

TOTAL SULFUR IN HEAVY OILS, TARS AND SOLIDS BY MICROCOULOMETRIC TITRATION, SINGLE ENTRY BOAT TECHNIQUE

UOP Method 731-74

SCOPE

This method is for determining total sulfur in heavy oils and viscous hydrocarbons in the range of 10 wt-ppm to greater than 2000 wt-ppm. Samples are analyzed directly by single entry boat insertion. Halides in excess of 10 times the sulfur level, nitrogen content greater than 10% and heavy metals interfere with the analysis.

OUTLINE OF METHOD

The sample is weighed into a quartz boat and placed in a magnetic sample ladle which, in turn, is inserted into a pyrolysis tube in a flowing oxygen-helium stream. The assembly is transported into the combustion zone by magnet. The sulfur dioxide formed passes into a titration cell and is titrated iodometrically. The iodine consumed is replaced coulometrically. The amount of current required to re-establish the iodine balance in the electrolyte is a measure of the total sulfur in the sample.

APPARATUS

Balance, analytical, micro, capable of weighing with a precision of ± 0.001 mg

Boats, quartz. Fabricate according to Fig. 3, Detail "D"

Bottle, glass, 8-oz

Burner, Meker type

Cylinders, graduated, borosilicate glass, 25-, 50- and 100-ml

Exit tube kit, quartz, Dohrmann, Division of Envirotech Corp., 1062 Linda Vista Ave., Mountain View, CA 94040. Cat. No. 511760¹

Flask, volumetric, 1000-ml

Furnace, pyrolysis. Available as Model S-300 from Dohrmann¹, or provide equivalent and arrange per photograph, Fig. 1

Gas inlet heater capillary and power supply Available as Model P-200 from Dohrmann¹

Magnet, of sufficient strength to use as ladle transporter in fabricated system

Microcoulometer, Dohrmann¹, Model C-200B

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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Pressure regulators. Two-stage, with stainless steel diaphragms for ultrahigh-purity helium and oxygen

Quartz wool

Recorder, Dohrmann, Model R-100-I recorder/integrator¹

Sample ladle, magnetic. Fabricate according to Fig. 3, Detail "B"

Single boat inlet, available as accessory SBI from Dohrmann, for use with MCTS 30 system

Stirrer, magnetic, Dohrmann Cat. No. 51640 or equivalent¹

Timer, scale divided into seconds by tenths or hundredths

Titration cell, Dohrmann Model T-300P¹

Titration cell enclosure, Dohrmann Cat. No. 523100¹

Tube, pyrolysis. Available from Dohrmann¹, or fabricate from quartz according to Fig. 3

Water bath

Wire, stainless steel or Nichrome

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. References to water mean deionized water of high purity, 5-6 megohm-cm resistivity.

Acetic acid, glacial

Acetone

Electrolyte solution. Weigh 0.50 g of potassium iodide and 0.60 g of sodium azide, transfer to a 1000 ml volumetric flask and dissolve in water. Add 5 ml of acetic acid and dilute to volume with water. Mix thoroughly.

Helium, Matheson ultrahigh purity

Hydrofluoric acid solution, 1:1. Dilute hydrofluoric acid (48-51%) with an equal volume of water.

Iodine, crystals, 20-mesh

Mineral oil, light, viscosity 80-90° Saybolt, sulfur-free

Oxygen, Matheson ultrahigh purity

Phenyl disulfide

Potassium iodide

Sodium azide, crystals

Sulfur standard, 3000 wt - ppm. Weigh 1.0216 g $\pm$ 0.1 mg of phenyl disulfide into a clean, 8-oz bottle. Add a small amount of mineral oil and place the bottle in a hot water bath at about 150 F to dissolve phenyl disulfide. After dissolution occurs, add mineral oil to bring the total weight to 100.00 g. This will make a standard containing 3000 wt-ppm sulfur.

¹ Available as a complete system from Dohrmann as MCTS, Total Sulfur System. If the complete system is purchased, the quartz tube, ladle, magnet, or quartz boats need not be fabricated.

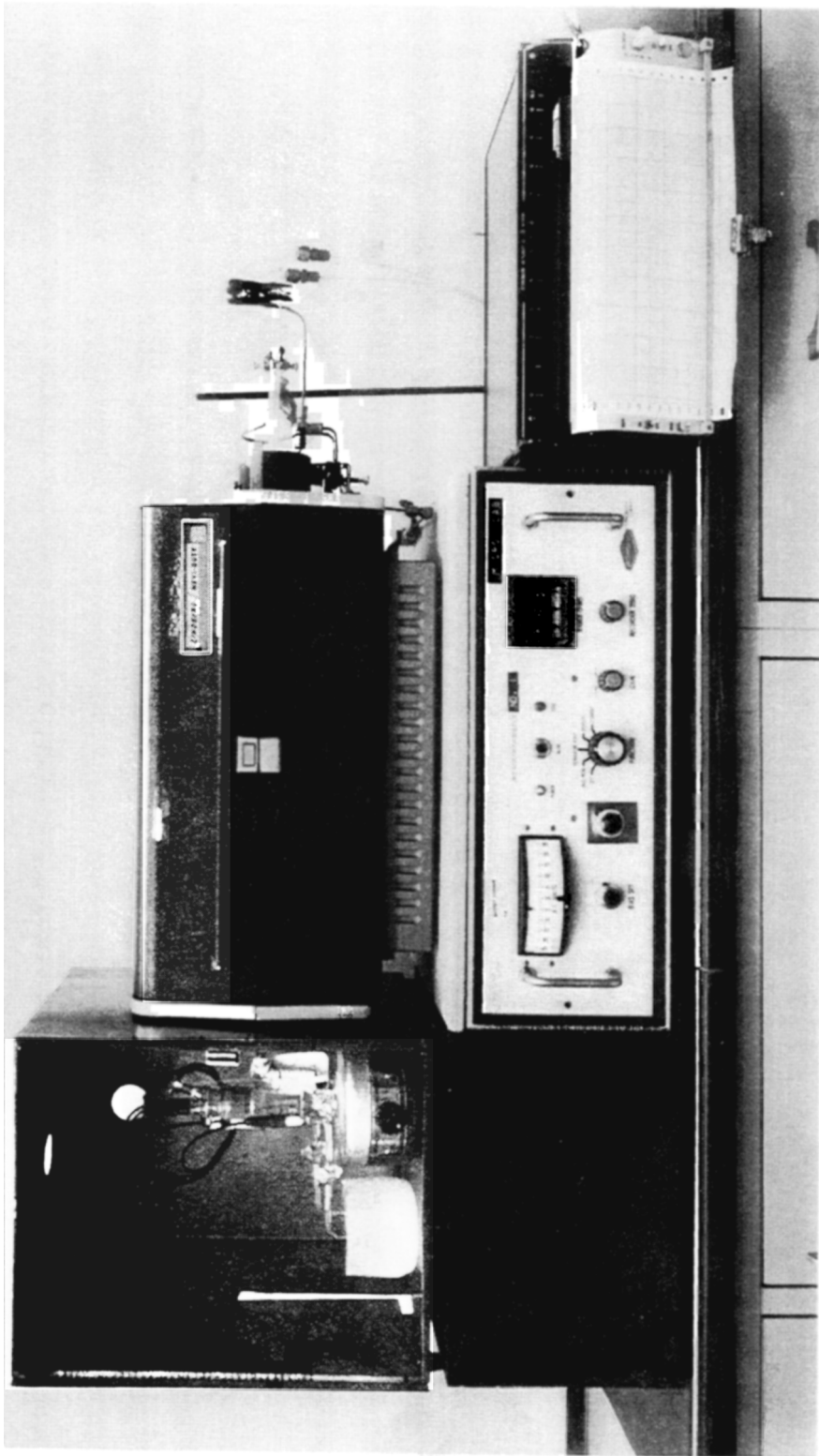


Figure 1
Apparatus Arrangement

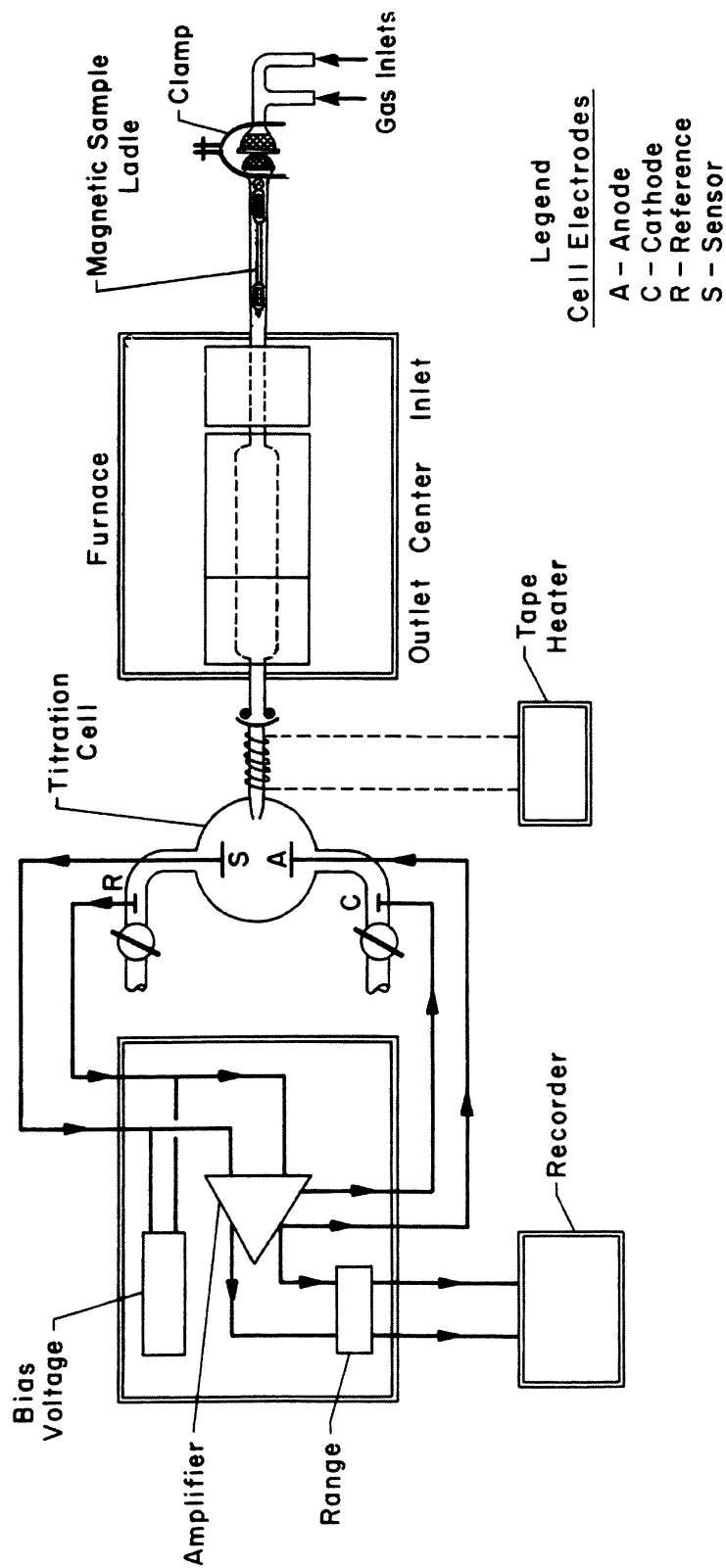


Figure 2
Flow Diagram of Pyrolysis Furnace, Titration Cell,
Microcoulometer and Recorder

Sulfur standards, less than 3000 wt-ppm. Dilute the 3000 wt-ppm sulfur standard as required with mineral oil to make more dilute standards for use in the analysis of samples having “low range” sulfur levels

PROCEDURE

Start-up and Operation

1. Prepare the titration cell according to the manufacturer's specifications and center it on the magnetic stirrer. Secure it in the centered position with tape or any suitable means. Position the cell head so that the platinum foil electrodes are parallel to the gas inlet flow and so that the generator anode also is adjacent to the generator cathode. Add the specified volume of electrolyte. Turn on the stirrer to create a moderate vortex. Excessive stirring speeds tend to cause the stirring bar to decouple and damage the platinum electrodes. Place heating tape on the capillary inlet of the titration cell.
2. Assemble the coulometer, pyrolysis furnace, recorder and cell enclosure in an arrangement suitable for efficient operation, connected as shown in Figs. 1 and 2.
3. Turn the coulometer function switch to “standby” position. Turn on the power to the recorder.
4. Precondition the furnace according to the manufacture's specifications. Fit the pyrolysis tube into the furnace and turn on the power. If using a fabricated system as shown in the photograph, Fig. 1, support the inlet section of the pyrolysis tube with a small ring stand and clamp arrangement.
5. Pack the quartz exit tube (see Fig. 3) with 51 mm of quartz wool and fit it into the rear of the pyrolysis tube so that the quartz wool is nearest to the hot zone. Clamp the adapter fitting in place.
6. Connect the pyrolysis tube to the appropriate gas supplies by means of the gas inlet cap and clamp in place to the 18/9 ground glass joint at the inlet end of the pyrolysis tube.
7. Adjust the operating parameters as follows:

Reactant gas flow (oxygen)	120^a
Carrier gas flow (helium)	80^a ml/minute
Furnace zone temperatures	
Inlet	700–800 C
Center	1000 C
Outlet	1000 C
Coulometer	
Bias voltage	140–160 mv
Gain	Low 50–400
Range	2–200 Ω
Recorder chart drive	1/2 inch/minute

^a Special applications will require changes in flow rates.

8. Flush the titration cell with fresh electrolyte 2 or 3 times, eliminating all bubbles in side-arms. Turn the function switch to the “operate” position. The recorder pen will deflect up-scale and return to zero baseline in a few seconds.

9. Connect the titration cell to the pyrolysis tube and allow the baseline to stabilize.

10. After the baseline has stabilized, disconnect the cell. Using any stainless steel or Nichrome wire of suitable stiffness, dip a small portion of a high sulfur standard into each of several quartz boats. Place the quartz boat in the magnetic sample ladle, disconnect the gas inlet cap and insert the ladle into the pyrolysis tube. Reconnect and clamp the gas inlet cap. Allow the baseline to stabilize, then, using a magnet, transport the ladle and sample forward into the combustion zone of the furnace. Repeat several standard samplings. These standard samplings will serve to “condition” the pyrolysis and exit tubes. Re-connect the titration cell and allow the baseline to stabilize. Turn on the capillary gas inlet heat tape, if necessary. Generally, the exit gases are hot enough to keep the capillary inlet sufficiently warm.

Calibration with Sulfur Standards

1. Select a sulfur standard in the approximate range of the samples to be analyzed. Using a dip-wire, weigh approximately 2 to 4 mg (to the nearest 0.001 mg) of the standard into a quartz boat. Record the weight.

2. Transfer the boat and its contents to the magnetic sample ladle, using forceps to avoid contamination.

3. Unscrew the clamp on the gas inlet cap and remove the cap. Place the magnetic sample ladle inside the front section of the pyrolysis tube and re-connect the gas inlet cap. This step should be done as expeditiously as possible. An air cooling jet installed at the front section of the pyrolysis tube helps to keep this section cool.

4. After the baseline has stabilized, carefully transport the magnetic ladle forward into the combustion zone of the pyrolysis tube by use of a magnet.

5. Weigh out portions of the standard to give the amount of sulfur approximately equal to that of the sample. When the instrument appears to be conditioned, average the 3 closest consecutive peak areas (Fig. 4) and calculate the recoveries as directed in the *CALCULATIONS* section. The average recovery of the standard should not differ from the extremes by more than $\pm 5\%$ relative. Recoveries of less than 65% are to be considered suspect. When the instrument is operating properly, recoveries are between 65 and 95%.

Analyzing Samples

Samples are analyzed by following the procedure used for the standards, taking care to match sample and standard as closely as possible. All parameters being the same, the peak area of the sample should not be less than one-half and not greater than twice the peak area of the standard used. See Fig. 3 for typical peaks and areas.

Approximate Range Settings

S Level, wt - ppm	Range Setting, ohms
3000	1
2000	2
1000	3
250-500	3-5
50-100	5-10
10-50	10-20

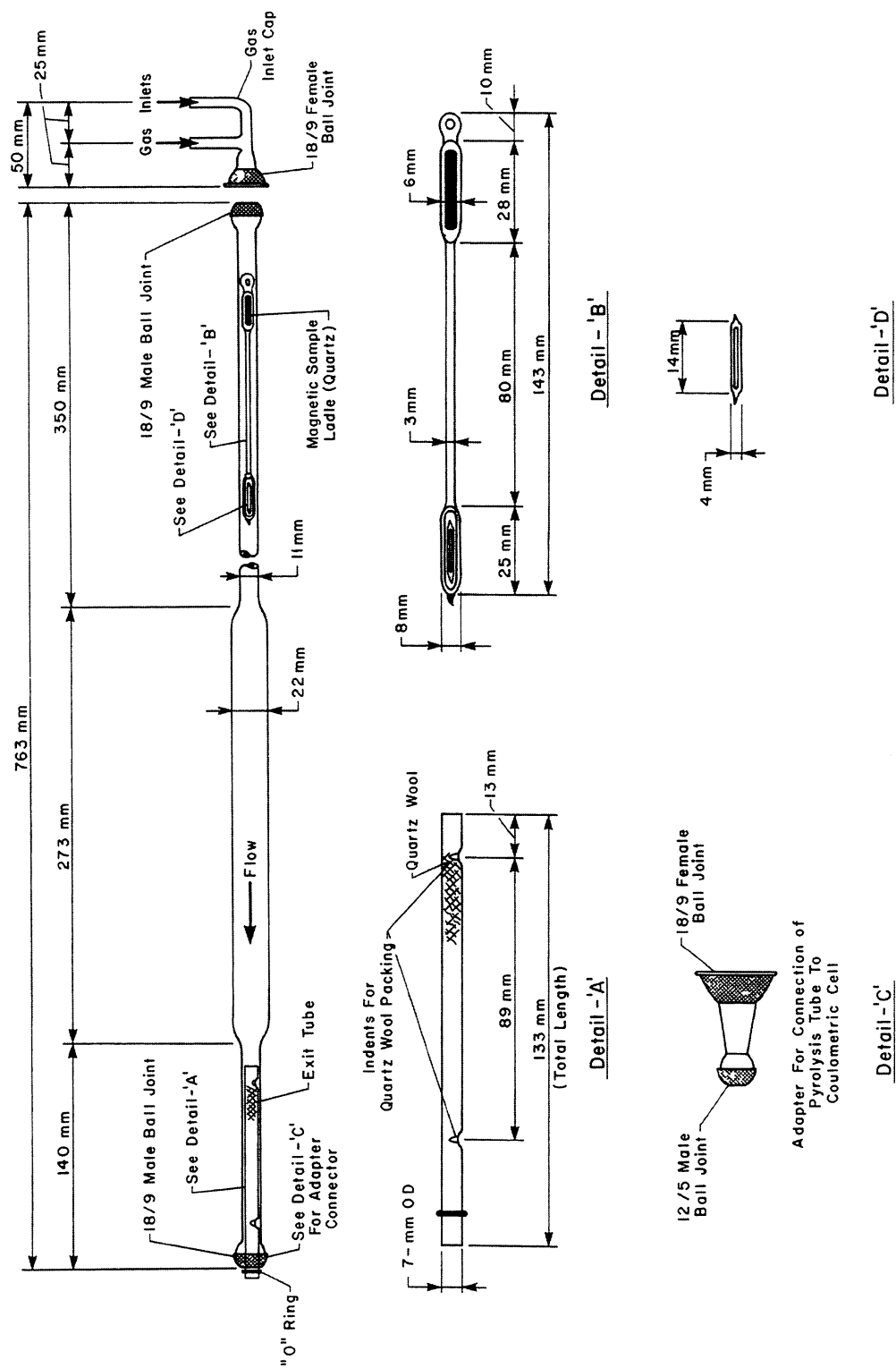


Figure 3
Pyrolysis Tube Detail

STANDARDS - PHENYL DISULFIDE IN WHITE OIL

25.0 wt-ppm S Wt. Combusted 2.704 mg Range 015 Ω Bias 152 mv Flow Rate—O₂ - 120 ml/min He - 80 ml/min Peak Area - 0.26 in² Recovery - 76% Factor - 260.208 ng S/in²	250 wt-ppm S Wt. Combusted 2.511 mg Range 005 Ω Bias 160 mv Flow Rate—O₂ - 120 ml/min He - 80 ml/min Peak Area - 1.15 in² Recovery - 73% Factor - 545.898 ng S/in²	2000 wt-ppm S Wt. Combusted 2.245 mg Range 002 Ω Bias 152 mv Flow Rate—O₂ - 120 ml/min He - 80 ml/min Peak Area - 3.44 in² Recovery - 76% Factor - 1337.258 ng S/in²
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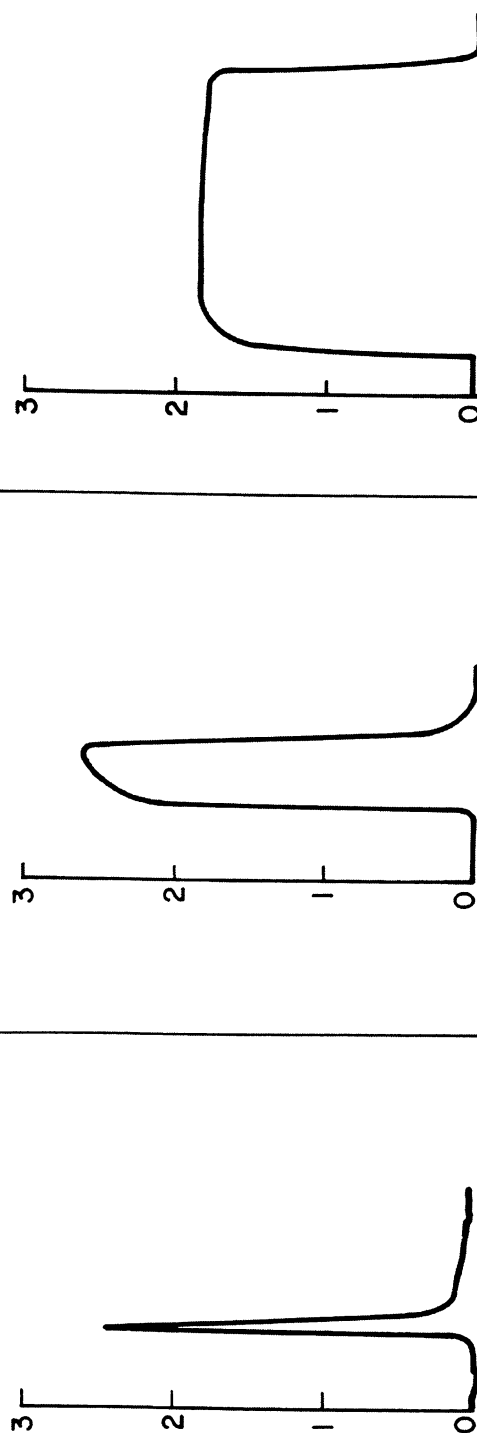


Figure 4
Examples of Typical Peak and Areas
At Three Sulfur Levels

When analyzing samples having different sulfur levels, it is advisable to make several samplings of the appropriate standard at the new level, rejecting the first peak areas. This is particularly important when changing from high to low level samples. Accept the consecutive peak areas which result from the later samplings.

Shut - down Procedures

Daily

1. Turn the coulometer function switch to standby position.
2. Turn off the recorder chart drive and disengage the chart paper carriage slightly so that the pen is off the paper.
3. Disconnect the titration cell from the pyrolysis tube and turn the stirrer to very low speed.
4. Remove the leads from the titration cell cap and remove the cap. Rinse the electrodes with water, then with acetone. Rinse again with water and finally with electrolyte.
5. Replace the cell cap, reconnect the leads, flush the titration cell with electrolyte, and fill it to a level just below the top of the inlet capillary.
6. Leave the furnace at operating temperatures.
7. Turn off the oxygen and helium.

Long Term Shut-down

1. Turn off the coulometer and recorder.
2. Turn off the stirrer.
3. Fill the titration cell with electrolyte. Plug the cell cap outlet and inlet capillaries. This will prevent excessive evaporation.
4. When not in use, frequently flush the cell with electrolyte.
5. Turn off all gas flows.

CALCULATIONS

Standards

$$\text{Recovery, \%} = \frac{1.99 \times 10^3 \times A_1 \times 100}{R B}$$

where:

- A_1 = peak area of the standard, sq in.
- B = total weight of sulfur in the weighed standard, ng
- R = range setting
- 1.99** = coulometric replacement of triiodide ion consumed in titration cell, as determined indirectly by Faraday's law

Percent recovery is not used in calculating sulfur content of samples. It serves only as an operational check.

Samples

$$\text{Sulfur, wt - ppm} = \frac{A_2 B}{A_1 W}$$

where:

A₂ = peak area of the sample, sq in.

W = weight of sample combusted, mg

A₁ and **B** as previously defined

NOTES AND PRECAUTIONS

1. Peak-tailing may be controlled by decreasing the stirring rate or increasing the bias voltage or gain. Make any adjustments in bias voltage with the function switch in “standby” or “generator read” positions.

2. When an overshoot occurs, increase the stirring rate or decrease the bias voltage by 2-mv increments or decrease the gain until a satisfactory peak shape results.

3. Increasing the level of electrolyte in the titration cell will also help eliminate overshoot.

4. Any adjustments, such as “bias voltage,” “gain” or “range-ohms,” are allowable in order to obtain a satisfactory peak, provided the standards and samples are run using identical parameters.

5. In some cases with samples having very low sulfur levels, a negative peak may be observed. This may sometimes be corrected by taking larger samples and increasing the oxygen content of the flow gases.

6. The titration cell may become erratic and desensitized occasionally. If this occurs, rinse the electrodes with water and acetone. Blow dry with air or nitrogen. Then, *very gently* and *with great care*, slowly heat the electrodes over a flame to a dull orange color. Allow them to cool gradually before returning them to the cell. Allow the cell to stabilize before starting an analysis.

7. Low recoveries may result from inadequate conditioning of a new pyrolysis tube or having carbon deposits in an old one. In the case of a new pyrolysis tube, continue to make conditioning runs until recovery reaches a maximum point and levels off. In the case of an old pyrolysis tube, remove the tube from the furnace and allow it to cool. After it is cool, rinse it with acetone to remove any hydrocarbon residue. Blow dry with air or nitrogen and wash with 1:1 hydrofluoric acid solution for 3 to 5 minutes. Rinse with water followed by acetone and blow the tube dry. Return the tube to the furnace, bring it to operating temperature and condition it with repeated insertions of standards of suitable sulfur levels.

8. The exit tube may cause erratic performance and/or varying or low recoveries. Remove the tube and clean it by rinsing with water, then with acetone and blow it dry with air or nitrogen. Repack the tube with quartz wool and replace it in the pyrolysis tube.

PRECISION

Samples of Paraffinic and Bottoms Fractions

Sulfur Level, wt-ppm S	No. of Pairs	Estimated Standard Deviation, wt-ppm S	Allowable Difference, wt-ppm S
10-50	31	1.5	4
50-100	14	3.0	9
100-400	17	5.8	18
400-700	9	12.2	40
700-1000	13	20.4	63
1000-2000	11	14.8	47
2000 Plus	5	30.0	112

TIME FOR ANALYSIS

The labor requirement is 0.90 man-hour and the elapsed time 0.90 hour per analysis.

REFERENCES

1. Martin, R. L. and Grant, J. A., *Anal. Chem.* **37**, 644 (1965)
2. Manual: "Sub-Micro Elemental Analysis by Microcoulometry", Dohrmann, (Mountain View, CA)
3. Drushel, H. V., *Anal. Chem.* **41**, 569 (1969)