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Petrochemical Application of Low Field Benchtop NMR: Characterization of Polyols and Epoxy Resins

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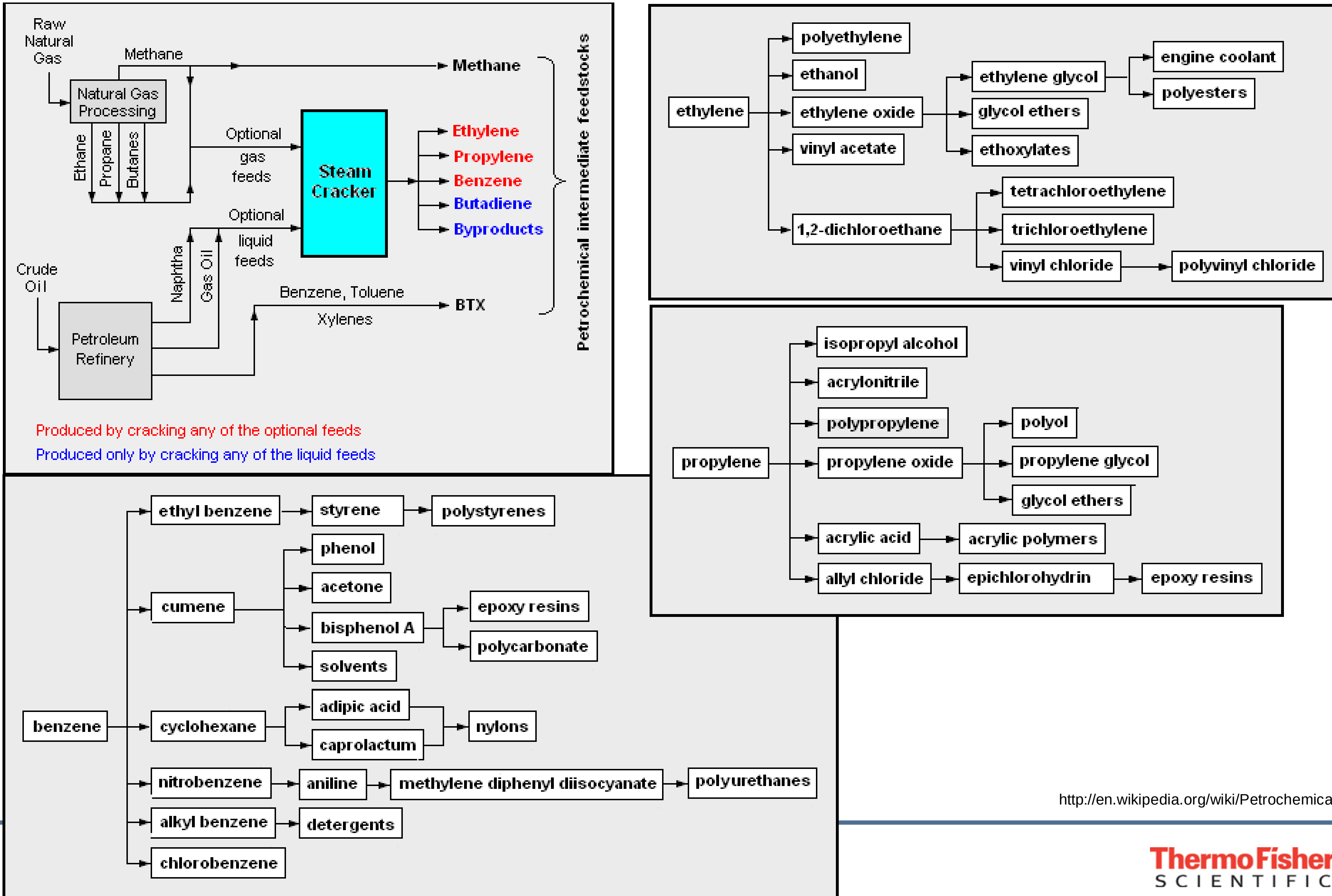
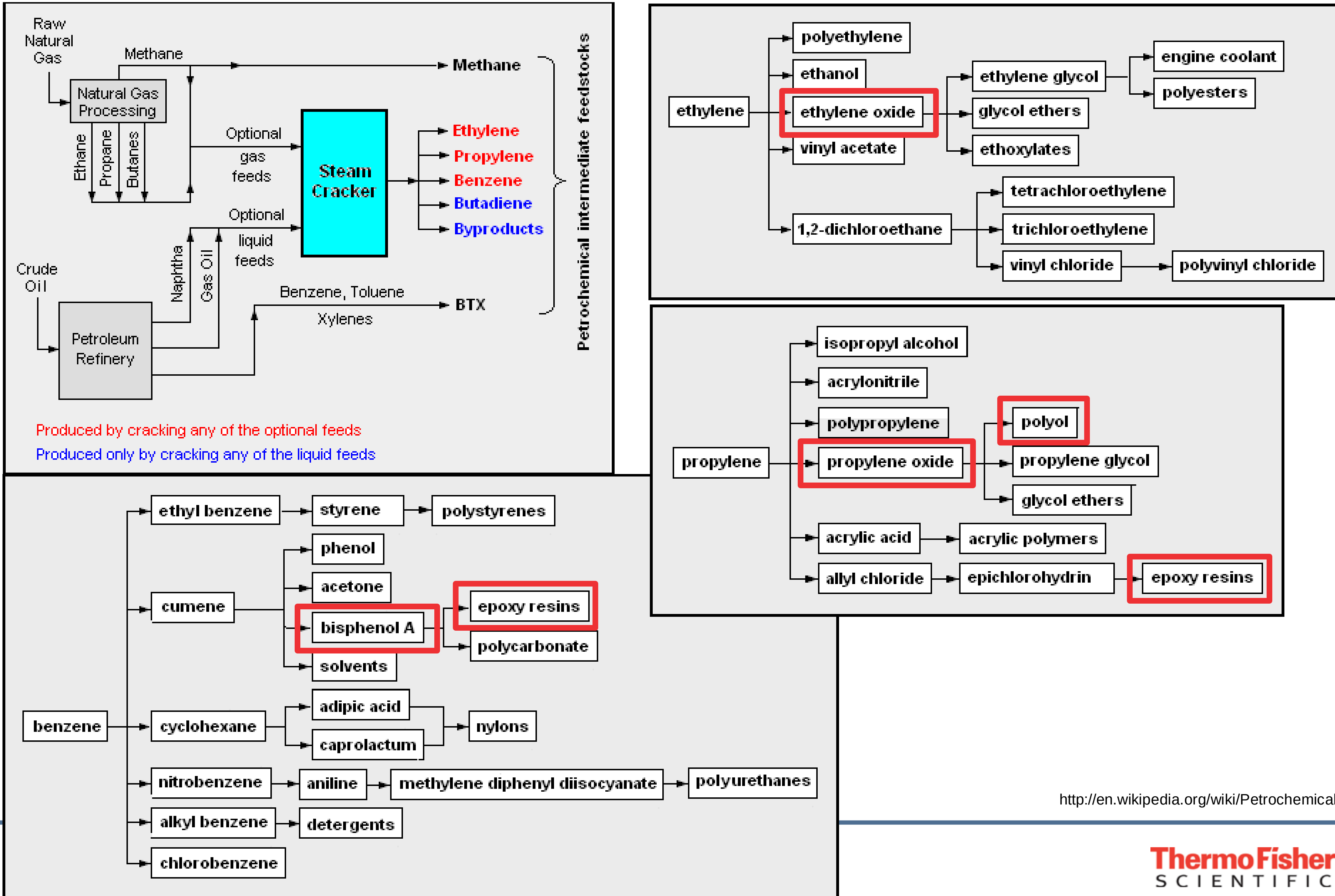
Overview of Petrochemical Industry



http://en.wikipedia.org/wiki/Petrochemical

Opportunity for NMR – Petrochemical Derivatives



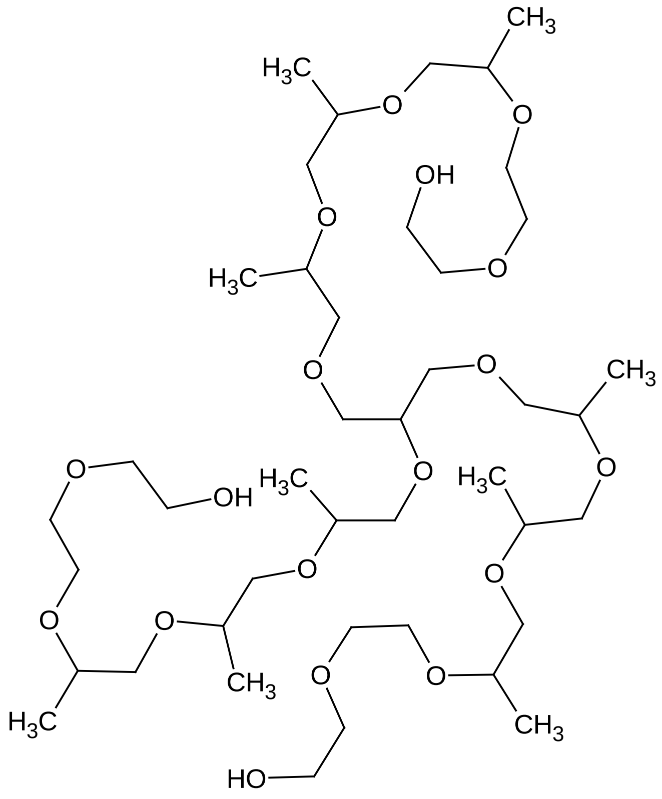
http://en.wikipedia.org/wiki/Petrochemical

Determining Ethylene Oxide (EO) Content of Polyether Polyols

What are Polyols?

- Polyols are based on alkylene oxides – ethylene (EO) and propylene oxide (PO)
  - Polyols contain multiple hydroxyl functional groups for organic reactions
- Used as the starting material with isocyanatse for the production of polyurethanes (PU)
- The name polyol refers to chemical compounds containing multiple hydroxyl groups

- Example polyol (triol) of propylene glycol and capped with ethylene oxide



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Understanding Polyol Features

- The propylene oxide (PO):ethylene oxide (EO) ratio and the overall molecular weight are major parameters defining the composition of different polyols, which affect the physical properties of the final polyurethane (PU) product
- A low molecular weight polyol with high EO content, which enhances reactivity, is ideally suited for fast-curing systems, such as thermoplastic urethanes (TPU), or reaction injection molded (RIM), or cast elastomers
- Using a polyol with low EO content and relatively high molecular weight results in polyurethanes suitable for coatings, adhesives or sealants
- ***The EO content of polyols dictates the characteristics of the final PU products***

Understanding Polyol Features

- Ethylene oxide is more hydrophilic, and thus polyether polyols with high ethylene (EO) content tend to produce polyurethanes that are more hydrophilic than those produced solely with propylene oxide (PO)
- By changing the polyol and isocyanate components, you can greatly impact the final properties of the polyurethane resin
- Polyurethane chemistry is very versatile, with multitude of uses from bowling balls to flexible foam and windmill adhesives

Characterization of Polyol EO Content by NMR

- The abundance of protons in the repeating structures of polyols and the dispersion of signals makes ^{1}H NMR spectroscopy ideally suited for rapid characterization of EO content
- ASTM method developed in 1988 (D4875 – 11)

INTERNATIONAL

Designation: D4875 – 11

Standard Test Methods of Polyurethane Raw Materials: Determination of the Polymerized Ethylene Oxide Content of Polyether Polyols[1]

This standard is issued under the fixed designation D4875; 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.

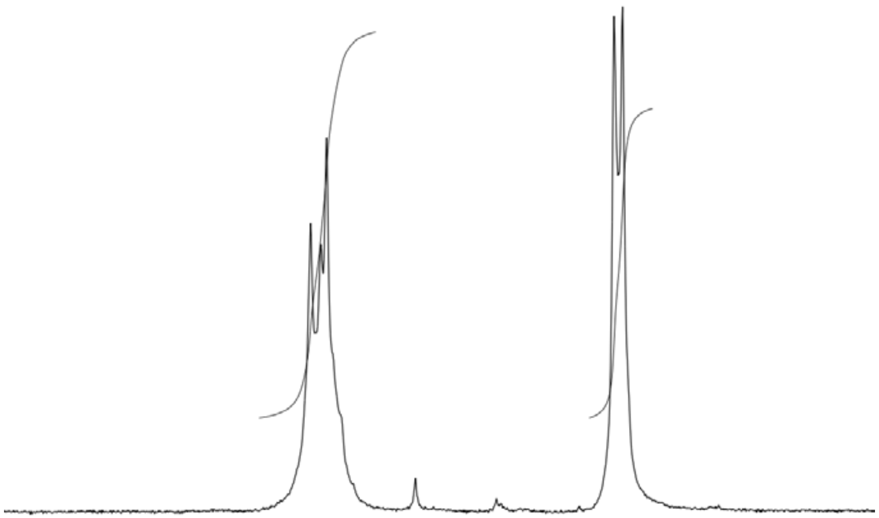
4. Summary of Test Methods

4.1 *Test Method A*—The ^{1}H NMR spectra of polyether polyols show two groups of resonance peaks corresponding to the methyl protons of propylene oxide (PO) and to the methylene and methine protons of EO and PO. The EO peak area is obtained by subtracting the area of the PO methyl peaks from the area of the methylene and methine peaks. Initiators other than glycols of EO and PO give systematic errors (see Note 2).

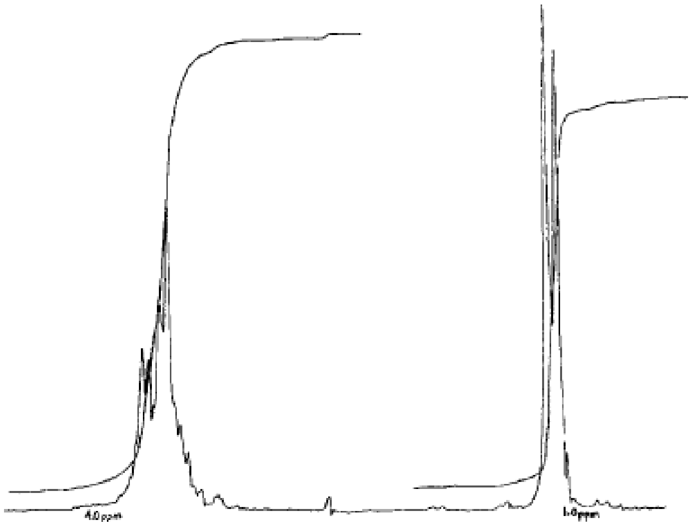
NOTE 2—The initiator error can be estimated by calculating the theoretical contribution of initiator protons to the EO and PO peak areas.

ASTM Standard D4875-11, **2011**, *ASTM International*, DOI:10.1520/D4875-11.

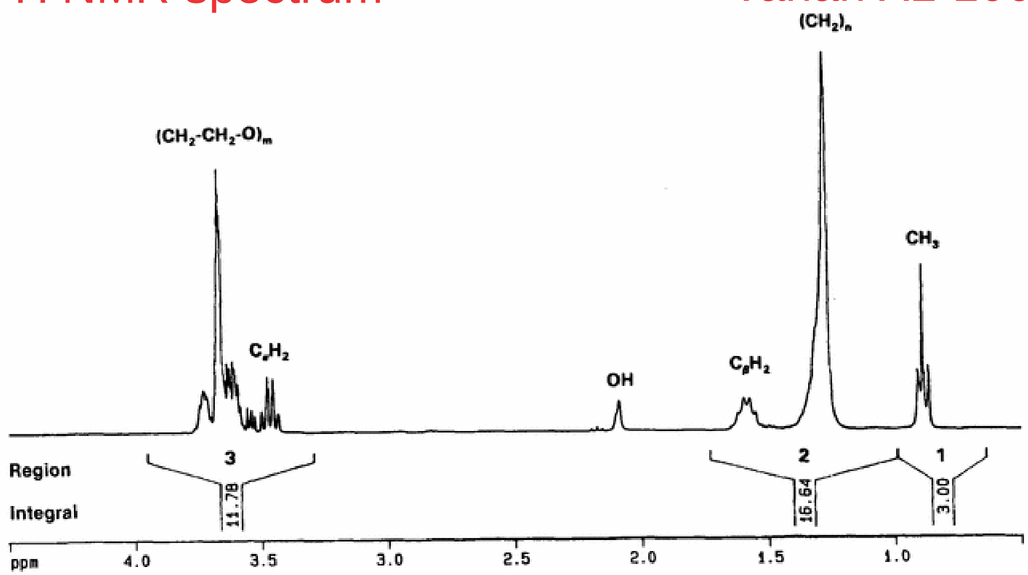
Example Polyol Proton NMR Spectra



picoSpin 80 ^{1}H NMR spectrum



Varian XL-100 FT ^{1}H NMR spectrum

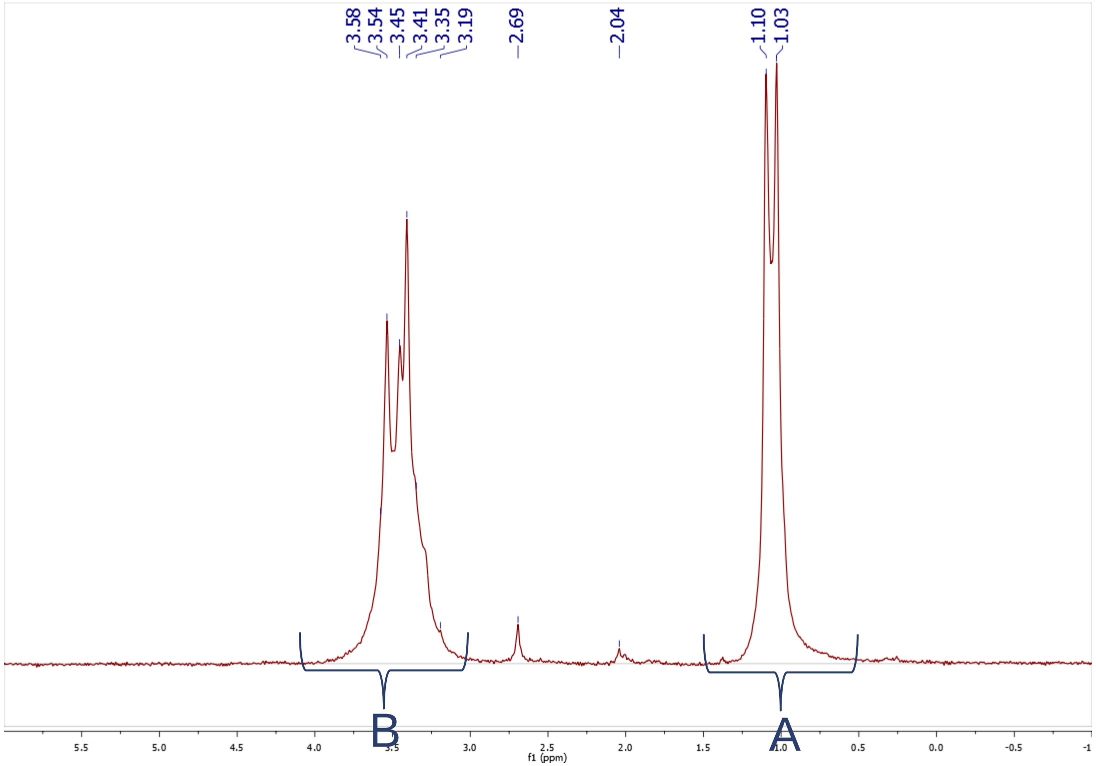


Bruker AMX 300
^{1}H NMR spectrum

ASTM Standard D4875-11, DOI:10.1520/D4875-11. Hammond, C. E.; Kubick, D. K. *J. Am. Oil Chem. Soc.* **1994**, *71*, 113-115.

Determining Weight Percent EO Content by NMR

- In the NMR spectrum, chemical shifts for the PO methyl proton resonances (area A) range from 0.6-1.6 ppm and chemical shifts for the EO and PO methylene and methine proton resonances (area B) range from 2.8-4.0 ppm



$$EO = \frac{33 \times Z}{33 \times Z + 58} \times 100$$

where:

$$Z = \left(B/A\right) - 1$$

33 = g EO/mol

(after weighting for the number of EO protons vs PO protons)

58 = g PO/mol

ASTM Standard D4875-11, DOI:10.1520/D4875-11.

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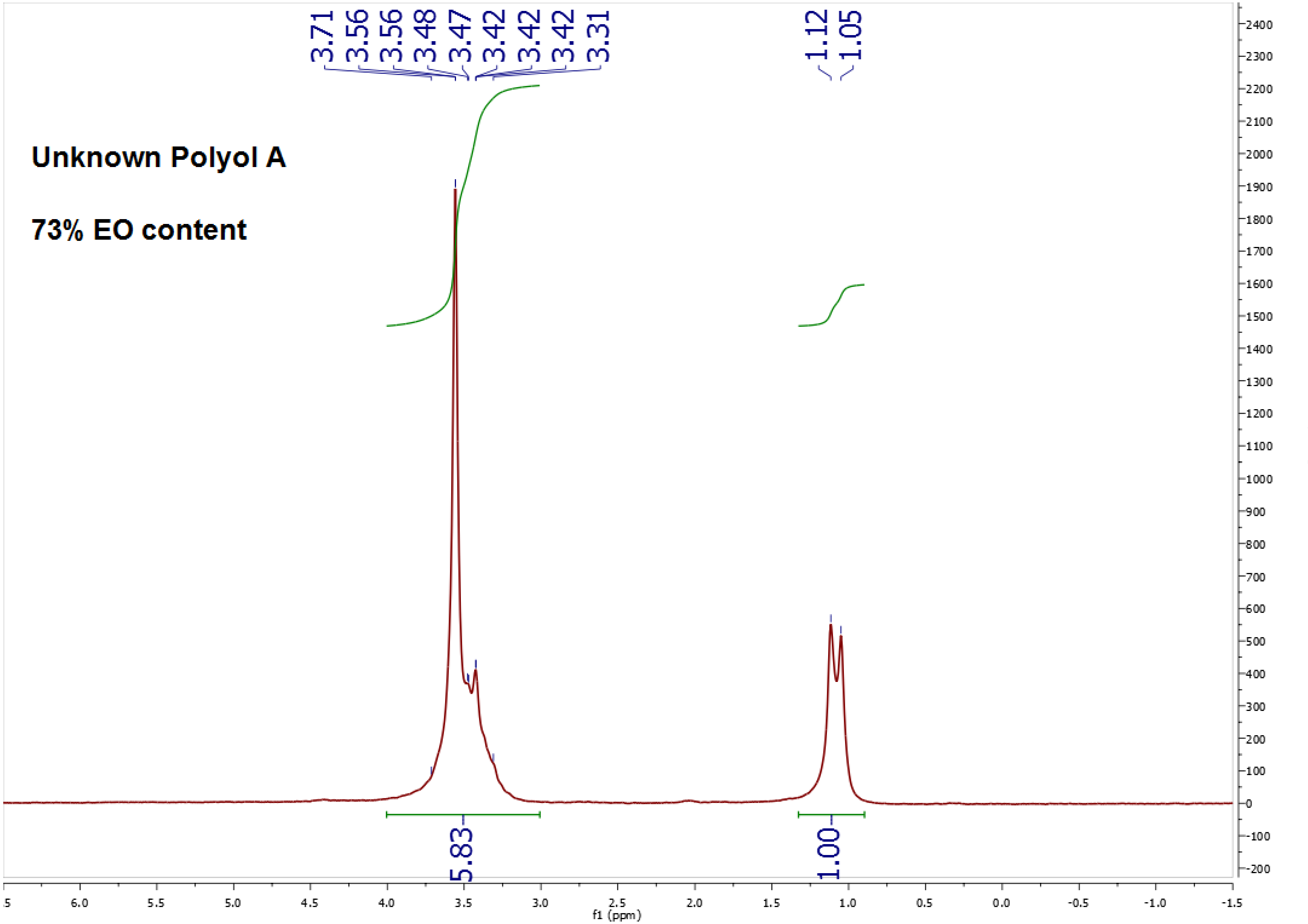
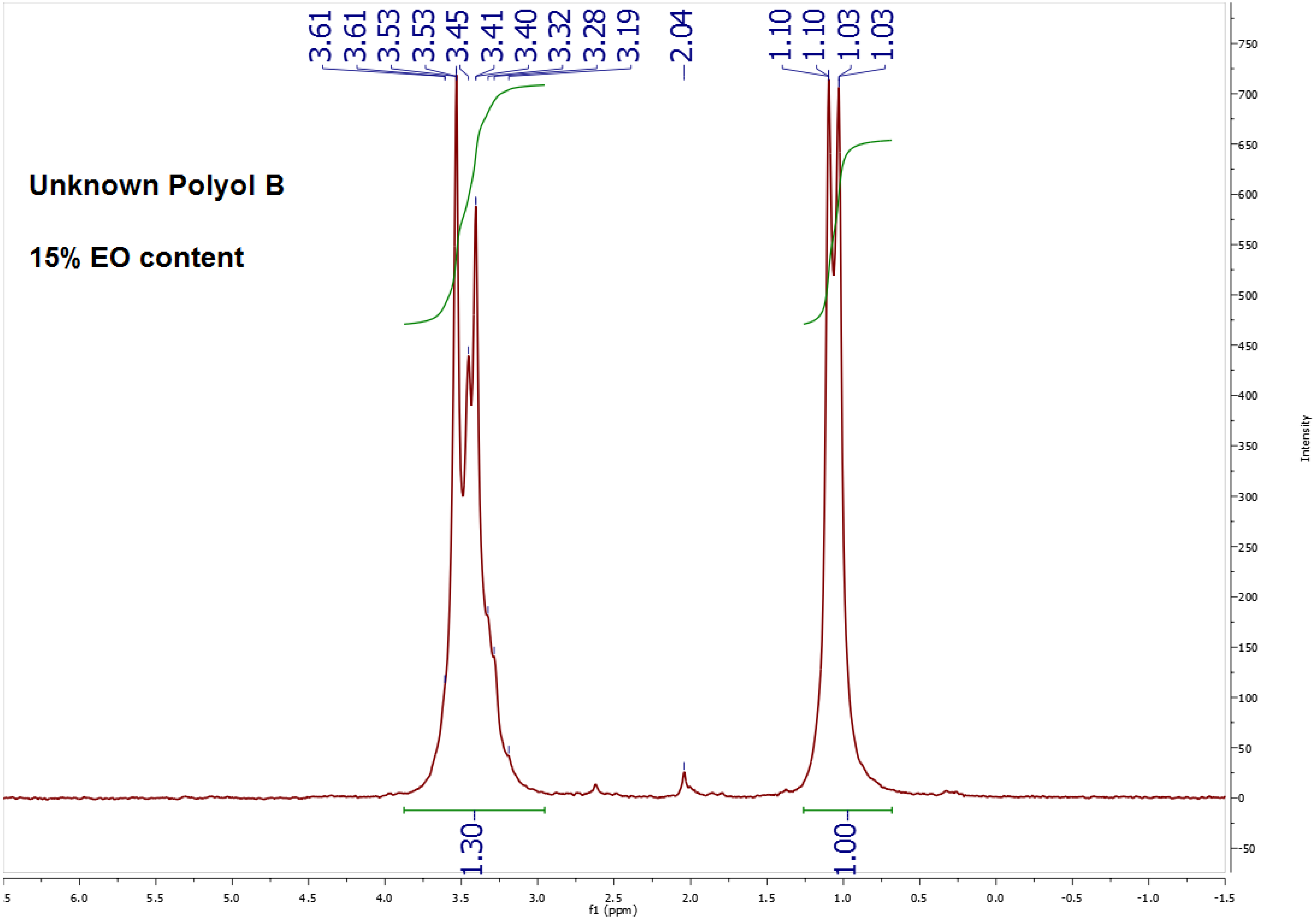
Unknown Polyol A – Thermo Scientific™ picoSpin 80™



Unknown Polyol B – Thermo Scientific™ picoSpin 80™



QA/QC of Incoming Vendor Materials: Characterizing Epoxy Resin

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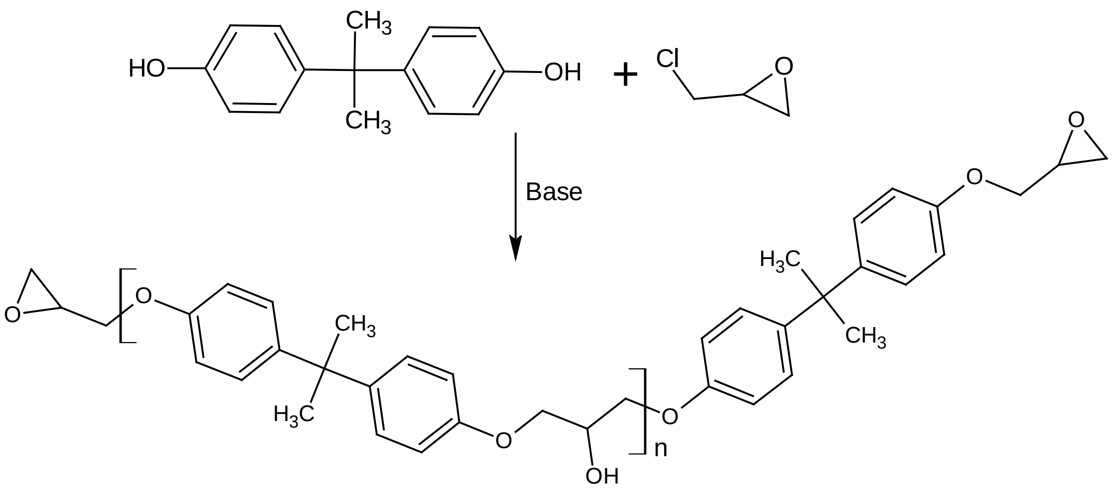
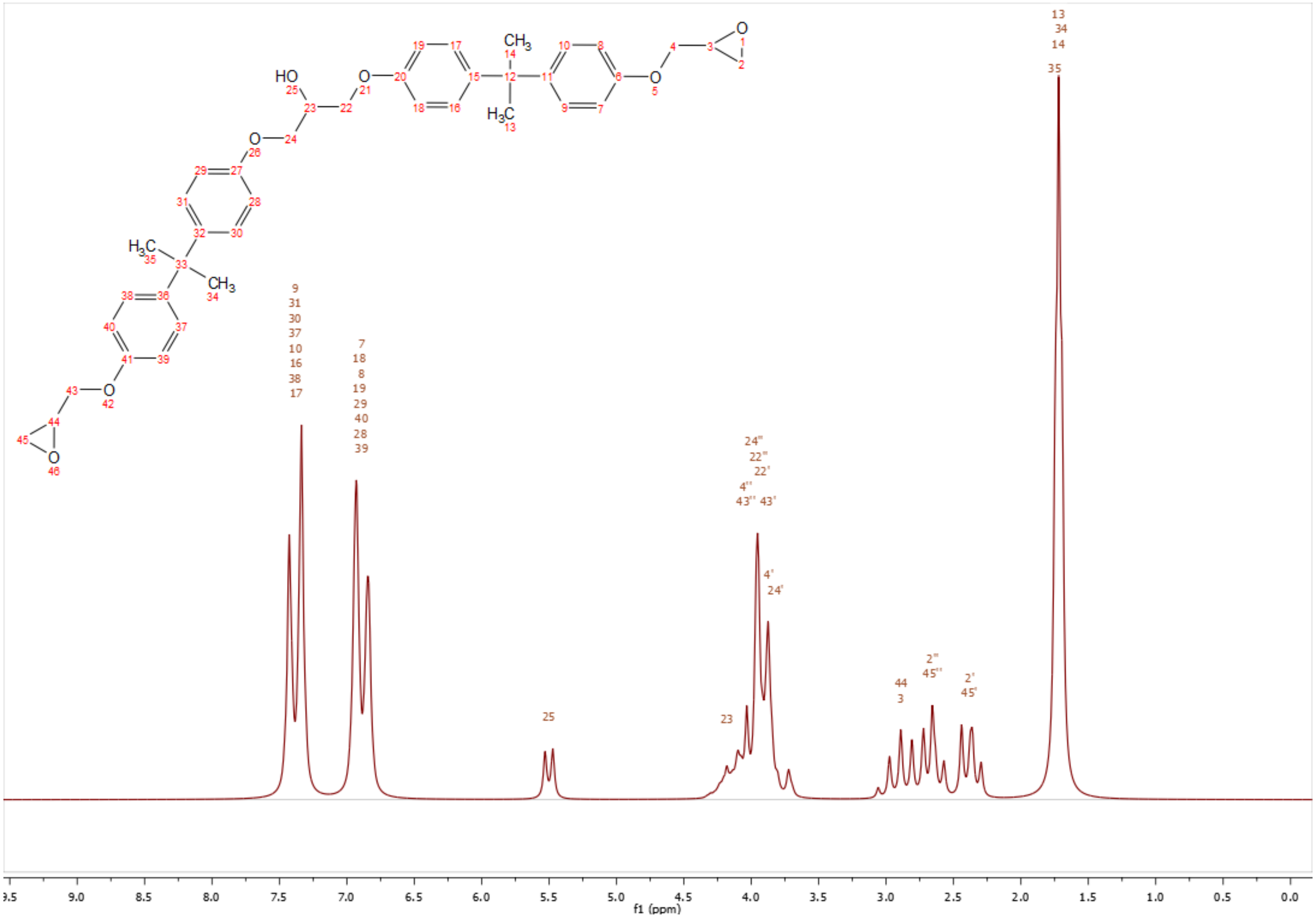
Understanding Epoxy Resin

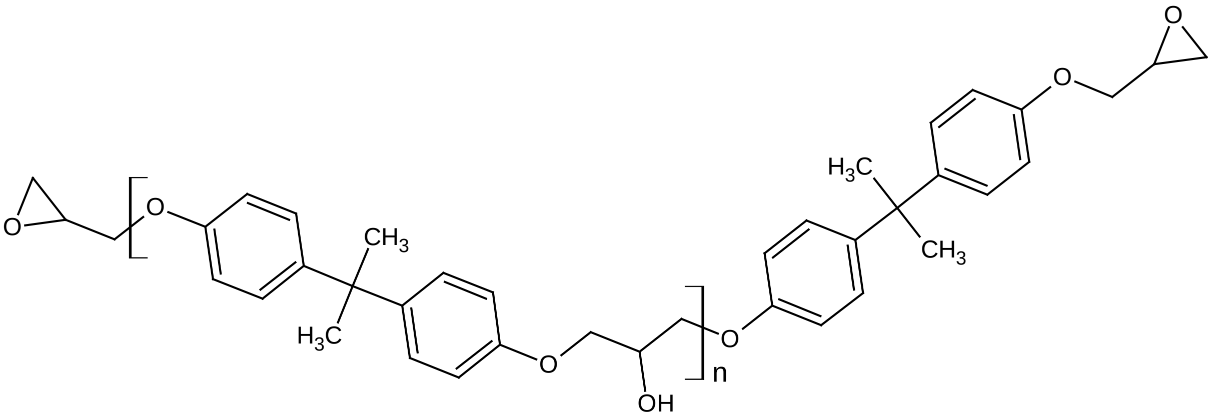
- Epoxies are thermosetting polymer resins where the resin molecule contains one or more epoxide groups
- The chemistry can be adjusted to perfect the molecular weight or viscosity as required by the end use
- One of the most common epoxy resins is created using bisphenol-A, and is synthesized in a reaction with epichlorohydrin

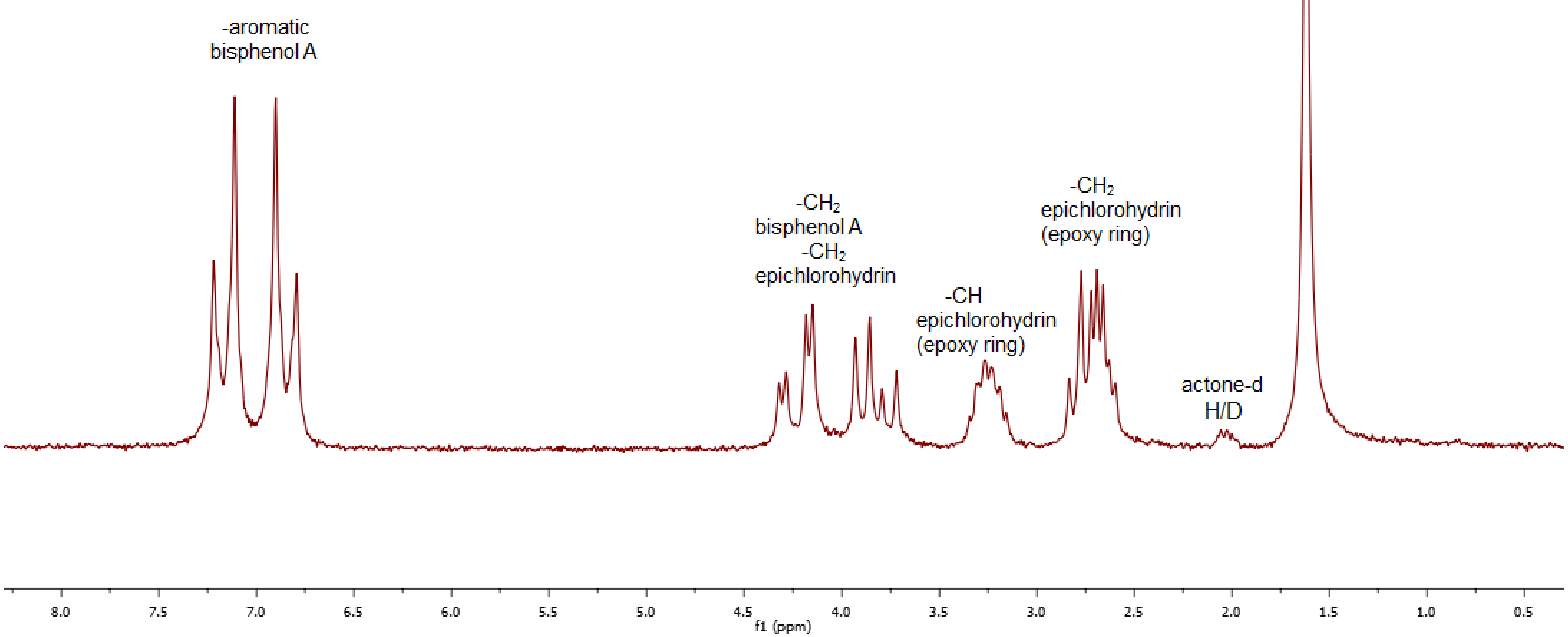


Mnova™ Predicted 82 MHz Proton NMR Spectrum

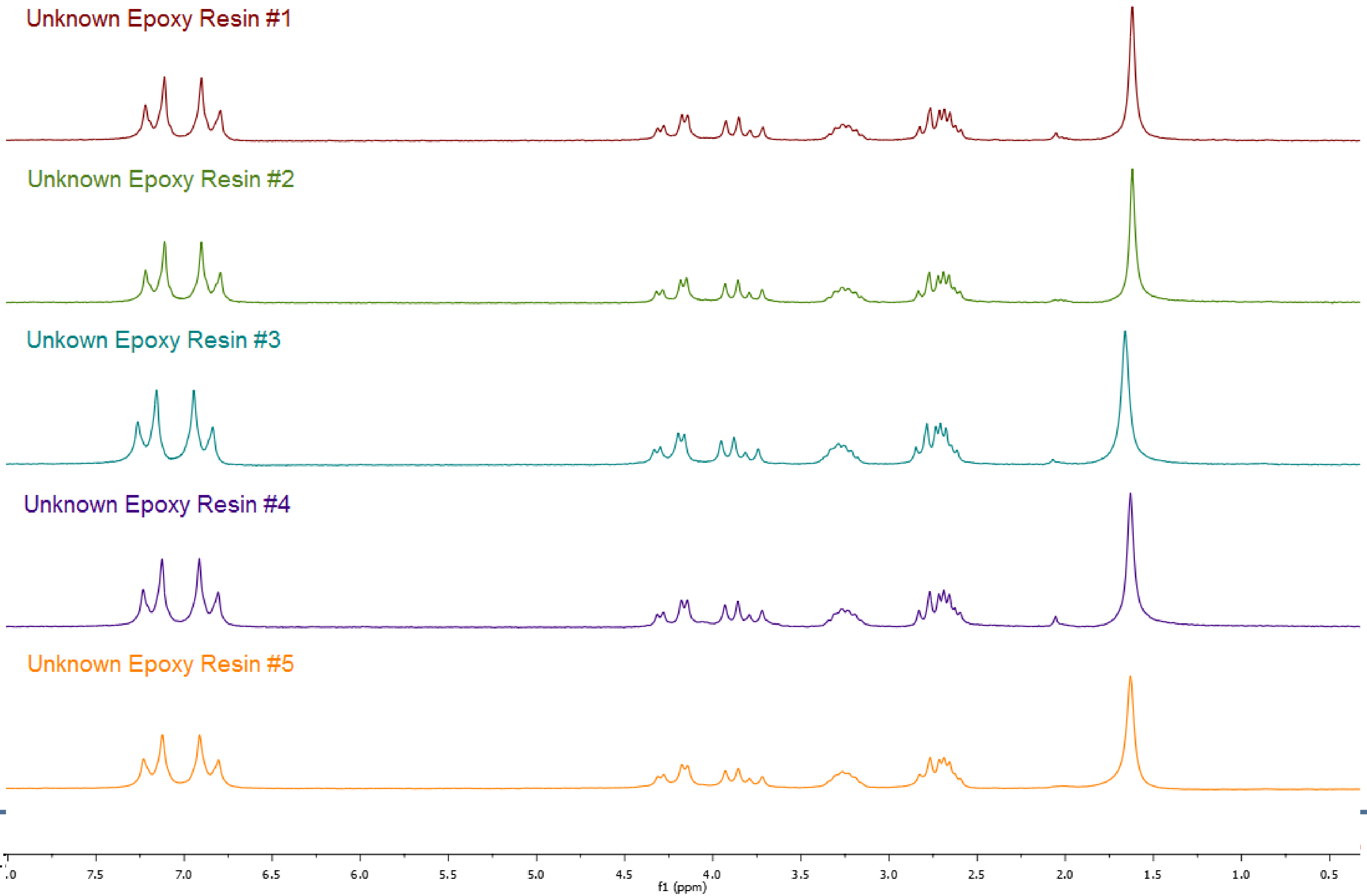


picoSpin 80 Epoxy Resin Proton NMR Spectrum





QA/QC Incoming Epoxy Resin Materials

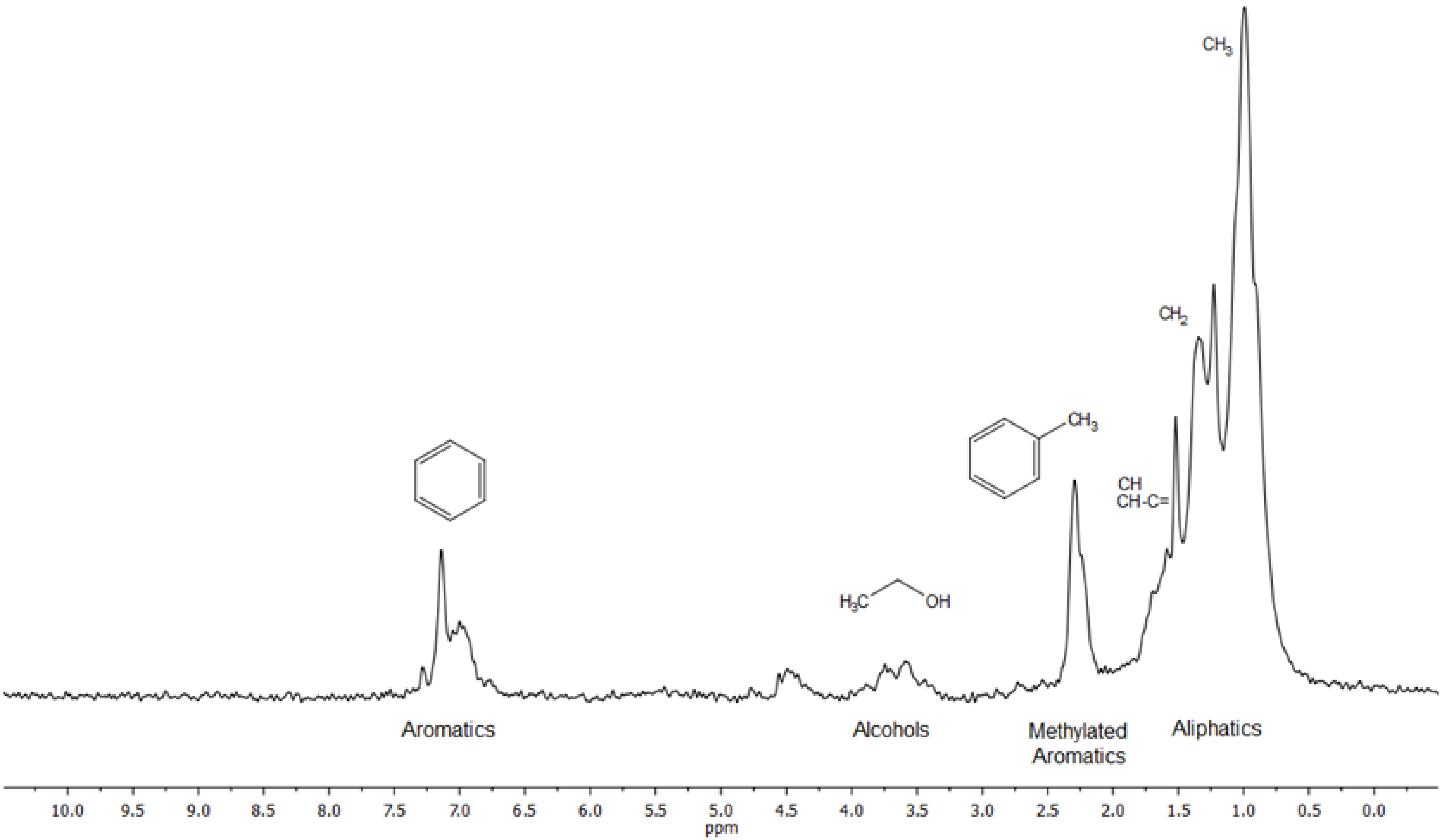


Characterization of Regular Unleaded Gasoline

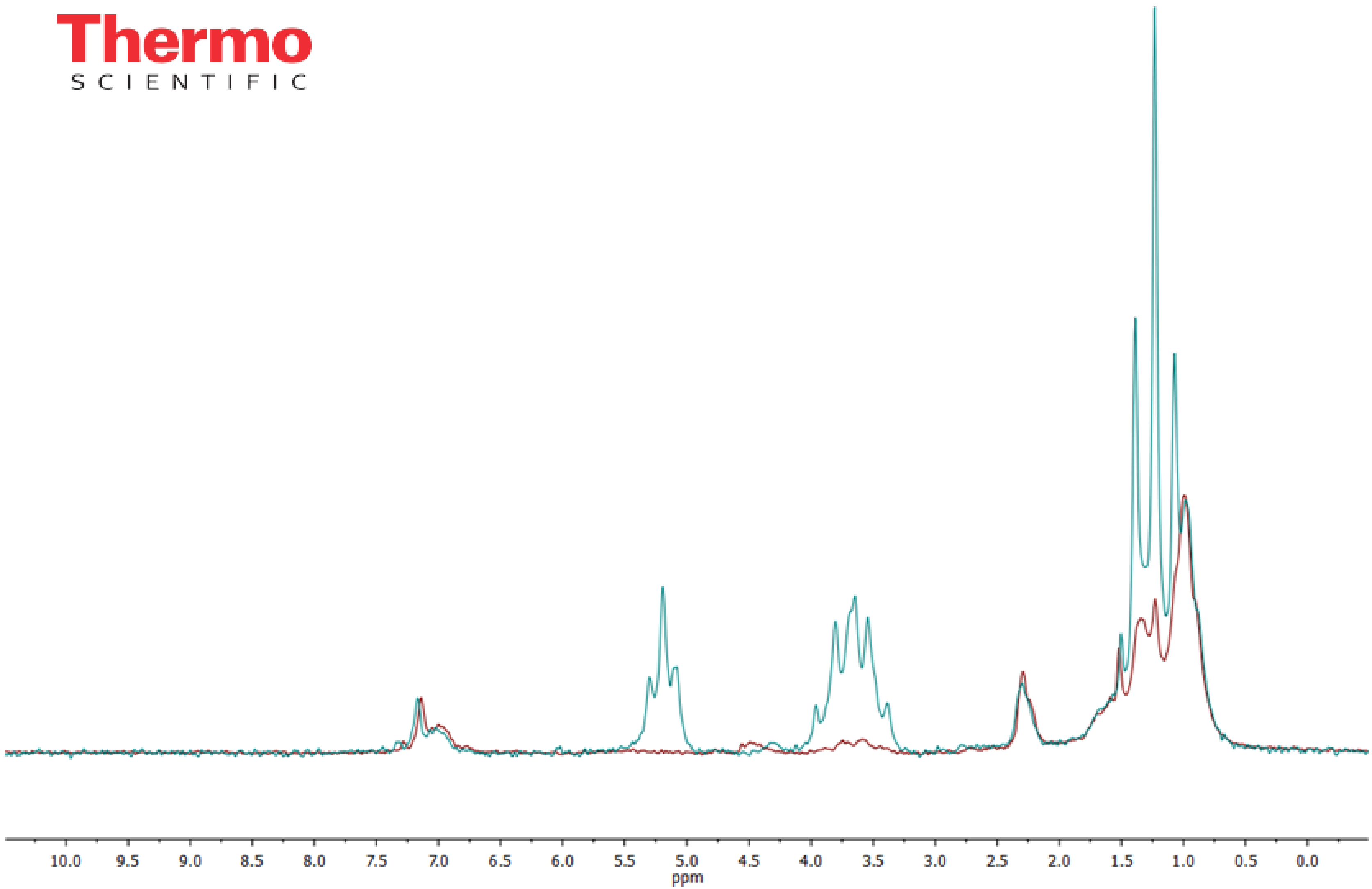
Characterization of E10 Gasoline

- Examine the complex spectrum of gasoline and estimate the amount of ethanol blended into the fuel
  - Gasoline is a complex mixture of hydrocarbons and additives
  - Ethanol is often added to gasoline as a way to incorporate more renewable energy sources into fuels while simultaneously improving the octane rating
- The regular unleaded gasoline we obtained was labeled as containing up to 10% ethanol (E10) by volume

^{1}H picoSpin 45 Spectrum of E10 Unleaded Gasoline



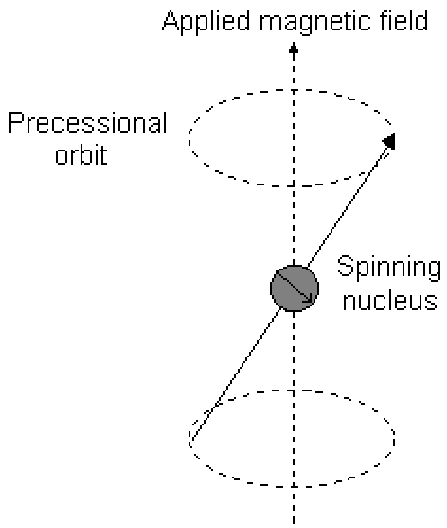
E10 Gasoline and Anhydrous Ethanol



Summary Characterization Petrochemical Derivatives

- The picoSpin 80 has been well received by scientists working with polymeric samples due to the **ease of use** and the **spectral resolution** provides the necessary chemical information
- Offers the capability of characterizing products in-house quickly, improving efficiency using the picoSpin NMR spectrometer
- picoSpin NMR spectrometer: affordable NMR spectroscopy, when you need it, where you need it

Questions ???



Thank you !!!