

FREE SULFUR IN PETROLEUM DISTILLATES AND LPG BY THE AC POLAROGRAPH

UOP Method 700-70

SCOPE

This is a method for determining free sulfur in petroleum distillates and liquefied petroleum gas (LPG) using the AC polarograph. The lower limit of detection is a function of the solubility of the sample in the supporting electrolyte and toluene mixture; in most cases it is 0.1 ppm. The method appears to be free of interferences by constituents found in distillates, e.g., peroxides, phenols and other sulfur compounds. Mercaptans interfere only when present at high concentration, such as 1000 times the free sulfur content.

OUTLINE OF METHOD

A sample of petroleum distillate or LPG is diluted with toluene and supporting electrolyte. This mixture is placed in a polarograph cell and the oxygen removed by purging with nitrogen. The sample is then scanned between -0.5 and $+0.5$ v. The same process is repeated with a known amount of sulfur (in solution in toluene) added to the sample, toluene and supporting electrolyte mixture. From this the concentration of free sulfur is calculated.

APPARATUS

Bath, circulating, 25 C constant temperature

Bottles, 250 - ml, gas scrubbing, with sintered glass tips

Cell, polarographic, constructed according to Fig. 1. This design provides for collection and withdrawal of used mercury. If the used mercury is not withdrawn, it interferes with the analysis. Do *not* attempt this analysis with the commercially available cell.

Cylinder, corrosion-resistant metal, 1-liter, referred to in the text as “sample bomb”

Electrode, silver-silver chloride, reference. Fill the electrode with 1.0-molar lithium chloride in methanol instead of the aqueous potassium chloride solution commonly employed. Do not use an electrode that has been in contact with potassium chloride solution. Place fresh methanolic lithium chloride in the bridge arm at least twice in an 8 - hr day when the electrode is in use.

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).

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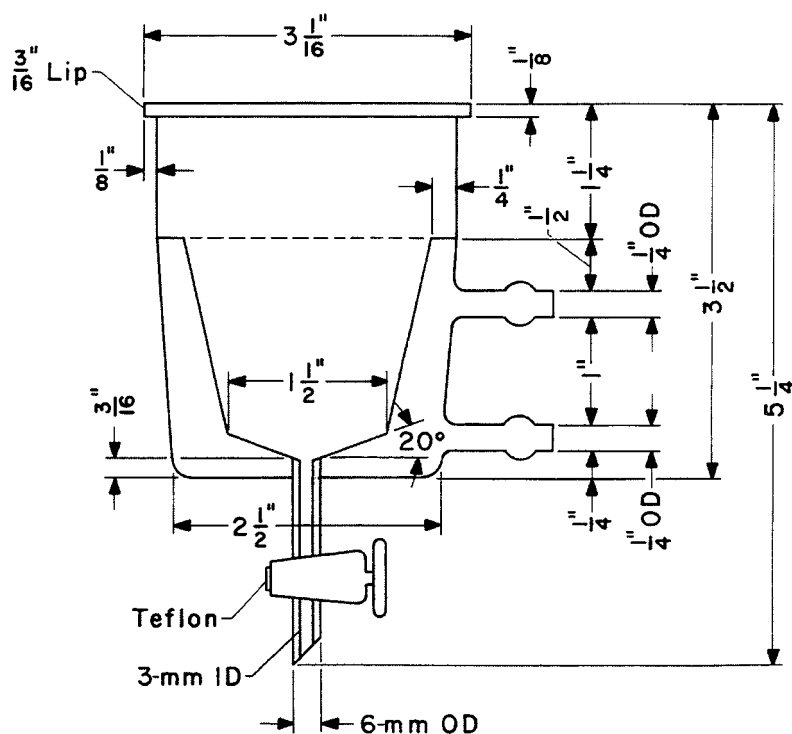


Figure 1
Polarographic Cell

Electrode, tungsten wire

Flask, Erlenmeyer, 500-ml

Flasks, volumetric, 25-, 50-, 100-, 1000-ml

Pipets, 1-, 2-, 3-, 5- and 10-ml

Pipets, Mohr, 0.1-, 0.5- and 10-ml

Polarograph, Metrohm Polarecord Model E 261, with AC Modulator, Model E 393, and forced dropping mercury electrode device

Stand, polarographic, Metrohm Model E 354; 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 specified.

Boiling chips

Lithium chloride, 1.0-*M* in methyl alcohol

Nitrogen

Supporting electrolyte. Mix 100 ml of the 1.0-*M* lithium chloride, 95 ml of pyridine, 5 ml of concentrated hydrochloric acid and dilute to 1 liter with methanol.

Toluene, free of free sulfur

Vanadous chloride solution. Boil a mixture of 2 g of ammonium metavanadate and 25 ml of concentrated hydrochloric acid, dilute to 200 ml and shake with 5 g of heavily amalgamated zinc; add a little more acid if a precipitate or turbidity forms. Divide the solution between two 250-ml gas washing bottles, each containing 25 g of heavily amalgamated zinc. Purge with nitrogen until the solution is a deep violet.

PREPARATION OF APPARATUS

Turn on the instruments, Polarecord E 261 and AC Modulator E 393, and let them warm up for an hour. Turn on and set the constant temperature bath at 25 C. Refill the lithium chloride electrode with fresh 1.0 *M* lithium chloride in methanol. Rinse down the electrodes and cell with methanol and wipe dry. Fill the bubbler of the stand with supporting electrolyte.

Refer to Fig. 2 in making the settings listed.

Instrument Settings

A. Polarecord E 261 from left to right, top to bottom:

1. Operation mode: mv setting
2. Sensitivity A/mm: does not apply
3. Starting voltage V: -0.5
4. Voltage range V: +1
5. Scanning voltage: fast
6. Paper advance: fast
7. mv Ranges: 500
8. Damping: does not apply
9. Compensating current: zero the instrument and set the pen on the paper.
10. Charging current compensation: 0

B. AC Modulator E 393 from left to right, top to bottom:

1. Mode switch: ~ P
2. Sensitivity Arms: see *PROCEDURE*
3. Applied AC voltage: see *PROCEDURE*
4. Calibration: to set C on the mode switch to read 250 on the Polarecord E 261 scale
5. Damping: see *PROCEDURE*

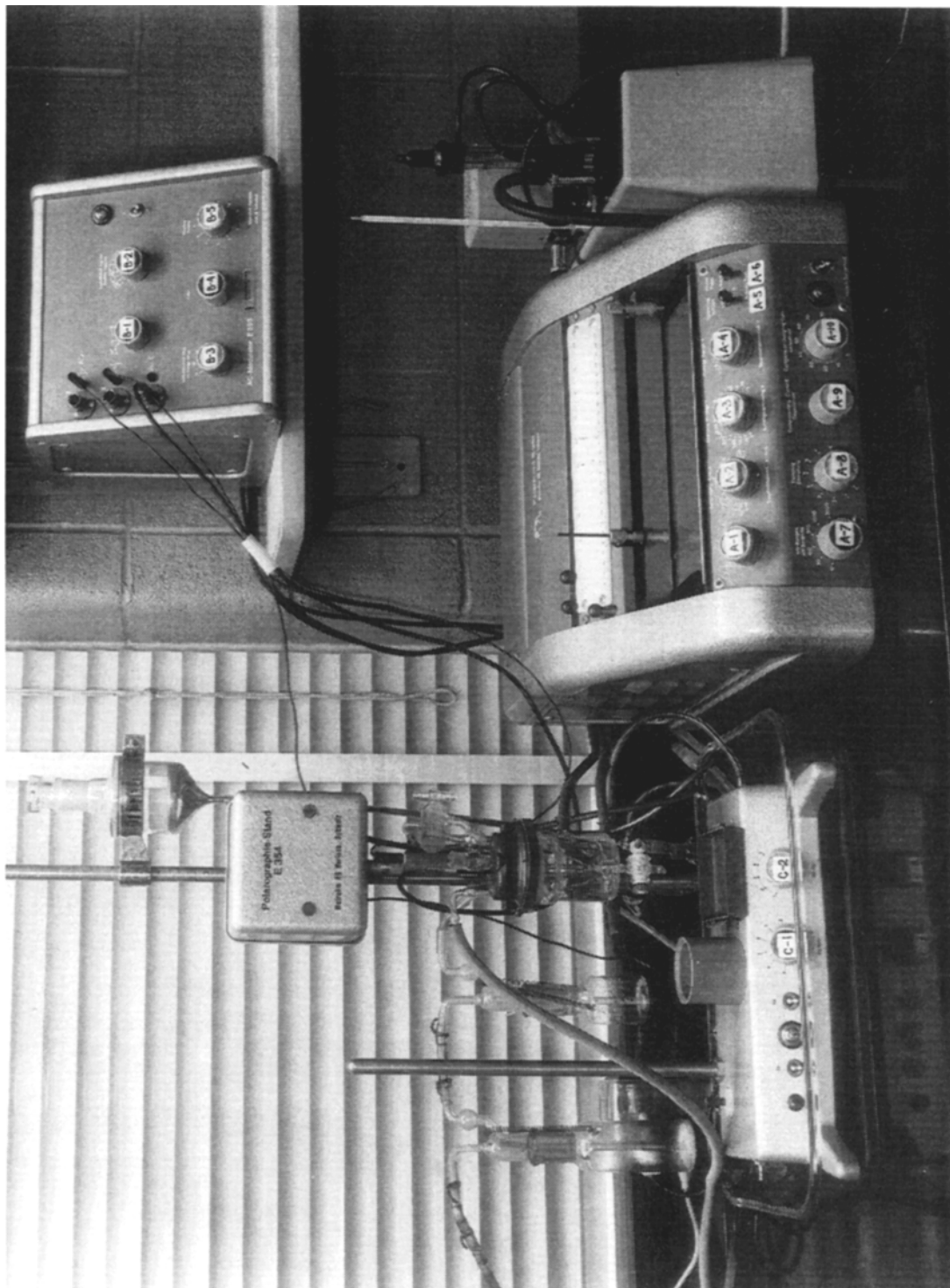


Figure 2
AC – DC Polarograph

C. Polarecord E 354 Stand, left to right:

1. Impulse strength control: see *PROCEDURE*
2. Mercury drop rate: see *PROCEDURE*

PROCEDURE

Petroleum Distillates

Pipet 1 ml of the sample into a 25-ml volumetric flask, add 9 ml of toluene, dilute to the mark with supporting electrolyte, and mix. Pour the solution into the clean cell. Purge the cell contents with oxygen-free nitrogen for 10 minutes. Start the mercury electrode dropping and activate the dropping controls. Set the impulse rate and controls so that the drops fall in a straight line and a regular flow of small mercury drops is produced.

Now zero the instrument by setting the mode switch (B1) on "zero" and moving the pen with compensating current control (A9) to zero on the Polarecord scale. Turn the mode switch (B1) to "C" and readjust the pen on the Polarecord current scale to read 250. Turn the stopcock to direct the nitrogen stream to the gas phase above the liquid in the cell. Set the applied AC voltage (B3) on 50 and the sensitivity to 2×10^{-9} (B2). Turn the mode switch (B1) to $\sim P$ and bring the pen on the current scale to about 30 with the compensating current switch (A9). Adjust the damping (B5) until the pen no longer vibrates. Scan the sample with the scanning voltage (A5) and the paper advance on "fast". The free sulfur peak appears between -0.4 and -0.3 volt. *Note:* the voltage scan must be in the direction -0.5 v to $+0.5$ v; do *not* reverse this.

If the peak is too high, greater than 70 mm, reset the AC voltage (B3) on 30 and scan on lower sensitivity (B2). If the peak is poor on the lower sensitivity use a smaller sample. If the peak on the first scan is less than 20 mm use a larger sample.

The total hydrocarbon content, toluene plus sample, in the supporting electrolyte should be 10 ml. However, the largest amount of sample that can be used is limited by the solubility of the sample in the resulting mixture of toluene and supporting electrolyte. As a typical example, a mixture of 3 ml of sample and 7 ml of toluene is used with most kerosines.

When the proper amount of sample and optimum setting have been determined do not change any of the instrument settings. Pipet a new sample and the proper amount of toluene into a 25-ml volumetric flask, dilute to the mark with the supporting electrolyte and mix. Pour the solution in the clean cell and purge with oxygen-free nitrogen for 10 minutes. After 10 minutes direct the nitrogen stream into the gas phase above the liquid in the cell. Turn the mode switch (B1) to $\sim P$ and bring the pen on scale at about 30 with the compensating current switch (A9). Scan the sample 3 times and take an average peak height in millimeters.

Repeat the above operations with a known addition of free sulfur to give an additional peak height of 20 to 30 mm.

LPG Samples

Add 50 ml of the sulfur-free toluene to a 500-ml Erlenmeyer flask. Attach the delivery tube to the LPG sample bomb and weigh the assembly to the nearest gram. Place the delivery tube tip in the bottom of the flask. Pass 200 to 300 ml of the gas into the flask as rapidly as possible without splattering the contents of the flask. This is done at room temperature. The purpose of the rapid sampling operation is to keep the

sample substantially liquid and to wash into the flask any sulfur which may crystallize in the delivery tube. Re-weigh the bomb to the nearest gram. Alternatively, the sampling may be done by means of a calibrated gas cylinder and the weight of the sample obtained by determining the volume and density.

Add several boiling chips to the flask and boil slowly on a steam bath in a well-ventilated hood until only the toluene-sulfur solution remains; i.e., the total volume is about 50 ml. Then transfer the solution to a 100-ml volumetric flask. Rinse the Erlenmeyer flask 3 or 4 times with toluene, placing the rinsings in the volumetric flask. Dilute to the mark and analyze an aliquot in the same manner as for petroleum distillates.

CALCULATIONS

Petroleum distillates:

$$\text{Free sulfur, ppm} = \frac{AM}{DV (B - A)}$$

Liquefied petroleum gas:

$$\text{Free sulfur, ppm} = \frac{100 AM}{GS (B - A)}$$

where:

- A** = peak height for sample, mm
- B** = peak height for sample plus free sulfur increment, mm
- D** = density of the sample (determined by any convenient means), g/ml
- G** = weight of LPG sample, g
- M** = free sulfur added, micrograms
- S** = volume of "LPG aliquot" analyzed, ml
- V** = sample volume, ml

PRECISION

Based on 5 replicate analyses of petroleum distillates, the estimated standard deviation calculated from the mean range was 0.10 ppm sulfur at the 4.5-ppm level. Duplicate determinations should not differ from each other by more than 0.36 ppm (or 8% of the determined value) at this level.

Based on duplicate and triplicate analyses of 9 distillates containing sulfur in the range of 0.05 to 200 ppm, duplicate determinations should not differ from each other by more than 10% of the determined value.

TIME FOR ANALYSIS

Petroleum Distillates

The estimated labor requirement is 2 man-hours. Estimated elapsed time is 2 hours.

Liquefied Petroleum Gas

The estimated labor requirement is 3 man-hours. Estimated elapsed time is 3.5 hours.