

## **MERCAPTAN SULFUR IN LPG BY MICROCOULOMETRY**

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### **UOP Method 772-77**

#### **SCOPE**

This method is for the determination of total mercaptan sulfur at the level of 0.1 to several hundred ppm sulfur in C<sub>1</sub> through C<sub>5</sub> hydrocarbons. Hydrogen sulfide at any concentration will falsify the results as H<sub>2</sub>S is titrated stoichiometrically in the cell. Carbonyl sulfide cannot be determined. Therefore, the method should be applied only to finished LPG, and not to untreated refinery streams.

#### **OUTLINE OF METHOD**

The sample is injected as a gas or liquid into a heated chamber where, if liquid, the hydrocarbon vaporizes, and the vapor is carried into a selective coulometric titration cell by an inert gas stream. The mercaptan is titrated by silver ions which cause a change in the electrode potential. The silver ions are coulometrically replaced to the original concentration which is directly proportional to the mercaptan concentration.

#### **APPARATUS**

*Balance*, analytical

*Bottle*, glass, 8-ounce

*Capillary gas inlet heater and power supply*, available as Model P-200 from Dohrmann, or equivalent

*Fittings*, stainless steel, various sizes to fit cylinders

*Furnace*, available from Sargent-Welch, Cat. No. S-36517, or equivalent. For use in the inert gas cleanup train, see Fig. 1

*Gauge*, 0-400 psig (28 kg/sq cm), mounted on stainless steel tee

*Heating tape*, 1/2 inch by 4 ft, 140W, 45V, 480 F (250 C) max.

*Microcoulometer*, Dohrmann, Model C-200B, or equivalent

*Quartz retainer*. To hold the copper for the inert gas cleanup train. See Fig. 1.

*Recorder*, Dohrmann, Model R-100-1 recorder/integrator, or equivalent

*Regulator, pressure*, two-stage, for helium or nitrogen

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*Septa*, Dohrmann, Cat. No. 523786, or equivalent

*Stirrer*, magnetic, Dohrmann, Cat. No. 51640, or equivalent

*Syringes*, 0.25 and 0.50 cm<sup>3</sup> Pressure-Lok available from Precision Sampling Corp.; 10-, 25-, 50- and 100 cm<sup>3</sup> Gastight available from Hamilton Co. Inc., or equivalent

*Titration cell*, Dohrmann, Model T-300S, prepared and plated by the manufacturer and ready for use. Model T-300P can also be used, however, it must be prepared and plated according to the manufacturer's directions before use.

*Transformer*, variable, Powerstat, Cat. No. S30940. Available from Sargent-Welch, or equivalent

*Valve*, needle, Whitey valve No. 2RF2, 316 stainless steel

*Vaporization chamber*, quartz, with injection port, see Fig. 2.

## REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society when such specifications exist, unless otherwise stated or specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

*Acetic acid*, glacial

*Acetic acid solution*. 70% v/v. Mix 7 parts glacial acetic acid with 3 parts water by volume.

*Copper*, available as "Cuprin" from Coleman, Cat. No. 29-120, or equivalent

*Electrolyte solution*. 0.1 N NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in 50/50 isopropanol and water. Weigh 8.200 g of the sodium acetate into a 1-liter volumetric flask. Add 500 cm<sup>3</sup> of water and mix until the sodium acetate is completely dissolved. Fill to the mark with isopropanol and mix thoroughly.

*Ethyl mercaptan*, pure grade

*Isopentane*, pure grade

*Isopropanol*, pure grade

*Mercaptan stock solution*. Bubble ethyl mercaptan into a flask containing 200-250 cm<sup>3</sup> of cold isopentane for about 20 seconds. Keep this solution cold and under a nitrogen blanket. Determine the RSH-S content by UOP Method 163. Check the concentration weekly.

*Mercaptan standard solution*. From the stock solution, prepare one day's supply of 0.5 and 2.5 wt-ppm RSH-S solutions. Keep solutions cold in a beaker of dry ice.

*Sodium acetate*, purified grade, available from J. T. Baker, or equivalent

*Silver acetate*, purified grade, available from J. T. Baker, or equivalent

## PROCEDURE

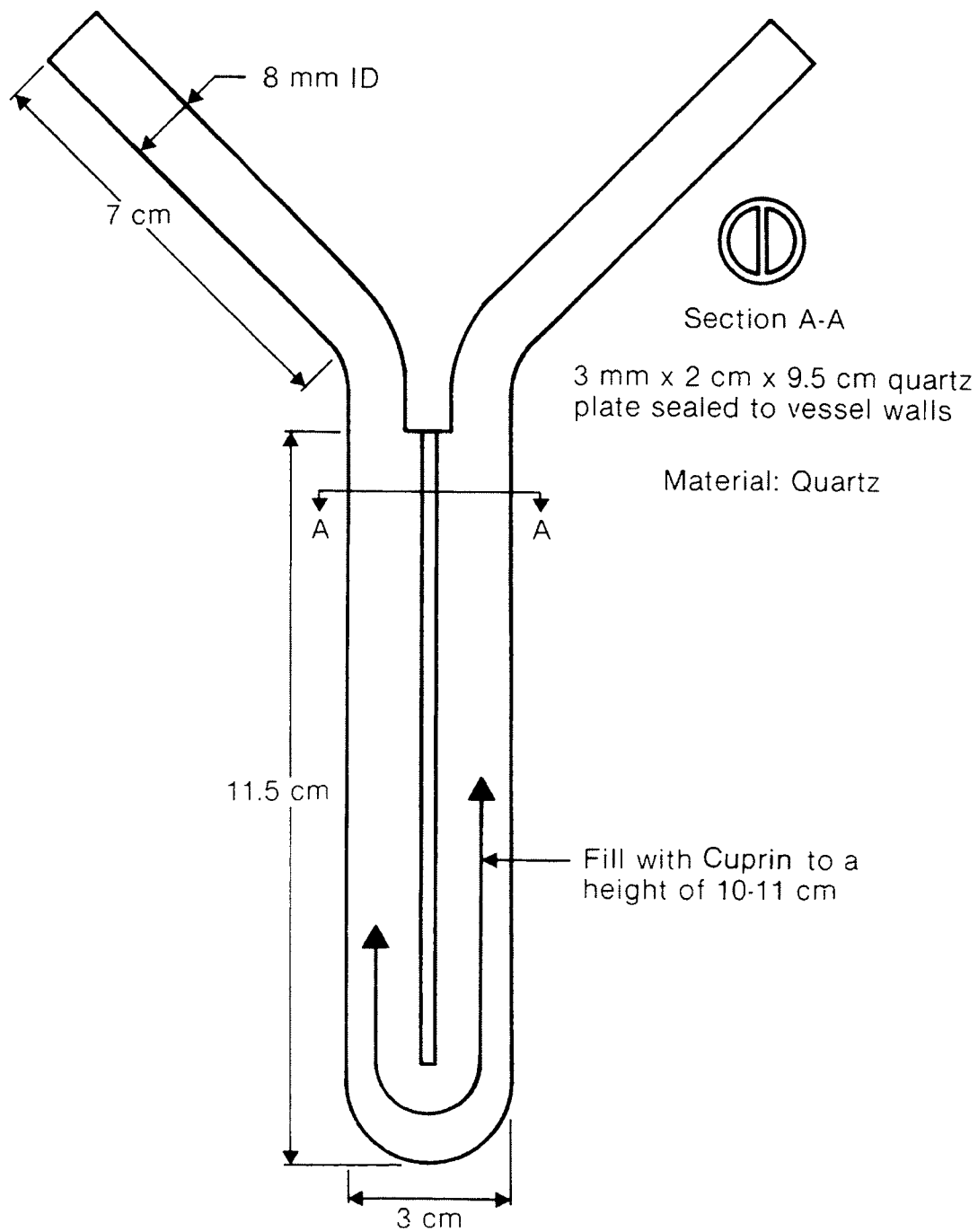
### Cell Preparation

If a Model T-300S cell is used, proceed to *Start-up and Operation*. If the Model T-300P is used, it must be plated; proceed as follows:

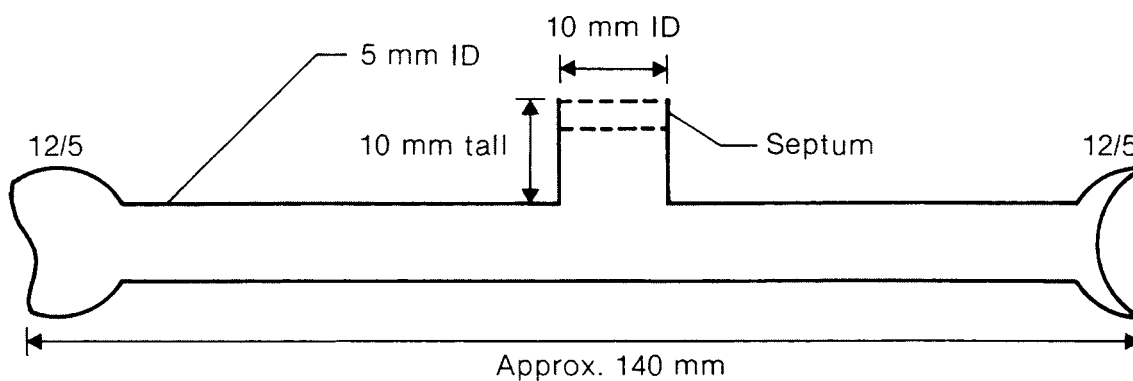
1. Take an unplated cell and clean it according to the manufacturer's specifications.
2. Again following the manufacturer's directions, silver-plate the cell head and reference electrodes. Condition the plated electrodes by placing them in 70% acetic acid solution for one hour.
3. Lightly grease the stopcocks so they move freely.
4. Add silver acetate to the reference half cell cavity up to the bottom of the ground glass surface.
5. Add the 70% acetic acid solution to the main cell body until the reference cavity is filled and the silver acetate is visibly wetted by the acid solution.
6. Grease the ground glass surface of the reference electrode making sure the silver acetate cavity is filled, and carefully insert the electrode into the cavity. Make sure there are no air bubbles and that the exposed wire portion (silver plated) of the electrode is completely surrounded by the silver acetate.
7. Attach a spring or rubber band to the "ears" to secure the electrode.
8. Flush out any silver acetate that may have been forced through the glass disk at the base of the reference cavity.
9. Flush out the cell with the 0.1 *N* NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> electrolyte 4 to 5 times. Place a stirring bar in the cell body.
10. Orient the cell head in the body as shown in Fig. 3.

### Start-up and Operation

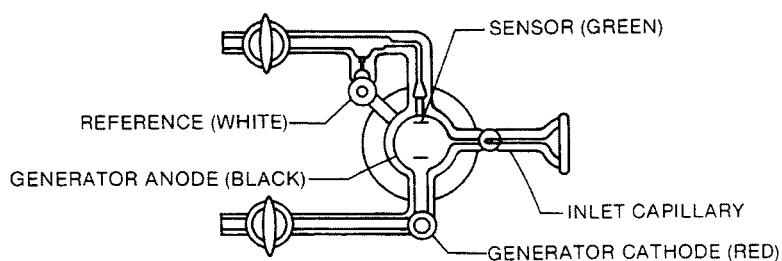
1. Assemble the apparatus as shown in Fig. 4, placing the titration cell on the magnetic stirrer. Secure it in the center with tape. Flush the cell 2 to 3 times with the 0.1 *N* NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> electrolyte. Connect the cell to the coulometer.
2. Wrap the heating tape around the glass tee and turn on the current to the tape. Place a septum in the vaporization chamber opening and make sure it fits tight.
3. Connect the carrier gas line to the tee and adjust the gas flow.
4. Connect the tee to the cell inlet with a clamp and turn on the function switch to operate.
5. Turn on the recorder.
6. Adjust the operating parameters as follows, and allow the system to stabilize.

**Figure 1**

Quartz Retainer for Inert Gas Cleanup

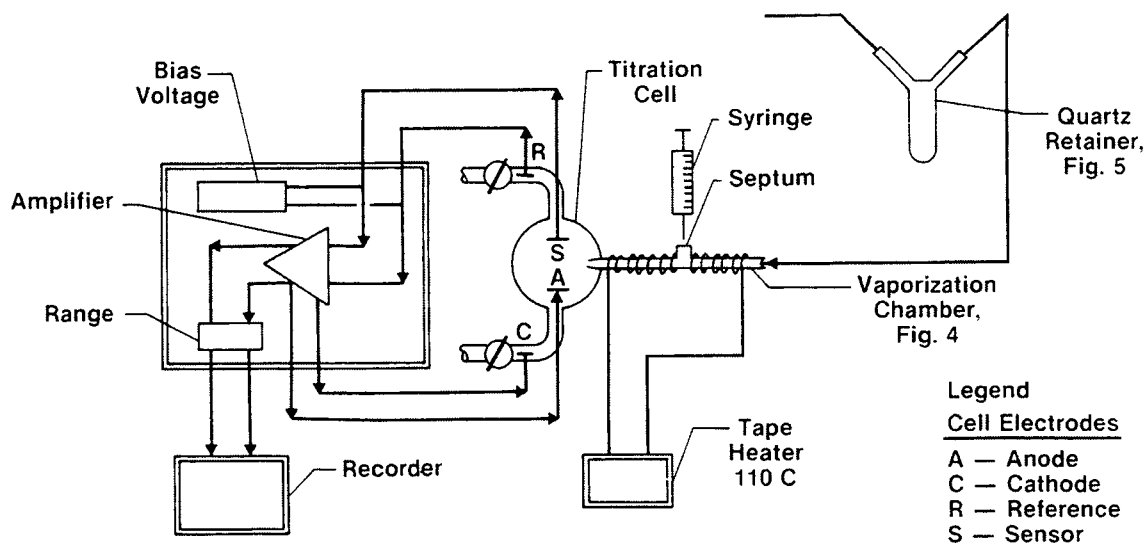


**Figure 2**  
Quartz Vaporization Chamber

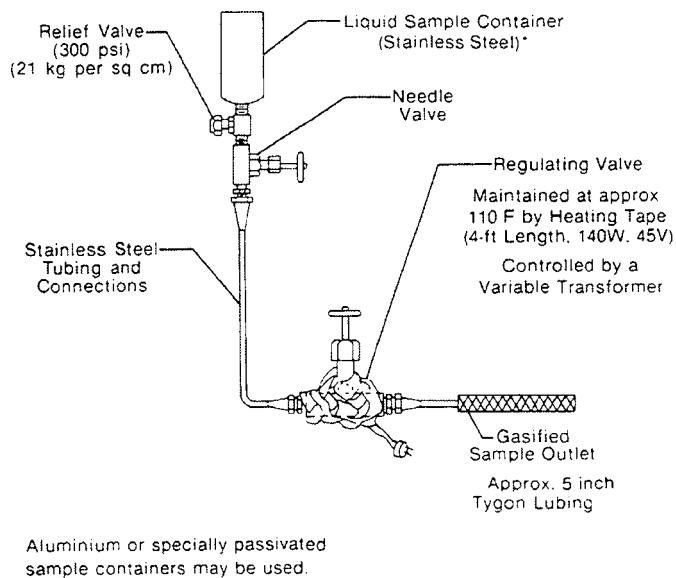


|                      |                                                                                                    |
|----------------------|----------------------------------------------------------------------------------------------------|
| Electrolyte:         | 0.1 <u>N</u> $\text{NaC}_2\text{H}_3\text{O}_2$<br>in 50/50 v/v. Isopropanol/ $\text{H}_2\text{O}$ |
| Sensor Electrode:    | Silver (Green Cap)                                                                                 |
| Reference Electrode: | Silver: Silver Acetate<br>Saturated (White Cap)                                                    |
| Generator Anode:     | Silver (Black Cap)                                                                                 |
| Generator Cathode:   | Platinum (Red Cap)                                                                                 |
| Bias Voltage:        | Approximately 250 mv                                                                               |

**Figure 3**  
Configuration of the Titration Cell

**Figure 4**

Flow Diagram of Injection Port Tee, Titration Cell Microcoulometer and Recorder

**Figure 5**

Scheme for Sampling C<sub>1</sub>-C<sub>4</sub> Hydrocarbons as Gases

### Operating Conditions

|                                    |                                   |
|------------------------------------|-----------------------------------|
| <b>Carrier gas flow (nitrogen)</b> | <b>100 cc/min</b>                 |
| <b>Coulometer</b>                  |                                   |
| <b>Bias voltage</b>                | <b>220-250 mv</b>                 |
| <b>Gain</b>                        | <b>High 700-1000</b>              |
| <b>Range</b>                       | <b>50–100 <math>\Omega</math></b> |

### Standardization

Inject 0.10 cm<sup>3</sup> of the 0.5 ppm RSH-S standard solution slowly into the vaporization chamber using a Pressure-Lok syringe. Repeat until there are three consecutive peak areas of consistent value.

Now inject 0.03 cm<sup>3</sup> of the 2.5 ppm RSH-S standard into the same vaporization chamber using a Pressure-Lok syringe. Again repeat until there are three consistent peaks.

Verify the linearity of the analysis by comparing the weight of mercaptan sulfur/square inch for the two standards, as determined under *CALCULATIONS*.

### Analysis of Sample

Set up the sample cylinder as shown in Fig. 5. Turn on the current to the heating tape on the regulating valve, and line out the temperature at approximately 110 F (45 C).

Open the cylinder valve and open the regulating valve just a small amount to allow a flow of the sample to the air.

Allow sufficient time for the lines to be purged. Draw a volume of gas from the tubing end using a Gastight syringe. Flush the syringe twice with the sample. Finally draw the proper size sample and inject it through the septum into the vaporization chamber inlet. Inject all of the sample within thirty seconds, while observing the peak area on the recorder. (NOTE: Choose the gas sample size according to Table 1.) Repeat this procedure until three consistent peak areas are obtained.

**Table 1**  
**Range Settings and Sample Size**

| <b>S Level,<br/>Wt-ppm S</b> | <b>Sample<br/>Size, cm<sup>3</sup></b> | <b>Range of Setting,<br/>ohms</b> |
|------------------------------|----------------------------------------|-----------------------------------|
| <b>0-0.5</b>                 | <b>100</b>                             | <b>100</b>                        |
| <b>0.5-1.0</b>               | <b>50</b>                              | <b>50-100</b>                     |
| <b>1.0-5.0</b>               | <b>10-50</b>                           | <b>20-50</b>                      |
| <b>5.0-50.0</b>              | <b>10-50</b>                           | <b>10-20</b>                      |
| <b>50.0-300</b>              | <b>10-50</b>                           | <b>1-10</b>                       |

The mercaptan concentration should be determined within twenty-four hours after the sample is taken, in a stainless steel sample cylinder, as the oxidation at very low RSH levels occurs rapidly, as illustrated in the following table.

**Mercaptan Stability at 0.5 ppm RSH-S Level  
Ethyl Mercaptan in Isobutane**

|       |          | <u>RSH-S,<br/>wt-ppm</u> |
|-------|----------|--------------------------|
| Day 1 | 9:30 AM  | 0.48                     |
| Day 1 | 12:10 PM | 0.51                     |
| Day 1 | 3:15 PM  | 0.45                     |
| Day 2 | 10:00 AM | 0.51                     |
| Day 2 | 1:30 PM  | 0.44                     |
| Day 3 | 10:00 AM | 0.35                     |
| Day 4 | 12:30 PM | 0.15                     |

**Shut-down Procedure**

1. Turn the coulometer function switch to Stand-by or Generator Read.
2. Turn off the recorder chart drive and disengage the chart paper slightly so that the pen is off the paper.
3. Turn off the heating tape.
4. Disconnect the cell from the tee and turn off the stirrer.
5. Turn off the gas at the cylinder.
6. Fill the titration cell with electrolyte to a level just below the inlet capillary.

**CALCULATIONS**

**Standard**

$$F = \frac{CV_1}{A_1}$$

**Samples**

$$\text{RSH-S, wt-ppm} = \frac{FA_2 \times 10^6}{V_2 D}$$

where:

**A<sub>1</sub>** = peak area of the standard, sq in

**A<sub>2</sub>** = peak area of the sample, sq in

**C** = concentration of standard, mg RSH-S/ml

**D** = weight of 1 ml of sample at 25 C, mg

**F** = factor from standard injection, mg RSH-S/in<sup>2</sup>

**V<sub>1</sub>** = volume of the standard injected, cm<sup>3</sup>

**V<sub>2</sub>** = volume of the sample injected, cm<sup>3</sup>

**Table 2**  
**Weight in Milligrams of 1 ml of Gas at 25 C**

|                      |              |                  |              |
|----------------------|--------------|------------------|--------------|
| <b>H<sub>2</sub></b> | <b>0.082</b> | <b>Propylene</b> | <b>1.718</b> |
| <b>Methane</b>       | <b>0.655</b> | <b>Butanes</b>   | <b>2.375</b> |
| <b>Ethane</b>        | <b>1.228</b> | <b>Butylenes</b> | <b>2.290</b> |
| <b>Ethylene</b>      | <b>1.145</b> | <b>Butadiene</b> | <b>2.215</b> |
| <b>Propane</b>       | <b>1.800</b> |                  |              |

## PRECISION

Based on replicate determinations, the estimated standard deviation (esd) in the table below was calculated for the components listed.

Results are satisfactory if duplicates do not differ by more than the differences indicated (95% probability).

| <b>Type of Sample</b>      | <b>Sulfur Level,<br/>Wt-ppm RSH-S</b> | <b>No. of<br/>Replicates</b> | <b>esd,<br/>Wt-ppm RSH-S</b> | <b>Allowable<br/>Difference,<br/>Wt-ppm RSH-S</b> |
|----------------------------|---------------------------------------|------------------------------|------------------------------|---------------------------------------------------|
| <b>Isopentane (liquid)</b> | <b>0.48</b>                           | <b>37</b>                    | <b>0.03</b>                  | <b>0.08</b>                                       |
| <b>Isopentane (liquid)</b> | <b>2.45</b>                           | <b>28</b>                    | <b>0.18</b>                  | <b>0.55</b>                                       |
| <b>Isobutane (gas)</b>     | <b>0.39</b>                           | <b>14</b>                    | <b>0.02</b>                  | <b>0.06</b>                                       |
| <b>Isobutane (gas)</b>     | <b>0.12</b>                           | <b>8</b>                     | <b>0.03</b>                  | <b>0.10</b>                                       |

## TIME FOR ANALYSIS

The labor requirement is 4.0 man-hours per sample. The elapsed time for 2 samples is 8 hours.

## SUGGESTED SUPPLIERS

J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ 08865  
 Coleman Instruments, Inc., Division of Perkin-Elmer Corp., 2000 York Rd., Oak Brook, IL 60521  
 Dohrmann Division of Envirotech Corp., 1062 Linda Vista Ave., Mountain View, CA 94040  
 Hamilton Co., P.O. Box 10030, Reno, NV 89510  
 Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA 70815  
 Sargent-Welch, 7300 Linder Avenue, Skokie, IL 60076  
 Whitey Research Tool Co., 5679 Landregan St., Emeryville, CA 94608