and the corresponding standard deviations for each line. Ten recordings of each spectrum were obtained at room temperature, using a Varian DP-60 spectrometer. To avoid signal saturation the radio field amplitude was set 60 db, below one-half watt. The external magnetic field was swept at the rate of 0.5 to 1.0 c.p.s./second. Spinning 5-mm. o.d. sample tubes were used to achieve maximum field homogeneity. Calibration of the spectra was accomplished by the usual side-band technique, using a Hewlett-Packard 200 CD wide band oscillator and a 522B counter. Tetramethylsilane (K & K Laboratories Inc., Jamaica, N. Y.) was used as an internal reference.

Several advantages attend the use of the time base generator described above. In addition to improved linearity and reproducibility, the time base generator affords greater convenience in the recording of NMR spectra, since the pen may be driven in the right-to-left direction. By convention NMR spectra are displayed with magnetic field strength increasing from left to right. Using tetramethylsilane as an internal reference, the reference signal normally occurs further upfield than all other spectral lines. Therefore, one can begin at the beginning with only an irrelevant change in the appearance of the spectrum.

The possibility of error due to the nonlinearity of the recorder slidewire has been eliminated. Consequently, line position measurements are more precise. Convenience also is achieved by correlating voltage with linear distance along the recorder slidewire. Linear distance on the chart paper need not be measured. Also, line positions are rapidly measured in digital form in terms of frequency.

Table I. Comparison of Two Methods of Measuring NMR Line Positions

	Conventional method		Electronic method	
	Line[a] position	Std. dev.[b]	Line[a] position	Std. dev.[b]
1,1,2-Trichloroethylene	387.4	0.32	387.3	0.21
Chloroform	434.5	1.44	434.8	0.30
Methylene of ester group of ethylcyanoacetate	243.3	1.25	243.4	0.50
	250.3	1.20	250.6	0.64
	257.7	1.17	257.8	0.60
	264.8	1.14	264.9	0.57
Methanol	197.8	0.73	197.8	0.70
	202.8	0.76	202.9	0.75
	252.9	0.78	252.7	0.77
	258.0	0.89	258.0	0.70
	263.0	0.89	263.2	0.75
	268.3	0.88	268.2	0.75
Methoxy group of methyl butyrate	216.8	1.32	216.2	0.70

[a] c.p.s. from tetramethylsilane, solvent–CCl_4
[b] Two sigma values.

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Mention of commercial products does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

Combining Gas Chromatography with Nuclear Magnetic Resonance Spectrometry

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GAS CHROMATOGRAPHY has been combined previously with nuclear magnetic resonance spectrometry (NMR) for the identification of effluent fractions from C_8 aldehydes (*4*), isoprenoid hydrocarbons (*2*), isomers of triisobutylene and tetraisobutylene (*3*), and C_7 olefins (*1*). In each of these cases conventional trapping procedures were used. They consist of trapping samples into one vessel and transferring them into another vessel for the NMR examination. These procedures require a relatively large amount of starting material and generally can take a long time (hours or more) to collect a sufficient amount of pure sample for identification. In the present investigation, a new procedure which eliminated the use of a second vessel was developed. Thus, the same vessel into which the sample was trapped could also be used for the NMR examination. As a result of this procedure less sample was required to obtain NMR spectra.

The new procedure of combining gas chromatography with NMR was developed with the use of glass microtubes (NMR Specialties, Inc., New Kensington, Pa.) that became commercially available only last year for NMR studies. These tubes are made of borosilicate glass and contain a bubble at about 15 mm. from the bottom of the tube to coincide with the position of the receiver coil in the spectrometer. The exact position can be determined by filling the bubble with chloroform and by noting the position that corresponds to the maximum signal for the proton resonance. A 1-mm. i.d. capillary leads from the top of the tube to the bubble whose volume is about 35 μl. After several attempts were made to trap effluents directly from a gas chromatograph into these tubes using a 22-gauge syringe needle that was eight inches long, it was found that this fine gauge needle caused a very large pressure drop at the exit of the gas chromatograph. Inefficient operation of the gas chromatograph resulted. To circumvent this difficulty, a pair of microtubes that had a 2-mm. i.d. capillary leading to the bubble were obtained on special request. With the larger capillary, a larger diameter syringe needle (17-gauge) could be used for trapping samples. Thus, less restriction to the helium flow and greater efficiency in trapping was made possible.

A picture of the microtube and equipment used for trapping samples directly from a gas chromatograph is shown in Figure 1. The 17-gauge needle that is eight inches long is seen inside the glass microtube. The tip of the needle is located inside the bubble near the bottom of the tube. The top of the needle is connected to a Luer lock which is silver soldered to a $^1/_4$-inch tubing T. By using a Luer lock connection, the needle can either be attached or removed very quickly and easily from the tubing T. The right side of the T is equipped to connect it to the exit port of a gas chromatograph. The left side is shown uncapped. Whenever a species to be trapped emerges from the exit port, the nut to the immediate left of the T is screwed on the T and tightened to force the carrier gas to pass through the needle in the

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tube. A "Triclene" and dry ice bath can be used conveniently for trapping the species in the bubble. As soon as the gas chromatograph indicates that the species being trapped is no longer exiting from the chromatograph, the nut is removed first to bypass the gas flow, and the needle is disconnected from the Luer lock.

The next step in the procedure is to add sufficient solvent to the microtube to fill the bubble for the NMR examination. A 50-μl. syringe without needle attached is filled to about the 35-μl. mark with the solvent to be used. Then, the syringe is connected to the 17-gauge needle, and the microtube which still contains the needle is removed from the dry ice–Triclene bath. The solvent is injected into the needle and the tube containing needle is returned to the cold bath. This technique has the effect of washing the inside of the needle with solvent and of dissolving the trapped species in one operation. If more solvent is needed to fill the bubble, the microtube is removed from the cold bath, a few more microliters of solvent are added, and the microtube is returned to the bath to wash the solvent into the bubble.

After the bubble is filled to volume, the needle is removed from the microtube and the trapped species is examined by NMR. Samples that range in boiling points from less than 100° C. to nearly 300° C. have been examined successfully with this procedure. The high boilers require external heating of the tubing T to get them into the needle and to be dissolved by the appropriate solvent.

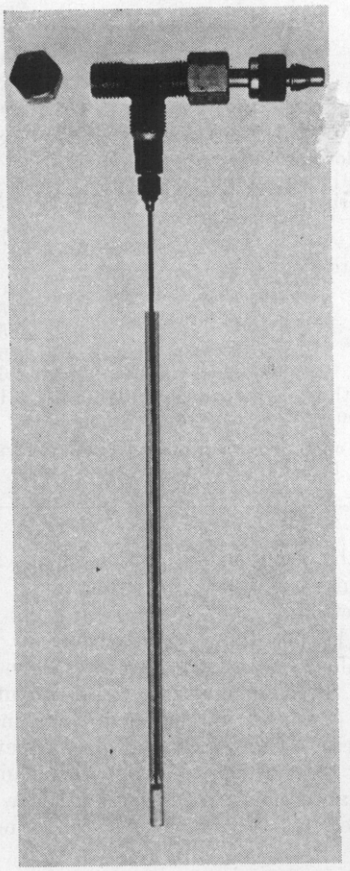

Figure 1. NMR microtube with 17-gauge syringe needle and $^1/_4$-inch tubing T

Results obtained from the use of tl direct trapping procedure indicate tl a minimum of about 100 to 400 μg. sample are required to obtain a gc NMR spectrum from an A-60 sp trometer. If computer averaging te niques are used or if one of the nev spectrometers such as an HA-100 strument is used to enhance the sign proportionately less sample is requir to obtain a good spectrum. Thus, the order of several micrograms of sample can readily be obtained as a minimum level of concentration through the use of this trapping procedure to combine gas chromatography directly with NMR.

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