A Microcell for NMR Spectral Measurements

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The necessity of handling the minute amounts of substances encountered by many chemsits has lead to the invention of a few micro- and semimicro-cells.[1] Some of them, however, can not be used at an elevated temperature, and they are usually expensive. We have been using a convenient and simple microcell made from a glass-capillary for measurements with a Varian A-60 spectrometer.

The sample tube consists of a capillary, 1 to 2 mm. in outside diameter and about 19 cm. long (similar to a normal melting point tube), which is fixed inside a standard-size NMR tube by means of two cylindrical plugs.[2] These plugs have concentric holes with a diameter slightly larger than that of the capillary. The sample solution, usually prepared from about 3 mg. of the substance and about 30 μl. of a solvent containing a trace of the internal reference, is introduced into the capillary tube (one end sealed) either by a process of warming and cooling or with the aid of a micro-syringe. The open end is then sealed. One of the plugs is placed at the bottom, and the other, about 50 mm. from the bottom of the NMR tube; the capillary is inserted into the tube and through the hole in each plug. The upper end of the capillary tube is stabilized by inserting it through a hole bored in the center of a plastic cap, which is then fitted over the mouth of the NMR tube. The

1) As far as we know, three types of these cells are commercially available, those made by Varian Associates, U. S. A., Nuclear Magnetic Specialities Inc., Canada, and Japan Electron Optics Laboratory Co., Japan.

2) For the sake of convenience, we have been using sections of the nylon upper-plug of a Varian microcell or the insulating cover of electric wire for measurements at room temperature, and sections of Teflon tubing at elevated temperatures (up to 130°C).

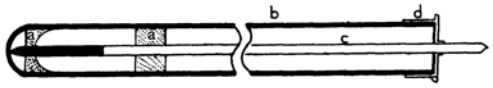

Fig. 1. Cross-section of the micro-cell.
a Nylon plugs
b Standard-size NMR sample tube
c Capillary
d Plastic cap

completely-assembled micro-cell is illustrated in Fig. 1.

The measurement of the NMR spectra is carried out in the normal way. The spectra obtained with the use of this cell are usually as good as those obtained with 5 to 10 times the amount of sample in an ordinary 5-mm. cell. Examples of spectra obtained with the use of this microcell and of those with the use of a standard cell are shown in Figs.

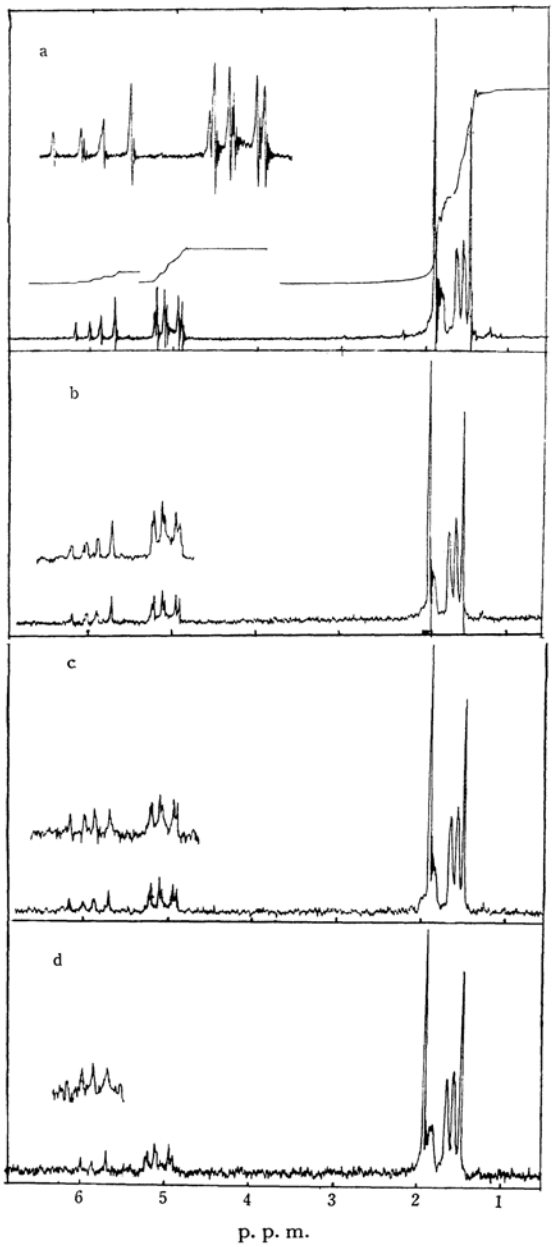

Fig. 2. NMR spectra of linalool in carbon tetrachloride
a 30 mg. in standard cell
b 8 mg. in microcell
c 5 mg. in microcell
d 3 mg. in microcell

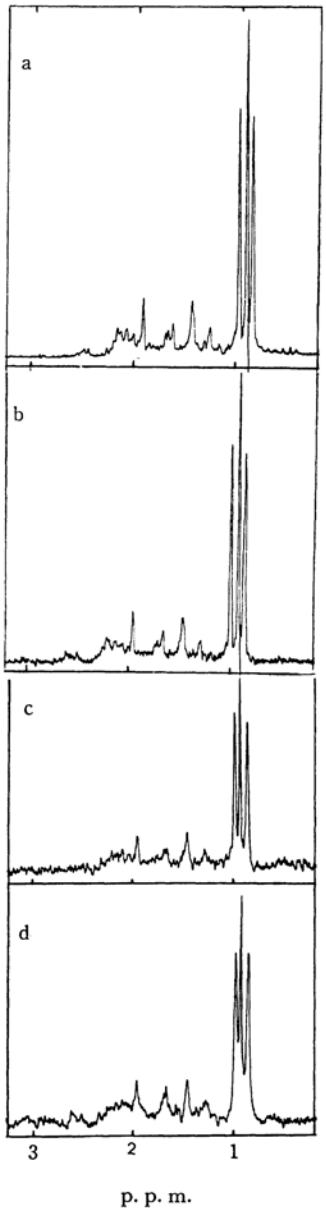

Fig. 3. NMR spectra of camphor in carbon tetrachloride.
a 30 mol.% in standard cell
b 30 mol.% in the microcell
c 10 mol.% in the microcell
d 3.2 mol.% in the microcell

2 and 3 in order to illustrate the limitations of this micro-cell.

In the case of linalool, the one proton quartet, due to the X part of the ABX system, is visible with 3 mg. of sample in about a 8 mol.% solution, whereas in the case of the methyl protons of camphor, the signal can be clearly recognized when 1.1 mg. of the sample (ca. 3.2 mol.% solution), or even as little as 0.35 mg. of the sample (1 mol.% solution), is used.

Although a certain degree of sensitivity is sacrificed because of the large diameter of the receiver coil, which has been designed for use with the larger standard NMR tubes, this cheap and simple micro-cell is very useful when only small quantities of sample are available.

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