Nuclear magnetic resonance probe for supercritical water and aqueous solutions

Markus M. Hoffmann and Mark S. Conradi
Departments of Physics and Chemistry—1105, Washington University, St. Louis, Missouri 63130-4899

(Received 20 May 1996; accepted for publication 7 October 1996)

A nuclear magnetic resonance (NMR) probe for high pressure, high temperature studies is presented. While applicable to many physical systems, the device is optimized for the study of the physics and chemistry of supercritical water and its solutions. The design is modular and is particularly simple, using readily available parts and materials. A new approach is presented for elimination of the magnetic field from the heater currents. The probe has been used to 600 °C and 400 bar. The rf performance is quite good; the NMR linewidth is about 0.1 ppm full width at half-height at any pressure and temperature. © *1997 American Institute of Physics.*
[S0034-6748(97)00301-8]

I. INTRODUCTION

Supercritical fluids have attracted a great deal of recent attention for both fundamental studies[1] and industrial applications.[2] The density and related properties such as dielectric constant and solvent ability are continuous, smooth functions of pressure and temperature. This opens up the opportunity of using environmentally benign substances such as CO_2 and H_2O as solvents in a pressure- and/or temperature-tuned supercritical state for chemical reactions and/or separation processes.

The critical point of water (T_c=374 °C, P_c=221 bar, and ρ_c=0.32 g/cm^3) is a particularly harsh set of conditions, compared to the critical point of many other simple fluids.[3] In addition, supercritical water is chemically aggressive; for example, it can dissolve silica glass.[4] Nevertheless, there are several exciting aspects of supercritical water's chemistry. One example is that controlled oxidation of toxic and hazardous organics to innocuous end products can be performed in supercritical water.[5,6] Another example is that Evilia *et al.*[7] and others[8,9] found massive deuteration of simple organics (e.g., benzene) in supercritical D_2O, with very little auxiliary reaction. Chemistry occurs in ocean floor hydrothermal vents at near-critical conditions; this chemistry has been implicated in the geologic formation of CH_4 natural gas.[10–13]

We report here a nuclear magnetic resonance (NMR) probe designed for use near and above the critical temperature and/or pressure of water. The apparatus allows not only for measurements of physical properties such as chemical shift, diffusion, and relaxation times, but it allows the dynamics of chemical reactions to be studied *in situ* in this novel medium. *In situ* measurements offer a substantial improvement over batch-mode techniques (e.g., run the reaction for N minutes and then analyze off-line, repeating for several values of N), principally in the rapidity with which data may be collected.

Several schemes have been published for NMR at high pressures. Merbach *et al.* have divided the designs into two groups.[14] In one group, the high pressure sample is held inside a strong vessel (necessarily an electrical insulator, for rf field penetration) located in a conventional NMR probe. This method offers the advantage of simplicity and a field resolution nearly as good as the commercial (ambient pressure) probe. In this group, Roe[15] and others[16,17] have reported designs based on single-crystal sapphire tubes, with pressures reported up to 400 bar. Glass capillary tubing has also been used successfully.[18–21] Very narrow fused silica capillaries of the type employed for capillary gas chromatography have been used to a remarkable 4000 bar.[22] But the chemical reactivity of supercritical water precludes the use of all but the sapphire tubes. Furthermore, the high critical pressure of H_2O is near the limit of the reported range of the sapphire designs. Also, the temperatures involved exceed the range of most commercial NMR probes. While, it may yet prove possible to work with supercritical water in a suitable sapphire or other vessel, our decision was that the second group of designs discussed by Merbach *et al.* would be safer and more likely to succeed.[14] In this second kind of high pressure probe, the rf coil, NMR sample, and pressurizing fluid are all contained in a strong metal pressure vessel.[23–29] The design reported here is of this kind. We note that DeFries and Jonas[29] have described such a NMR probe for use with supercritical water. Jonas and co-workers subsequently reported measurements of water's spin-lattice relaxation time[30,31] and diffusion coefficient[32] over a wide range of temperature and pressure.

This article first presents a broad overview of the NMR probe design. Then, details are provided about many aspects of the device. Finally, the performance of the probe is demonstrated. Suppliers of many of the materials are specified in the references as an aid to the reader but not as an endorsement of specific vendors or products.

II. OVERVIEW OF THE NMR PROBE

The basic design makes liberal use of ideas from probes described by Jonas and co-workers.[28,29] Thus, the pressure vessel (Fig. 1) is a titanium alloy, Ti-6-4. Large Ti-alloy nuts secure the end plugs. The resistance-wire furnace for the NMR sample is internal, keeping the pressure vessel cooler and stronger. The vessel is pressurized with argon gas, transmitted to the water or aqueous solution sample by a pressure balance.

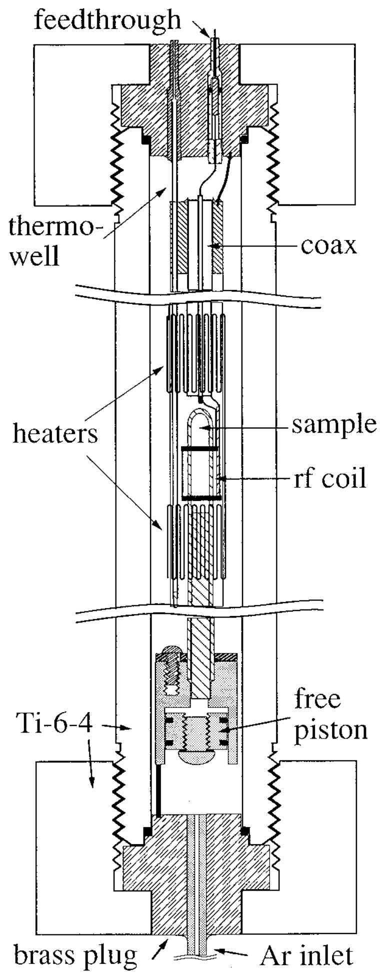

FIG. 1. Overall side cut-away view of NMR probe, not drawn to scale. The titanium alloy Ti-6-4 vessel is pressurized with argon gas; the pressure is transmitted to the sample through the free piston.

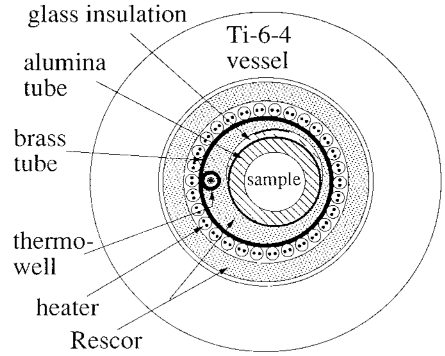

FIG. 2. Cross-sectional view of NMR probe, at the approximate height of the rf coil. The leads of the rf coil are separated by the thin glass insulation. The heater is serpentine (zig–zag) in the double-hole ceramic spacer tubes.

There are several significant design improvements which make the present device cheaper and simpler to build, compared to the DeFries and Jonas apparatus.[29] The probe described here uses a single pressure vessel, instead of two. The end closures are sealed by rubber O-rings instead of specialized metallic C-seals. The rubber can tolerate virtually any quality of surface finish. The present electrical feedthroughs are simpler and use O-rings. The sample vessel described here is made from stock ceramic tube and rod; the previous design used a machined ceramic vessel and C-seal closures with polished finishes on metal and ceramic. A free-piston with rubber O-rings is used as the pressure balance, instead of a bellows device. The free-piston can pop out the end of its cylinder, providing automatic protection against excess gas formation (e.g., by decomposition of an organic solute). The heater is driven by high-frequency ac, eliminating the effect of residual magnetic fields on the NMR. A thermowell provides an easy mechanism for measuring axial temperature profiles. Furthermore, the present equipment is intended for use only to 400 bar, instead of 2000 bar. This simplifies the pressure generation (no compressor, just a high-pressure cylinder) and substantially decreases the risk of rupture, both to humans and the magnet. Nevertheless, 400 bar includes much of the interesting chemistry that has been reported in supercritical water.

To complete the overview, the NMR coil is a saddle-coil connected through a short internal coaxial line to a tuning box located just above the upper closure nut. The entire probe is located in a 4.5 T (186.6 MHz protons) superconducting magnet of 98 mm bore with room temperature shims (about 82 mm i.d.). A more traditional 89 mm magnet would be adequate.

III. DETAILS OF THE NMR PROBE

The **pressure vessel** (Fig. 1) is made of titanium alloy Ti-6-4 (6 wt % Al, 4% V). The outer diameter (o.d.) is 1.5 in. (used as received) and the inner diameter (i.d.) is 0.875 in. (Fig. 2). The overall length with the end closure nuts is 22 in. While the central hole could be bored or even gun-bored, our vessel was simply drilled from both ends, leaving a small ledge of no consequence. (For field homogeneity, the ledge is best located at least 2 in. from the rf coil position.) With these dimensions, the vessel should be capable of an internal pressure greater than 2000 bar, providing a large safety margin over our highest working pressure, 400 bar. Before use, the vessel was tested at 670 bar with hydraulic oil and a hand-pump.

The **end closures** use brass plugs, rubber O-ring seals, and massive Ti-6-4 alloy **closure nuts**. The o.d. of the nuts is 3.0 in. and they are internally threaded 1.500 in. by six threads per in., to match the external threads on the ends of the vessel. For strength, we used 85% of the full, theoretical thread depth. As shown in Fig. 1, the O-ring seal is trapped between two ledges; this seal has been very reliable. The closure nuts need only be tightened by hand (no wrench flats are provided). Immediately after depressurization, the closure nuts are difficult to remove, presumably because of some stretching of the O-rings under pressure. A few hours delay at room pressure eases removal of the nuts. The O-rings eventually relax to their correct size and can be reused.

The **pressure vessel** and **closure nuts** contribute most of the probe's mass, about 6 Kg. In 1995, the Ti-6-4 alloy stock cost $200.[33]

There are two **brass end plugs** (Fig. 1). The lower plug has only one feature, an inlet for the argon pressurizing gas. A 0.25 in. o.d. by 0.063 in. i.d. stainless steel 304 tube is thoroughly silver-soldered into the plug, to avoid catastrophic ejection under pressure. For safety reasons, a stainless plug and a threaded joint might be superior. A rupture disk[34] rated at 550 bar is located on the gas supply tubing, within 10 in. of the bottom plug. We warn that the vessel must have a low impedance path to the rupture disk, for safety.

The **upper brass end plug** carries five identical electrical feedthroughs and a thermowell (Fig. 1). The **thermowell** is a *closed* tube into which the thermocouple is inserted, with no need for a sliding seal. The tube is $\frac{3}{32}$ in. o.d. brass with 0.064 in. i.d.[35] The tube is soft-soldered into a stepped hole in the brass end plug. The stepped hole prevents ejection under pressure. During soldering, the brass tube must be fully seated on the step; if not, application of pressure will seat the tube, shearing the solder joint. The lower end of the tube is plugged by a short brass rod, silver-soldered into place. At the pressures and temperatures used here, the brass tube will collapse eventually. To avoid this, a long ceramic insulator[36] is placed the entire length of the thermowell. The $\frac{1}{16}$ in. o.d. ceramic insulator fits snugly and supports the brass. The $\frac{1}{32}$ in. i.d. is adequate for a 0.020 in. o.d. type E **thermocouple**,[36] with stainless 316 external jacket (18 in. long). The thermocouple is easily moved up and down to determine the temperature profile. To facilitate this from outside the magnet bore, a set of guide tubes is employed. Because of the magnetic susceptibility of the thermocouple jacket, it is raised away from the rf coil region during signal acquisition.

The **electrical feedthroughs** [Fig. 1 and detail in Fig. 3(b)] are constructed of Torlon, a strong and easily machined plastic. Three feedthroughs are used for the two-section heater, one is for the rf, and one is a spare. Except when the upper brass end plug was allowed to become too hot, these feedthroughs have been very reliable. A possible improvement would be to use a stainless steel screw in place of Torlon, with insulating tubing over the wire. The hole in the brass end plug is threaded 8–32 only at the bottom, allowing the O-ring a smooth surface upon which to seal.

The **sample vessel** [Fig. 1 and detail in Fig. 3(a)] is a ceramic closed-end tube[37] (99.8% alumina, $\frac{1}{4}$ in. o.d., and $\frac{3}{16}$ in. i.d.). Alumina is one of the few insulating materials impervious to supercritical water.[4,38] Excess volume in the tube is removed by an alumina rod.[37] At the bottom, cool end, the alumina tube is rubber O-ring sealed to a stainless steel 304 cylinder-**free piston** device.[17,39,40] Because the internal and external pressures are equalized, the ceramic tube need not be strong. The free piston carries two O-rings to help piston alignment and to prevent leakage. An O-ring sealed screw in the piston provides access and venting for filling the tube with a sample. One could also use liquid Hg to separate the argon and the sample.[39]

The **free piston** arrangement works well, though one must keep the sealing surfaces free of scratches. We routinely check for infusion of argon into the sample by measuring the piston location with a micrometer depth gauge before and after a high pressure/high temperature experiment. Any argon gas finding its way into the sample would cause these positions to differ. We are frankly surprised that the net piston displacement is unmeasurably small (<0.001 in.) when pure water is run at supercritical conditions. Chemical reactions from solutes may also generate products that will be in the gas phase upon return to room conditions. If too much gas is generated, the free piston will be pushed out the bottom end of the cylinder [Fig. 3(a)], protecting the sample vessel.

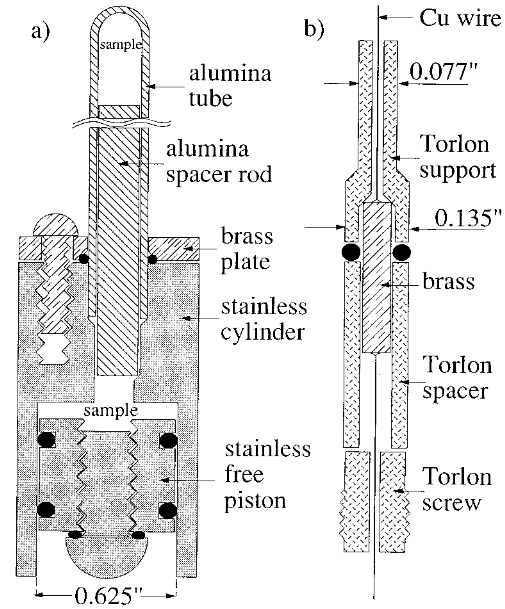

FIG. 3. (a) Detail of the ceramic sample tube and free-piston pressure balancing arrangement. The stainless-steel cylinder and piston are far from the heated region and remain cool. (b) One of the five electrical feedthroughs, located in the upper brass end plug (see Fig. 1). The screw has small wrench flats to assist tightening.

The **rf coil** consists of a two-turn saddle coil, one turn on each side of the sample vessel. The coil is made from copper foil 0.003 in. thick. It is cut by scissors and folded at a bend; the bend receives a touch of silver solder for stiffness. The two coil leads exit from the rf coil fairly close together, to reduce stray rf fields (which would generate signals from unwanted regions of the sample with lower field homogeneity). A thin piece of glass separates the leads (Fig. 2). The coil is fixed to a Rescor[41] (an inexpensive machinable ceramic) piece with a light application of cement (heat treated to 100 °C while evacuating to remove excess water).[42]

To convey the rf coil wires the distance of about 9 in. (which length is required for the end plug to remain cool) to the rf feedthrough in the upper brass end plug, a **coaxial line** is employed. This follows the ideas and designs of McKay[43,44] and resulted in substantial rf performance improvement, compared to simple 0.8-mm-diam copper wires. To reduce thermal conduction, thin-wall tubes are used. We used 0.003 in. wall Everdur copper alloy tubing which happened to be available: $\frac{1}{4}$ in. o.d. for the outer conductor and $\frac{1}{16}$ in. o.d. for the inner conductor. Quartz tubing (fused silica) is used as the dielectric and spacer between the conductors. The ends of the inner tube are plugged with silver-solder to prevent convection through the tube, but the tube must be vented somewhere to prevent collapse under pressure. Alternatively, readily available hard-drawn copper tubing[35] could be drilled from both ends to a wall thickness of 0.008 in. or less. The outer tube could be constructed from copper foil rolled around the silica dielectric and then tacked together at the seam with a small amount of silver-solder.

An **external tuning box** is located immediately above the upper brass end plug. In our case, the net impedance at that point at 186.6 MHz was near series resonance (zero impedance). A series inductor of copper ribbon is used to make the impedance inductive, so that a conventional tuning capacitor (1–10 pF) forms a tuned circuit.[45] Matching to the external 50 Ω line was accomplished with a series capacitor connected to a tap on the inductor.

The **heater** is in two sections, upper and lower, to allow the temperature profile to be adjusted.[29] Each section is 1.5 in. long, with chromel resistance wire passed up and down through two-hole alumina tubes (''thermocouple insulation tubes'')[36] closely packed around the perimeter of the $\frac{1}{2}$ in. o.d. brass support tube (Figs. 1 and 2). The spacing between the sections is 1.1 in. Each section has a resistance of 30 Ω. The two sections are in series, with an external, adjustable resistor in parallel with the upper section. Because of convection in the high pressure argon, the upper heater requires less current than the lower one. Simple rf filters outside the pressure vessel eliminate any rf noise picked up by the heater wiring.

Even though the heater is nominally noninductive (Fig. 1), the heater current produces sufficient magnetic field to disturb a high-resolution experiment. One solution to the problem is simply to turn off the heater for the duration of data acquisition of each free induction decay.[25] Thus, we use a field-effect transistor (FET) switch controlled by the spectrometer's pulse generator through an opto-isolator to turn off the heater for 0.20 s, starting 0.01 s before the inspection rf pulse. This works well, but it is not elegant. Furthermore, changes in the pulse repetition rate will cause a change in the duty cycle of the heater (always greater than 90%), changing the temperature.

A better solution is to convert the dc power to the heater into high frequency ac. An H-bridge of four switching power field effect transistors (FETs) with IR2110 drivers produces 10 kHz ac square-wave power to the heaters.[46] The stability of the temperature is determined by the current regulated dc source which supplies the dc–ac converter. At such a high frequency, any magnetic field from the heater produces only very weak sidebands in the NMR spectrum. The 10 kHz spacing guarantees that the sidebands cannot be confused for chemically shifted lines. A capacitor in series with the heaters ensures that no dc component is present. No rf noise is introduced by this scheme.

Convection of the argon is a substantial problem at high pressure. To reduce convection, the space between the $\frac{1}{2}$ in. o.d. brass heater support tube and the sample vessel (or, higher up, the coaxial line) is filled with a stack of 11 Rescor pieces[41] (not shown in Fig. 1 but represented in Fig. 2). The rf coil is fixed to one of these 11 (see above). Between the heater and the pressure vessel, Rescor pieces (not shown in Fig. 1 but represented in Fig. 2) are used as thermal insulation. Small amounts of ceramic cement[42] are used near the heater to plug convection paths. Nevertheless, the power required to reach 400 °C rises from 92 W at 19 bar to 200 W at 400 bar internal pressure. The hottest spot also moves up, requiring a readjustment of the division of power to the heater sections. We used additional Rescor pieces to reduce the unused volume and stored energy in the pressure vessel.

Water cooling coils of $\frac{1}{8}$ in. o.d., $\frac{1}{16}$ in. i.d. copper tubing are wound over the lower and upper sections of the pressure vessel. The central five inches are not cooled directly, but remain cooler than 100 °C during operation. As an afterthought, a copper clamp in contact with cooling coils was added to the upper closure nut. The coils are not soldered to the vessel or clamp; rather, a thin layer of grease aids thermal contact, but it is not critical. Thus, the cooling coils are easily removed or repositioned.

A long aluminum tube surrounds the copper cooling coils and slides over them from one end. This tube carries the **gradient coils** ($\partial H_z/\partial z$) required for field gradient measurement of diffusion coefficients. The cooling coils thus also provide cooling to the gradient windings. The gradient coil is wound on the 2 in. o.d. aluminum tube and has four sections consisting of two antisense pairs. The inner pair has 7 turns per section, separated 0.60 in.; the outer pair has 70 turns per section, separated 2.30 in. These values were taken from a computer calculation of the Biot–Savart law to yield the most uniform gradient.

The **argon pressurizing gas** is obtained from a commercially available large cylinder (size BX) at 400 bar. Compared to any compressor equipment, this approach is inexpensive and easy. The pressure is reduced through a valve (Whitey, Kel-F tipped stem)[47] and measured with an ordinary Bourdon gauge and a more accurate pressure transducer.[36] At these pressures, Cajon VCO-4 fittings (O-ring face-sealed)[48] work well and easily. We prefer small bore piping ($\frac{1}{16}$ in. o.d. by 0.030 in. i.d., stainless 316)[34] because it restricts both the maximum flow rate in the event of a rupture or ejection and the volume of gas involved. This tubing is also very convenient because it is so flexible. The stainless tubing is silver-soldered into the VCO fittings with the aid of stainless bushings. It is prudent to tie down all tubing to prevent whipping in case of ejection from a fitting.

Because of the possibility of rupture under pressure, we ensure that the ends of the magnet bore are relatively open, offering a low impedance path for escaping gas. Above the upper closure nut, a $\frac{1}{4}$-in.-thick wall aluminum tube is used to protect the magnet bore. Immediately surrounding the probe, the room temperature shim assembly offers some protection. We also recommend an additional safety shield between the 2 in. aluminum tube and the room temperature shims.

IV. PERFORMANCE OF THE NMR PROBE

The $\pi/2$ pulse length for protons at 186.6 MHz is 30 μs at all temperatures in this probe for an rf power of about 18 W. For comparison, we constructed a test probe with a similar size sample with tuning and matching components located near the rf saddle coil; this probe had 10 μs $\pi/2$ pulses. Thus, the rf performance is more than adequate (the chemical

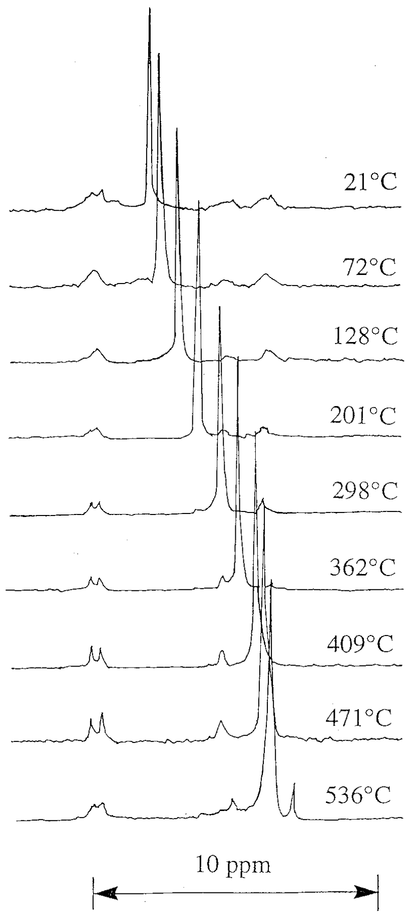

FIG. 4. Proton NMR spectra of a dilute solution of *para*-ethyl phenol in water, all at 250 bar (above the critical pressure). The spectra have been slightly shifted to keep the ring resonances (at left) of the solute in a fixed location on the spectra. As the temperature is increased, the water resonance shifts to lower frequency (to the right) because of the disruption of the hydrogen-bond network.

shift range for protons is only about 10 ppm, or 2000 Hz). The rf tuning changes only slightly with temperature changes, but the dielectric constant of dense argon produces a ~3 MHz tuning change upon pressurization to 400 bar.

The main limitation to high-resolution is that the materials near the sample have nonvanishing magnetic susceptibilities. This probe exhibits a linewidth of 0.1 ppm, about 20 Hz, full width at half-maximum, independent of pressure and temperature. Greater attention to material selection and location could improve this linewidth. The field shim coils need only small adjustments as the temperature of the probe is increased. NMR spectra of H_2O at varying temperatures are presented in Fig. 4. *Para*-ethyl phenol has been added at about 2 mol % to provide chemical shift reference lines. The H_2O resonance shifts to decreasing frequency (to the right in the figure) as the hydrogen bonding network is disrupted at higher temperatures. Because the frequency shift is measured with respect to an *internal* reference, a change in the chemical shift of water and/or the solute is occurring, not just a change in magnetic susceptibility. Because there is essentially no change in the relative shifts of the solute lines, it is the shift of the *water* that is changing. We are currently studying the hydrogen bonding in supercritical water as a function of temperature and density, by means of the chemical shift. New lines at the highest temperature in Fig. 4 indicate that the solute has undergone chemical changes.

The axial temperature profile in the sample region shows good uniformity for such a short furnace. The peak-to-peak variation is 3 °C in the central 0.7 in. region, centered on the rf coil center. Over the central 1.25 in., this becomes 8 °C, all at a central temperature of 470 °C. A chart is maintained in the laboratory that provides the optimum value of the adjustable shunt resistor to obtain the best temperature uniformity at each temperature and pressure setting. To date, the probe has been used to 600 °C and 400 bar. No chemical reactions with the sample vessel have been found.

V. POSSIBLE IMPROVEMENTS

In today's world of highly efficient and well-regulated switching power supplies, one should be able to design a compact, self-contained source of 10 kHz square-wave power for the heater, without any need for a regulated dc source. Pulse-width modulation would be an appropriate technique.

The sample vessel we have used to date requires that all the sample chemicals be put into the vessel at room conditions; then the vessel is sealed. It would be advantageous to be able to inject small amounts of solute into the cell while at supercritical conditions. A narrow bore teflon tube could be connected between the free piston and the bottom end plug to allow this, along the lines of the filling tube in a recent design.[17]

ACKNOWLEDGMENTS

The authors gratefully acknowledge the skillful machining of the Department of Physics Machine Shop and the electronic construction of the dc–ac converter by J. Ash. The work was partially supported by NSF Grant No. DMR 94-03667.

[1] J. F. Brennecke, in *Supercritical Fluid Engineering Sciences: Fundamentals and Applications: ACS Symp. Series 514*, edited by E. Kiran and J. F. Brennecke (American Chemical Society, Washington, DC, 1993), p. 201.
[2] J. F. Brennecke and C. A. Eckert, AIChE. J. **35**, 1409 (1989).
[3] R. W. Shaw, T. B. Brill, A. A. Clifford, C. A. Eckert, and E. U. Franck, Chem. Eng. News **69**, 26 (1991).
[4] G. M. Anderson and C. W. Burnham, Am. J. Sci. **265**, 12 (1967).
[5] D. M. Harradine, S. J. Buelow, P. C. Dell'Orco, R. B. Dyer, B. R. Foy, J. M. Robinson, J. A. Sanchez, T. Spontarelli, and J. D. Wander, Hazard. Waste Hazard. Mater. **10**, 233 (1993).
[6] W. R. Killilea, K. C. Swallow, and G. T. Hong, J. Supercritical Fluids **5**, 72 (1992).
[7] J. Yao and R. F. Evilla, J. Am. Chem. Soc. **116**, 11229 (1994).
[8] T. C. Hoering, Org. Geochem. **5**, 267 (1984).
[9] B. Kuhlmann, E. A. Arnett, and M. Siskin, J. Org. Chem. **59**, 3098 (1994).
[10] F. D. Mango, J. W. Hightower, and A. T. James, Nature (London) **368**, 536 (1994).
[11] E. L. Shock, Nature (London) **368**, 499 (1994).
[12] E. L. Seewald, Nature (London) **370**, 285 (1994).
[13] L. C. Price, Nature (London) **370**, 253 (1994).
[14] H. Vanni, W. L. Earl, and A. E. Merbach, J. Magn. Reson. **29**, 11 (1978).
[15] D. C. Roe, J. Magn. Reson. **63**, 388 (1985).
[16] I. T. Horváth and E. C. Ponce, Rev. Sci. Instrum. **62**, 1104 (1991).
[17] S. Bai, C. M. Taylor, C. L. Mayne, R. J. Pugmire, and D. M. Grant, Rev. Sci. Instrum. **67**, 240 (1996).
[18] H. Yamada, Rev. Sci. Instrum. **45**, 640 (1974).

[19] H. Yamada, M. Nakatsuka, H. Yamochi, M. Sawamura, and A. Sera, Rev. Sci. Instrum. **62**, 700 (1991).
[20] J. K. Tison and E. R. Hunt, J. Chem. Phys. **54**, 1526 (1971).
[21] J. von Jouanne and J. Heidberg, J. Magn. Reson. **7**, 1 (1972).
[22] C. R. Yonker, T. S. Zemanian, S. L. Wallen, J. C. Linehan, and J. A. Franz, J. Magn. Reson. A **113**, 102 (1995).
[23] J. Jonas, Rev. Sci. Instrum. **43**, 643 (1972).
[24] W. L. Earl, H. Vanni, and A. E. Merbach, J. Magn. Reson. **30**, 571 (1978).
[25] S. Shimokawa and E. Yamada, J. Magn. Reson. **51**, 103 (1983).
[26] J. W. Rathke, J. Magn. Reson. **85**, 150 (1989).
[27] U. Frey, L. Helm, and A. E. Merbach, High Pressure Res. **2**, 237 (1990).
[28] J. Jonas, Science **216**, 1179 (1982).
[29] T. H. DeFries and J. Jonas, J. Magn. Reson. **35**, 111 (1979).
[30] J. Jonas, T. DeFries, and W. J. Lamb, J. Chem. Phys. **68**, 2988 (1978).
[31] W. J. Lamb and J. Jonas, J. Chem. Phys. **74**, 913 (1981).
[32] W. J. Lamb, G. A. Hoffman, and J. Jonas J. Chem. Phys. **74**, 6875 (1981).
[33] President Titanium Co., Inc., Hanson, MA.
[34] High Pressure Equipment Co., Erie, PA.
[35] Small Parts, Inc., Miami Lakes, FL.
[36] Omega Engineering, Inc., Stamford, CT.
[37] Coors Ceramic Co., Golden, CO.
[38] K. W. Downey, R. H. Snow, D. A. Hazlebeck, and A. J. Roberts, in *ACS Symposium Series 608: Innovations in Supercritical Fluids*, edited by K. W. Hutcheson and N. R. Foster (American Chemical Society, Washington, DC, 1995), pp. 313–326.
[39] R. Folland, S. M. Ross, and J. H. Strange, Mol. Phys. **26**, 27 (1973).
[40] W. C. Allen, N. Liu, and J. Jonas, J. Chem. Phys. **63**, 3317 (1975).
[41] Rescor 960 from Cotronics Corp., Brooklyn, NY.
[42] Sauereisen No. 8, Sauereisen RIDC, Pittsburgh, PA.
[43] R. A. McKay, U.S. Patent No. 4,446,431 (1 May 1984).
[44] M. S. Conradi, Concepts Magn. Reson. **5**, 243 (1993).
[45] E. Fukushima and S. B. W. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach* (Addison-Wesley, Reading, MA, 1981).
[46] *IR Power Semiconductors Product Digest* (International Rectifier, El Segundo, CA, 1992).
[47] Whitey Co., Highland Heights, OH.
[48] Cajon Co., Macedonia, OH.