Designation: E2977 – 15

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 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

2.2 *ISO Standard:*[3]

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**).[4] 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.

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.

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

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

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- 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 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.

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.

LD&D Laboratories

110 Maple St.

Quahog, RI 11959 USA

(401) 555-7734

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

6.1.5 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.