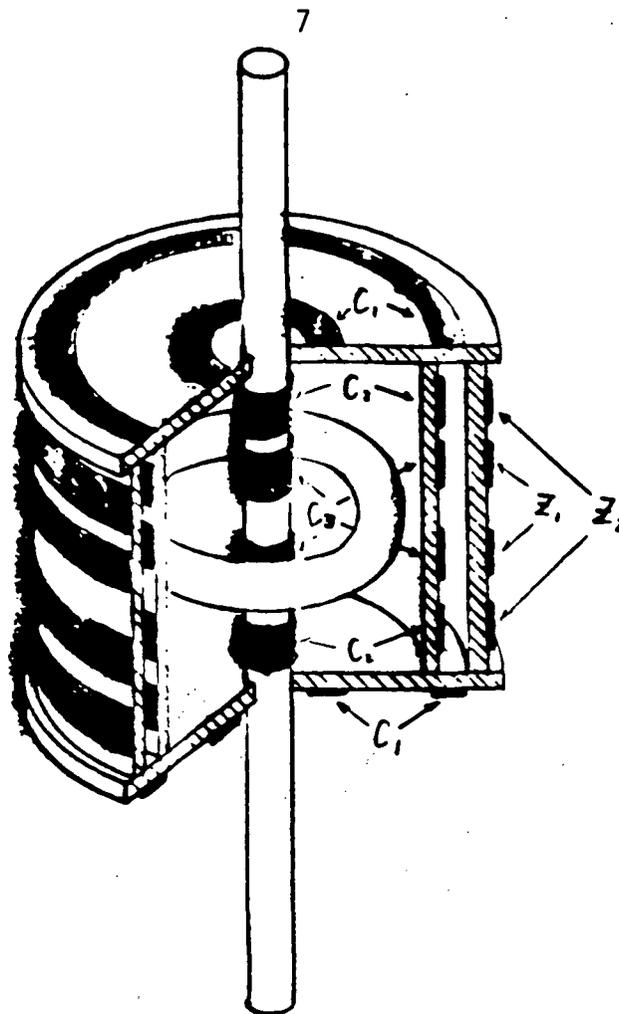
Figure 2. Sketch of toroid shim system. The inner two pairs of C_2 and C_3 shims were wound on a rod (d=4 mm) symmetrically placed 3.5 and 8.5 mm, respectively, above and below the torus plane. The outer two pairs of C_2C_3 shims were wound on a glass cylinder (d=22 mm) at the same position as indicated for the inner pairs of C_2 and C_3 shims. The outer Z_1 and Z_2 shims were wound on a 30 mm glass cylinder in similar fashion. The planar shims C_1 are 14 mm above and below the torus plane. The glass toroid sample container has a volume ($CHCl_3$) of 225 µl with an inner and outer diameter of 6 and 7.5 mm, respectively. The receiving and transmitting coil was wound about this glass container (not indicated in sketch).
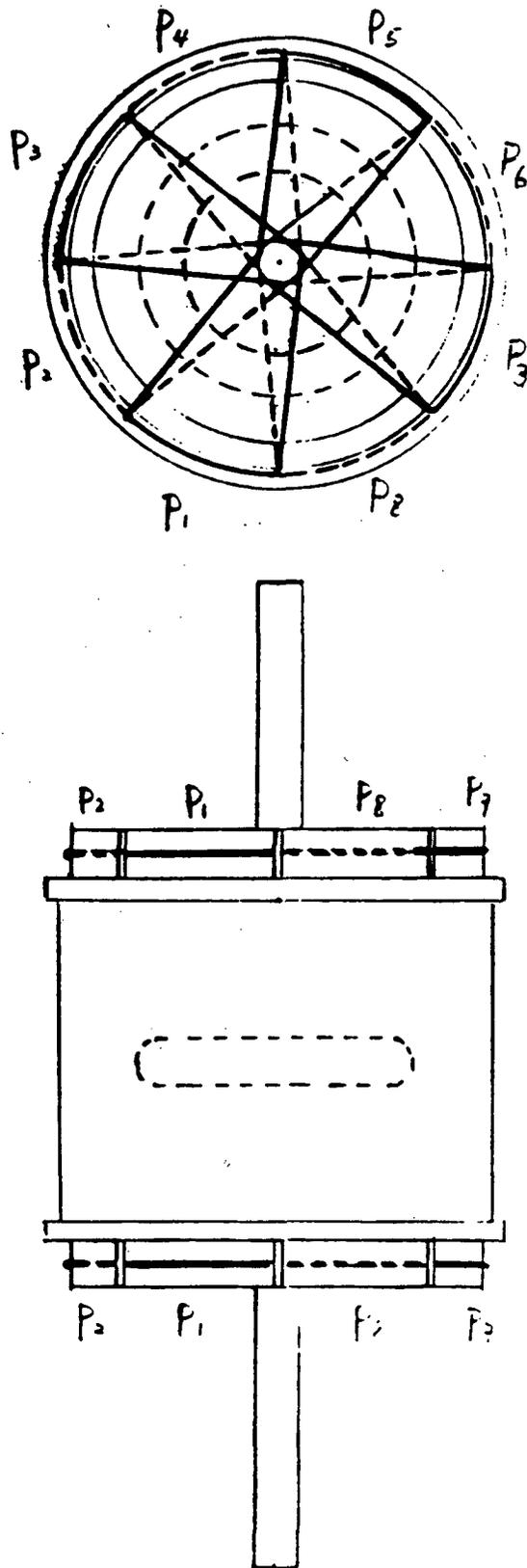
Figure 3. Sketch of point shims P_1 ...P_8 (see Figure 2 for overall dimensions).
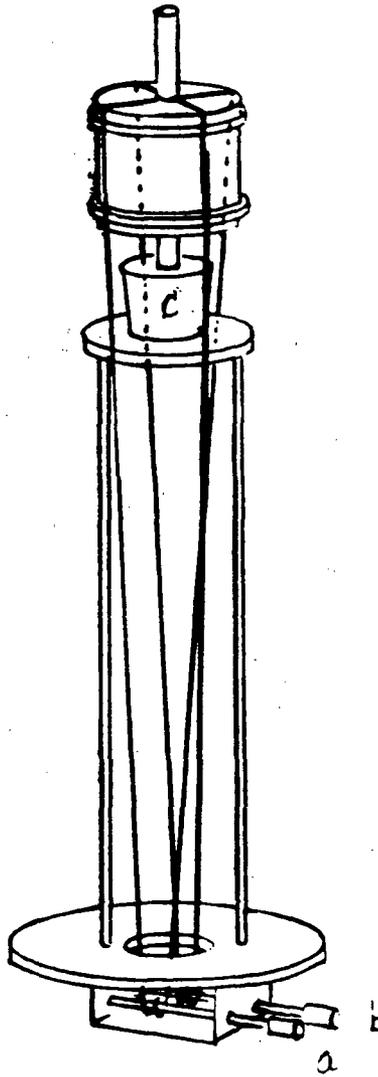
Figure 4.   Sketch of mechanical linkage for positioning toroid shim system in the xy plane of B_o.
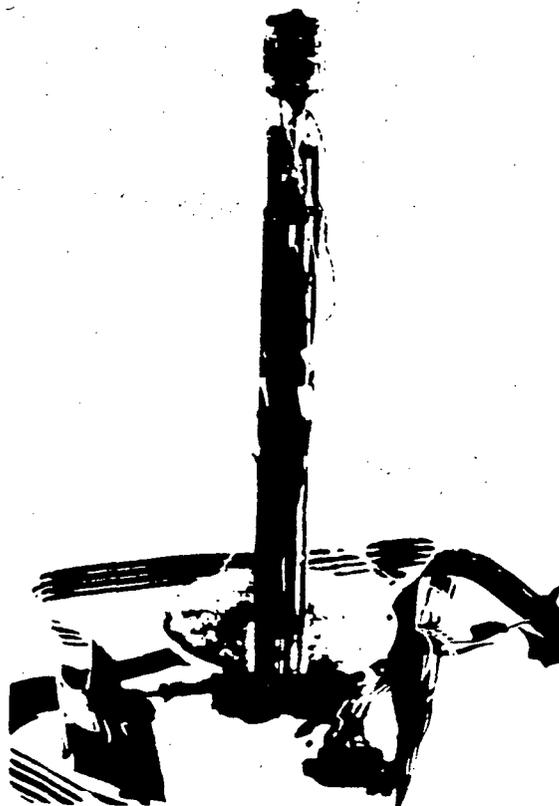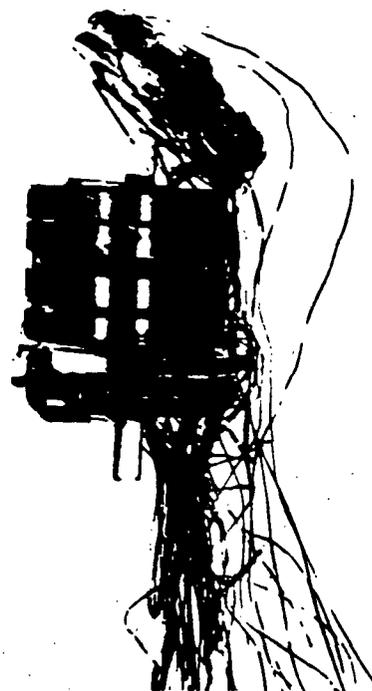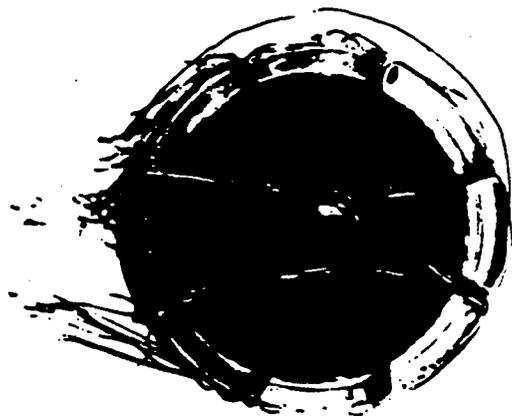
ORIGINAL PAGE IS
OF POOR QUALITY

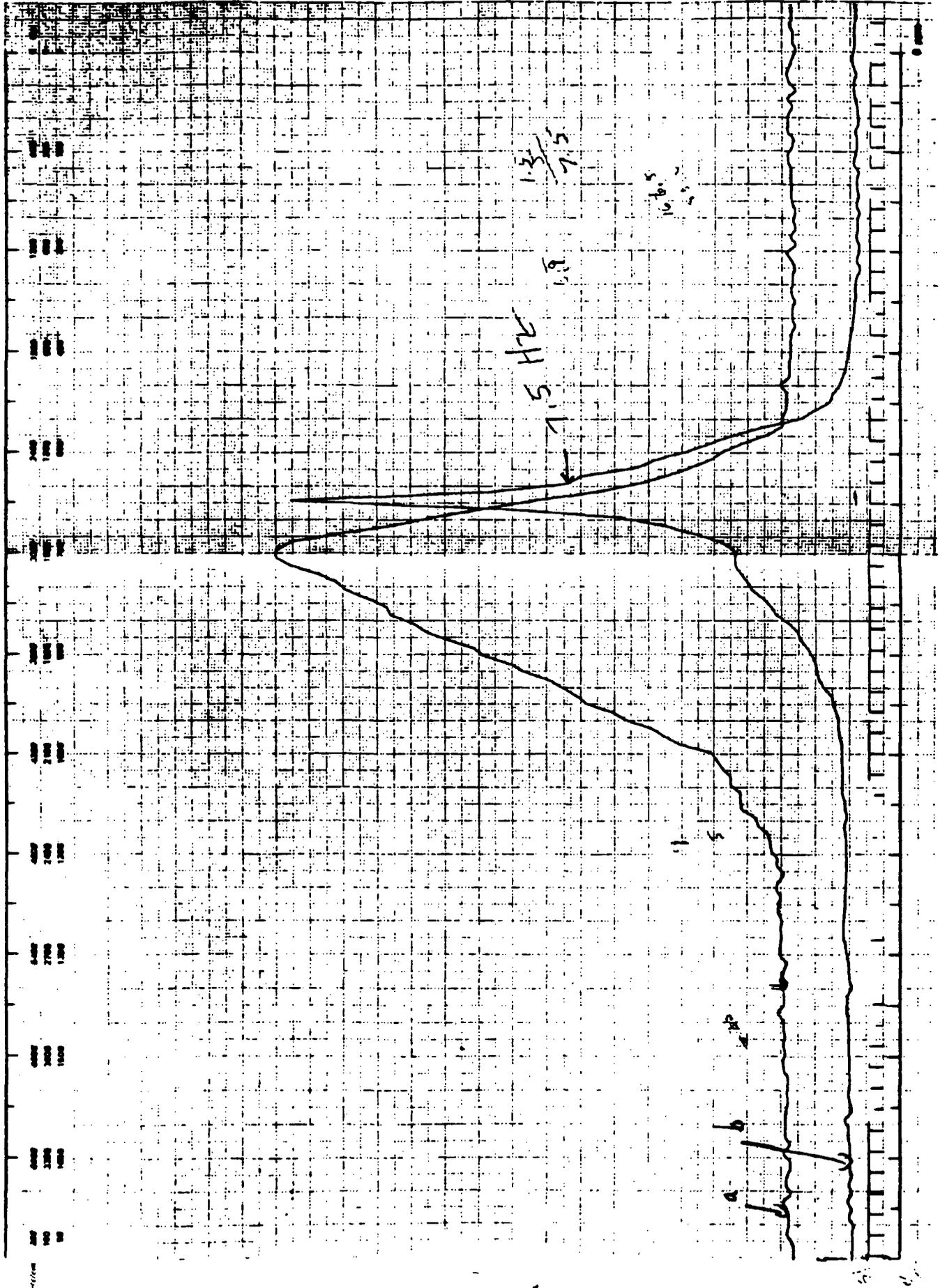Figure 5.   Photograph of assembled ^{1}H NMR flow probe and components.

Figure 6. The ^{1}H 200 MHz NMR spectrum for $HCCl_3$ with (a) and without (b) experimental shim system. The half linewidth in (B) is ~7.5 Hz.
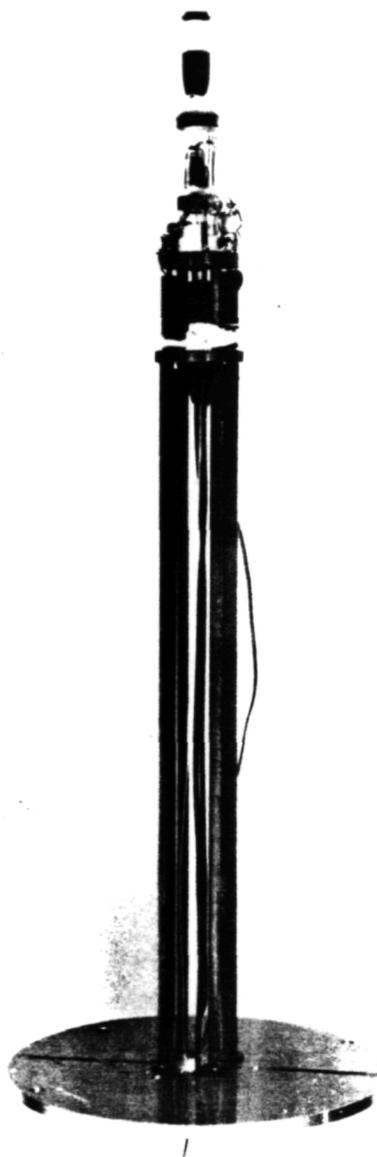
Figure 7. Photograph of assembled ^{13}C NMR flow probe B.
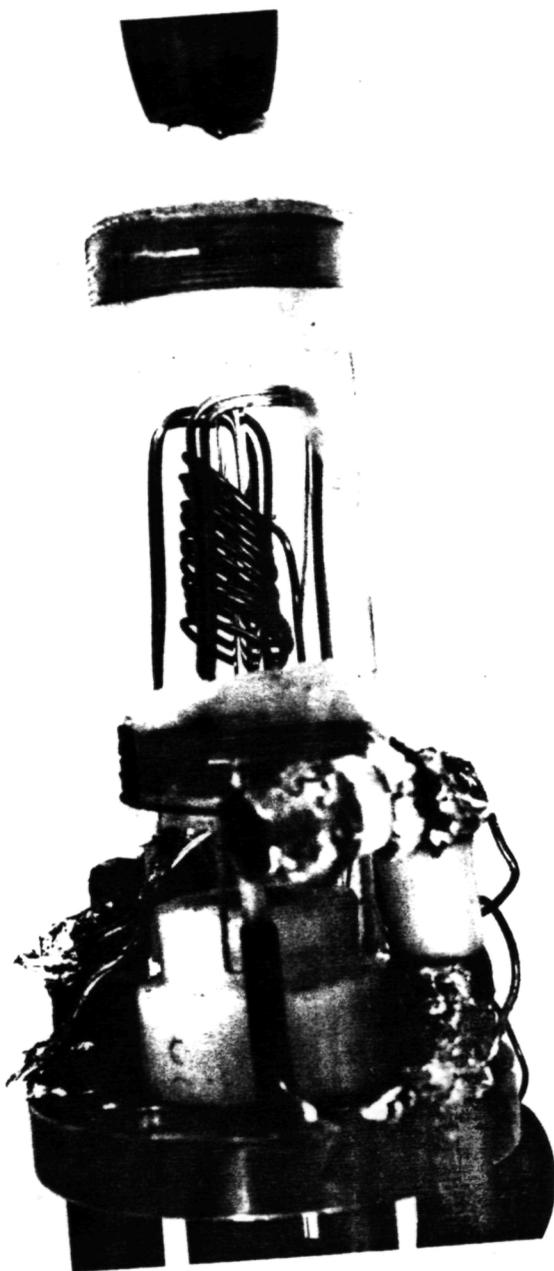
Figure 8. Photograph of close-up view of ^{13}C NMR flow probe B including Helmholtz ^{1}H coil and tilted ^{13}C coil.

solenoid coil tuned to 50 MHz (^{13}C) and a Helmholtz coil for ^{1}H decoupling 200 MHz. Although not clearly indicated, a pyrex glass cell with volume of ~250 µl was used for the ^{13}C NMR flow experiments.

RESULTS AND DISCUSSION

The results for experimental probe A and shim coil system provide a significant improvement in the B_0 homogeneity for the toroid-shaped sample volume. Using only shim coil groups C_1 and C_2 the static ^{1}H NMR linewidths can be reduced from ~50 Hz to ~7.5 Hz (see Figure 6). The resolution of (~.05 ppm) obtained with this shim system is certainly adequate for certain NMR nuclides (e.g., ^{17}O, ^{14}N, etc.) which are broadened by quadropolar interactions [18]. However, this is unsatisfactory for high resolution ^{1}H NMR and marginally acceptable for ^{13}C studies. The resolution appears to be limited by magnetic susceptibility distortions and/or discontinuities between the glass, sample, copper, and surrounding medium of the torus region.

Initial results for probe B are presented in Figure 9. The flow ^{13}C NMR spectrum for neat isooctane was obtained in 16 scans at a flow rate of 2 ml/min. Other conditions for this spectrum are indicated in Figure 9. In addition, the linewidths are artificially broadened by experimental weighing of the F.I.D. to enhance the (S/N).

The next step in this study would involve direct coupling of a high performance liquid chromatography (HPLC) to the ^{13}C NMR flow detector. Unfortunately, further work on this study was terminated after the first year of this project.
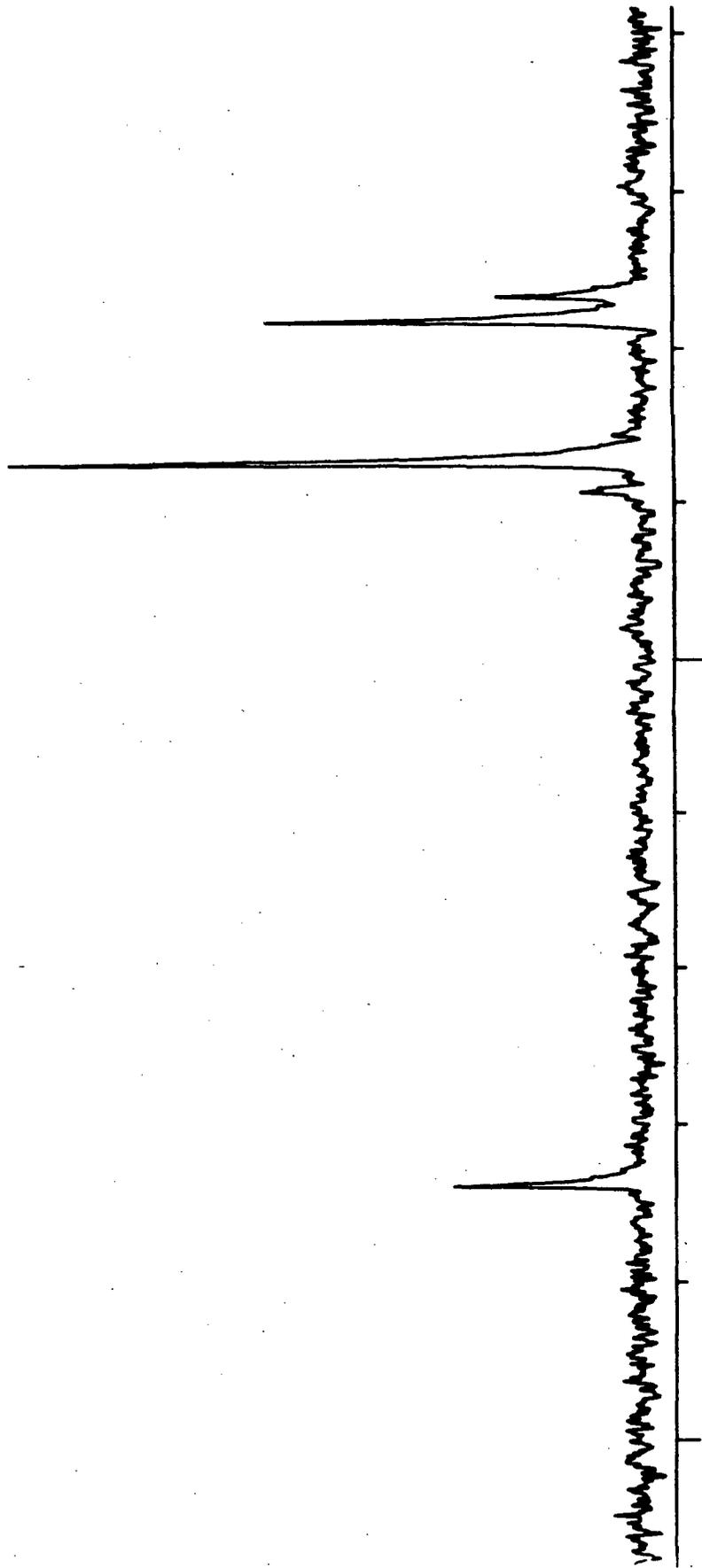
Figure 9. Flow 50 MHz ^{13}C NMR Spectrum of Isooctane. 16 scans were obtained for this spectrum (1085) at a flow rate of 2 ml/min. The cell size is ~250 μl and a pre-equilibration volume of 2 ml was employed before NMR detection. MLEV-16 ^{1}H decoupling was used with 0.5 watts of power.

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