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**NMR METHOD
FOR THE QUANTITATIVE PURITY ANALYSIS
OF NEAT FEED STOCK SAMPLES**

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PREFACE

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NMR METHOD FOR THE QUANTITATIVE PURITY ANALYSIS OF NEAT FEED STOCK SAMPLES

1. INTRODUCTION

This procedure is based on the previously published ERDEC-TR-449.¹ This procedure utilizes an internal standard to establish an absolute weight percent for the analytes in question. Identifying the structures of other components in the mixture is not necessary. The weight percent calculations are not negatively affected by the presence of undetectable components in the sample (elemental sulfur, inorganic salts, etc.).

2. PROCEDURE

2.1 Sample Preparation.

This procedure should be performed under appropriate engineering controls, in accordance with all appropriate surety and safety regulations.

a. Tare a screw-cap vial and cap. Dispense ~100 μ l of neat internal standard (usually TEP for acidic samples, TEP or HMPA for neutral or basic samples) of known purity into the vial and replace the cap. The exact weight is determined using an analytical balance capable of measuring to the hundredth of a milligram. Record the weight, and tare the balance.

b. Add ~100 μ l of the neat sample into the vial. Replace the cap and record the weight.

c. Mix the sample vial on a vortexing apparatus to assure homogeneity.

d. Transfer between 60 and 80 μ l of the above mixture into the Stem Coaxial Insert² tube, placing the liquid just above the capillary portion (Figure 1).

e. Option A. If the freeze-pump-thaw method^{3,4,5} is to be used, the insert tube is attached to WILMAD's NMR TIP-OFF MANIFOLD, which was in turn connected to a specialized high vacuum manifold/system, all of which was contained within engineering controls. The insert was subjected to at least 3 cycles of a Freeze-Pump-Thaw method, using liquid nitrogen for the freezing. The insert was then flame sealed under vacuum using WALE APPARATUS CO.'s "Little Torch," catalog no. 900, fitted with a "Twin Flame Tip," catalog no. 902.⁶

Option B. If the sample is to be sealed under atmospheric conditions, then the mixed sample is shaken down to the capillary end of the insert. The sample must be uniform, therefore, air voids must be eliminated. The insert is then placed in a beaker of ice or a salt and ice mixture to drop its vapor pressure. The insert is then sealed, using a jeweler's size sealing torch as in Option A.

f. Into a standard 8 in., 5-mm NMR tube (Figure 1), ~535 μL of D_2O is placed. The insert is then pushed down into the 5-mm tube. This 5-mm tube is then sealed under atmospheric conditions.

2.2 Obtaining NMR Spectra.

a. Place the NMR tube into the spinner, using vendor supplied depth gauge to orient sample at maximum sensitivity position to the coils inside the probe. Lower the sample into the magnet, lock onto the deuterium signal, and shim to maximize lock signal.

b. Call up the data file for inversion-recovery experiment for nucleus of interest if T_1 's of the nuclei of interest are not known. Perform experiment, process data, and determine the longest T_1 value for the nuclei of interest. For quantitative analysis, flip angles of 90° recycle times of eight times the longest T_1 (determined). The 32k total data point acquisition and spectral widths of 200 ppm for ^{31}P are appropriate starting points. If decoupling is required, use inverse gated-decoupling during acquisition.

c. Tune probe for optimal frequency and impedance match for the sample.

d. Enter sample name and information into NMR operating system and acquire data.

e. Perform at least seven replicates of the same sample for quantitative analysis.

2.3 Spectral Data Analysis.

a. Apply appropriate window functions such as exponential multiplication to enhance signal-to-noise (line broadening for ^{31}P should be 1-5 Hz).

b. Fourier transform the resulting data to convert from time to frequency and produce the NMR spectrum.

c. Correct the baseline and phase all peaks in the spectrum.

d. Reference the chemical shift against the internal standard (TEP should have a shift of 0.01 ppm).

e. Integrate all peaks in the spectrum to obtain areas.

Where the primary nucleus is C-13, a variation of the above method is used. For the blister-type surety material, equal amounts of the blistering material and an internal standard of known purity are combined. A convenient amount is 250 μL of each, with the exact weight determined on an analytical balance. Using the vial method as before, this mixture is thoroughly vortexed. Next, approximately 500 μL of CDCl_3 is added and again the mixture is vortexed.

The weight of the CDCl_3 is unimportant. This mixture is then transferred to a 4-mm O.D. NMR tube. The sample is chilled using ice or salt and ice to decrease the flash point of the chemicals involved. The tube is then air-sealed or purged with an inert gas and then sealed. The easiest way to seal the tube is to attach a small rod to the lip of the NMR tube using the torch, then gently pull the rod while applying the flame of the sealing torch to just below the rod, until a seal is formed. Gently here means just enough to pull the molten glass away from the NMR tube, but not enough to pull the tube out of the ice. Once cooled, this 4-mm tube can be pushed into a 5-mm NMR tube which is then simply air sealed.

3. CALCULATION, CALIBRATION, AND DOCUMENTATION

The NMR standard (ethyl benzene or Triphenylphosphate) is analyzed to assure that the spectrometer meets sensitivity specifications and chemical shift criteria, as defined for the instrument.

The weight percent of each Analyte for the sample can be calculated with the following equation when an internal standard (IS) is used :

$$\frac{\text{Area under Analyte Peak}}{\text{Area under IS Peak}} \times \frac{\text{Molecular Weight of Analyte}}{\text{Molecular Weight of IS}} \times \frac{\text{Weight of IS}}{\text{Weight of Analyte}} \times 100\% = \text{Wt. \% Analyte}$$

If analytical precision is to be reported, from at least seven replicates calculate the mean and standard deviation. The mean value ± 2 standard deviations will provide a 95% confidence range.

4. CONCLUSIONS AND DISCUSSION

The procedures above were performed in laboratory hoods, under engineering controls, operating at 100 cfm face velocity. The addition of an internal standard assists in total quantitative analysis. The final vessel is a double contained and double sealed standard. The insert samples also have D_2O surrounding the primary sealed vessel as a lock in the 5-mm tube. Aqueous samples can also be flame sealed, but not by the Freeze-Pump-Thaw method. Water, upon freezing, expands and breaks the NMR tube. For aqueous samples and for our secondary container, we flame sealed under atmospheric conditions. Major nuclei can be observed in a reasonable amount of time. Proton, carbon, and phosphorous nuclei were analyzed by this method using PW90's (90° pulse) and $8 \times T_1$ (eight times the T_1 relaxation delay) on NMR's of 300 and 500 MHz.

The sample can be neat and un-adulterated by solvents, and still have a lock solvent present within the magnetic field of the spectrometer. Aqueous samples can also be flame sealed under atmospheric conditions. Reducing the sample volume down to 80 μL of neat material benefits this operation in several ways. First it allowed observation at proton nuclei on high field instruments using PW90s and $8 \times T_1$, both of which are required for quantitative NMR spectroscopy.⁷ Though smaller in volume than a regular 5-mm NMR tube requiring 500-800 μL ,

there was still adequate material for observation of C-13 and P-31 nuclei in less than an hour for each spectra. Finally, the smaller volume and double containment of neat material allowed us to conduct a much safer operation for the NMR analysis.

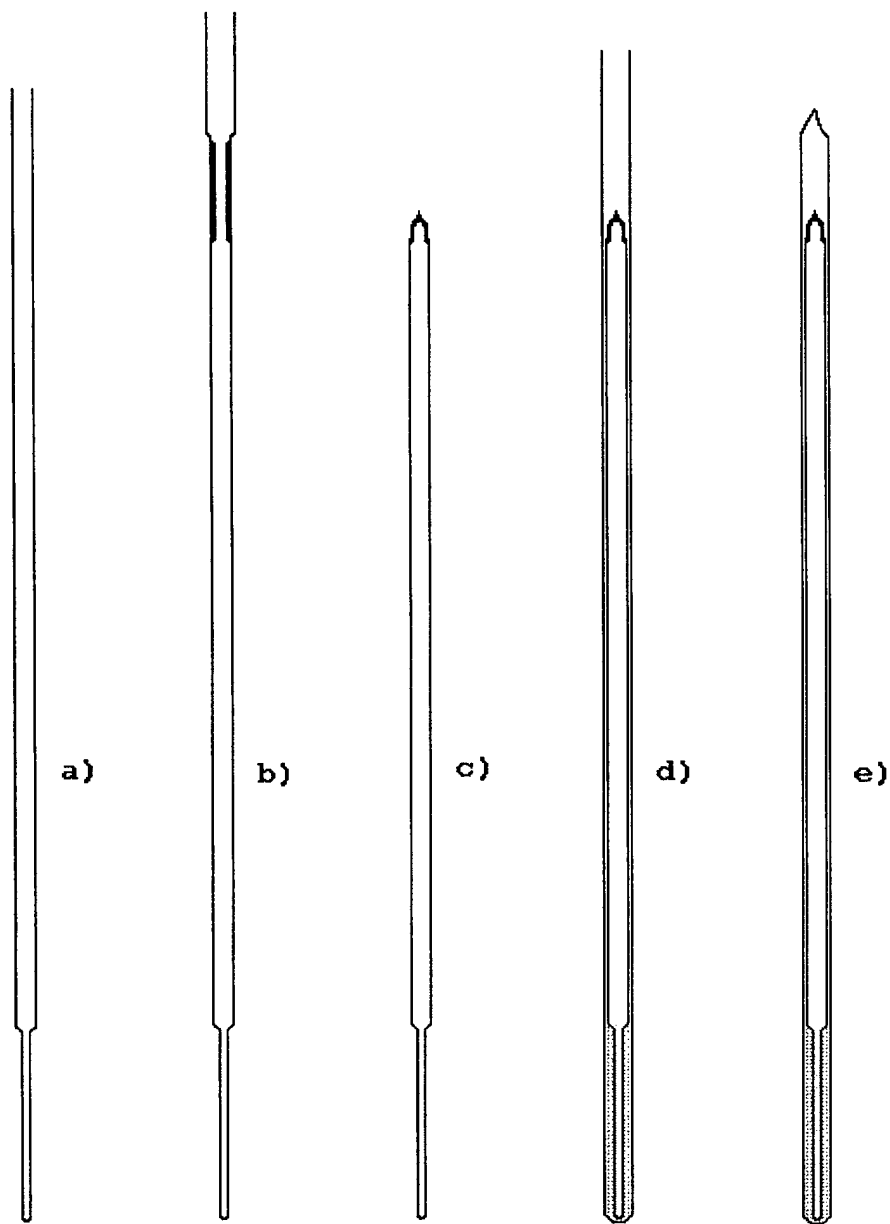


Figure 1. a) Original insert. b) Modified insert. c) Insert containing $\sim 60 \mu\text{L}$ sample, freeze-pump-thawed, then flame sealed under vacuum. d) Insert within a Wilmad 535-pp containing $\sim 0.600 \text{ mL D}_2\text{O}$. e) Secondary tube sealed under atmospheric conditions.

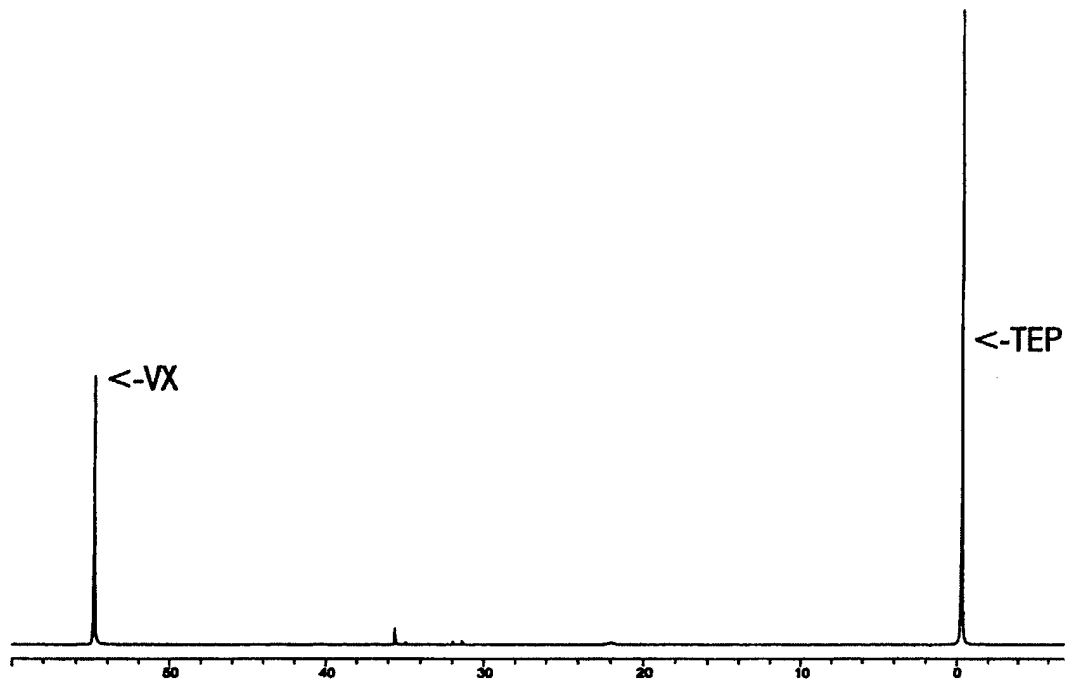


Figure 2. Representative P-31 spectra of VX with TEP internal standard.

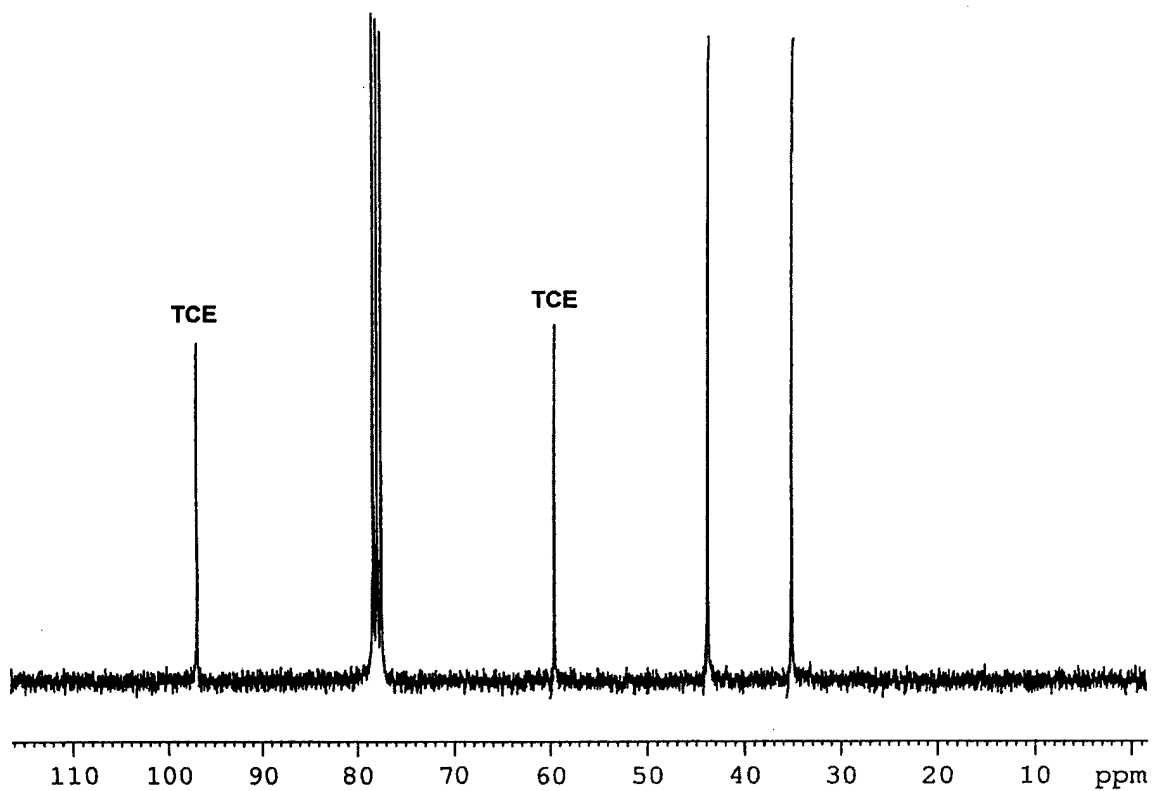


Figure 3. Representative C-13 spectrum of HD with TCE (1,1,1,2-tetrachloroethane) internal standard and d-chloroform as the solvent.

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