

# MERCAPTAN TYPES IN KEROSENE BY NMR

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## UOP 935-94

### SCOPE

This method is for determining primary, secondary and tertiary mercaptans (thiols) in kerosines up to several thousand mass-ppm, based on the procedure previously suggested by E. Rafii, et al. (1,2). The lower limit of detection by  $^{119}\text{Sn}$  {H} decoupled, refocused Insensitive Nucleus Enhancement by Polarization Transfer (INEPT) Nuclear Magnetic Resonance (NMR) spectroscopy without preconcentration is 40 mass-ppm per mercaptan type in the kerosine. Lower concentrations can be determined using a specified distillation procedure. The only known interferences are thiophenols and branched alcohols, such as isopropyl and butyl alcohols (see *NOTE*). The method relies upon the quantitative preparation of soluble tri-*n*-butyl tin derivatives of all of the thiols present.

### OUTLINE OF PROCEDURE

UOP Method 163 (3) is performed to determine the total mercaptan sulfur content of the kerosine sample. The mercaptans are derivatized by reaction with *bis*(tributyltin) oxide (TBTO) to form the corresponding organo-sulfur-tributyltin compounds. If required, vacuum distillation is performed to concentrate the mercaptan-derivatives to greater than 40 mass-ppm for each type in the kerosine bottoms. The derivatized sample or concentrate is diluted 50/50 (vol/vol) in a perdeuterobenzene ( $\text{C}_6\text{D}_6$ )/chromium (III) acetylacetonate solution and analyzed by  $^{119}\text{Sn}$  NMR spectroscopy using a proton decoupled, refocused INEPT procedure. The NMR areas assignable to each mercaptan type are determined by a specified integration procedure. The area fraction attributable to each type is then multiplied by the total mercaptan sulfur in the sample to determine the concentration of primary, secondary and tertiary thiols.

### APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

*Adapter*, universal, with gas inlet and 24/40 standard taper joints, Fisher Scientific, Cat. No. K179750-2114

*Balance*, readability 0.01-g, 1800-g capacity

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).</p> |
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*Caps*, NMR tube, pressure, Wilmad Glass, sized appropriately for the NMR tube (see *PROCEDURE, Instrument Specification*)

*Clamps*, 3-prong, utility, Fisher Scientific, Cat. No. 05-769

*Cylinder*, graduated, 250-mL, Class A, Fisher Scientific, Cat. No. 08-557E

*Derivatization apparatus*, Dean-Stark, 24/40 standard taper joints, Fisher Scientific, Cat. No. K535800-0000

*Flask*, boiling, round bottom, 500-mL, 24/40 standard taper joint, with thermometer well, Fisher Scientific, Cat. No. 10-069A

*Flask*, volumetric, Class A, 10-mL

*Heating mantle*, spherical, 500-mL flask size, with cord, Fisher Scientific, Cat. No. 11-472B

*Heat tape*, 610- x 13-mm (2-feet x 1/2-inch), Fisher Scientific, Cat. No. 11-463-54A

*Nuclear Magnetic Resonance Spectrometer*, capable of time-averaged, proton decoupled, refocused INEPT analysis of  $^{119}\text{Sn}$ . See *PROCEDURE, Instrument Specification* for additional information.

*Pipet*, Mohr, Class B, 1-mL

*Pipet*, volumetric transfer, Class A, 5-mL

*Plug*, vortex, glass, Wilmad Glass, sized appropriately for NMR tube (see *PROCEDURE, Instrument Specification*)

*Pump*, vacuum, mechanical, Fisher Scientific, Cat. No. 01-182

*Rotary Evaporator*, with reflux condenser and oil bath, Fisher Scientific, Cat. No. 09-548-224

*Regulator*, gas, for supply of nitrogen gas for derivatization, Fisher Scientific, Cat. No. 10-574N

*Ring stand*, with rectangular base, 250- x 230-mm with 890-mm rod, Fisher Scientific, Cat. No. 14-679

*Stirrer*, magnetic bar, 32-mm (1.25-inch), Teflon covered, egg-shaped, Fisher Scientific, Cat. No. 14-511-58A

*Stirrer*, motor, magnetic, 50/60 Hz, Fisher Scientific, Cat. No. 11-501-4S

*Temperature controller*, stepless, 120 V, 2 required, Fisher Scientific, Cat. No. 13-931-12

*Thermometer*, mercury, 76-mm immersion, calibrated from -5 to 400°C, Fisher Scientific, Cat. No. 15-166C

*Thermometer*, mercury, 76-mm immersion, 10/30 standard taper, calibrated from -10 to 360°C, Fisher Scientific, Cat. No. 15-002F

*Trap*, vacuum distillation, borosilicate glass, 50/50 standard taper joints, Fisher Scientific, Cat. No. 11-184-1E

*Tube*, NMR sample, reusable, Ultra or Royal Imperial Quality Class, Wilmad Glass, sized appropriately for NMR spectrometer (see *PROCEDURE, Instrument Specification*)

*Tubing*, vacuum, rubber, red, Fisher Scientific, Cat. No. 14-173D

## REAGENTS AND MATERIALS

Unless otherwise specified, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

*Acetone*, free of alcohols, Fisher Scientific, Cat. No. A929-11

*Bis(tributyltin) oxide*, 96% purity, Aldrich, Cat. No. B5,338-3

*Chromium(III) acetylacetonate*, 97% purity, Aldrich, Cat. No. 20-223-1

*Chromium(III) acetylacetonate solution*, 0.1-M. Weigh 0.349 g chromium(III) acetylacetonate into a 10-mL volumetric flask. Dilute to volume with C<sub>6</sub>D<sub>6</sub>. Mix thoroughly to dissolve.

*Dry ice*

*Grease*, high vacuum, silicone, Fisher Scientific, Cat. No. 14-635-5D

*Nitrogen*, gas, 99.9% minimum, <2 ppm H<sub>2</sub>O, Matheson Gas Products, Extra Dry

*Perdeuterobenzene*, benzene-d<sub>6</sub>, C<sub>6</sub>D<sub>6</sub>, 99.6 atom-%, Cambridge Isotope Laboratories, Cat. No. DLM-1

*Pump oil*, vacuum, Fisher Scientific, Cat. No. 01-184-150A

*Tetramethyltin*, 99+% purity, Aldrich, Cat. No. 14,647.1

*Tetramethyltin solution*, 0.084-M. Weigh 0.15 g tetramethyltin into a 10-mL volumetric flask containing approximately 5-mL C<sub>6</sub>D<sub>6</sub>. Dilute to volume with C<sub>6</sub>D<sub>6</sub>. Mix thoroughly.

*Thread*

*Toluene*, 99.8% minimum purity, Fisher Scientific, Cat. No. T291-4

## PROCEDURE

Handle all reagents in a fume hood using the appropriate safety equipment.

### Mercaptan Sulfur Analysis

A 50-g sample is required for analysis by UOP Method 163 to obtain the thiol-sulfur content (total mercaptan value) of the sample. This value will be used to determine the amount of TBTO to use in *PROCEDURE, Preparation of Sample*, and in *CALCULATIONS*.

### Preparation of Sample

1. Clean the 500-mL round bottom flask with acetone, follow with a toluene rinse and dry with nitrogen gas.
  - If extensive concentration is anticipated, because one or more of the mercaptan types are below 40 mass-ppm, then it is desirable to concentrate more than 200 g of kerosine at a time. If so, then proportionally more kerosine, toluene, TBTO and a larger flask and heating mantle should be used during derivatization.
2. Add the stir bar to the flask and weigh the flask and bar to the nearest 0.01 g.
3. Measure approximately 200 g of sample into the tared 500-mL flask using a graduate cylinder, record the volume ( $\pm 1$  mL) and weigh to the nearest 0.01 g.
4. Calculate to 4 significant figures the millimols of thiol-sulfur present in the sample portion as follows:

$$S = \frac{10^{-3} G M}{32.06} \quad (1)$$

where:

**G** = concentration of thiol-sulfur from *Mercaptan Sulfur Analysis*, mass-ppm  
**M** = mass of sample, g  
**S** = millimols of thiol-sulfur  
**32.06** = grams of sulfur/mol  
 **$10^{-3}$**  = factor required to convert from mass-ppm to millimols

5. Calculate to the nearest 0.01 g the quantity of TBTO required as follows:

$$T = 1.191 S \quad (2)$$

where:

**S** = previously defined (Eq. 1)  
**T** = quantity of TBTO required, g  
**1.191** = factor to convert millimols of thiol-sulfur to grams of TBTO required with a four-fold molar excess ( $2 \times 0.59538$  g of tin compound per millimol)

6. Add the quantity of TBTO determined in Step 5 to the 500-mL flask, weighing the reagent to the nearest 0.01 g.
7. Add 20±1 g of toluene to the 500-mL flask.
8. Cap and swirl the flask to mix the contents.
9. Place the 500-mL flask in a spherical heating mantle, turn on the nitrogen flow and purge the condenser and the 500-mL flask with nitrogen (see Fig. 1).
10. Complete the assembly of the apparatus as indicated in Fig. 1, after purging the apparatus with nitrogen and lubricating the standard taper joints with vacuum grease.
  - The nitrogen atmosphere in the apparatus should be maintained during the derivatization by continuing the nitrogen flow to prevent air oxidation of mercaptans.
11. Clamp the apparatus securely to the ring stand and place the stirring motor under the derivatization flask.

### Derivatization of Sample

1. Turn on the water to the condenser.
2. Wrap heating tape around the distillation head (see Fig. 1), plug the tape into a temperature controller, turn on and adjust to maintain the distillation head at a temperature between 170 to 180°C.
  - The temperature of the distillation head is set using the standard taper immersion thermometer.
3. Plug the heating mantle into another temperature controller.
4. Turn on the heating mantle temperature controller and adjust to maintain the distillation flask thermometer temperature at 170 to 180°C and hold that temperature for 30 minutes, collecting and measuring the mass (±0.01 g) and volume (±1 mL) of any distillate produced.
  - The distillation temperature of kerosines vary, depending on the sample. If initial boiling temperatures lower than 170 to 180° C are observed, distill the sample until the boiling point of the sample is in the target range and hold for 30 minutes. If the initial boiling temperature is higher than 180°C, maintain 170 to 180°C for 30 minutes to complete the derivatization without distillation of the kerosine.
5. Turn the temperature controller switches off, remove the heating mantle from the flask and permit the flask to cool to room temperature, while continuing the nitrogen flow (Fig. 1).
  - If the minimum concentration of each of the mercaptan types is greater than 40 mass-ppm, skip *Sample Concentration* steps and proceed as indicated in *<sup>119</sup>Sn NMR Analysis*.
  - If the minimum concentration of each of the mercaptan types is unknown, estimate the approximate concentration of the mercaptan types by proceeding immediately as indicated in *<sup>119</sup>Sn NMR Analysis* and then repeat the analysis, concentrating the sample, if appropriate.
  - If concentration is required, estimate the volume of kerosine that must be removed to attain the needed concentration from the volume and mass of overhead collected and the original volume and mass of the sample.
  - Since the organo-sulfur-tributyltin compounds are not volatile, the degree of concentration can be determined from the mass of the kerosine bottoms in the derivatization flask and the initial charge.

6. Transfer the sample to an appropriately sized nitrogen purged glass bottle and seal with a polyseal screw cap.
  - If desired, the derivatization flask used above may also be used for the vacuum distillation after removal of the thermometer and the stir bar. If this is to be done, then this step should be skipped.
  - If desired, the sample may be stored indefinitely at room temperature under nitrogen until the NMR analysis is performed.
  - Traces of precipitates or haze may be observed in some samples, particularly concentrated samples, due to the presence of heavy hydrocarbons. Therefore, the sample should be mixed well before transferring to the glass bottle to ensure representative sampling.

### Sample Concentration

1. Mark the receiver flask at the liquid level of distillate to be removed, place the sample in the vacuum distillation flask and assemble the rotary evaporator as indicated in Fig. 2 and according to the manufacturer's instructions.
  - Any convenient marker may be used to calibrate the receiver, and the calibration need only be accurate to within several mL.
  - If desired, the derivatization flask used in *Derivatization of Sample* may be used for the vacuum distillation after removal of the thermometer and the stir bar.
2. Turn on the rotary evaporator, adjust the rotation speed, establish a vacuum and heat the vacuum distillation flask to distill sufficient kerosine from the sample, using either the heating mantle or the oil bath that is part of the rotary evaporator equipment.
  - If extensive concentration is required, it is desirable to concentrate more than 200 g of kerosine at a time. In that case, proportionately more kerosine, toluene, TBTO and a larger flask and heating mantle should be used during *Derivatization of Sample* and an appropriately larger flask should be used here.
3. Turn off and remove either the heating mantle or the oil bath once the required concentration has been completed and permit the flask to cool to room temperature.
4. Remove the flask from the rotary evaporator.
  - If desired, the sample may be transferred to an appropriately sized bottle, capped, purged with nitrogen and stored indefinitely at room temperature under nitrogen until the NMR analysis is performed.
  - Traces of precipitates or haze may be observed in some samples, particularly concentrated samples, due to the presence of heavy hydrocarbons. The hydrocarbon heavies do not affect the analysis.

### Instrument Specification

The NMR spectrometer must be capable of performing time-averaged fourier transform (FT), proton decoupled, refocused INEPT analysis of  $^{119}\text{Sn}$ . The NMR must be sensitive enough to detect primary, secondary and tertiary mercaptan types that have been reacted with TBTO at 40 mass-ppm per mercaptan type. Sample volume versus magnetic field considerations make it impractical to consider magnetic fields below 4.7 Tesla when attempting to achieve the indicated sensitivities. Table 1 shows signal-to-noise measurements that were obtained on two spectrometers that had sufficient sensitivity to perform this analysis. In addition, spectrometers equipped with autosamplers are suggested as a means of more efficient operation.

**Table 1**  
**<sup>119</sup>Sn INEPT Sensitivity (TBTO)**

| <b>Instrument</b>                     | <b>Bruker CXP-200</b> | <b>Bruker ACP-300</b> |
|---------------------------------------|-----------------------|-----------------------|
| <b>Signal/Noise</b>                   | <b>333:1</b>          | <b>450:1</b>          |
| <b>TBTO Concentration, mass-%</b>     | <b>22.4</b>           | <b>22.4</b>           |
| <b>Pulse Width</b>                    | <b>90°</b>            | <b>90°</b>            |
| <b>Sweep Width, ppm</b>               | <b>129</b>            | <b>125</b>            |
| <b>Line Broadening, Hz</b>            | <b>4*</b>             | <b>1</b>              |
| <b>Number of Data Points</b>          | <b>8k</b>             | <b>8k</b>             |
| <b>Zero Filled</b>                    | <b>16k</b>            | <b>16k</b>            |
| <b>Pulse Program</b>                  | <b>INEPT</b>          | <b>INEPT</b>          |
| <b>Magnetic Field Strength, Tesla</b> | <b>4.7</b>            | <b>7.05</b>           |
| <b>Number of Scans</b>                | <b>1</b>              | <b>1</b>              |
| <b>Sample Tube Diameter, mm</b>       | <b>20</b>             | <b>10</b>             |

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\* Natural Line Width

The pulse sequence for the INEPT data acquisition is shown below. The pulse program for a Bruker CXP-200 equipped with an ASPECT 3000 computer as well as the automation program for a Bruker ACP-300 equipped with an ASPECT 3000 computer and a B-ACS 60 autosampler is included in the *APPENDIX*.

<sup>1</sup>H: P<sub>90</sub>(<sup>1</sup>H) - 1/4J - P<sub>180</sub>(<sup>1</sup>H) - 1/4J - P<sub>90</sub>(<sup>1</sup>H) - δ/2 - P<sub>180</sub>(<sup>1</sup>H) - ----- - Waltz Decouple  
<sup>119</sup>Sn P<sub>180</sub>(<sup>119</sup>Sn)- 1/4J - P<sub>90</sub>(<sup>119</sup>Sn)- δ/2 - P<sub>180</sub>(<sup>119</sup>Sn) - δ/2 - Acquire .....Wait

### Calibration of the Spectrometer

- Set up the NMR as described in *<sup>119</sup>Sn NMR Analysis* except change the pulse program sequence to proton decoupled Bloch decay.
  - The spectrometer calibration is required to be done once to set the spectral reference for the samples. The calibration should be repeated if the sample matrix changes or if the spectrometer field is changed.
  - The pulse program needs to be changed to proton decoupled Bloch decay in place of INEPT otherwise, the tetramethyltin would not be detected.
- Pipet 5-mL of sample into a vial.
- Pipet 5-mL of 0.1-M chromium(III) acetylacetonate in C<sub>6</sub>D<sub>6</sub> and 0.1-mL of 0.084-M tetramethyltin (TMT) into the same vial. Mix the solutions thoroughly.

4. Transfer into the appropriately sized NMR tube enough of the mixed solution to just fill both the decoupler and receiver coils.
5. Place a glass vortex suppressor in the NMR tube with the suppressor positioned to prevent formation of a vortex in the sample. Cap the tube.
  - If the glass vortex suppressor sinks into the sample, hold it in place with a piece of thread
6. Record the time-averaged, proton decoupled Bloch decay of  $^{119}\text{Sn}$  NMR spectrum over a period of 16 hours.
7. Plot the NMR spectral features using a line broadening parameter of 1-ppm.
8. Determine the spectral reference (SR) by assigning the chemical shift of the TMT peak to 0 ppm.
  - The TMT peak can be assigned by comparing the spectrum of the above sample containing TMT with the spectrum of the same sample, run by INEPT, without TMT.
  - Tin NMR uses TMT as a chemical shift reference at 0 ppm. Once the chemical shift reference is set at 0 ppm a SR will be obtained which can be used for subsequent samples.

### $^{119}\text{Sn}$ NMR Analysis

1. Set up and tune the NMR according to the manufacturer's instructions and the operating parameters of Table 2 to record the time averaged, refocused INEPT  $^{119}\text{Sn}$  spectrum.
  - The operating conditions are for the instruments indicated equipped as described. Other conditions and instruments may be used provided they produce the required sensitivity.
2. Pipet 5-mL of sample into a vial.
3. Pipet 5-mL of 0.1-M chromium(III) acetylacetonate in  $\text{C}_6\text{D}_6$  into the same vial and mix the solutions thoroughly.
4. Transfer into the appropriately sized NMR tube enough of the mixed solution to just fill both the decoupler and receiver coils.
5. Place a glass vortex suppressor in the NMR tube with the suppressor positioned to prevent formation of a vortex in the sample. Cap the tube.
  - If the glass vortex suppressor sinks into the sample, hold it in place with a piece of thread.
6. Record the time-averaged, proton decoupled, refocused INEPT  $^{119}\text{Sn}$  NMR spectrum over a period of 16 hours.
7. Plot the NMR spectral features using a line broadening parameter of 1-ppm and calculate the integral areas for each resonance detected.
  - If a prominent resonance from excess TBTO at a chemical shift of 83 - 86 ppm does not appear in the NMR spectrum, the *PROCEDURE* must be started over, adding more TBTO (*Preparation of Sample*).
8. Identify the resonances attributable to primary, secondary and tertiary organo-sulfur derivatives by consulting Table 3 and Fig. 3. Record the integral areas associated with each type.

**Table 2**  
**NMR Operating Conditions**

| <b>Spectrophotometer</b>                                                       | <b>Bruker<br/>CXP-200</b> | <b>Bruker<br/>ACP-300</b> |
|--------------------------------------------------------------------------------|---------------------------|---------------------------|
| <b>Transmitter Channel Frequency, MHz</b>                                      | <b>74.599</b>             | <b>111.92</b>             |
| <b>Pulse Program Sequence</b>                                                  | <b>INEPT</b>              | <b>INEPT</b>              |
| <b>90° Pulse Width of Tin, μsec</b>                                            | <b>29.28</b>              | <b>19.95</b>              |
| <b>90° Pulse Width of Proton Decoupler at Maximum Power Setting, μsec</b>      | <b>36</b>                 | <b>23.3</b>               |
| <b>90° Pulse Width of Composite Pulse Decoupler at 10H Power Setting, μsec</b> | <b>100</b>                | <b>101</b>                |
| <b>Delay Time Between Pulses, sec</b>                                          | <b>3</b>                  | <b>2.5</b>                |
| <b>Refocus Delay (δ/2), msec</b>                                               | <b>2.31</b>               | <b>2.26</b>               |
| <b>Number of Scans (16 hr)</b>                                                 | <b>16,800</b>             | <b>20,736</b>             |
| <b>Tube Size, mm</b>                                                           | <b>20</b>                 | <b>10</b>                 |
| <b>Probe Temperature</b>                                                       | <b>ambient</b>            | <b>ambient</b>            |
| <b>Line Broadening (1 ppm), Hz</b>                                             | <b>75</b>                 | <b>112</b>                |

**Table 3**  
**Chemical Shifts for Mercaptan Classes**

| <b>Class</b>                | <b>Chemical Shift, ppm</b> |
|-----------------------------|----------------------------|
| <b>Primary Mercaptans</b>   | <b>70-80</b>               |
| <b>Secondary Mercaptans</b> | <b>60-70</b>               |
| <b>Tertiary Mercaptans</b>  | <b>40-60</b>               |

## **CALCULATIONS**

Calculate the mole-fraction of each mercaptan type found in the sample to 4 decimal places using Eq. 3:

$$A = \frac{B}{C} \quad (3)$$

where:

**A** = mole-fraction of each mercaptan type present in the sample

**B** = calculated NMR integral area for the individual mercaptan type from Step 8, *<sup>119</sup>Sn NMR Analysis*

**C** = sum of calculated NMR integral areas associated with the primary, secondary and tertiary mercaptan-tin derivatives, from Step 8, *<sup>119</sup>Sn NMR Analysis*

Calculate the concentration of the individual mercaptan types, to the nearest 1 mass-ppm below 100 mass-ppm or to 3 significant figures at or above 100 mass-ppm using Eq. 4:

$$D = AE \quad (4)$$

where:

**A** = defined above (Eq. 3)

**D** = primary, secondary or tertiary mercaptan concentration, mass-ppm

**E** = total mercaptan sulfur concentration measured by UOP Method 163, mass-ppm

## NOTE

To prevent interference with the determination of primary mercaptans, the sample must contain less than 40 mass-ppm of thiophenol, isopropyl and butyl alcohols. When derivatized with TBTO, such contaminants exhibit chemical shifts in the same region as the primary mercaptan derivatives. Such contamination of kerosines is rare, but if it is suspected, the sample may be analyzed by Gas Chromatography to verify that interferences are present. If present, the mercaptan types cannot be unambiguously determined.

## PRECISION

### Repeatability

Based on eight tests performed by one analyst, the within-laboratory estimated standard deviations (esd) were calculated for mercaptans at the concentrations indicated in Table 4. Two tests performed in the same laboratory on different days by the same analyst should not differ by more than the allowable differences shown in Table 4 at the concentrations listed (95% probability).

**Table 4**

| <b>Mercaptan Concentration<br/>(without Concentration)</b> | <b>In Feed,<br/>mass-ppm</b>    | <b>esd,<br/>mass-ppm</b> | <b>Allowable<br/>Difference,<br/>mass-ppm</b> |
|------------------------------------------------------------|---------------------------------|--------------------------|-----------------------------------------------|
| <b>Primary</b>                                             | <b>18</b>                       | <b>1.7</b>               | <b>6</b>                                      |
| <b>Secondary</b>                                           | <b>291</b>                      | <b>6.0</b>               | <b>20</b>                                     |
| <b>Tertiary</b>                                            | <b>63</b>                       | <b>4.1</b>               | <b>14</b>                                     |
| <b>Mercaptan Concentration<br/>(without concentration)</b> | <b>In Product,<br/>mass-ppm</b> | <b>esd,<br/>mass-ppm</b> | <b>Allowable<br/>Difference,<br/>mass-ppm</b> |
| <b>Primary</b>                                             | —                               | —                        | —                                             |
| <b>Secondary</b>                                           | <b>9</b>                        | <b>0.65</b>              | <b>2</b>                                      |
| <b>Tertiary</b>                                            | <b>10</b>                       | <b>0.69</b>              | <b>2</b>                                      |

### Reproducibility

There is insufficient data to determine the between-lab reproducibility at this time.

## TIME FOR ANALYSIS

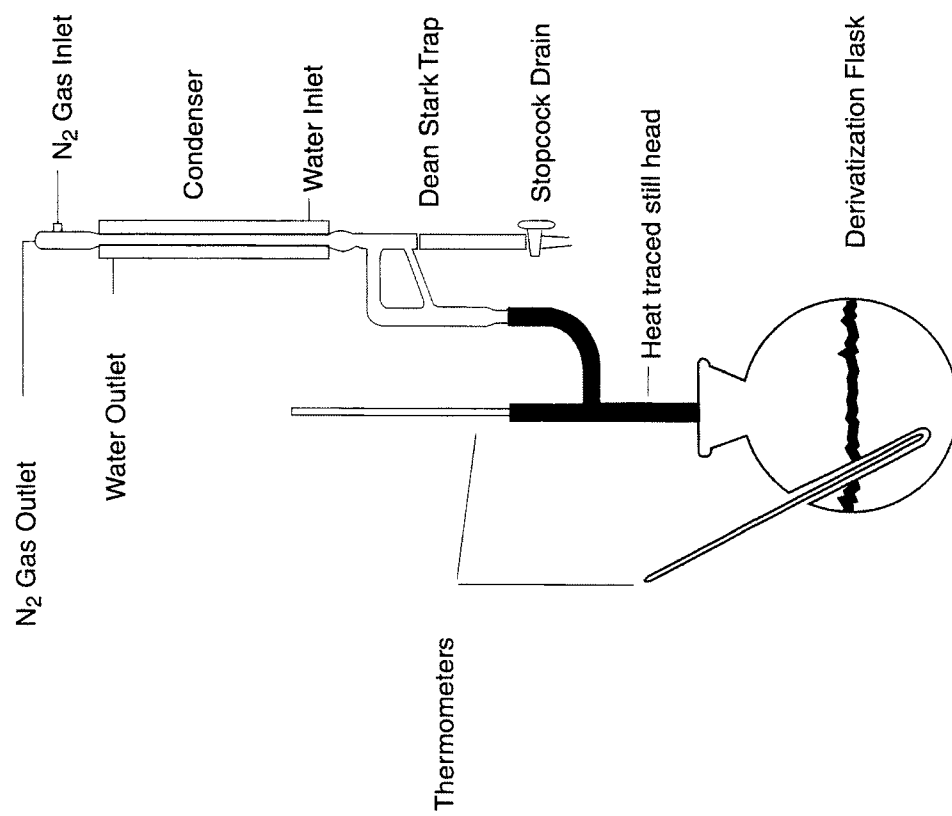
For one analysis, the time for sample preparation is the same as the elapsed time of 1 hour. Distillation, if required, consumes an additional one to two hours of labor, depending on the degree of concentration required. The labor requirement for the  $^{119}\text{Sn}$  NMR Analysis is approximately 1 hour. The elapsed time for one NMR analysis is 16 to 17 hours.

## REFERENCES

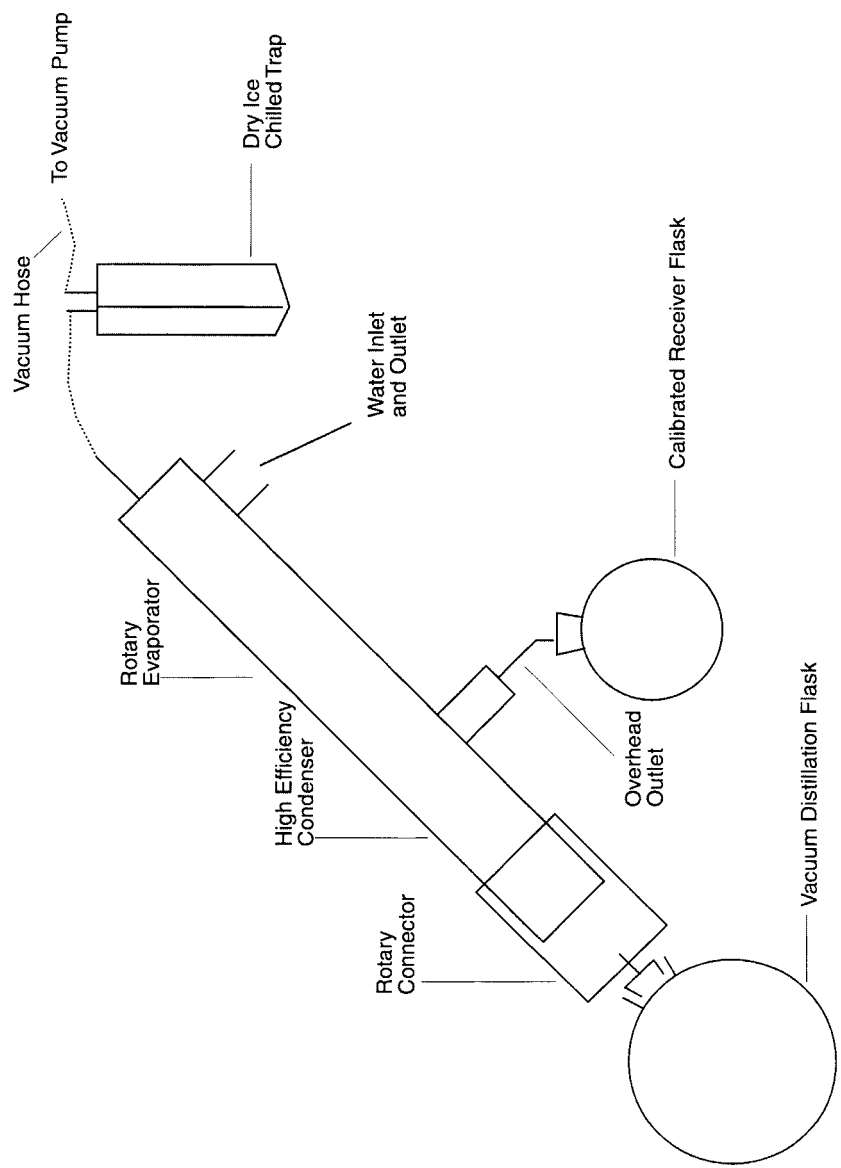
1. Rafii, E., Ngassoum, M., Faure, R., Foon, R., Lena, L. and Metzger, J., "Structural Characterization of Sulphur Compounds in Petroleum Fractions by  $^{119}\text{Sn}$  Nuclear Magnetic Resonance Spectrometry," *Fuel*, **70**, pp 132-135, January 1990
2. Rafii, E., Faure, R., Lena, L., Vincent, E. and Metzger, J., "Characterization of Phenols from Coal Liquefaction Products by  $^{119}\text{Sn}$  Nuclear Magnetic Resonance Spectrometry," *Anal. Chem.*, **57**, 2854-2858 (1985)
3. UOP Method 163, "Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons"

## SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)  
Cambridge Isotope Laboratories, 20 Commerce Way, Woburn, MA 01801 (617-938-0067)  
Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)  
Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)  
Wilma Glass Co., Rte. 40 and Oak Rd., Buena, NJ 08310 (609-697-3000)



**Figure 1**  
derivatization Equipment



**Figure 2**  
Vacuum Distillation Equipment

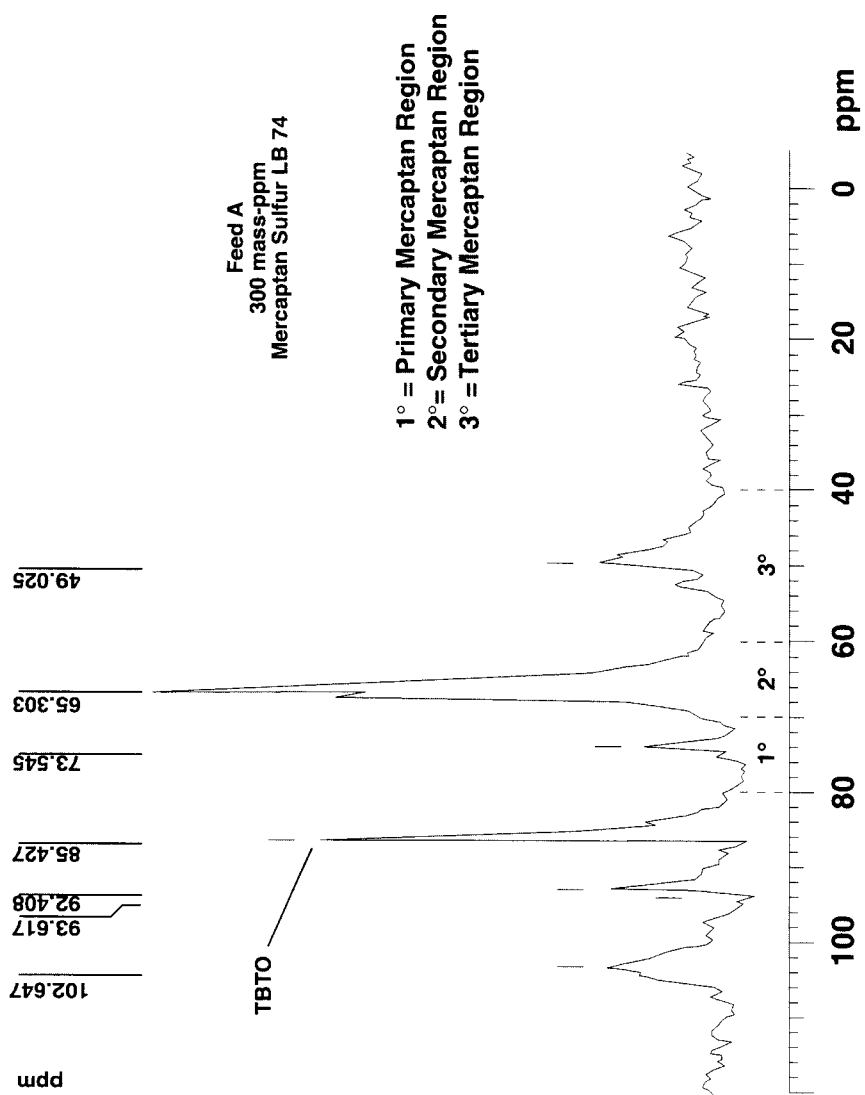


Figure 3  
Typical NMR Spectrum

**APPENDIX**  
**Automation Program for Bruker ACP-300 NMR**  
**Equipped with an ASPECT 3000 Computer and a B-ASC 60 Autosampler**

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; INEPT FOR NON-SELECTIVE POLARIZATION TRANSFER FROM
; 1H TO X-NUCLEI VIA J(XH).
; WITH REFOCUSING FOR DECOUPLED SPECTRA
; WITH ADDITIONS TO RUN IN AUTOMATION
; 1H: D1 - 90 - D2 - 180 - D2 - 90 - D3 - 180 - D3 - BB
; X:          180      90      180      FID

1 II ;INITIALIZE INTERFACE
2 TU4 ;SHIM ON Z1 AND Z2, TUNING VERSION
3 ZE ;ZERO MEMORY
4 D1 S1 D0 ;RELAXATION DELAY FOR 1H, PREPARE DEC. POWER
;FOR PULSING
5 (P1 PH1 D2):D ;90° PULSE FOR 1H, THEN DELAY
;FOR EVOLUTION OF SHIFTS AND COUPLINGS
6 (P2 PH2 D2):D P4 PH4 ;SIMULTANEOUS 180° PULSES TO 1H AND X,
;TO REFOCUS SHIFTS BUT COUPLING EVOLVES
;FURTHER TO GIVE ANTI-PARALLEL 1H
;DOUBLET
7 (P1 PH3):D (P3 PH5 D3) ;90° 1H PULSE (90° PHASE SHIFT)
;CAUSES POLARIZATION TRANSFER, 90° X
;PULSE GENERATES DETECTABLE X, Y-MAGN.
;DELAY ALLOWS EVOLUTION OF ANTIPHASE
;X MULTIPLETS
8 (P2 PH2):D (P4 PH6 D3 S2) ;180° PULSES FOR 1H AND X TO
;REFOCUS SHIFTS, SET DEC. POWER
9 GO=4 PH7 CPD ;ACQUIRE X-NUCLEUS FID WITH DECOUPLING
;SIGNAL PHASE AND INTENSITY DEPENDS ON J(XH),
;CHOICE OF D3, AND X-H MULTIPLICITY.
;LOOP TO 4
;STORE FID UNDER DIALOGUE DEFINED NAME

10 WR @
10 D2 DO
11 EXIT ;EXIT WITH DEC. OFF

PH1=B0 B0 B0 B0 B0 B0 B0 B0
B2 B2 B2 B2 B2 B2 B2 B2
PH2=B0 B2
PH3=B1 B1 B3 B3
PH4=A0 A2
PH5=A0 A0 A0 A0 A1 A1 A1 A1
A2 A2 A2 A2 A3 A3 A3 A3
PH6=A0 A2 A0 A2 A1 A3 A1 A3
PH7=R0 R0 R2 R2 R1 R1 R3 R3

;D1 = 1-5*T1 FOR 1H
;S1 = 0H NORMALLY FOR MAX. PULSE POWER
;S2 = POWER SETTING FOR GOOD DECOUPLING WITH CPD
;P1,P2 = 90°, 180° FOR 1H DECOUPLER
;P3,P4 = 90°, 180° FOR X-NUCLEUS
;P9 = 90° DEC. PULSE FOR POWER S2
;D2 = 0.25/J(XH) FOR MAX, TRANSVERSE POLARIZATION OF 1H
;D3 IS VARIABLE DEPENDING ON DESIRED MULTIPLICITY SELECTION:
; E.G. D3 = 0.125/J GIVES XH, XH2, XH3 POSITIVE
; = 0.25/J GIVES XH ONLY
; = 0.375/J GIVES XH, XH3 POS. AND XH2 NEG.
;NS=4*N, RD=PW=0

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# Pulse Program for Bruker CXP-200 NMR Equipped with an ASPECT 3000 Computer

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; INEPTD.PC
; REFOCUSED INEPT PULSE SEQUENCE WITH WALTZ DECOUPLING
; ON CXP-200
; REF. MORRIS AND FREEMAN, J.MAG.RES. 41, 341 (1981)
; SET S2 FOR WALTZ S2=10H FOR 20MM PROBE

DE=DW*3/4
EVOLVE=(0.25S)/K2      ; SET K2 = J (X,H)
SELECT=(0.125S)*K3/K2  ; SET K3 = 1, 2 OR 3
PROT F1 F2 XT

START,30U              ; SET DECOUPLER TO S1
  D15                  ; RELAXATION
  D11 [F2 @ PLS1]      ; 1H P1/2 PULSE
EVOLVE                 ; 1/4J
  D12 [F2 @ PLS2]      ; 1H P1 PULSE
  D2 [F1 @ PLS4]       ; X-NUCLEI P1/2 PULSE
EVOLVE                 ; 1/4J
  D11 [F2 @ PLS3]      ; 1H P1/2 PULSE
  D1 [F1 @ PLS5]       ; X-NUCLEI P1/2 PULSE
SELECT                 ; MULTIPLY SELECTION
  D12 [F @ PLS2]       ; 1H P1 PULSE
  D2 [F1 @ PLS6]       ; X-NUCLEI P1 PULSE
RELEASE F1 XT          ; RELEASE F2 OUTPUTS
SELECT                 ; REFOCUSING DELAY
DE [STA DEC]
AQ [DEC]               ; ACQUIRE WITHIN BB-DECOUPLING
++PLS1++PLS2++PLS4++
PLS3++PLS5++PLS6
10U
GOTO START
BEGIN LISTS
PLS1,8(+X) 8(-X)
PLS2,+X -X
PLS3,+Y +Y -Y -Y
PLS4,+X -X
PLS5,4(+X) 4(+Y) 4(-X) 4(-Y)
PLS6,+X -X +X -X +Y -Y +Y -Y
RLS,+X +X -X -X +Y +Y -Y -Y
END LISTS

; RECEIVER MODE : RPN
; TRIGGER MODE:: NT
; NS = 4 * N

; D1, D2 = 90°, 180° X-NUCLEI PULSE
; D11, D12 = 90°, 180° PROTON PULSE
; FOR CORRECT EVOLUTION DELAY SET K2 = AVERAGE C-H COUPLING
; FOR SELECTION DELAY AND REFOCUSING DELAY
;
; =1/8J :GIVES XH, XH2, XH3 POS., SET K3=1
;
; =1/4J :GIVES XH ONLY, SET K3=2
;
; =3/8J :GIVES XH, XH3 POS. AND XH2 NEG., SET K3=3

; S1, S2 : DECOUPLER SWITCH
; S1 = 0-10H (DEPENDS ON PROBEHEADS), ABOUT 5H FOR 10MM PROBE
; S2 = 13-25H (DEPENDS ON PROBEHEADS), ABOUT 16H FOR 10MM PROBE
; CRITICAL PARAMETERS ARE ALL PULSE ANGLE SETTINGS AND
; K2 FOR OPTIMUM POLARIZATION AND OPTIMUM SUPPRESSION
; AND PHASE OF PEAKS

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