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# picoSpin™ 45/80: Simple Distillation of a Toluene-Cyclohexane Mixture

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## 1. Introduction

There are four basic distillation techniques for separating and purify the components of a liquid mixture: simple distillation, fractional distillation, vacuum distillation and steam distillation. The chosen distillation method and extent of purification will depend on the nature of the mixture, and specifically the difference of the boiling points of miscible liquids. In distillation, the mixture is heated, vaporizing a substance. Under boiling reflux, the vapor phase becomes richer in the lower boiling component as vapors continue to condense and move up the distillation head, purifying the mixture.

Simple distillation is most effective when applied to mixtures where the liquid components differ in their boiling points by at least 75°C. As the first component distills, the temperature is measured from vapor condensing on the bulb of a thermometer positioned just below the sidearm of the distilling head. With simple distillation, the rate of change of temperature is slow while the composition of the boiling liquid changes as distillation progress. Thus, the range over which liquid is purified is not sharp. The temperature of the distilling liquid is observed to plateau and then drop before rising again, as the process of distilling the second component begins. Here, the temperature will plateau near the boiling point of the second lowest boiling liquid in the mixture, thus distilling the second fraction. The process continues for each subsequent component, leaving the highest boiling liquid in the distilling flask. By carefully controlling the rate of distillation, it is possible to affect reasonably good separation. If distillation is rapid, then separation of the components of the mixture is poorer than if the mixture is distilled slowly.

## 2. Purpose

The purpose of this experiment is to separate components of a mixture using traditional simple distillation. A miscible liquid mixture is heated in a round bottom flask fitted with a distilling head, thermometer and condenser. The large surface area of the heating flask allows for transfer of sufficient thermal energy to distill components of a mixture. Under typical boiling conditions, as the solution is heated equilibrium develops between the vapor and liquid phase, separating out in the vapor phase the lower boiling component. By distilling to rapidly, added heat and excess vapors disrupts the equilibrium, causing higher-boiling components to distill in early fractions. As the distillation proceeds, the condensation line moves up the cold surface of the flask, heating it and distilling the first component. Reaching the thermometer bulb the

vapor-phase temperature is measured just before it condenses and liquefies in an air or water-cooled condenser tube. Condensed, purified liquid then flows to a collection flask.

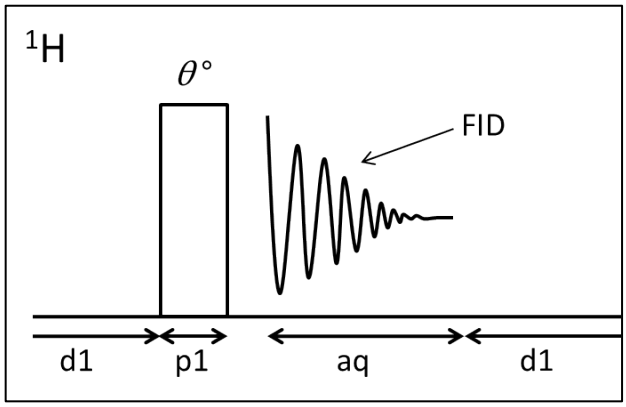
In this experiment, a 50:50 mixture of cyclohexane and toluene will be distilled, separating the lower boiling component from the mixture. The initial mixture, the distillate and the pot residue will be analyzed using the Thermo Scientific™ picoSpin™ 45 or 80 NMR spectrometer. Samples will be quantified but integrating resonance signals in the spectra to determine the molar ratio of the initial mixture, distillate and pot residue, and to evaluate the efficiency of simple distillation of our choice of liquid samples.

## 3. Literature

Adapted from Williamson, K. L.; Minard, R.; Masters, K. M. Macroscale and Microscale Organic Experiments, 5th ed., Houghton Mifflin Co., 2007.

## 4. Pulse Sequence

In this experiment, we use a standard 90° single pulse experiment. The recycle delay time (d1) is adjusted to maximize signal intensity prior to signal averaging the next FID.




Sequence: d1–[$\theta$°–aq–d1]$_{ns}$
$\theta$°: Pulse rotation angle (flip angle)
FID: Free induction decay
d1: Recycle delay (μs) for spin-lattice relaxation
p1: R.F. transmitter pulse length (μs)
aq: Acquisition time (ms)
ns: # of scans (individual FIDs)

## 5. Procedures and Analysis

*Time requirements*: 2 hrs

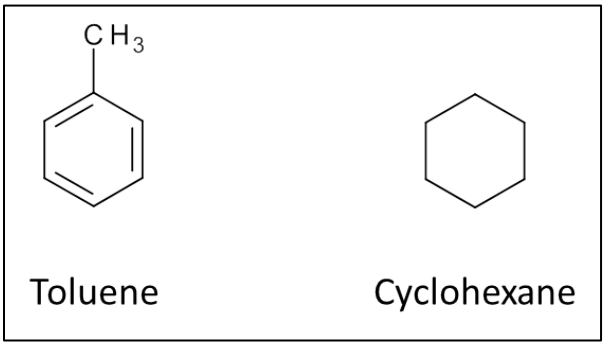
*Difficulty*: Easy

*Sample*: Cyclohexane, toluene

*Equipment/materials*:

- Thermo Scientific™ picoSpin™ 45 or 80
- Cyclohexane ($C_6H_{12}$)
- Toluene ($C_5H_5CH_3$)
- Tetramethylsilane (TMS; $(CH_3)_4Si$)
- Simple distillation apparatus
  - 100 mL round bottom flask
  - 25 mL Erlenmeyer flask
  - Condenser
  - Three-way adapter
  - Vacuum adapter
  - Clamps (flask or Keck)
  - Ring stand, ring clamp, iron ring
- Thermometer
- Thermometer adapter
- Boiling chips
- Mnova NMR Processing Suite
- picoSpin accessory kit:
  - Port plugs
  - Syringe port adapter
  - Drain tube assembly
- 25 mL beaker
- 1 mL polypropylene syringes
- 22 gauge blunt-tip dispensing needles
- 2 and 7 mL vials

*Molecules:*




*Physical data*:

| Substance | FW (g/mol) | Quantity | MP (°C) | BP (°C) | Density (g/mL) |
|---|---|---|---|---|---|
| toluene | 92.14 | 10 mL | -95 | 111 | 0.8669 |
| cyclohexane | 84.16 | 10 mL | 6.47 | 80.74 | 0.779 |
| tetramethylsilane (TMS) | 88.22 | 3 drps | -99 | 26-28 | 0.648 |
| chloroform-d ($CDCl_3$) w/1%TMS | 120.384 | 1 mL | -64 | 61 | 1.50 |
| acetone-$d_6$ (Ac-$d_6$) w/ 1%TMS* | 64.12 | 1 mL | -94 | 56 | 0.872 |

*Optional NMR solvents

## Safety Precautions

**CAUTION** Eye protection should be worn at all times while using this instrument.

**CAUTION** Avoid shock hazard. Each wall outlet used must be equipped with a 3-prong grounded outlet. The ground must be a noncurrent-carrying wire connected to earth ground at the main distribution box.

### Experimental

*Reaction procedure*

- Set up a simple distillation apparatus (Figure 1).

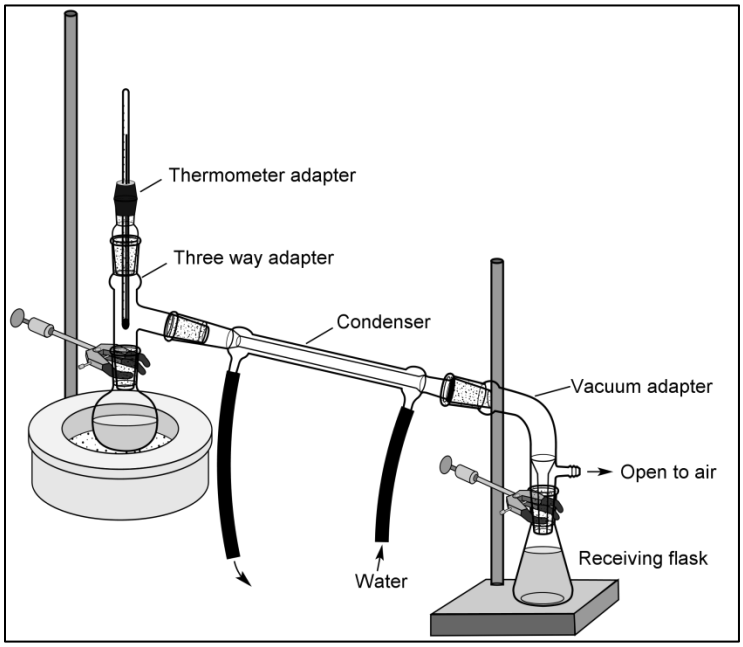



**Figure 1** Simple distillation apparatus

- Use a sand bath as a heat source.
- To a 50 mL round bottom flask, add approximately 10 mL of toluene, 10 mL of cyclohexane, and a boiling chip.
- Swirl the mixture then take a 0.25 mL aliquot for Sample 3 and transfer it to a 2mL vial.
- Place the thermometer bulb so it reaches below the sidearm of the three-way adapter.
- Use water to cool the condenser.
- Place a receiving vial at the outlet of the vacuum adapter.
- Place the vial in a 25 mL beaker filled with ice.
- Control heating of the round bottom flask by piling up or removing hot sand.

- As distillation begins, vapors will rise and condense on the cold glass.
- Control the boiling rate by removing some sand so that only about 2 drops per minute is collected in the receiving flask.
- Record the temperature as the first drops of liquid are collected. This temperature reflects the boiling point of the cyclohexane distillate.
- Collect distillate until distillation of cyclohexane stops and the observed temperature drops (approximately 7 mL)
- Do not distill to dryness.
- Turn off the sand bath.
- Prepare samples for NMR analysis

*Preparing Samples*

Several samples will be prepared for analysis. Samples can be analyzed as neat liquids. Since the $^{1}$H NMR chemical shifts of toluene and cyclohexane are well known, we can use their signals as an internal chemical shift reference. Alternatively, a few microdrops of TMS (0 ppm) can be added to the test samples. The sample preparation guide and spectra presented are for neat samples with added TMS.

- Sample 1: To a labeled vial measure about 0.20 mL of toluene, add a couple microdrops of TMS. Cap and save for NMR analysis.
- Sample 2: To a labeled vial measure about 0.20 mL of cyclohexane, add a couple microdrops of TMS. Cap and save for NMR analysis.
- Sample 3: To a labeled vial measure about 0.20 mL of the initial mixture of toluene and cyclohexane from the round bottom flask, add a couple microdrops of TMS. Cap and save for NMR analysis.
- Sample 4: To a labeled vial measure about 0.20 mL of distillate from the receiving flask, add a couple microdrops of TMS. Cap and save for NMR analysis.
- Sample 5: To a labeled vial measure about 0.20 mL of residue from the round bottom flask, add a couple microdrops of TMS. Cap and save for NMR analysis.
-

**Instrumental procedure**

The general procedure for sample analysis using a picoSpin NMR spectrometer is as follows:


*Shim*

- Ensure the NMR spectrometer is shimmed and ready to accept samples.

*Pre-sample preparation*

- Displace the shim fluid from the picoSpin capillary cartridge with air.

- Flush the cartridge with 0.1 mL of chloroform, and then displace the solvent with an air push. A small signal in your sample spectrum may appear at 7.24 ppm due to residual chloroform, it can be used to shift reference the spectrum.
- Set up the *onePulse* script according to parameters listed in the Pulse Script table.

*Injection*

- Using a 1 mL disposable polypropylene syringe fitted with a 1.5" long, 22 gauge blunt-tip needle, withdraw a 0.2 mL aliquot of sample.
- Inject about half the sample. Ensure all air bubbles have been displaced from the cartridge by examining the drain tube.
- Cap both the inlet and outlet ports with PEEK plugs.

*Acquire*

- Execute the onePulse script according to the values in the table of parameters provided
- Once the onePulse script has finished, prepare the cartridge for the next user by displacing the sample from the cartridge according to the following protocol: air, solvent, air.

*Pulse Script*: onePulse

Acquisition parameters apply to both the picoSpin 45 and picoSpin 80 spectrometers. Use the tx frequency (tx) and pulse length (p1) appropriate for each system.

| Parameter | Value |
|---|---|
| tx frequency (tx) | proton Larmor frequency (MHz) |
| scans (ns) | 4 |
| pulse length (p1) | Instrument specific 90° pulse length |
| acquisition time (aq) | 750 ms |
| rx recovery delay (r1) | 500 µs |
| T1 recycle delay (d1) | 6 s |
| bandwidth (bw) | 4 kHz |
| post-filter atten. (pfa) | 10 (11)[a] |
| phase correction (ph) | 0 degrees (or any value) |
| exp. filter (LB) | 0 Hz |
| max plot points | 400 |
| max time to plot | 250 ms |
| min freq. to plot | -200 Hz |
| max freq. to plot | +1000 Hz |
| zero filling (zf) | 8192 |
| align-avg. data | ✓ |
| live plot | ✓ |
| JCAMP avg. | ✓ |
| JCAMP ind. | Unchecked |

[a] Choose the instrument's default pfa values

## 6. Processing

Download the experimental JCAMP spectra files and open them by importing into Mnova. The free induction decay (FID) will undergo automatic Fourier transformation and a spectrum will be displayed. To each spectrum, apply the following processing steps using the given settings:

| Function | Value |
|---|---|
| Zero-filling (zf) & Linear Predict (LP) | 16 k |
| Forward predict (FP) | From aq → 16 k |
| Backward predict (BP) | From -2 → 0 |
| Phase Correction (PH) | PH0: Manually adjust |
| | PH1: 0 |
| Apodization | |
| Exponential (LB) | 0 Hz |
| First Point | 0.5 |
| Shift reference (CS) | Manually reference |
| Peak Picking (pp) | Manually Select Peaks |
| Integration (I) | Automatic Selection |
| Multiplet Analysis (J) | - |

- Import each data file into the same workspace in Mnova. Manually apply Ph0 phase correction to each spectrum.
- Manually shift reference each spectrum using Mnova's TMS tool. Assign the TMS signal (0 ppm), residual chloroform signal (7.24 ppm), cyclohexane signal (1.38 ppm), or toluene signals (2.09 or 6.98 ppm).
- Identify and assign each signal in the spectra.
- Integrate each signal group associated with toluene and cyclohexane, and determine the relative molar concentrations of each component of the initial mixture, distillate and pot reside.
- Save the Mnova document, print each spectrum and paste into your lab notebook.

## 7. Results

The 45 MHz and 82 MHz $^{1}H$ NMR spectra of toluene (neat) are presented in Figure 2. The spectrum contains two signals, one downfield signal centered at 7.00 ppm due to five aromatic protons ($C_6H_5$), and a second upfield signal at 2.09 ppm arising from excitation of the methyl group ($CH_3$) attached to the phenyl ring. The methyl protons do not coupling owing to the lack of neighboring protons. Spin-spin coupling isn't observed in the aromatic ring protons of toluene in the 45 MHz spectrum, but at 82 MHz the slight differences in the chemicals shift position of *ortho* (7.04 ppm), *meta* (7.08 ppm) and *para* (7.01 ppm) protons are observable (Figure 2, bottom). Integration of the signals reveals an expected 5:3 proton ratio.

Shown in Figure 3 are the 45 MHz (top) and 82 MHz spectra of neat cyclohexane. The spectrum is dominated by a single resonance due to 12 equivalent protons ring protons appearing at 1.44 ppm. Integrating the peak yields an expected integral value of 12.

In Figure 4, we see the first spectrum of our mixture; it shows both the 45 MHz (top) and 82 MHz $^{1}$H NMR spectrum of the initial mixture of toluene and cyclohexane. The signals attributable to each species are identified in the spectra. Initially, we measured roughly equal volumes of the two compounds. Looking at the 45 MHz spectrum, if we integrate individual signals and normalize the cyclohexane signal to 12, due to its 12 chemically equivalent protons, we obtain an integral ratio of 5.78:3.76:12.00. Were the sample exactly a 50:50 mixture of the two components we would expect a ratio of 5:3:12. To estimate the molar ratio of the two compounds, compare the integration of the methyl group in toluene (3.76 at 2.24 ppm) to the integration of the cyclohexane signal (12 at 1.44 ppm); the ratio is 3.76:12. Normalizing this ratio to account for 3 protons in the methyl group of toluene and 12 protons in cyclohexane, we get a ratio of 1.25:1, which gives us a molar ratio of 55% toluene to 45% cyclohexane, very close to the intended 50:50 ratio. We can apply the same approach using the aromatic signal but then its relative integral value would need to be normalized for the 5 protons its signal contains. We can also evaluate the 80 MHz spectrum in the same way.

The NMR spectrum of the distillate is shown in Figure 5. The cyclohexane signal is easily identifiable as the largest signal at 1.44 ppm. Qualitatively, the toluene signals appear considerably smaller when compared to their size in the initial mixture spectrum. However, a quantitative measure will give a better estimate of molar ratio of components in the distillate. Applying the same approach, we compare the relative ratio of the methyl proton signal from toluene to that of cyclohexane and we obtain 1.46:12. Normalizing for the number of protons comprising each signal we get a normalized ratio of 0.49:1 from the 45 MHz spectrum. This yields an estimated molar ratio of 33% toluene to 67% cyclohexane. Visually the minor species looks considerably smaller than the 33% just calculated. However, there are 12 protons in the cyclohexane signals whereas there are only 3 in the methyl group signal, and it is difficult to visually normalize these differences.

Finally, we evaluate the pot residue; its spectrum is presented in Figure 6. Here we see a spectrum very similar to those in Figures 4 & 5; signals attributed to toluene (7.00 ppm & 2.38 ppm) and cyclohexane (1.44 ppm) are easily identifiable. What may seem surprising however, are that the signal intensities look similar to the initial mixture spectrum (Figures 4). Simple distillation is effective for mixtures where the components have a boiling point difference of about 75°C; the boiling points of our sample are 88°C and 111°C for cyclohexane and toluene, respectively. Owing to the closely spaced boiling points, simple distillation is less effective at separating the two components and we expect to see a higher concentration of toluene in the vapor phase condensing along with cyclohexane. Quantitative analysis of the 45 MHz spectrum of the residue yields a normalized molar ratio of 1.65:1, or 62% toluene to 38% cyclohexane.

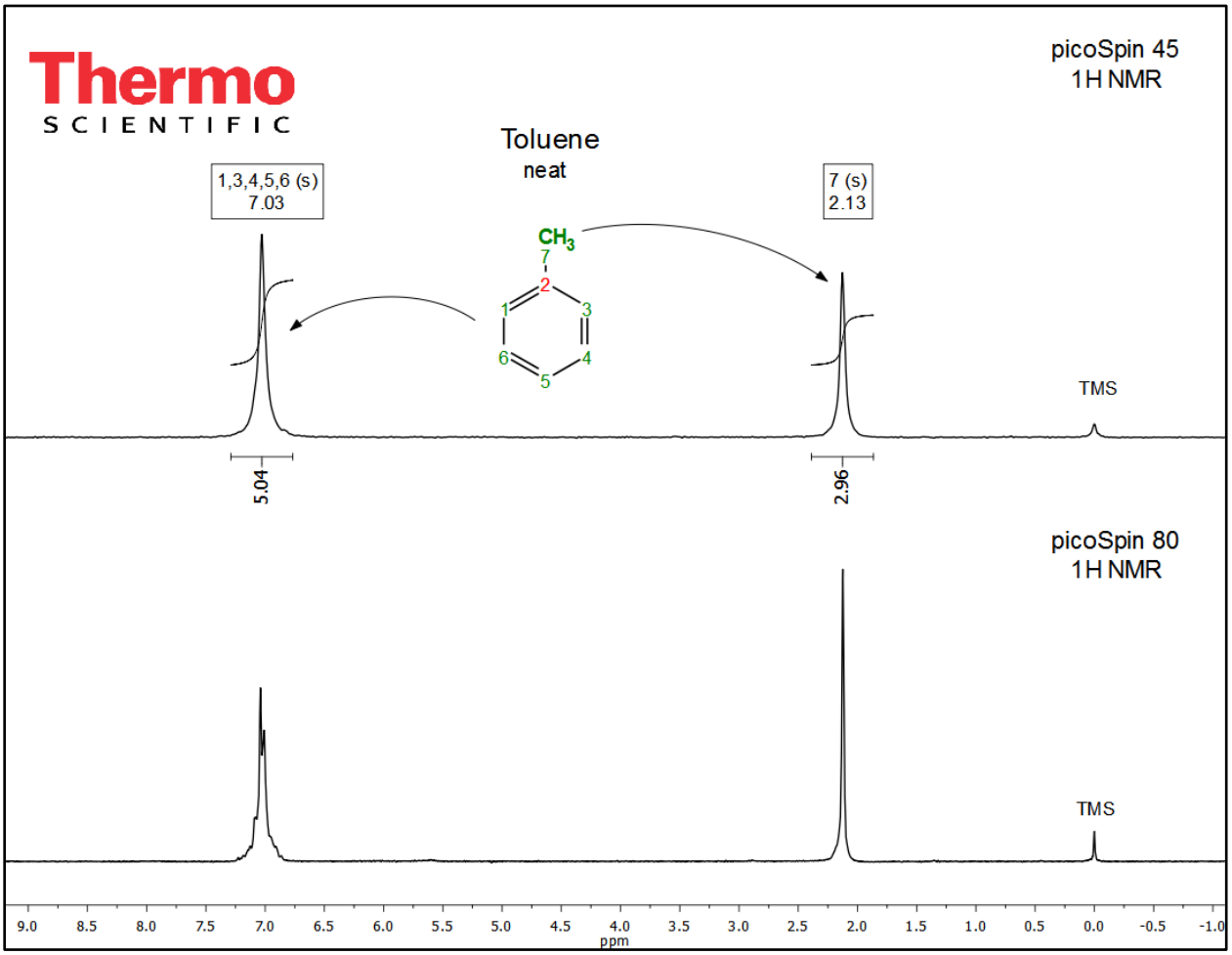



**Figure 2** Stacked, full $^{1}$H NMR 45 MHz (top) and 82 MHz (bottom) spectra of toluene (neat) with TMS

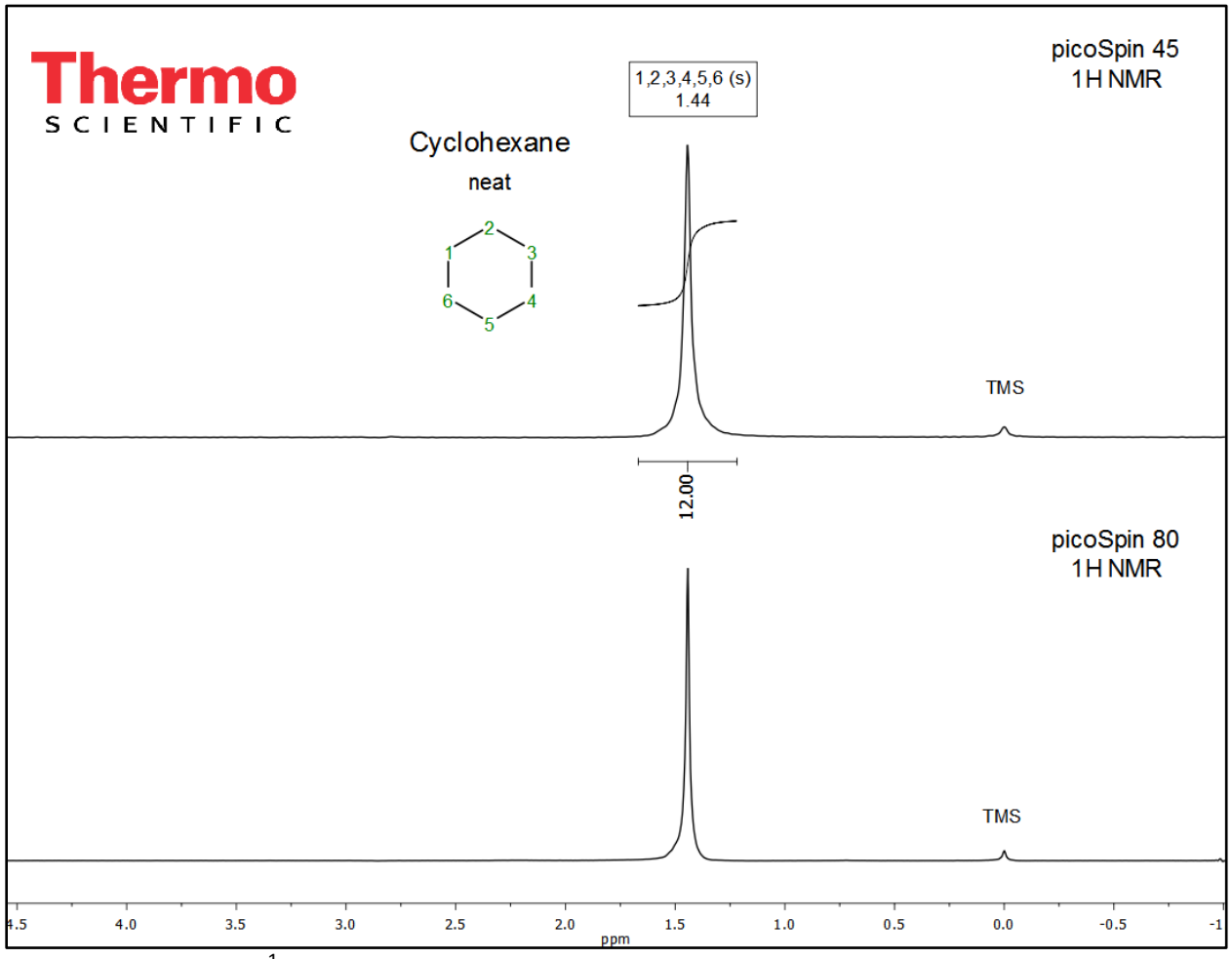



**Figure 3** Stacked, full $^{1}$H NMR 45 MHz (top) and 82 MHz (bottom) spectra of a cyclohexane (neat) with TMS

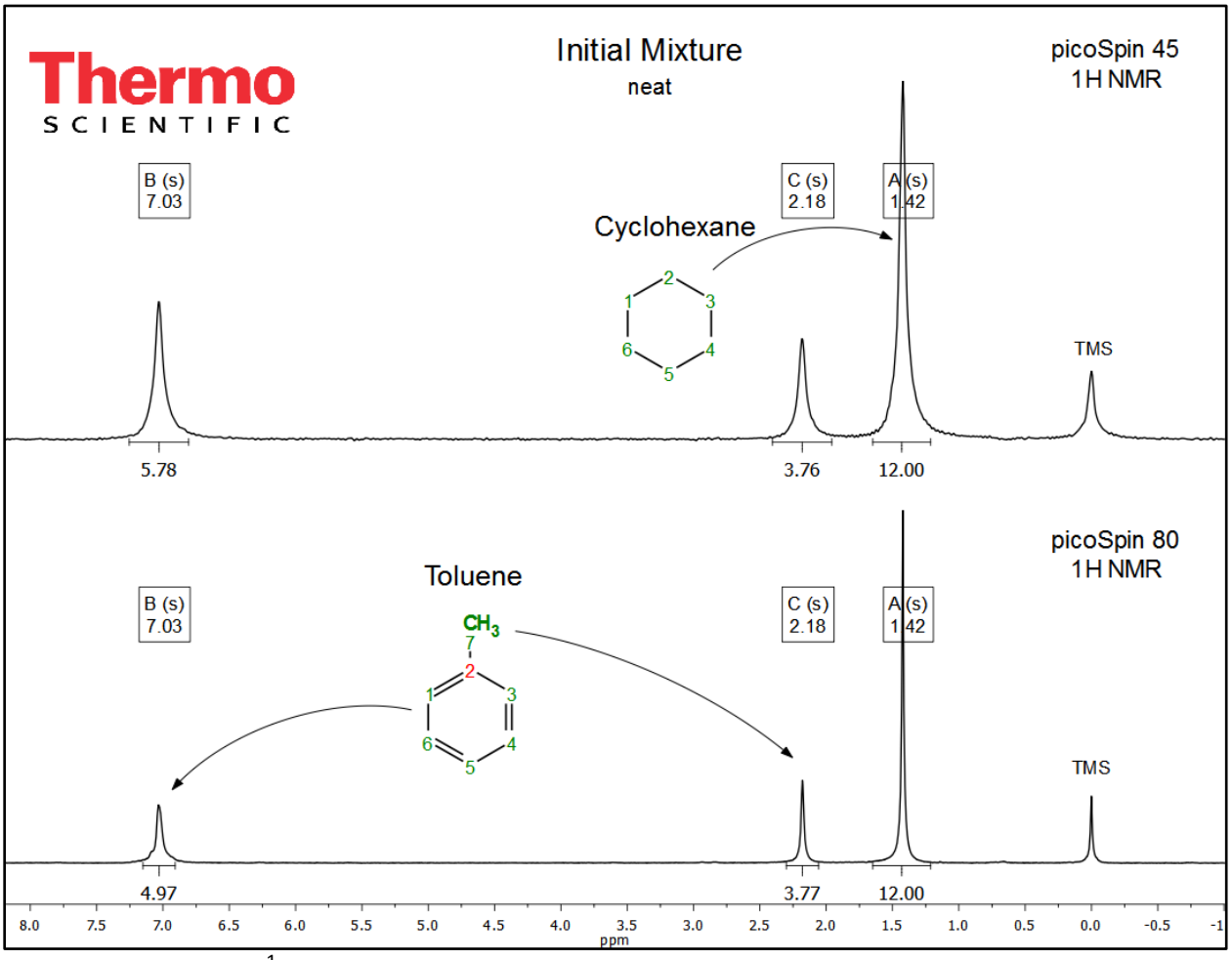



**Figure 4** Stacked, full $^{1}$H NMR 45 MHz (top) and 82 MHz (bottom) spectra of the initial distillation mixture with TMS

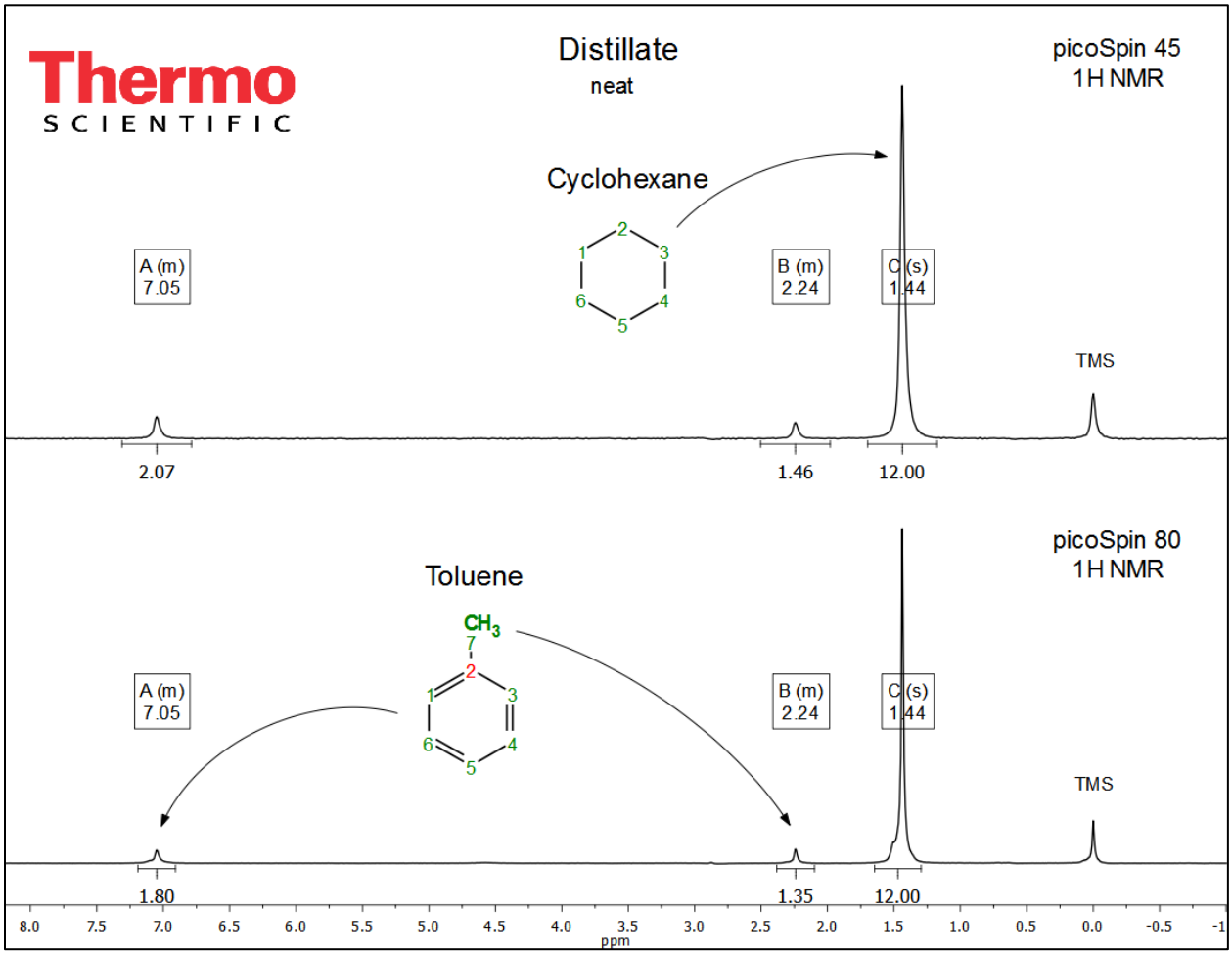



**Figure 5** Stacked, full $^{1}$H NMR 45 MHz (top) and 82 MHz (bottom) spectra of distillate with TMS

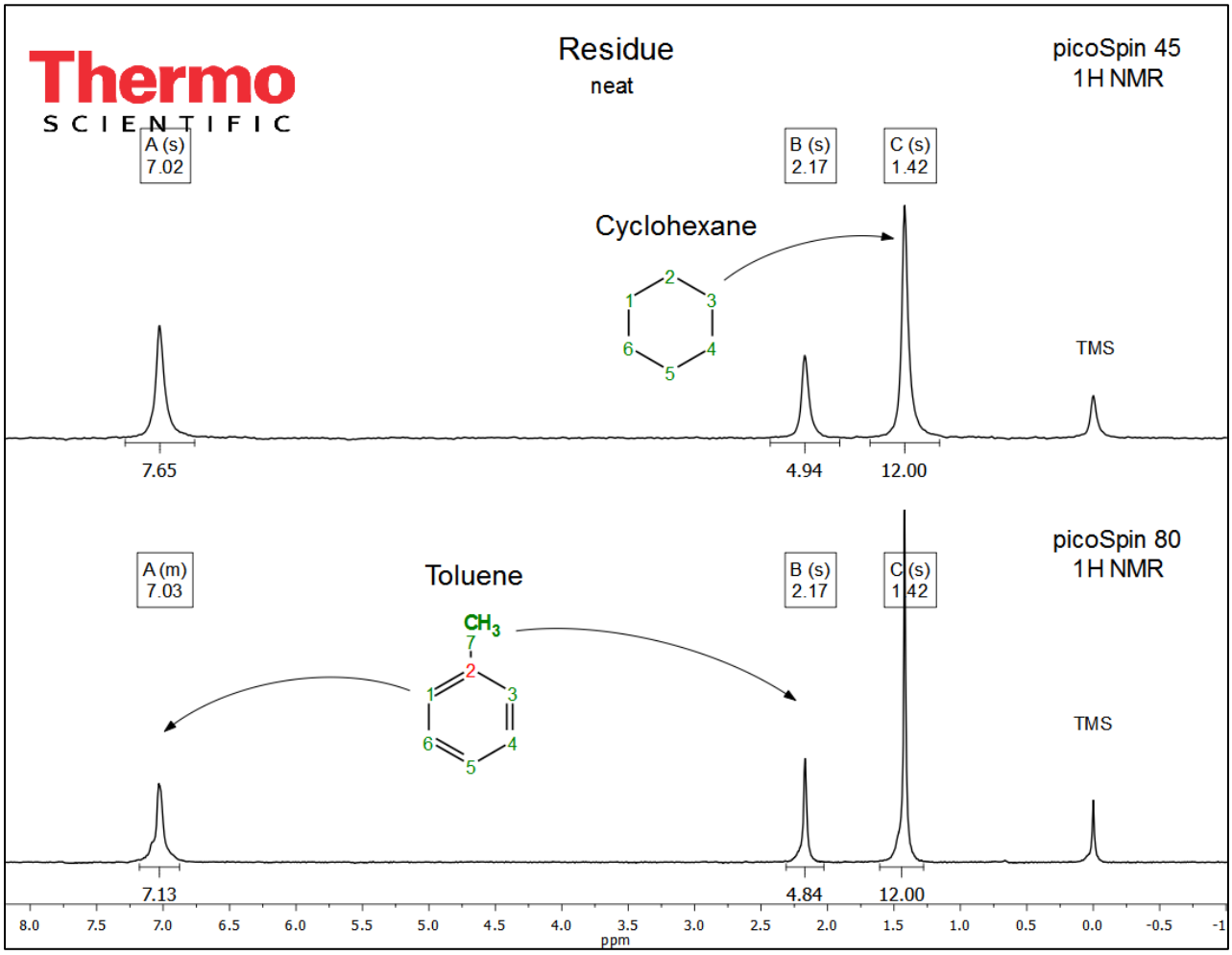



**Figure 6** Stacked, full $^{1}$H NMR 45 MHz (top) and 82 MHz (bottom) spectra of distillate with TMS

Table 1. $^{1}$H NMR Spectral Data

| Figure | Compound | Signal Group | Chemical Shift (ppm) | Nuclides | Multiplicity |
|---|---|---|---|---|---|
| 2-6 | TMS | $Si(CH_3)_4$ | 0 | 12 H | Singlet |
| 2, 4-6 | Toluene | $C_6H_5CH_3$ | 2.24 | 3 H | Singlet |
| | | $C_6H_5CH_3$ | 7.08(m), 7.04(o), 7.01(p) | 5 H | Singlet |
| 3-6 | Cyclohexane | $C_6H_{12}$ | 1.44 | 3 H | Singlet |
| | Chloroform | $CHCl_3$ | 7.24 | 1 H | Singlet |
| | Acetone | $O=C(CH_3)_2$ | 2.05 | 6 H | Singlet |

## 8. Comments

This lab offers no specific challenges.

## 9. Own Observations



| | | | |
|---|---|---|---|
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