Designation: E2977 – 15 (Reapproved 2023)

Standard Practice for Measuring and Reporting Performance of Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) Spectrometers for Liquid Samples[1]

This standard is issued under the fixed designation E2977; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers procedures for measuring and reporting the performance of Fourier-transform nuclear magnetic resonance spectrometers (FT-NMRs) using liquid samples.

1.2 This practice is not directly applicable to FT-NMR spectrometers outfitted to measure gaseous, anisotropically structured liquid, semi-solid, or solid samples; those set up to work with flowing sample streams; or those used to make hyperpolarization measurements.

1.3 This practice was expressly developed for FT-NMR spectrometers operating with proton resonance frequencies between 200 MHz and 1200 MHz.

1.4 This practice is not directly applicable to continuous wave (scanning) NMR spectrometers.

1.5 This practice is not directly applicable to instruments using single-sideband detection.

1.6 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E131 Terminology Relating to Molecular Spectroscopy

E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy (Withdrawn 2015)[3]

2.2 *ISO Standard:*[4]

ISO Guide 31 Reference Materials—Contents of Certificates and Labels

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E131, Practice E386, and Refs **(1-4)**.[5] Chemical shifts are usually given in the dimensionless quantity, δ, commonly expressed in parts per million. For a given nucleus, the chemical shift scale is relative and is commonly pegged to the resonance of an agreed upon reference material as described by Eq 1.

$$\delta_{sample} = (\nu_{sample} - \nu_{reference}) \div \nu_{reference} \quad (1)$$

3.1.1 Frequencies are given in Hertz. Because the numerator is very small compared with the denominator, it is usually convenient to express δ in parts per million.

3.1.2 As the location of a resonance is determined in part by the ratio of the magnetic field to the radio frequency at which it is observed, chemical shifts and spectral regions are often designated as lower frequency (increased shielding) or higher frequency (decreased shielding) relative to a reference point. Defined in this manner, chemical shifts are independent of either the magnetic field or the radio frequency used. Coupling constants, which are independent of the magnetic field or radio frequency used, are expressed in Hertz.

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.15 on Analytical Data.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

3.1.3 *nuclear magnetic resonance (NMR) tube camber, n*—maximum total deflection of any part of the outer wall of the tube held at the ends and rotated 360°; a measure of the bow in the tube.

3.1.4 *NMR tube concentricity, n*—maximum variation in wall thickness of the tube; a measure of how centered the tube inside diameter is relative to the tube outer diameter.

4. Significance and Use

4.1 This practice permits an analyst to compare the performance of an NMR spectrometer for a particular test on any given day with the instrument's prior performance for that test. The practice can also provide sufficient quantitative performance information for problem diagnosis and solving. If complete information about how a test is carried out is supplied and sufficient replicates are collected to substantiate statistical relevance, the tests in this practice can be used to establish the setting and meeting of relevant performance specifications. This practice is not necessarily meant for the comparison of different instruments with each other, even if the instruments are of the same type and model. This practice is not meant for the comparison of the performance of different instruments operated under conditions differing from those specified for a particular test.

5. Test Samples

5.1 In general, the test samples called for in this practice are commercially available materials made explicitly for the testing of NMR spectrometer performance. The particular samples chosen are those that have been widely accepted by the NMR community of users and vendors for these purposes. However, in certain instances, especially with higher field instruments, the commonly accepted samples may exhibit characteristics that render them less than ideal for such uses.

5.2 Each sample shall be uniquely identifiable, and a certificate containing information about the sample shall be available (ISO Guide 31). In addition to the information required elsewhere in this practice, the certificate shall list the manufacturer of the sample, the date of manufacture, the name of the sample, and a reference number (for example, sample serial or lot number) (see Fig. 1).

5.3 *Sample Tubes*—Although sample tubes with sizes ranging from about 1 mm to 25 mm outside diameter (OD) are used in modern NMR spectrometers, the 5 mm OD tube remains the most common size. To avoid detailing test procedures for all possible tube sizes, this practice specifies tests for use with 5 mm OD sample tubes. Users requiring sample tubes of differing size should scale the quantities, dimensions, and volumes given here to the requirements of their spectrometers taking into account any specific recommendations of the instrument's manufacturer.

5.3.1 The inside diameter of the sample container shall be stated along with tolerances from the manufacturer.

5.3.2 The quality of the tube in terms of its concentricity and camber shall be stated. The concentricity and camber of the tube should be smaller than 0.025 mm and 0.013 mm, respectively.

5.4 *Analytes, Solvents, and Chemical Shift Standards*—Analyte concentration is defined as a volume percentage (v/v) at 25 °C, that is, the volume of the analyte divided by the total volume of the solution.

5.4.1 Unless otherwise specified, the chemical purity of each component for standard samples used to test sensitivity shall be ≥99.5 weight % and the purity of each component for all other standard samples shall be ≥99 weight %. The resonances of impurities observed in the spectrum of the standard sample should not interfere with the resonances of interest in the standard sample. This usually means that the impurity peaks shall not appear within the region of the satellite peaks, particularly for resolution standard samples. However, samples with higher water content may still be usable so long as the water signal does not interfere with the spectral test. Water content may be determined by Karl Fischer titration or by ^{1}H NMR spectroscopy (protic water only). The purity of the analyte(s) shall be stated.

5.4.2 Except as noted, the sample solvent should be deuterated to provide a field/frequency lock for the spectrometer, of the highest purity commonly obtainable, and have an atom-percent deuteration of at least 99 %. The solvent's purity and level of deuteration shall be stated.

5.4.3 When used, chemical shift standards should be of the highest purity commonly available and added to the sample to achieve a concentration approximately one tenth that of the analyte. The purity and concentration of the chemical shift standard shall be stated.

5.5 *Sample Preparation*—Either a m/m method or a v/v method may be used for sample preparation; however, care shall be taken to assure better than 1 % accuracy in the measurements. If a v/v method is used, the densities used for the liquid components shall be stated. Unless specified otherwise, any impurities in the final sample (including water) should be less than 10 mol % of the analyte concentration. The final analyte concentration and its uncertainty shall be stated.

5.5.1 The sample should be sealed under nitrogen or argon taking care that the final sample is near atmospheric pressure.

5.5.2 Each sample tube shall bear a label stating its content and reference identifier.

5.5.3 For long-term storage, samples should be maintained in the dark to prevent photolysis. Except as noted, samples may be stored at room temperature. For long-term storage, samples containing chloroform should be kept between −25 °C and 8 °C unless the sample is known to have been deoxygenated.

6. Preliminary Experimental Procedures

6.1 To achieve consistent results, the following shall be completed before the performance measurement:

6.1.1 The sample temperature should be stabilized at approximately 25 °C, controlled during the measurement (8.16), and specified in the report.

6.1.2 The magnetic field homogeneity shall be adjusted to the best achievable on the sample to be used (8.9 – 8.12).

6.1.3 The observe radio frequency (rf) circuitry shall be well-tuned and matched to the sample to be used. If decoupling is used, the decoupling rf circuitry shall be tuned and matched to the sample to be used.

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Certificate of Analysis

NMR Performance Evaluation Standard

60 % (v/v) benzene-d_6 (C_6D_6) in *p*-dioxane

LD&D Part Number: ^{13}C-SNR1-5

Sample ID (tube label): 60 % C_6D_6 in *p*-dioxane; LD&D ^{13}C-SNR1-5; 11C1304

Date of Manufacture: 08/11/2011

Date of Qualification: 12/13/2011

Lot Number: 11C1304

Tube Parameters: borosilicate; 5.0 mm O.D.; 4.24 mm I.D.; 190 mm length; ≤0.025 mm concentricity; ≤0.013 mm camber

Constituent Purities (including water):

p-dioxane: 99.7 % pure by ^{1}H NMR

benzene-d_6: 99.6 % pure by GC; 99.6 atom % deuteration by ^{1}H NMR; 1.08 atom % ^{13}C by MS

Degassing: helium sparge of bulk sample prior to tube filling and sealing

Sealant Gas: nitrogen

Analyte Concentration: 60 % ± 0.08 % (v/v) benzene-d_6 by GC

Sample Filling Height: 50 mm ± 2.5 mm

Usage: determination of coupled ^{13}C NMR Sensitivity and ^{13}C NMR resolution and lineshape

Storage: keep in the dark between 10 °C and 30 °C

Stability: If handled and stored properly, this sample should be indefinitely useable. Sample stability may be monitored by appropriate quantitative NMR techniques.

FIG. 1 Example of a Certificate of Analysis for an NMR Test Sample

6.1.4 The 90° pulse for the probe to be used should be measured and reported. If decoupling is used, parameters, such as peak power in Hertz, mean power level in Hertz, and the decoupling modulation pattern shall be measured and reported. The decoupling power is defined in Hertz as one divided by the duration of the decoupling channel 360° pulse in seconds at the power level being used for decoupling.

6.1.5 The T_1 relaxation time of the specific sample resonance of interest should be measured on each sample to assure that the equilibration period is adequate. As T_1 relaxation times are dependent on the specific resonance observed, sample concentration, sample temperature, magnetic field strength, and the concentration of certain impurities (most notably dissolved oxygen), basing the equilibration period on literature T_1 values is insufficient. Unless experimental conditions such as temperature or field strength are changed, the T_1 need only be determined once for a sealed sample.

6.1.6 For sensitivity tests in which the signal-to-noise ratio (S/N) is insufficient, signal averaging may be used. If multiple transients are collected, the resulting sensitivity value shall be adjusted as described in 7.2.

6.1.7 In cases in which the natural abundance of the measured isotope is low, it may be necessary to correct the S/N for the actual abundance of the measured isotope in the sample itself. Examples of this are S/N determinations for ^{13}C, ^{15}N, and ^{29}Si.

6.1.8 For both sensitivity and resolution tests, decoupling should not be used unless specified.

7. Reporting Results

7.1 *General Tests*—Results may be reported from determinations made by single procedures.

7.2 *Signal Averaging*—If signal averaging is used, the measured sensitivity value shall be adjusted by dividing by the square root of the number of transients.

7.3 *Tests for Establishing and Meeting Specifications*—Specification-level test results shall be reported as the average along with the standard deviation of the results from ten replications of the specified test made with no intervening adjustments. For specification results, actual analyte concentrations and their uncertainties and tube dimensions (specifically, either the internal diameter or the external diameter and wall thickness) shall be reported.

8. Specific Test Procedures

8.1 *^1H Sensitivity*—This practice describes the determination of the proton sensitivity of the NMR system.

8.1.1 *Sample*—The sample is 0.1 % (v/v) ethylbenzene in deuterochloroform (chloroform-*d*) containing 0.003 % (v/v) to 0.1 % (v/v) tetramethylsilane (TMS). The density of ethylbenzene is 0.86702 g/cm^3 at 20 °C, 0.862 64 g/cm^3 at 25 °C, and 0.858 28 g/cm^3 at 30 °C (**5**). The density of chloroform-*d* is 1.5007 g/cm^3 at 20 °C (**6**), 1.4999 g/cm^3 at 25 °C, and 1.4906 g/cm^3 at 30 °C (**7**). The density of TMS is 0.6386 g/cm^3 at 20 °C, 0.6329 g/cm^3 at 25 °C, and 0.6274 g/cm^3 at 30 °C (**8**). The ethylbenzene shall be 99.95 % pure and free from chlorinated by-products, such as (2-chloroethyl)benzene (**9**) and (1-chloroethyl)benzene (in chloroform-*d*—5.12 and 1.88 ppm) (**10**), and care shall be taken to ensure that it has not reacted with air to produce oxygenated products (**11**), such as the hydroperoxide [chloroform-*d*—8 ppm to 9 ppm (s, 1H), 5.05 ppm (q, 1H), 1.45 ppm (d, 3H)] (**12**), *sec*-phenethyl alcohol (**13**), acetophenone (**14**), and benzaldehyde (**15**). The total contribution from all impurities (excluding water) in the final sample shall be less than 1 mol % of the ethylbenzene concentration. The peak height of the signal from dissolved water in the sample shall be smaller than that of the methyl triplet. For very high-sensitivity systems, a more dilute sample may be used. Sensitivity shall then be converted to and clearly reported as "equivalent to 0.1 % (v/v) ethylbenzene at 25 °C." The final concentration and its uncertainty shall be specified.

8.1.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.1.2.1 *Spectral Region*—The larger of 30-ppm or 11-kHz (for proton frequencies below 400 MHz) width centered on the methylene resonance of ethylbenzene.

8.1.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the ethylbenzene methylene resonance reduced by the acquisition time.

8.1.2.3 *Pulse Flip Angle*—90°.

8.1.2.4 *Data Acquisition Time*—4 s to 8 s.

8.1.2.5 *Number of Transients*—One.

8.1.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.1.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.1.3 *Data Processing*—The following data processing parameters shall be used:

8.1.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (line broadening) = 1 Hz and t = time value for each acquired data point.

8.1.4 Zero fill to at least twice the size of the data table. Calculate the FT using sufficient data points to yield a digital resolution of ≤0.05 Hz per data point. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 2).

8.1.5 No data smoothing or other types of data manipulation may be applied except as specified in 8.1.3.1.

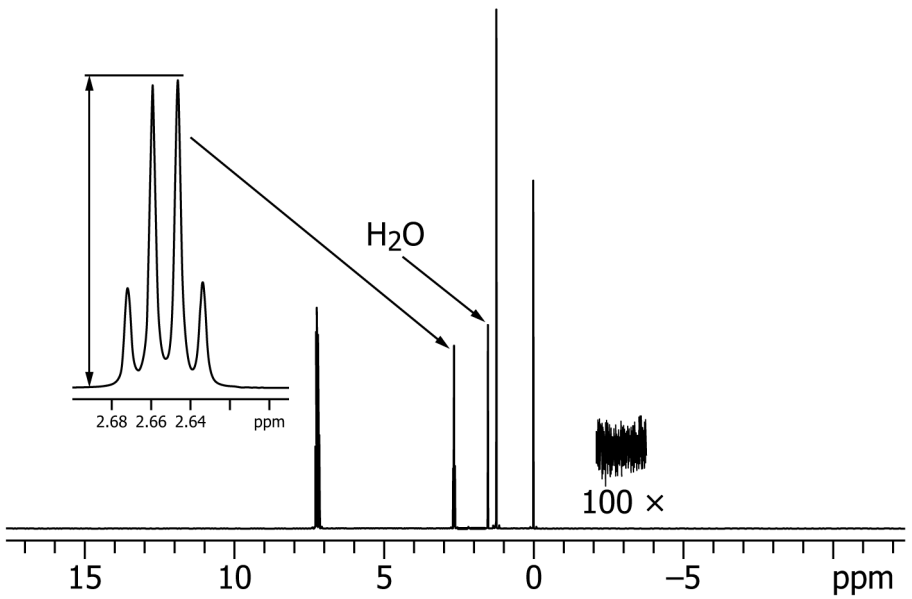

FIG. 2 600.1 MHz ^1H Sensitivity Test Spectrum of 0.1 % Ethylbenzene with Tetramethylsilane in Chloroform-*d*

8.1.6 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.1.6.1 Signal is defined as the amplitude of the tallest peak in the methylene resonance (2.65 ppm) of the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- (offset) and first-order (slope) baseline corrections should be applied to a region of 1 ppm around the signal.

8.1.6.2 Noise is defined as two times the root mean square (rms) noise in the region of 1 kHz starting at −2 ppm from the TMS signal and going to lower frequency where minimal interference from resonances of chemical impurities is found. Zero- and first-order baseline corrections should be applied to the 1 kHz noise region.

8.1.6.3 To calculate rms noise, use:

$$\text{rms noise} = \{[\Sigma\ (\text{amplitude})^2]/(N\ -\ 1)\}^{1/2} \quad (2)$$

(1) The amplitude of each point measured from the zero-intensity line in the selected 1 kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.1.6.4 The S/N is equal to: signal ÷ (2 × rms noise).

8.1.6.5 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.1.7 *Reporting Sensitivity*—The results of ^{1}H sensitivity measurements shall be reported as described in Section 7. If sample concentrations other than those in 8.1.1 are used, sensitivity results should be corrected for concentration and reported as "equivalent to 0.1 % (v/v) ethylbenzene."

8.2 *Decoupled ^{13}C Sensitivity*—This practice describes the determination of the decoupled carbon-13 sensitivity of the NMR system.

8.2.1 *Sample*—The sample is 10 % (v/v) ethylbenzene in chloroform-*d*. The densities and purities of the sample constituents are given in 8.1.1. The ethylbenzene shall be 99.95 % pure and free from chlorinated by-products, such as (2-chloroethyl)benzene **(16)** and (1-chloroethyl)benzene **(17)**, and care shall be taken to ensure that it has not reacted with air to produce oxygenated products **(11)**, such as the hydroperoxide (in chloroform-*d*—20.4 ppm, 84.0 ppm, 126.8 ppm, 128.5 ppm, 128.9 ppm, and 141.7 ppm) **(12)**, *sec*-phenethyl alcohol **(18)**, acetophenone **(19)**, and benzaldehyde **(20)**. The sample shall be prepared from ethylbenzene of known ^{13}C isotopic abundance near that of the natural mean abundance at positions 2 and 3 of the benzene ring. The ^{13}C abundance and the means of measuring this shall be reported on the certificate. The total contribution from all impurities in the final sample (including water) should be less than 10 mol % of the ethylbenzene concentration. The final concentration and its uncertainty shall be specified.

8.2.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.2.2.1 *Spectral Region*—A 200 ppm width with the transmitter frequency set to 100 ppm with chloroform-*d* referenced to approximately 77 ppm.

8.2.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the ethylbenzene C2 or C3 resonances reduced by the acquisition time.

8.2.2.3 *Pulse Flip Angle*—90°.

8.2.2.4 *Data Acquisition Time*—5 s.

8.2.2.5 *Number of Transients*—One.

8.2.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.2.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.2.2.8 *Decoupling Conditions*—Decoupling parameters such as peak power in Hertz, mean power levels in Hertz, and decoupling modulation pattern shall be specified. The parameters chosen should result in all the ethylbenzene peaks appearing as singlets with line widths less than 1 Hz. The decoupling frequency shall be centered at approximately 4.3 ppm relative to the proton signal of chloroform at 7.26 ppm. The same decoupling conditions shall be maintained during the acquisition and the relaxation delay.

8.2.3 *Data Processing*—The following data processing parameters shall be used:

8.2.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB\cdot t\cdot\pi}$ where LB (also known as width) = 0.3 Hz and t = time value for each acquired data point. Zero fill to at least double the size of the data table. Calculate the FT using sufficient data points to yield a digital resolution of ≤0.02 Hz per data point. If the instrument cannot achieve this resolution, the highest achievable resolution should be used. Apply phase corrections as needed to produce the pure absorption mode spectrum (see Fig. 3).

8.2.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.2.3.1.

8.2.5 *S/N Calculation*—The calculations for S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.2.5.1 Signal is defined as the amplitude of the tallest aromatic resonance of ethylbenzene (approximately 128 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of 10 ppm around the signal.

8.2.5.2 Noise is defined as two times the rms noise in the region between 80 ppm and 120 ppm with the central peak of chloroform-*d* referenced at approximately 77 ppm. Zero- and first-order baseline corrections should be applied to the noise region.

8.2.5.3 Use Eq 2 to calculate rms noise.

8.2.5.4 The amplitude of each point measured from the zero-intensity line in the selected 40 ppm region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.2.5.5 The corrected S/N is equal to:

$$\text{signal} \div (2\ \times\ \text{rms noise}\ )\ \times\ (1.105\ \div\ \text{the measured}\ \ ^{13}C\ \ \text{abundance}) \quad (3)$$

NOTE 1—Corrected for the average natural abundance of ^{13}C **(21)**.

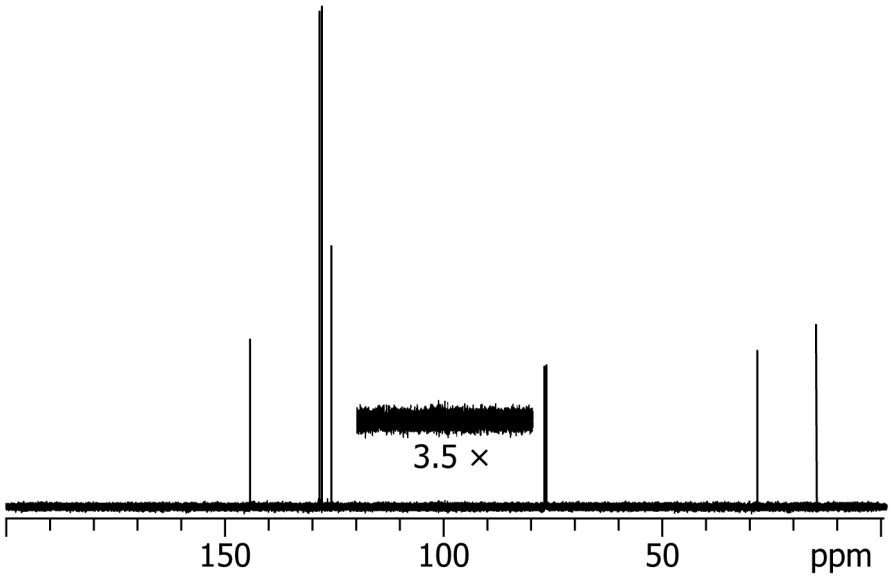

FIG. 3 125.8-MHz ^{1}H Decoupled ^{13}C Sensitivity Test Spectrum of 10 % Ethylbenzene in Chloroform-*d*

8.2.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.2.6 *Reporting Sensitivity*—The results of the decoupled ^{13}C sensitivity measurements shall be reported as described in Section 7.

8.3 *Coupled ^{13}C Sensitivity*—This practice describes the determination of the coupled ^{13}C sensitivity of the NMR system.

8.3.1 *Sample*—The sample is 60 % (v/v) benzene-d_6 in *p*-dioxane (also known as 1,4-dioxane). The density of benzene-d_6 is 0.9494 g/cm^3 at 20 °C, 0.9436 g/cm^3 at 25 °C, and 0.9378 g/cm^3 at 30 °C (**22**). The density of *p*-dioxane is 1.0336 g/cm^3 at 20 °C, 1.0280 g/cm^3 at 25 °C, and 1.0224 g/cm^3 at 30 °C (**23**). The benzene-d_6 shall be at least 99 % deuterated. The *p*-dioxane shall be at least 99 % pure, and care shall be taken to ensure that it has not reacted with air to produce oxygenated products. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the *p*-dioxane concentration. The final concentration and its uncertainty shall be stated. For routine use (not for specification purposes), a relaxation agent, such as 0.2 % Cr(acac)$_3$, may be added to the sample to permit more rapid data acquisition, provided its use is reported.

8.3.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.3.2.1 *Spectral Region*—A 100 ppm width with the transmitter frequency set at 100 ppm ± 10 ppm.

8.3.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the benzene-d_6 resonance reduced by the acquisition time.

8.3.2.3 *Pulse Flip Angle*—90°.

8.3.2.4 *Data Acquisition Time*—1 s.

8.3.2.5 *Number of Transients*—One.

8.3.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.3.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.3.2.8 No decoupling.

8.3.3 *Data Processing*—The following data processing parameters shall be used:

8.3.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB\cdot t\cdot\pi}$ where LB (also known as width) = 3.5 Hz and t = time value for each acquired data point.

8.3.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 4).

8.3.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.3.3.1, unless its use is specifically described in the resulting report.

8.3.5 *S/N Calculation*—The calculations for the S/N ratio are carried out on the real part of the pure phase absorption mode spectrum.

8.3.5.1 Signal is defined as the amplitude of the tallest benzene-d_6 resonance (approximately 128 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of 10 ppm around the signal.

8.3.5.2 Noise is defined as two times the rms noise in the region between 80 ppm and 120 ppm. For spectrometers with proton frequencies less than 350 MHz, this will result in fewer than 1000 zero crossings within the noise region, which will reduce the precision of the noise measurement. Zero- and first-order baseline corrections should be applied to the noise region.

8.3.5.3 Use Eq 2 to calculate rms noise.

8.3.5.4 The amplitude of each point measured from the zero-intensity line in the selected 40 ppm region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

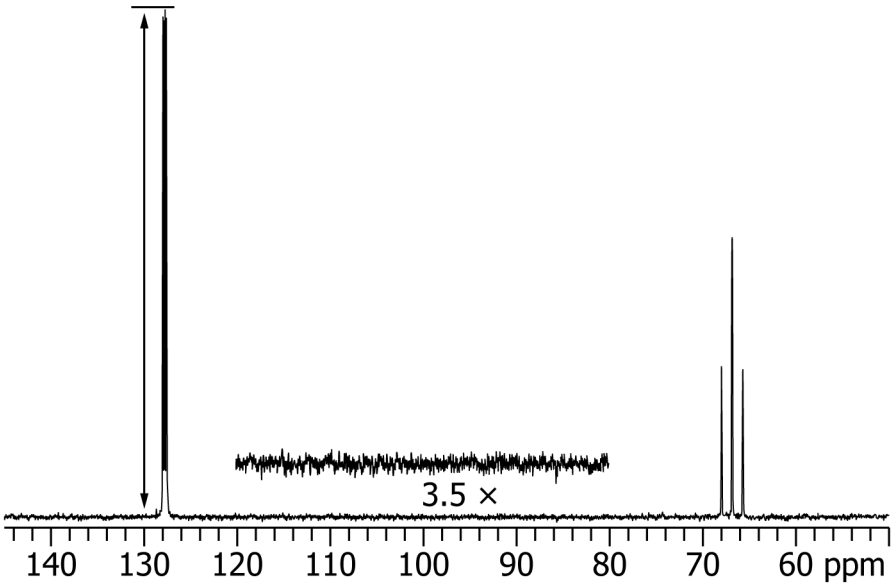

FIG. 4 125.8 MHz Coupled ^{13}C Sensitivity Test Spectrum of 60 % Benzene-d_6 and 40 % *p*-Dioxane

8.3.5.5 The corrected S/N is equal to:

$$\text{signal} \div (2 \times \text{rms noise}) \times (1.105 \div \text{the measured } {}^{13}C \text{ abundance}) \quad (4)$$

NOTE 2—Corrected for the average natural abundance of ^{13}C (**21**).

8.3.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.3.6 *Reporting Sensitivity*—The results of the coupled ^{13}C sensitivity measurements shall be reported as described in Section 7.

8.4 *^{31}P Sensitivity*—This practice describes the determination of the ^{31}P sensitivity of the NMR system.

8.4.1 *Sample*—The sample is 0.0485 mol L^{-1} triphenylphosphate in acetone-d_6 or chloroform-*d*. The molecular mass of triphenylphosphate is 326.28 g. The triphenylphosphate shall be at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the triphenylphosphate concentration. The final concentration and its uncertainty shall be stated.

8.4.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.4.2.1 *Spectral Region*—A 40 kHz width with the transmitter frequency set to approximately the resonance of triphenylphosphate.

8.4.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the triphenylphosphate resonance reduced by the acquisition time.

8.4.2.3 *Pulse Flip Angle*—90°.

8.4.2.4 *Data Acquisition Time*—1 s.

8.4.2.5 *Number of Transients*—One.

8.4.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.4.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.4.2.8 No decoupling.

8.4.3 *Data Processing*—The following data processing parameters shall be used:

8.4.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 5 Hz and t = time value for each acquired data point.

8.4.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 5).

8.4.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.4.3.1.

8.4.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.4.5.1 Signal is defined as the amplitude of the triphenylphosphate resonance (approximately −18 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±5 kHz around the signal.

8.4.5.2 Noise is defined as two times the rms noise in the 5 kHz region starting from −5 kHz to −10 kHz from the triphenylphosphate resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.4.5.3 Use Eq 2 to calculate rms noise.

8.4.5.4 The amplitude of each point measured from the zero-intensity line in the selected 5 kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.4.5.5 The S/N is equal to: signal ÷ (2 × rms noise).

8.4.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.4.6 *Reporting Sensitivity*—The results of the ^{31}P sensitivity measurements shall be reported as described in Section 7.

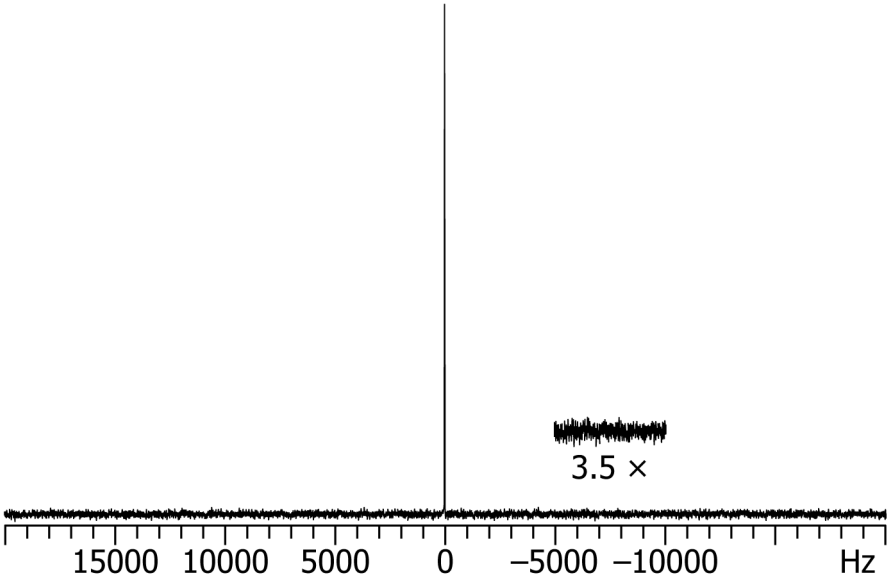

FIG. 5 202.5 MHz ^{31}P Sensitivity Test Spectrum of 0.0485 mol/L Triphenylphosphate in Acetone-d_6

8.5 *^{19}F Sensitivity*—This practice describes the determination of the ^{19}F sensitivity of the NMR system.

8.5.1 *Sample*—The sample is 0.05 % (v/v) α,α,α-trifluorotoluene [also known as trifluorotoluene, benzotrifluoride, (trifluoromethyl) benzene, or phenylfluoroform] in benzene-d_6 or chloroform-*d*. The density of trifluorotoluene is 1.1884 g/cm^3 at 20 °C, 1.1815 g/cm^3 at 25 °C, and 1.1743 g/cm^3 at 30 °C (**24**). The density of benzene-d_6 is given in 8.3.1. The density of chloroform-*d* is given in 8.1.1. The trifluorotoluene shall be at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the trifluorotoluene concentration. The final concentration and its uncertainty shall be stated.

8.5.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.5.2.1 *Spectral Region*—A 16 kHz width with the transmitter frequency set to approximately the resonance of trifluorotoluene.

8.5.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the trifluorotoluene resonance reduced by the acquisition time.

8.5.2.3 *Pulse Flip Angle*—90°.

8.5.2.4 *Data Acquisition Time*—At least 4 s.

8.5.2.5 *Number of Transients*—One.

8.5.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.5.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.5.2.8 No decoupling.

8.5.3 *Data Processing*—The following data processing parameters shall be used:

8.5.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 2 Hz and t = time value for each acquired data point.

8.5.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 6).

8.5.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.5.3.1.

8.5.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.5.5.1 Signal is defined as the amplitude of the trifluorotoluene resonance (approximately −63 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±2 kHz around the signal.

8.5.5.2 Noise is defined as two times the rms noise in the 2 kHz region from −2 kHz to −4 kHz from the trifluorotoluene resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.5.5.3 Use Eq 2 to calculate rms noise.

8.5.5.4 The amplitude of each point measured from the zero-intensity line in the selected 2 kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.5.5.5 The S/N is equal to: signal ÷ (2 × rms noise).

8.5.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.5.6 *Reporting Sensitivity*—The results of the ^{19}F sensitivity measurements shall be reported as described in Section 7.

8.6 *^{29}Si Sensitivity*—This practice describes the determination of the ^{29}Si sensitivity of the NMR system.

8.6.1 *Sample*—The sample is 25 % (v/v) hexamethyldisiloxane in benzene-d_6. The density of hexamethyldisiloxane is 0.7636 g/cm^3 at 20 °C, 0.7584 g/cm^3 at 25 °C, and 0.7536 g/cm^3 at 30 °C (**25**). The density of benzene-d_6 is given in

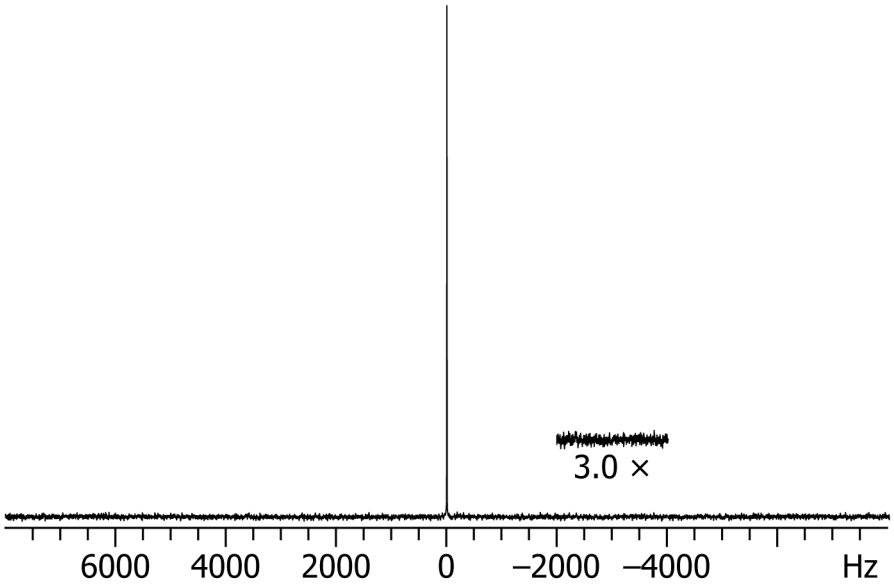

FIG. 6 470.6 MHz ^{19}F Sensitivity Test Spectrum of 0.05 % α,α,α-Trifluorotoluene in Chloroform-*d*

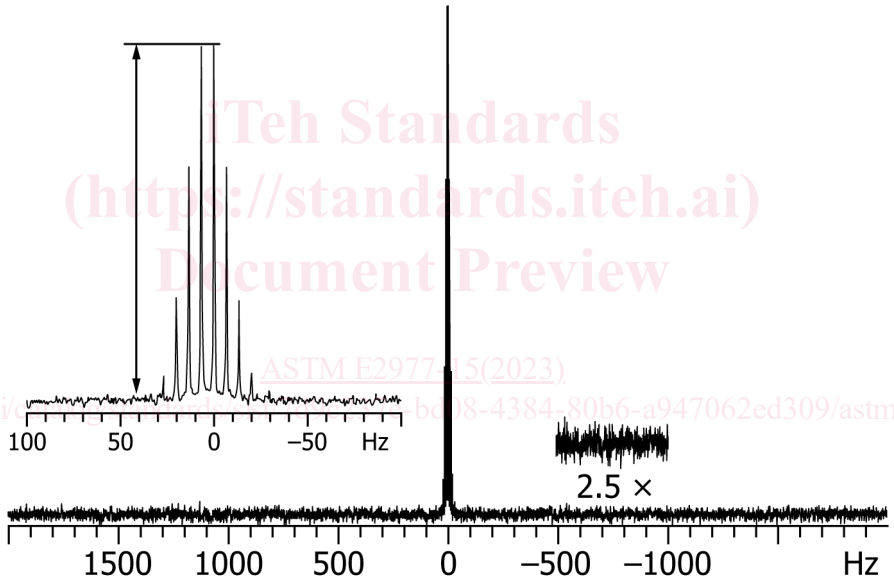

FIG. 7 119.2 MHz ^{29}Si Sensitivity Test Spectrum of 25 % Hexamethyldisiloxane in Benzene-d_6

8.3.1. The hexamethyldisiloxane shall be anhydrous and at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the hexamethyldisiloxane concentration. The final concentration and its uncertainty shall be stated.

8.6.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.6.2.1 *Spectral Region*—A 4 kHz width with the transmitter frequency set to approximately the resonance of hexamethyldisiloxane.

8.6.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the hexamethyldisiloxane resonance reduced by the acquisition time.

8.6.2.3 *Pulse Flip Angle*—90°.

8.6.2.4 *Data Acquisition Time*—At least 4 s.

8.6.2.5 *Number of Transients*—One.

8.6.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.6.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.6.2.8 *No Decoupling*—This test is run without decoupling to avoid issues resulting from the negative nuclear Overhauser enhancement (NOE) of ^{29}Si.

8.6.3 *Data Processing*—The following data processing parameters shall be used:

8.6.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 0.5 Hz and t = time value for each acquired data point.

8.6.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 7).

8.6.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.6.3.1.

8.6.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.6.5.1 Signal is defined as the amplitude of the hexamethyldisiloxane resonance (approximately 6 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±500 Hz around the signal.

8.6.5.2 Noise is defined as two times the rms noise in the 500 Hz region from −500 Hz to −1000 Hz from the hexamethyldisiloxane resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.6.5.3 Use Eq 2 to calculate rms noise.

8.6.5.4 The amplitude of each point measured from the zero-intensity line in the selected 500-Hz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.6.5.5 The S/N is equal to:

$$\text{signal} \div (2 \times \text{rms noise}) \times (4.685 \div \text{the measured } {}^{29}\text{Si abundance}) \quad (5)$$

NOTE 3—Corrected for the average natural abundance of ^{29}Si (**21**).

8.6.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.6.6 *Reporting Sensitivity*—The results of the ^{29}Si sensitivity measurements shall be reported as described in Section 7.

8.7 *^{15}N Sensitivity*—This practice describes the determination of the nitrogen-15 sensitivity of the NMR system.

8.7.1 *Sample*—The sample is 90 % (v/v) formamide in dimethyl sulfoxide-d_6. The density of formamide is 1.1334 g/cm^3 at 20 °C, 1.1330 g/cm^3 at 25 °C, and 1.1246 g/cm^3 at 30 °C (**26, 27**). The density of dimethyl sulfoxide-d_6 is 1.195 g/cm^3 at 20 °C (**7**), 1.190 g/cm^3 at 25 °C (**28**), and 1.185 g/cm^3 at 30 °C (**7**). The formamide shall be anhydrous and at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the formamide concentration. The final concentration and its uncertainty shall be stated.

8.7.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.7.2.1 *Spectral Region*—A 2.4 kHz width with the transmitter frequency set to approximately the resonance of formamide.

8.7.2.2 *Equilibration Delay*—At least seven times the T_1 relaxation time of the formamide resonance.

NOTE 4—This is seven rather than five times T_1 and not reduced by the acquisition time to allow sufficient time for the decay of the strongly negative nuclear Overhauser effect (NOE).

8.7.2.3 *Pulse Flip Angle*—90°.

8.7.2.4 *Data Acquisition Time*—6 s.

8.7.2.5 *Number of Transients*—At least one. (The low sensitivity of ^{15}N may mean that more than one transient is required to obtain an accurate result.)

8.7.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.7.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.7.2.8 *Decoupling Conditions*—Decoupling parameters such as peak power in Hertz, mean power levels in Hertz, and decoupling modulation pattern shall be specified. The parameters chosen should result in the signal appearing as a singlet with line widths less than 0.6 Hz after the application of apodization as described in 8.7.3.1. From the proton spectrum of the sample, determine the mean frequency of the amide signals and set the decoupling frequency to this value. The same decoupling conditions shall be maintained only during the acquisition. Because of the negative NOE of ^{15}N, no decoupling should be applied during the relaxation delay.

8.7.3 *Data Processing*—The following data processing parameters shall be used:

8.7.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 0.3 Hz and t = time value for each acquired data point.

8.7.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 8).

8.7.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.7.3.1.

8.7.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.7.5.1 Signal is defined as the amplitude of the formamide resonance (approximately 113 ppm relative to Ξ = 10.132 911 1 %) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±300 Hz around the signal.

8.7.5.2 Noise is defined as two times the rms noise in the 300 Hz region from −300 Hz to −600 Hz from the formamide resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.7.5.3 Use Eq 2 to calculate rms noise.

8.7.5.4 The amplitude of each point measured from the zero-intensity line in the selected 300-Hz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.7.5.5 The corrected S/N is equal to:

$$\text{signal} \div (2 \times \text{rms noise}) \times (0.366 \div \text{the measured } {}^{15}\text{N abundance}) \quad (6)$$

NOTE 5—Corrected for the average natural abundance of ^{15}N (**21**).

8.7.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.7.6 *Reporting Sensitivity*—The results of the ^{15}N sensitivity measurements shall be reported as described in Section 7.

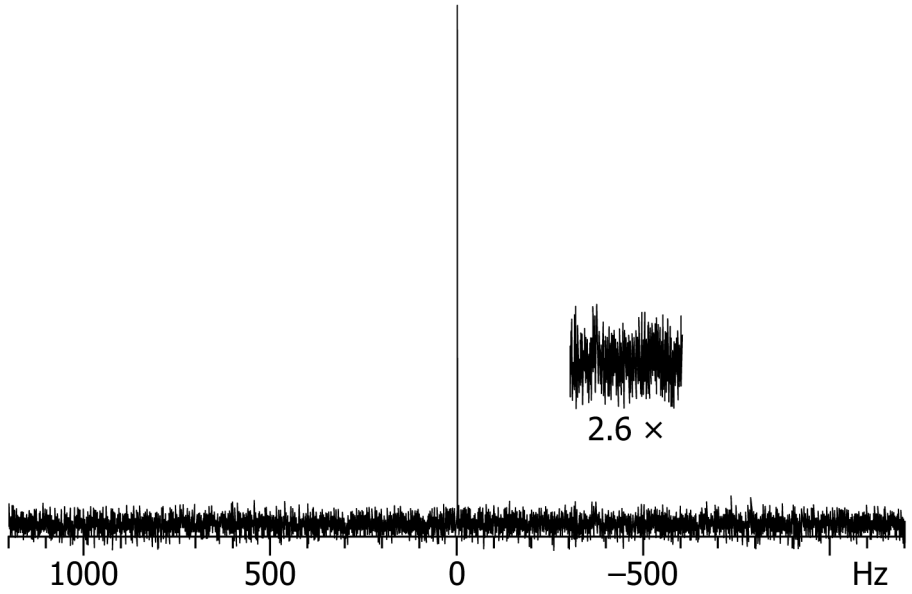

FIG. 8 50.7 MHz ^{15}N Sensitivity Test Spectrum of 90 % Formamide in Dimethyl sulfoxide-d_6

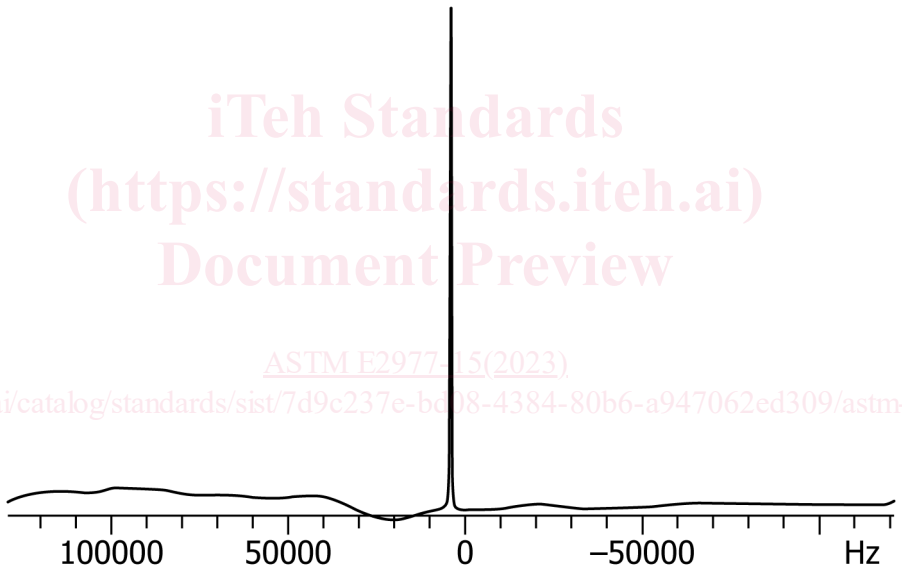

FIG. 9 36.1 MHz ^{14}N Sensitivity Test Spectrum of 90 % Formamide in Dimethyl Sulfoxide-d_6 without Acoustic Ringing Suppression

8.8 *^{14}N Sensitivity*—This practice describes the determination of the nitrogen-14 sensitivity of the NMR system.

8.8.1 *Sample*—The sample is 90 % (v⁄v) formamide in dimethyl sulfoxide-d_6 and is described in 8.7.1.

8.8.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.8.2.1 *Spectral Region*—A 250 kHz width with the transmitter frequency set to approximately the resonance of formamide.

8.8.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the formamide resonance reduced by the acquisition time.

8.8.2.3 *Pulse Flip Angle*—90°.

8.8.2.4 *Data Acquisition Time*—30 ms.

8.8.2.5 The pre-acquisition delay to allow for dead time should be set so that the S/N without acoustic ringing suppression is maximized.

8.8.2.6 *Number of Transients*—Sixty-four. If acoustic ringing distortion is present, the test may be carried out with acoustic ringing suppression **(29, 30**, pp. 235-236**)**. If acoustic ringing suppression is used (Fig. 9), the associated pulse sequence shall be specified.

8.8.2.7 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.8.2.8 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.8.2.9 No decoupling.

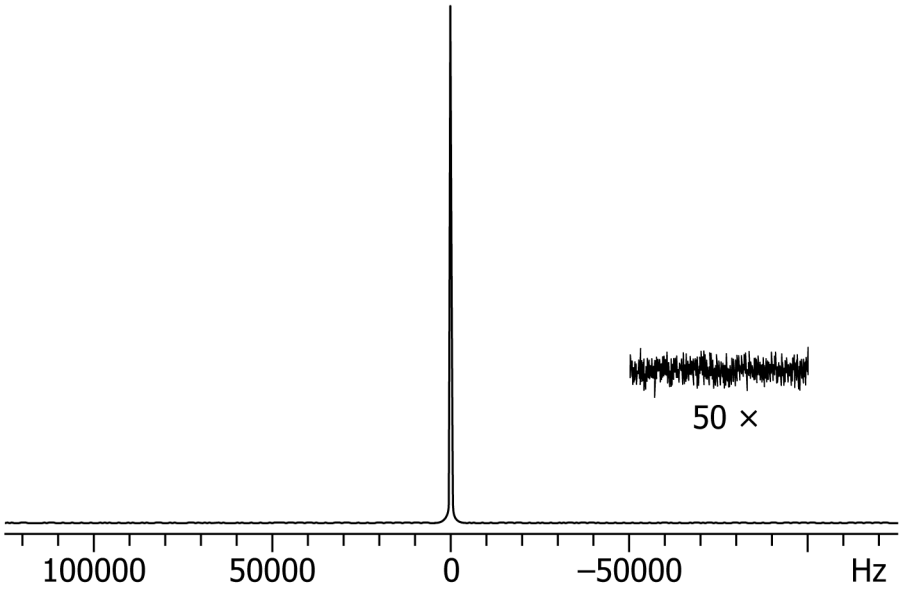

FIG. 10 36.1 MHz ^{14}N Sensitivity Test Spectrum of 90 % Formamide in Dimethyl Sulfoxide-d_6 with Acoustic Ringing Suppression

8.8.3 *Data Processing*—The following data processing parameters shall be used:

8.8.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 50 Hz and t = time value for each acquired data point.

8.8.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 10).

8.8.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.8.3.1.

8.8.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.8.5.1 Signal is defined as the amplitude of the formamide resonance (approximately 114 ppm relative to Ξ = 7.22 356 1 %) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region ±50 kHz around the signal.

8.8.5.2 Noise is defined as two times the rms noise in the 50 kHz region from −50 kHz to −100 kHz from the formamide resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.8.5.3 Use Eq 2 to calculate rms noise.

8.8.5.4 The amplitude of each point measured from the zero-intensity line in the selected 50 kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.8.5.5 The measured S/N is equal to: signal ÷ (2 × rms noise).

8.8.5.6 As 64 transients are used, the measured S/N ratio is divided by 8 to yield an S/N ratio reported as the equivalent to that from a single-scan measurement.

8.8.5.7 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.8.6 *Reporting Sensitivity*—The results of the ^{14}N sensitivity measurements shall be reported as described in Section 7.

8.9 *Primary Proton Resolution and Line Shape*—This practice describes the measurement of the proton resolution and line shape of the NMR system. It is useful for spectrometers with proton resonances between 200 MHz and 1200 MHz. As the measured resolution and line shape are critically dependent on the shimming of the spectrometer, it is not possible to separate unambiguously the instrument performance from operator performance.

8.9.1 *Sample*—The sample is 0.003 to 0.1 % (v/v) (depending on instrument sensitivity) TMS in chloroform-*d*. The TMS concentration is defined as a volume percentage (v/v) at 25 °C. The densities of TMS and chloroform-*d* are given in 8.1.1. The concentration need not be precise. However, low-signal intensity will reduce the accuracy of the measurements, and a signal that is too intense will lead to line broadening from radiation damping (**30**, p. 75). The TMS should be at least 99.9 % pure, and the chloroform-*d* should be at least 99.8 % deuterated. For long-term storage, samples should be maintained in the dark at room temperature to prevent photolysis. Photolysis is indicated by peaks at 0.128 ppm, 2.768 ppm, 0.437 ppm, and 2.210 ppm.[6] If the spectrometer has sufficient sensitivity, the same sample used for the ^{1}H NMR sensitivity measurement—0.1 % (v/v) ethylbenzene in chloroform-*d* containing 0.01 % TMS—may be used for the TMS resolution and line shape standard.

8.9.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.9.2.1 *Spectral Region*—A ≥500-Hz spectral width with the transmitter centered 50 Hz ± 10 Hz off the resonance frequency of the TMS.

8.9.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the TMS resonance reduced by the acquisition time.

[6] R. E. Hoffman, personal communication.