

SUMMARY SHEET 15
Reduced Sulfur Compounds

		Run #1	Run #2	Run #3	Avg
Client/Plant Name	FDS 15				
Job No.	FDS 15				
Sampling Location	FDS 15				
Run ID #	FDS 15				
Test Date	FDS 15				
Run Start Time	FDS 15				
Run Finish Time	FDS 15				
Concentration H ₂ S, ppm	H ₂ S	FDS 15			
Concentration COS, ppm	COS	FDS 15			
Concentration CS ₂ , ppm	CS ₂	FDS 15			
Avg SO ₂ Equivalent, ppm	SO _{2e}	FDS 15			
Sample Line Loss Ratio	LR	FDS 15			
Corr Avg SO ₂ Equivalent, ppm	SO _{2ec}	SS 15			
Post-test Calibration Checks					
Flow Meter Calibration	FDS 15				
Dilution Factor	FDS 15				

$$SO_{2ec} = \frac{SO_{2e}}{LR}$$

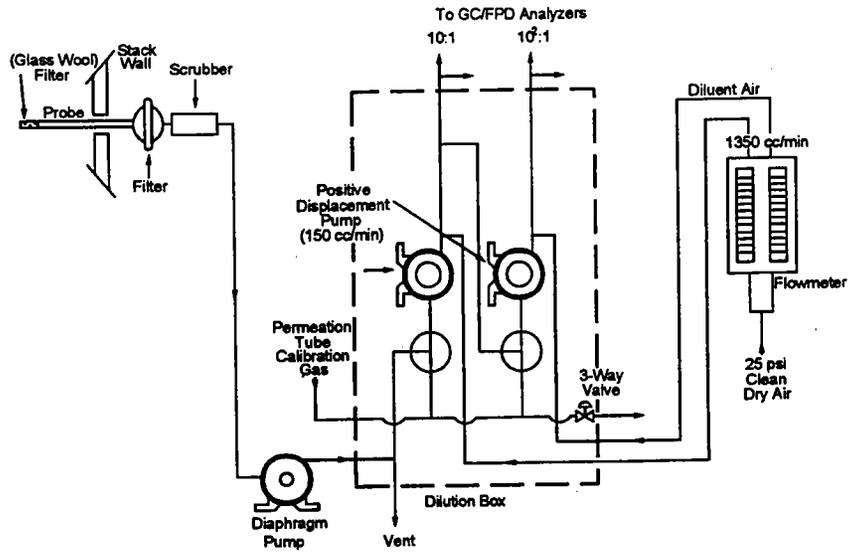


Figure F15-1. Sampling and Dilution Apparatus.

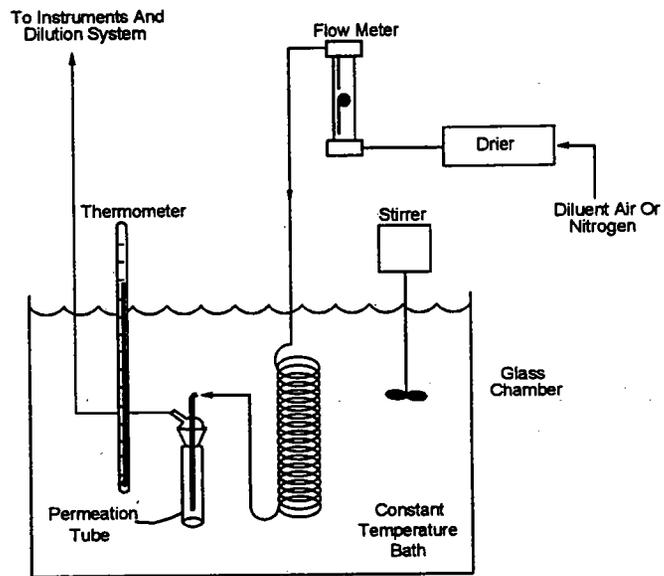


Figure C15-1. Apparatus for Field Calibration.

FIELD PROCEDURE 15
Reduced Sulfur Compounds

Note: Methods 15 and 16 are identical except for the reduced sulfur compounds being analyzed. Method 15 is used to determine hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) from tail gas control units of sulfur recovery plants. Method 16 is used to determine H_2S , methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS).

The forms in this section contain the information required by the test method; we are aware that some of the technology specified in the test method is obsolete. In these cases, the user should modify the forms to make them consistent with the technology used.

A. Optional Pretest Procedures

1. Leak-check all components, sample lines, and connections.
 - a. For components upstream of the sample pump, use FP 3c, section A, except conduct the leak-check at >2 in. Hg vacuum and 1 min.
 - b. For components after the pump, use FP 3c, section E.
2. Observe the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertain the response to be within predicted limits.

B. Calibration

1. Equilibrate the permeation tubes (H_2S , COS, and CS_2) for 24 hr at the calibration temperature ($\pm 0.1^\circ C$). (For Method 16, use permeation tubes for H_2S , MeSH, DMS, and DMDS.)
2. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.5 to 10 ppm for a 1-mL sample) for each of the sulfur compounds.
3. Bypassing the dilution system, inject the standards into the GC/FPD analyzers until the response of any one of three injects at each concentration varies no more than $\pm 13\%$ from their average (hereafter called precision). For Method 16, the precision requirement is $\pm 5\%$.
4. Generate a least squares equation of the concentrations vs. the appropriate GC/FPD response units (log-log relationship).
5. Calibrate each stage of the dilution system using a known concentration of H_2S from the permeation tube system. (See Figure C15-1.) Determine from the GC/FPD the concentration of the diluted calibration in ppm to within $\pm 13\%$ (or $\pm 5\%$ for Method 16) precision. Then calculate the dilution factor.

C. Sampling and Analysis Procedure

1. Assemble the apparatus as shown in Figure F15-1. Calibrate the system before the first run as in section B.
2. Insert the sampling probe into the test port; plug off open areas to prevent dilution air from entering the stack. Begin sampling, and dilute the sample approximately 9:1. Condition the entire system with sample for at least 15 min before analyzing.
3. For each sample run, analyze 16 individual injects of the diluted sample on the GC/FPD analyzer over 3 to 6 hr.
4. If sample concentrations decreases during a sample run and the decrease is not due to process conditions, check for clogging in the sample probe. If the probe is clogged, invalidate the test run, and restart the run.
5. After each run, inspect the sample probe.

D. Post-test Procedures

1. Determine the sample line loss as follows:
 - a. Introduce into the sampling system at the probe inlet H_2S of known concentration (using permeation tubes or H_2S /air mixture in a gas cylinder, traceable to permeation tubes) within $\pm 20\%$ of the applicable standard.
 - b. Compare the resulting measured concentration with the known value (must be $\leq 20\%$ loss).
2. After each run, or after a series of runs made within a 24-hr period, recalibrate the GC/FPD analysis and dilution system using only H_2S (or other permeant). Compare against the calibration curve obtained before the test runs. If the means of the triplicates differ $\geq 5\%$, either void the intervening runs or use the calibration data set that gives the highest sample values.

3. After a complete test series, calibrate each flowmeter in the permeation tube flow system with a wet test meter or soap bubble meter (must agree within $\pm 5\%$ of the initial calibration).

3. Section B. Calibrate the GC/FPD system by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. A separate determination of the dilution factor is not necessary, however, precision of $\pm 13\%$ still applies.

E. Alternatives

1. Step B1. Inject samples of calibration gas at 1-hr intervals until three consecutive hourly samples agree within $\pm 13\%$ of their average.
2. Step B4. Plot the GC/FPD response in current (amperes) vs. their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound.

FIELD DATA SHEET 15
Reduced Sulfur Compounds

Method (✓) 15 ___ 16 ___

Client/Plant Name _____ Date _____ Job # _____

City/State _____ Personnel _____

Calibration (✓) Initial ___ Post-Test ___ (Post-test requires calibration with only H₂S; must be ≤ 5% of initial)

Conc. Level	Conc., C (ppm)	GC/FPD Response: %Dev = ≤ ± 13% for FP 15; ≤ ± 5% for FP 16				
		Inject #1	Inject #2	Inject #3	Average	High % Dev
1	H ₂ S					
2						
3						
1	___					
2						
3						
1	___					
2						
3						
1	___					
2						
3						

Note: Plot response vs. concentration; attach graph.

Use only if dilution is necessary.

Stage	H ₂ S Conc. (ppm)	GC/FPD Resp: % Dev = ≤ ± 13% for FP 15; ≤ ± 5% for FP 16					Meas. Conc. (ppm)	Dilution Factor
		Inject #1	Inject #2	Inject #3	Average	% Dev		
1								
2								

Sample Line Loss:

Ref Gas _____ Ref Conc, C_r _____ ppm

Meas. Conc, C_m _____ ppm LR = C_m/C_r = _____ (0.80 to 1.20 ?)

Post-test Flow Meter Calibration (permeation tube flow system):

Initial Cal Factor, Y_i _____ Post-Test Cal Factor, Y_f _____ Y_f/Y_i = _____ (0.95 to 1.05 ?)

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
Personnel (Signature/Date)

_____ Team Leader (Signature/Date)

SUMMARY SHEET 15A
Reduced Sulfur Compounds

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 15A			
Job No.		FDS 15A			
Sampling Location		FDS 15A			
Run ID #		FDS 15A			
Test Date		FDS 15A			
Run Start Time		FDS 15A			
Run Finish Time		FDS 15A			
Barometric Pressure, mm Hg	P_b	FDS 15A			
Average Sample DGM Temp., °C	t_{ms}	FDS 15A			
Average Combustion DGM Temp., °C	t_{mc}	FDS 15A			
Sample DGM Calibration Factor	Y_s	FDS 15A			
Combustion DGM Calibration Factor	Y_c	FDS 15A			
Vol. of Metered Sample Gas, dL	V_{ms}	FDS 15A			
Vol. of Metered Combustion Gas, dL	V_{mc}	FDS 15A			
Vol. of Metered Sample Gas, dsL	$V_{ms(std)}$	SS 15A			
Vol. of Metered Combustion Gas, dsL	$V_{mc(std)}$	SS 15A			
Sample					
Normality of Titrant, meq/mL	N	LDS 6			
Volume of Aliquot, mL	V_a	LDS 6			
Volume of Solution, mL	V_s	LDS 6			
Volume of Titrant, mL	V_t	LDS 6			
Volume of Titrant for Blank, mL	V_{tb}	LDS 6			
System Performance (COS)					
DGM Calibration Factor	Y_p	LDS 15A			
Avg DGM Temperature, °C	t_{mp}	LDS 15A			
Vol. of Metered Gas, dL	V_{mp}	LDS 15A			
Vol. of Metered Gas, dsL	$V_{mp(std)}$	SS 15A			
Normality of Titrant, meq/mL	N	LDS 6			
Volume of Aliquot, mL	V_a	LDS 6			
Volume of Solution, mL	V_s	LDS 6			
Volume of Titrant, mL	V_t	LDS 6			
Volume of Titrant for Blank, mL	V_{tb}	LDS 6			
Sample Concentration of TRS as SO ₂ , ppm	C_{TRS}	SS 15A			
Recovery Gas Ref Concentration, ppm	C_{RG}	FDS 15A			
Recovery Gas Measured Concentration, ppm	C_{RGm}	SS 15A			
Recovery Efficiency, %	R	SS 15A			
Audit Relative Error, %	RE	QA1			
Post-test Calibration Checks					
Temperature and Barometer		CDS 2d			
Metering System		CDS 6			

$$V_{ms(std)} = 0.3858 V_{ms} Y_s \frac{P_b}{(t_{ms} + 273)}$$

Use the above equation to calculate $V_{mp(std)}$; using the appropriate data.

$$V_{mc(std)} = 0.3858 V_{mc} Y_c \frac{(P_b + P_{mc})}{(t_{mc} + 273)}$$

$$C_{TRS} = 12025 \frac{(V_t - V_{tb}) N \left(\frac{V_s}{V_a} \right)}{[V_{ms(std)} - V_{mc(std)}]}$$

Use the above equation to calculate C_{RGm} ; using the appropriate data.

$$R = \frac{C_{RGm}}{C_{RG}} \times 100$$

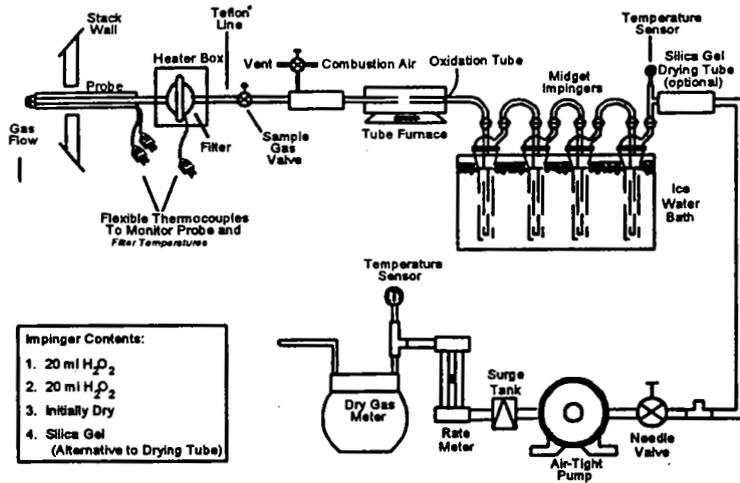


Figure F15A-1. Sampling Train.

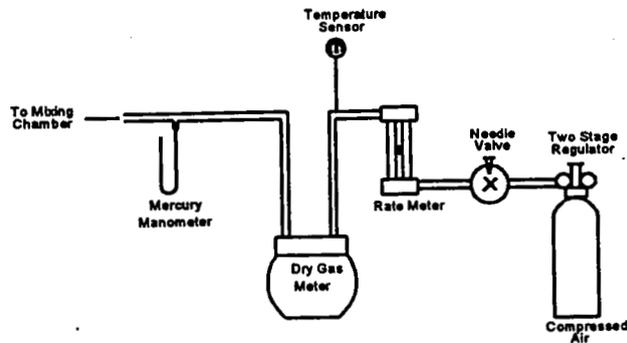


Figure F15A-2. Combustion Air Delivery System.

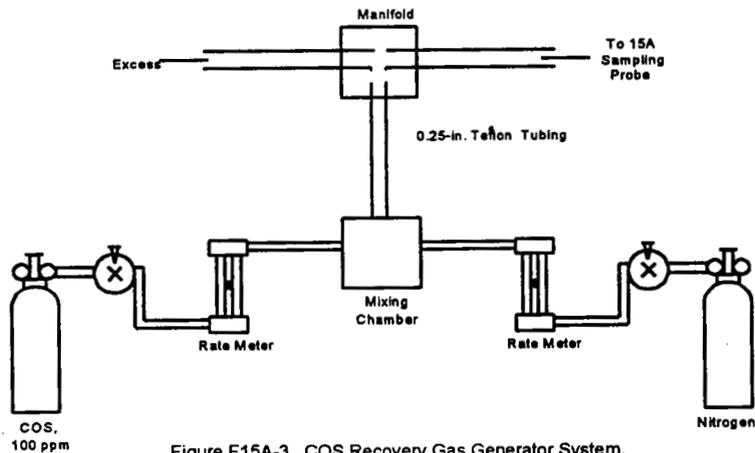


Figure F15A-3. COS Recovery Gas Generator System.

FIELD PROCEDURE 15A
Reduced Sulfur Compounds

Note: FP 15A is a procedure in which Method 6 is used after a dilution and oxidation system to convert reduced sulfur compounds to SO₂.

A. Sampling Train Preparation

1. Set up the sampling train as shown in Figure F15A-1. Prepare the Method 6 part of the train as in FP 6, except use 20 mL H₂O₂.
2. Set the oxidation furnace at 1100 ± 50°C and the probe and filter temperature high enough to prevent visible condensation of moisture.
3. *Optional:* Leak-check the sampling train as in FP 3c, sections C and D, including the combustion air delivery system from the needle valve forward.
4. *Optional:* Conduct two 30-min system performance checks in the field according to section C.

B. Sample Collection

1. Adjust the pressure on the second stage of the regulator on the combustion air cylinder to 10 psig and the combustion air flow rate to 0.50 L/min (± 10%). See Figure F15A-2.
2. Inject combustion air into the sampling train, start the sample pump, and open the stack sample gas valve (do all these operations within 30 sec to avoid pressurizing the sampling train).
3. Sample as in Method 6 at 2.0 L/min (± 10%) for 1 hr (three 1-hr samples are required for each run) or for 3 hr.
4. Monitor and record the combustion air manometer reading at regular intervals during sampling.

5. At the end of sampling, turn off the sample pump and combustion air simultaneously (within 30 sec of each other).
6. *Mandatory:* Leak-check the sampling train (see FP 3c, section C).
7. Recover the sample as in FP 6, except do not purge the sample.
8. *Mandatory:* Conduct a performance system check after each 3-hr run or after three 1-hr samples. See section C.
9. *Optional:* Rinse and brush the probe and replace the filter before the next run.

C. System Performance Check

1. Adjust the flow rates to generate COS concentration in the range of the stack gas or within ± 20% of the applicable standard at a total flow rate of at least 2.5 L/min. See Figure F15A-3, if dilution is required.
2. Calibrate the flow rate from both sources with a soap bubble flow tube.
3. Collect 30-min samples, and analyze in the normal manner. Collect the samples through the probe of the sampling train using a manifold or some other suitable device. Do not replace the particulate filter and do not clean the probe before this check.
4. Analyze the samples as in LP 6. Analyze field audit samples, if applicable.

FIELD DATA SHEET 15A (Continued)
System Performance Check

Client/Plant Name _____ Job # _____

City/State _____ Date/Time _____

Train ID# _____ Personnel _____

DGM Calibration Factor, Y_p _____

Rotameter Calibration			
Train ID# _____	COS		N ₂
Rotameter Rdg L/min			
Bubble Meter Vol, V _{sb} L			
Time, θ sec			
Bar. Press., P _b mm Hg			
Amb Temp., t _{amb} °C			
Flow Rate, Q _{std} L/min			
Average \bar{Q}_{std} L/min			

Samplg time (min)	COS Rotam Rdg (L/min)	N ₂ Rotam Rdg (L/min)	DGM Rdg (L)	Temperature (°C)		Flow Rate Deviation	
				DGM	Imp. Exit	ΔV_m	$\Delta V_m / \bar{\Delta V}_m$
0							
5							
10							
15							
20							
25							
30							
Total Time, θ_s	Avg	Avg	Volume, V _{mp}	Avg, t _{mp}	Max $\leq 20^\circ C?$	Avg	0.90 - 1.10?

Reference COS Cylinder Concentration, C_{COS} _____ ppm

$$Q_{std} = 23.13 \frac{V_{sb}}{\theta} \frac{P_b}{(t_{amb} + 273)}$$

$$C_{RG} = C_{COS} \frac{Q_{COS}}{Q_{COS} + Q_{N_2}}$$

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____

Personnel (Signature/Date)

Team Leader (Signature/Date)

