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Advanced Sulfur Control Concepts in Hot-Gas Desulfurization Technology

Quarterly Report
October 1 - December 31, 1997

By
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For
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DISCLAIMER

EXECUTIVE SUMMARY

After months of frustration, final alterations in the reactor system and the flame photometric detector were completed to permit quantitative measurements of low concentrations of H_2S during the prebreakthrough period. Two reduction/sulfidation runs were then completed. The first yielded approximately 15 ppmv H_2S, and, after additional stainless steel parts which might be contaminated by sulfur from previous experiments were removed from the system, prebreakthrough H_2S concentrations of about 5 ppmv were achieved in the second run. Then another calamity struck. The quartz liner which had been fabricated to minimize contact between the pressure vessel and reactor product gas containing H_2S, SO_2, and/or S_2 broke while the reactor was being cooled after the second run using the FPD.

Since replacing the quartz insert was expected to take a considerable amount of time, we decided to turn attention to sorbent durability studies by beginning a multicycle run. This necessitated that the FPD be replaced by the TCD since the time corresponding to active breakthrough rather than minimum prebreakthrough concentration was of primary interest. The TCD then had to be recalibrated after the numerous system changes made while making the FPD operational. By the end of the quarter, nineteen complete cycles had been completed with little or no evidence of sorbent deactivation. Prebreakthrough H_2S concentrations below the TCD detection limit of about 100 ppmv were achieved in all cycles. The time, $t_{0.5}$, required for the H_2S concentration in the product gas to reach 0.5% (50% of the inlet concentration) varied only between 97 and 106 minutes in the 19 cycles. Significantly, $t_{0.5}$ for the 19th cycle was 103 minutes, among the largest of all cycles. SO_2 breakthrough during regeneration showed similar good reproducibility. $t_{0.5}$ for regeneration only varied between 20.6 and 22.9 minutes. The concentration of elemental sulfur (considered as S_2) in the product gas exceeded 10% for more than 15 minutes in each cycle. By the end of December, the sorbent had been exposed continuously to temperatures ranging from 600°C to 800°C for more than one month in gas compositions ranging from 100% H_2 to air, and from 1% H_2S/10% H_2/N_2 to 12% SO_2/N_2. Between regeneration and sulfidation, the system was purged by nitrogen. The sorbent was at the highest temperature of 800°C for about 90% of that time. These sorbent durability results are considered to be quite favorable.

FLAME PHOTOMETRIC DETECTOR (FPD) OPERATION AND CALIBRATION

At the end of the previous quarter, even after months of adjustments and consultations with Shimadzu personnel, the FPD was still not providing the necessary H_2S sensitivity. Excessive tailing at the 5 ppmv concentration level was the primary problem. This problem was eventually solved by replacing all possible stainless steel parts with teflon. Specifically, the stainless steel column used to trap trace quantities of H_2O was replaced with a teflon column and the thermal conductivity detector (TCD) was removed, thereby permitting column effluent to flow directly into the FPD. Satisfactory analysis of 5 ppmv H_2S was then possible as shown in Figure 1 by the sharp peak having a retention time of 2.5 minutes. Analytical reproducibility was also satisfactory as shown in Figure 2. The variation in area counts for the ten duplicate samples was from 151 to 166.

After achieving satisfactory results at the 5 ppmv level, the FPD was calibrated over the range

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Method : C:\EZCHROM\METHODS\SUL003.MET
Sample ID : trial05b.016

	Sample Amount	ISTD Amount	Mult. Factor
Calibration :	1.000	1.000	1.000
Run :	1.000	1.000	1.000

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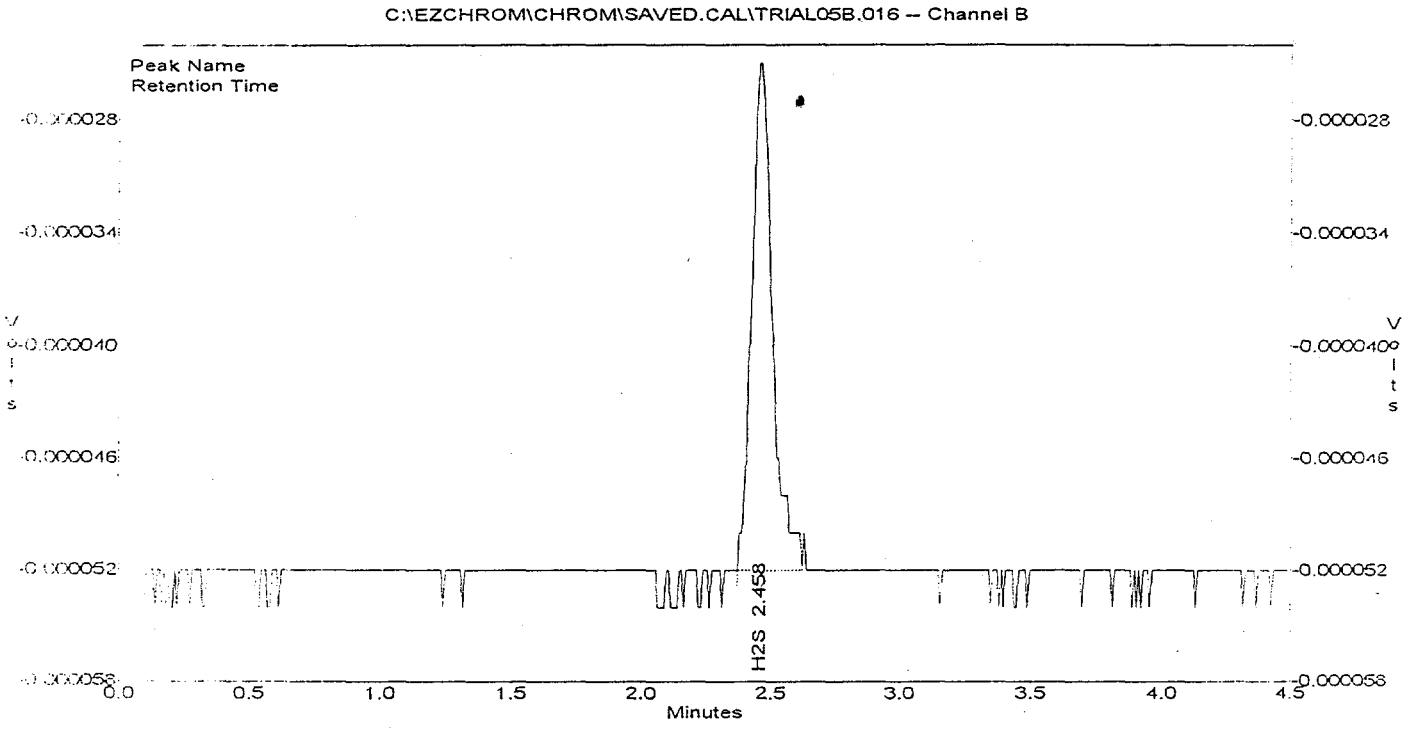
Printed : Jan 21, 1998 13:02:54
User : Yiding



Channel B Results

Peak	Name	Time	Area	Area %	ESTD Conc	NORM Conc
1	H2S	2.46	151	100.000	0.000	0.000
Totals :			151	100.000	0.000	0.000

Figure 1. FPD Chromatogram for 5 ppmv H_2S

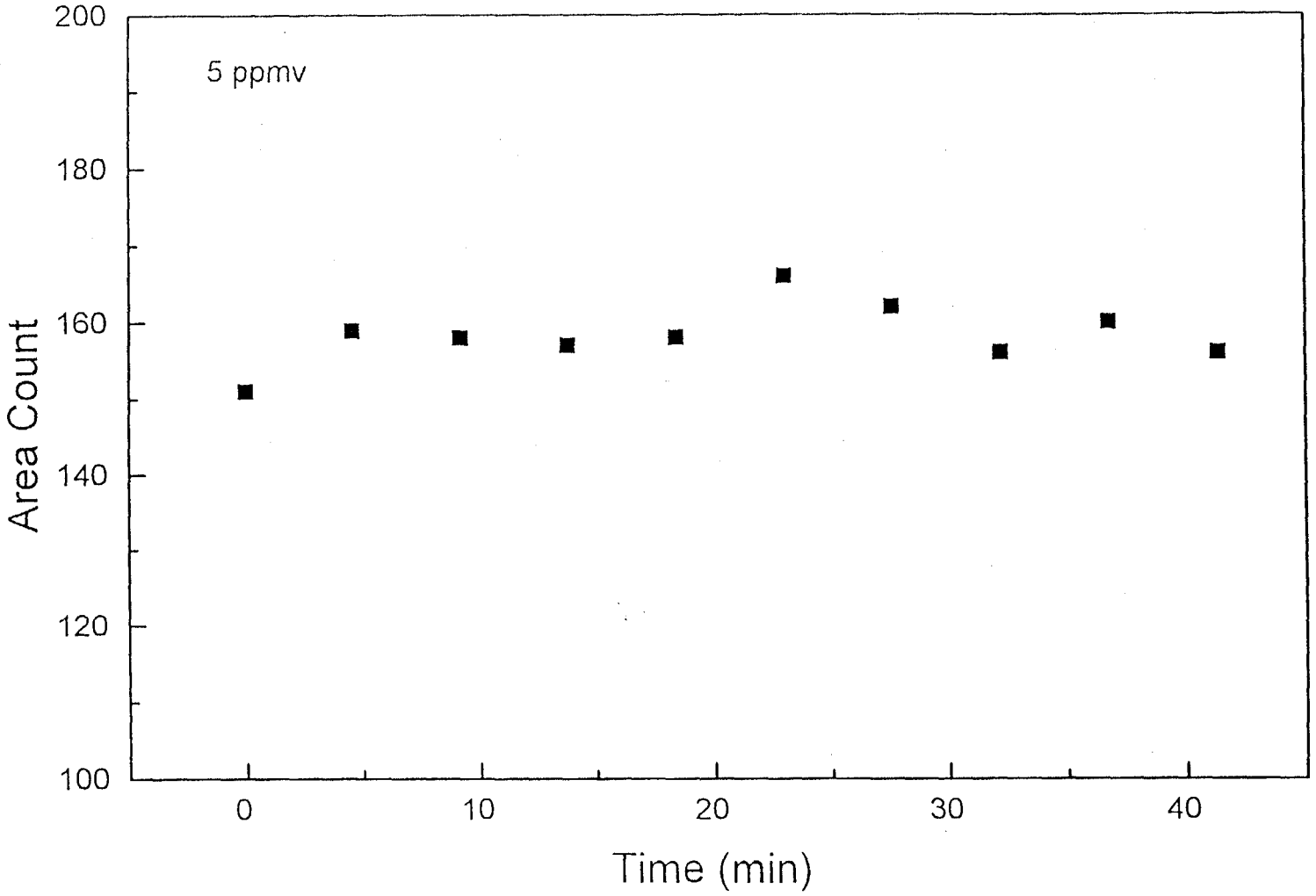


Figure 2. Reproducibility of the FPD Response to 5 ppmv H_2S

of 0 to 108 ppmv H_2S. Results are shown in Figures 3 and 4. Figure 3 shows the calibration results over the entire concentration range while Figure 4 shows results over the low concentration range of 0 to 10 ppmv H_2S. Calibration data were fit with quadratic equations and both the data and equations are shown in the figures. Figure 4 results are used when the H_2S concentration is below 10 ppmv while Figure 3 results are used between 10 and 108 ppmv.

PREBREAKTHROUGH H_2S CONCENTRATIONS

At this point we planned to begin an extensive study to determine minimum prebreakthrough H_2S concentrations which could be achieved as a function of temperature, pressure, and gas composition during both the reduction and sulfidation phases. Unfortunately, after only two runs, the quartz insert used to minimize contact between product gases and the stainless steel pressure vessel broke. Most likely the reactor was cooled too rapidly after the second run, and differences in thermal expansion coefficients caused the breakage.

However, results from the two tests were quite favorable. In the first test, Ce201s01, a standard mixture of 6g of Rhone Poulenc CeO_2 and 3g of Al_2O_3 was added to the reactor. The sorbent was reduced in 400 sccm of 10% H_2/N_2 at 800°C and 5 atm for 12 hours. 1% H_2S was then added and effluent H_2S concentrations as a function of time are shown in Figure 5. In the first four samples (4.5 to 18 minutes), the H_2S concentration was approximately 15 ppmv. The concentration then dropped to about 5 ppmv in the next two samples before increasing to a value beyond the FPD calibration range in the eighth sample at 31.5 minutes. The results were encouraging in that the sub-20 ppmv target level was reached during early stages of the test, but discouraging in that the sub-20 ppmv level was not maintained for a longer time. FPD breakthrough occurred at the relatively small dimensionless time of $t^* \sim 0.25$ while TCD breakthrough of about 2000 ppmv occurred in previous tests at $t^* \sim 1.0$.

Additional changes were made in the reactor system prior to the second run to determine if still lower prebreakthrough H_2S concentrations could be achieved. Specifically, the back pressure regulator, filter, and ball valve were removed from the product line. This left a single fitting and the chromatograph sampling value as the only steel parts in contact with the product gas. Without the back pressure regulator, reactor pressure was limited to 1 atm. Consequently, the reactor feed rate was reduced to 100 sccm from 400 sccm so that the reactor residence time was reasonably constant. Other than pressure and gas flow the conditions of the two runs were the same. Results from run Ce202s01 in the form of product H_2S concentration as a function of time are shown in Figure 6. The H_2S concentration remained below 10 ppmv for almost 100 minutes. Active breakthrough then began and the run was terminated after 125 minutes when the H_2S concentration exceeded the FPD calibration range. The reduced prebreakthrough concentration is attributed to the removal of the back pressure regulator, filter, and ball valve from the system. These parts had been exposed to numerous previous sulfidation and regeneration cycles and may have become contaminated with sulfur. The beginning of active breakthrough was reasonably consistent in both runs. That is, the breakthrough time of 100 minutes at 100 sccm is comparable to the 25 minute breakthrough time at 400 sccm.

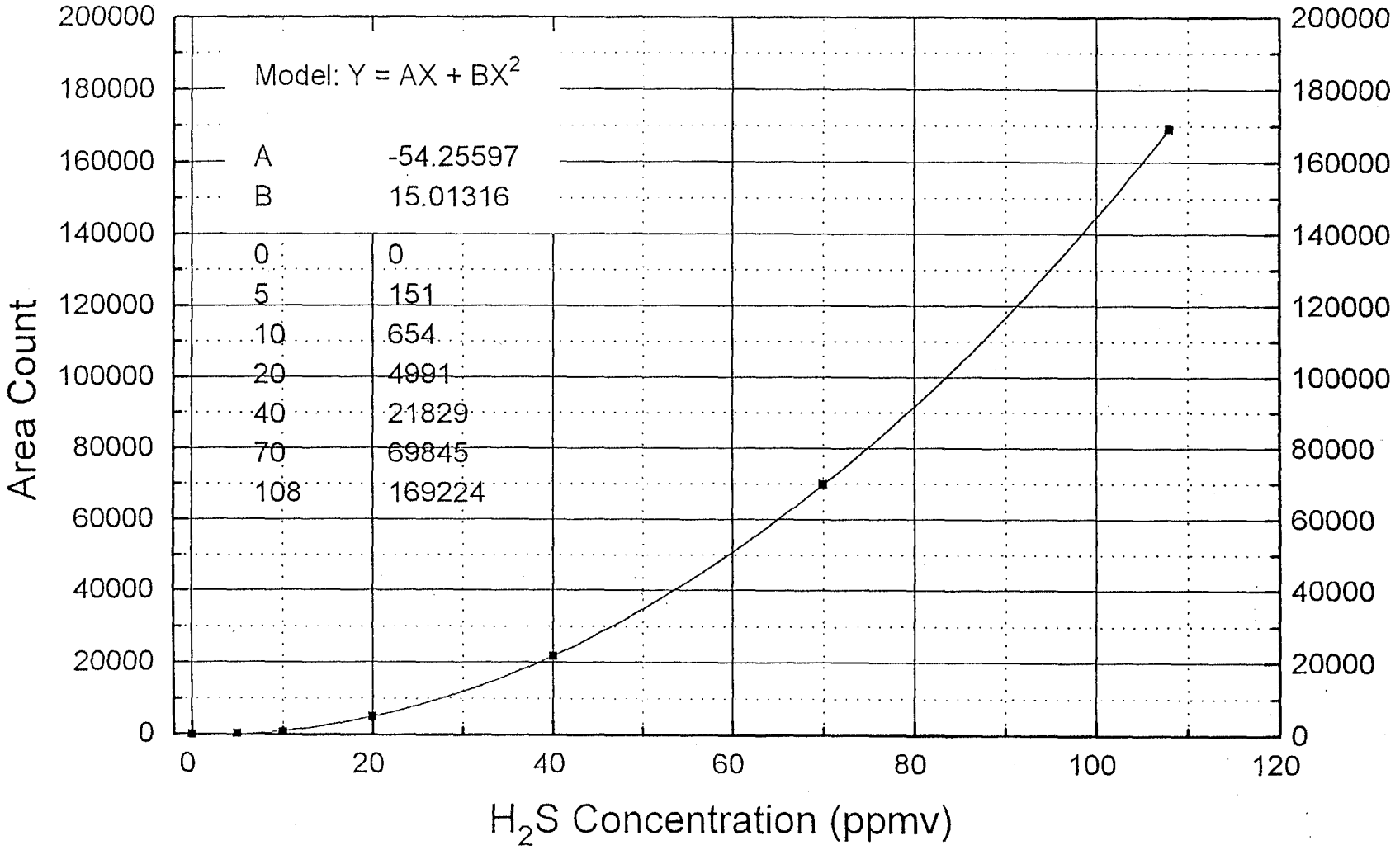


Figure 3. FPD Calibration Curve for H_2S Between 10 and 108 ppmv

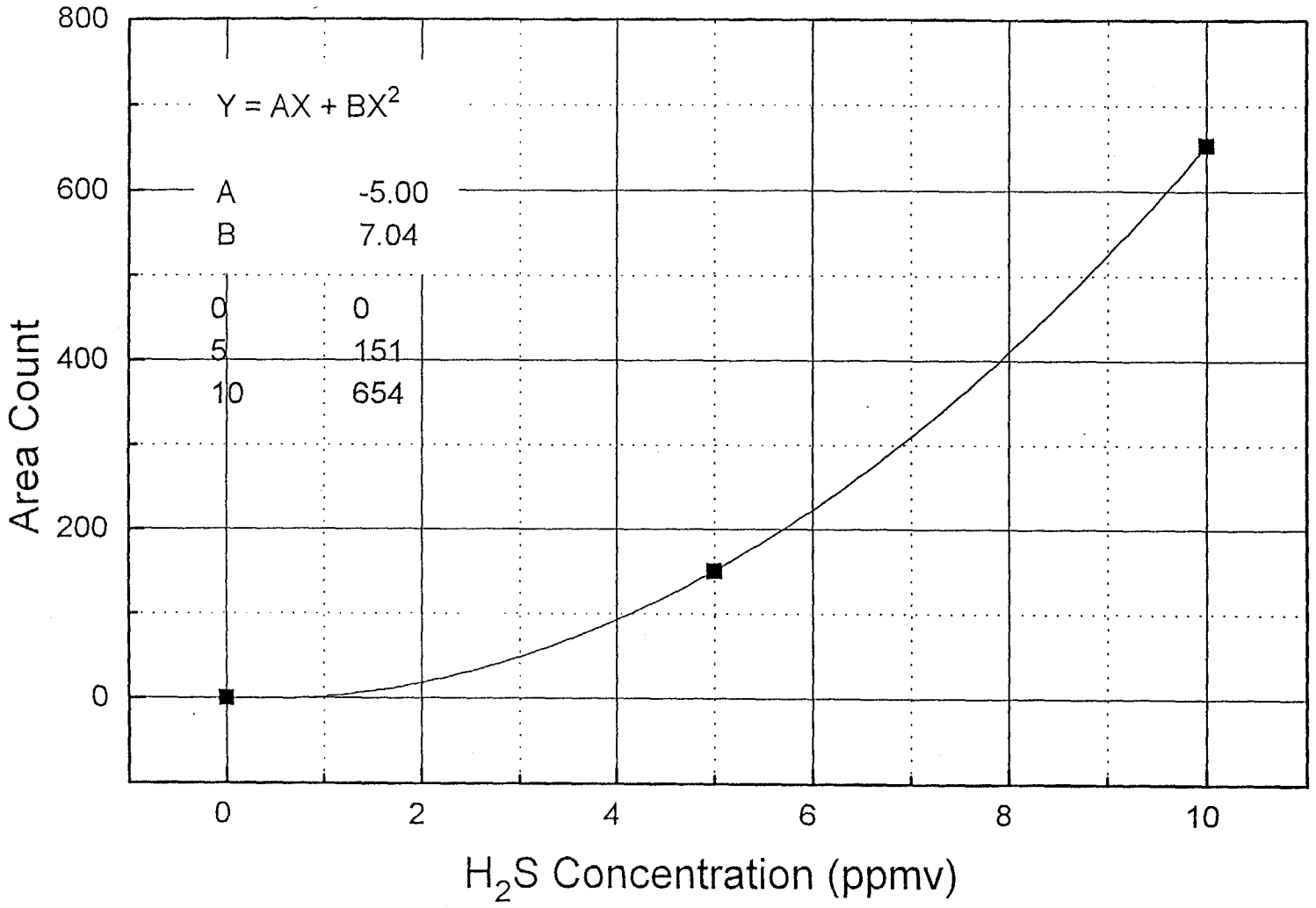


Figure 4. FPD Calibration Curve for H_2S Less Than 10 ppmv

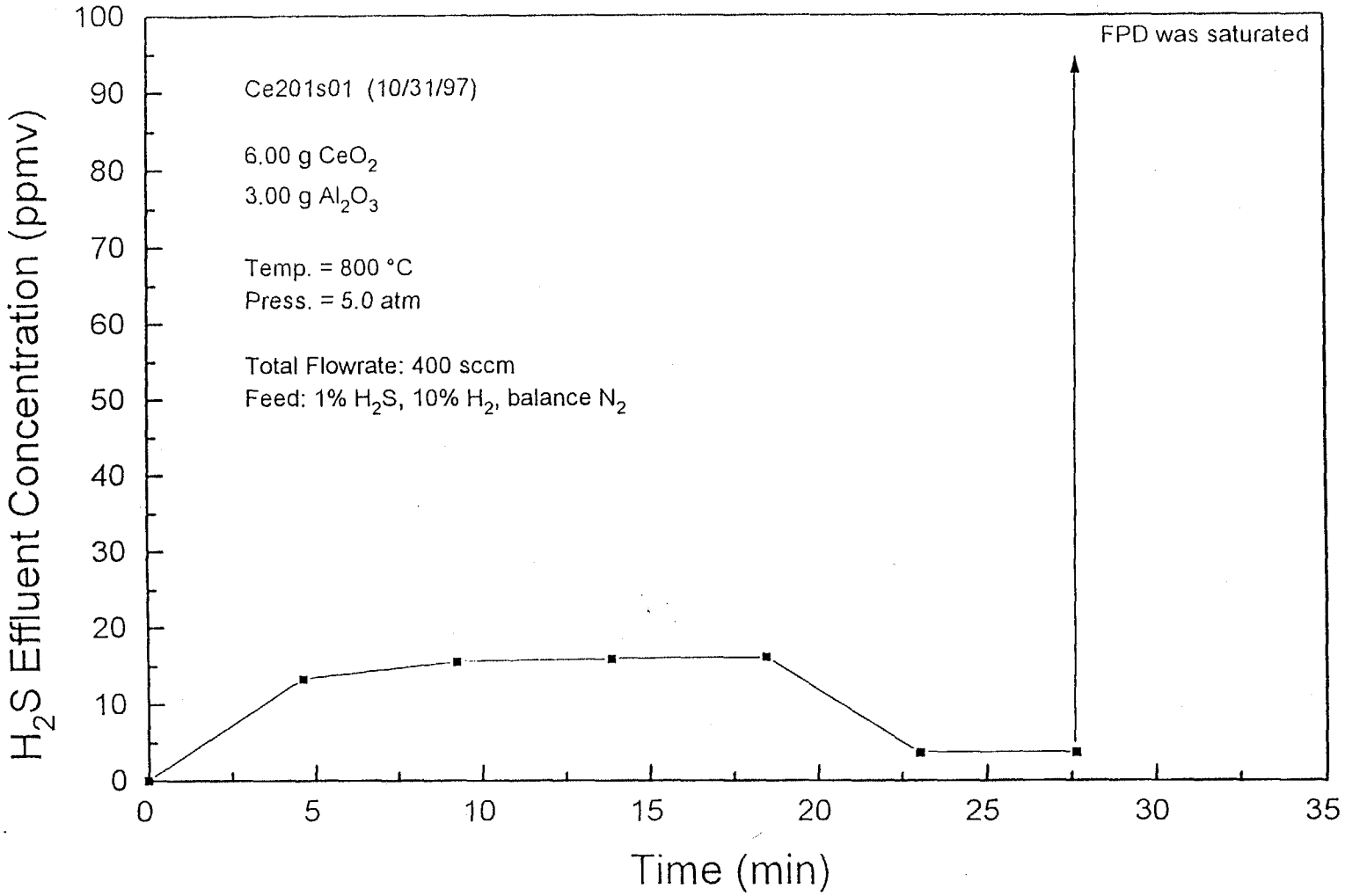


Figure 5. Fixed-Bed Reactor Response: Run Ce201s01

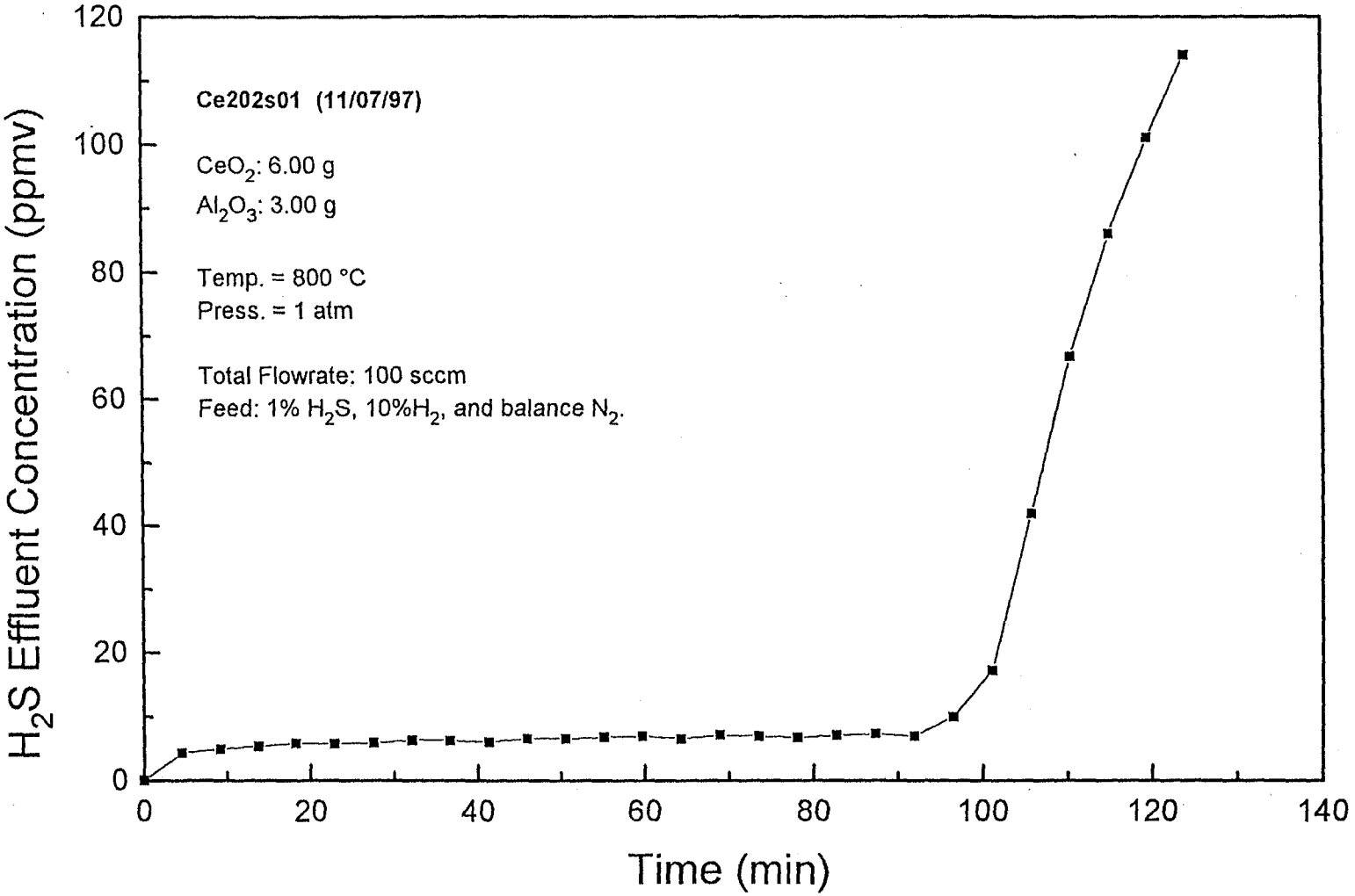


Figure 6. Fixed-Bed Reactor Response: Run Ce202s01

SORBENT DURABILITY TEST

Since an extended time period would be required before a replacement quartz liner could be obtained, we decided to address the question of sorbent durability in an extended multicycle run. The FPD was replaced by the TCD since the overall shape of the breakthrough curve instead of minimum prebreakthrough concentration was of primary interest. However, because of the numerous changes made while installing and using the FPD, recalibration of the TCD was required.

Recalibration results for H_2S over the concentration range of 0 to 1.3% are shown in Figure 7 while similar results for SO_2 between 0 and 19% are presented in Figure 8. As expected, both calibration curves were linear through the origin. The relationship between % H_2S and chromatograph peak area shown in Figure 7 is

$$\% H_2S = 2.681 \times 10^{-5} \text{ Area}$$

and the SO_2 calibration equation from Figure 8 is

$$\% SO_2 = 2.590 \times 10^{-5} \text{ Area}$$

Correlation coefficients for the calibration curves are 0.9972 for H_2S and 0.9981 for SO_2.

Nineteen sulfidation-regeneration cycles were completed by the end of the quarter. Each cycle consisted of four phases at the following conditions:

1. A standard sorbent mixture of 6g Rhone Poulenc CeO_2 and 3g Al_2O_3 was reduced at 800°C and 5 atm. In cycles 1 through 15 the reduction gas contained 10% H_2 in N_2 at a flow rate of 400 sccm. In cycles 16 through 19 reduction was carried out in 100% H_2 at a flow rate of 50 sccm. Reduction in pure H_2 had a positive effect on sulfidation performance. The reduction phase was generally carried out overnight.

2. Sulfidation at 800°C and 5 atm in 1% H_2S/10% H_2/N_2 at a rate of 400 sccm. Each sulfidation cycle was continued until the concentration of H_2S in the product gas reached 1%, typically 2 hours.

3. Regeneration at 600°C and 1 atm in 12% SO_2/N_2 at a rate of 200 sccm. Regeneration was continued until the concentration of SO_2 reached 12%, typically about 30 minutes.

4. Reactor cleaning at 800°C and 5 atm using air at 50 sccm. The purpose of the oxidative cleaning phase was to remove, to the extent possible, any elemental sulfur deposited during regeneration. As a further means of preventing contamination, different reactor exit lines were used during the sulfidation and regeneration phases. During sulfidation, the product gases flowed through teflon-lined tubing and a 7μ stainless steel filter to the back pressure regulator and then through teflon tubing to the chromatograph sample valve (stainless steel). Stainless steel in contact with the sulfidation product gas consisted of three fittings, one filter, the back pressure regulator, and the chromatograph sampling valve. During regeneration, product gases flowed through heat-traced

Method : C:\EZCHROM\METHODS\SULHI01.MET * - Replicate Not Used
Printed : Jan 21, 1998 13:04:35
Channel : A
Peak : H2S

Level	Area	Amount	RF	Rep Area 1	Rep Area 2	Rep Area 3	Rep Area 4	Rep Area 5	StdDe
1	4061	0.1	2.463e-005	4061					
2	35647	1	2.805e-005	35647					
5	3763	0.1	2.658e-005	3763					
6	15790	0.4	2.533e-005	15790					
7	26125	0.7	2.679e-005	26125					
8	36785	1	2.718e-005	36785					
9	48401	1.3	2.686e-005	48401					
10	38345	1	2.608e-005	38345					
11	29993	0.8	2.667e-005	29993					
12	22965	0.6	2.613e-005	22965					
13	15663	0.4	2.554e-005	15663					
14	8248	0.2	2.425e-005	8248					
5	4109	0.1	2.434e-005	4109					
16	10000	0.3	3e-005	10000					

Average RF: 2.63166e-005
Std Dev: 1.53862e-006
%RSD: 5.84656

Definition: Amount / Area
Weighting Method: None
Through Zero: Yes

Linear Fit: Amount = 2.681e-005 x Area + 0.000e+000
R^2 = 0.9972

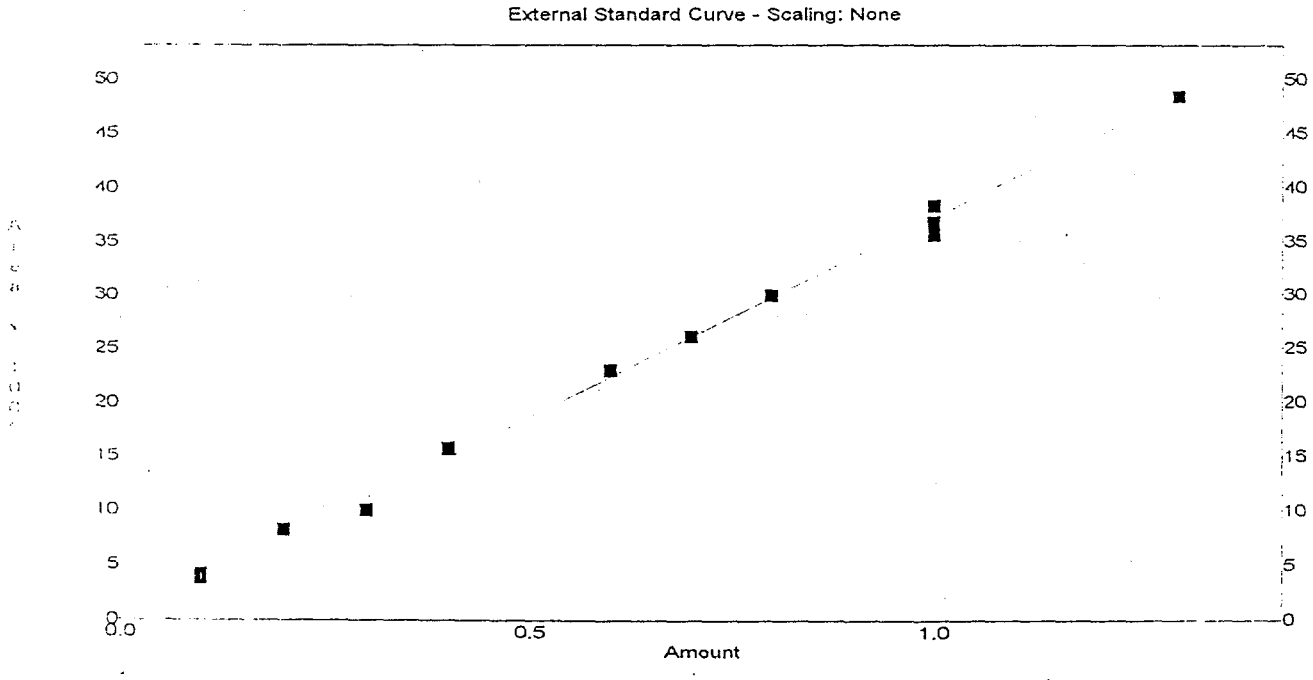


Figure 7. TCD Recalibration for H_2S

Method : C:\EZCHROM\METHODS\SULHI01.MET

Acquired : Jan 21, 1998 13:04:46

Channel : A

Type : SO2

* - Replicate Not Used

Level	Area	Amount	RF	Rep Area 1	Rep Area 2	Rep Area 3	Rep Area 4	Rep Area 5	StdDe
3	28218	1	3.544e-005	28218					
4	415513	11	2.647e-005	415513					
5	30704	1	3.257e-005	30704					
6	108499	3	2.765e-005	108499					
7	185817	5	2.691e-005	185817					
8	263442	7	2.657e-005	263442					
9	333373	9	2.7e-005	333373					
10	425883	11	2.583e-005	425883					
11	507844	13	2.56e-005	507844					
12	585413	15	2.562e-005	585413					
13	657740	17	2.585e-005	657740					
14	738388	19	2.573e-005	738388					
2	327376	8	2.444e-005	327376					
1	374348	10	2.671e-005	374348					

Average RF: 2.73133e-005

RF StDev: 2.99461e-006

RSD: 10.9639

Definition: Amount / Area

Weighting Method: None

Through Zero: Yes

Linear Fit: Amount = 2.590e-005 x Area + 0.000e+000

R^2 = 0.9981

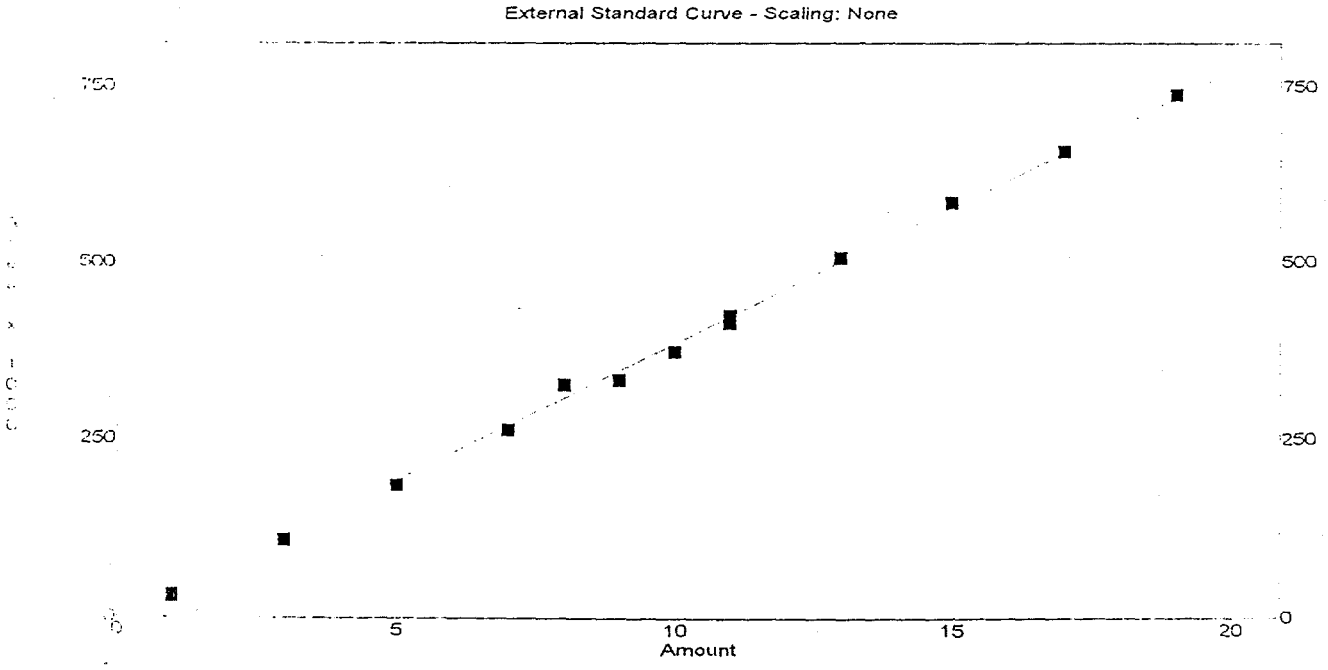


Figure 8. TCD Recalibration for SO_2

stainless steel lines to the condenser and then through a series of stainless steel filters and stainless steel tubing to the sampling valve. The back pressure regulator was not used during the atmospheric pressure regeneration tests and the only stainless steel parts exposed to both sulfidation and regeneration product gases were one fitting and the chromatograph sampling valve.

Complete H_2S breakthrough curves for the 19 sulfidation cycles are shown in Figure 9. With a single exception, the concentration-time curves are quite similar and show no evidence of sorbent deterioration. The delayed breakthrough time observed in Ce202s16 is attributed to reduced H_2S feed rate caused by a malfunction in the mass flow controller.

The time, $t_{0.5}$, required for the product H_2S concentration to reach 0.5% (one-half of the feed concentration) provides a good measure of sorbent disability. $t_{0.5}$ values for each cycle (excluding s16) are shown in Figure 10. The total variation in $t_{0.5}$ was only between 97 and 106 minutes with an average of 101 minutes. This level of variation is felt to be within the normal experimental error.

Figure 11 shows the H_2S breakthrough curves from the 19 sulfidation cycles using expanded concentration and time scales, thereby providing a clearer view of the prebreakthrough portion of the cycle. During the initial period of all cycles the H_2S concentration was below the TCD detection limit of about 100 ppmv. The first detectable H_2S in the product occurred in the 20 to 50 minute time span in cycles s01 through s15 (with the exception of cycle s11) and at about 90 minutes in cycles s16 through s19. The time increase beginning in s16 is associated with changing the composition of the reducing gas from 10% H_2/N_2 to 100% H_2. We believe that the stronger reducing gas increased the extent of reduction of CeO_2. That is, the final value of x in CeO_x was smaller in the stronger reducing atmosphere, and this led to improved H_2S removal. Initial appearance of H_2S after 80 minutes in cycle s11 is the exception since the reducing composition in that cycle should have been 10% H_2/N_2. However, there is reason to suspect that the H_2 content of the reducing gas was, by mistake, larger than the intended 10%. Overall, it appears from Figure 11 that the prebreakthrough performance was poorest in cycle 01, that cycles 02 through 15 (excluding cycle 11) formed an intermediate group with random variation within the group, and that the best performance was achieved in cycles 16 through 19.

Complete regeneration breakthrough curves for the 19 cycles shown in Figure 12 also indicate good reproducibility. Active breakthrough began at about 18 minutes and regeneration was effectively complete less than 10 minutes later. The rapid decrease in SO_2 concentration near the end of regeneration cycles r06 and r10 was caused by elemental sulfur plugging the product lines, thereby terminating the flow of feed gas. However, the characteristics of the SO_2 breakthrough curves were fully established by that time. Plugging in regeneration cycle r08 prevented any SO_2 breakthrough data from being acquired; complete regeneration was achieved, however, as indicated by the H_2S breakthrough curve in the subsequent sulfidation cycle (s09).

The time, $t_{0.5}$, required for the SO_2 concentration in the product gas to reach 6% (50% of the feed concentration) is shown as a function of cycle number in Figure 13. The overall variation was only between 21 and 23 minutes and the 18-cycle average was 22 minutes.

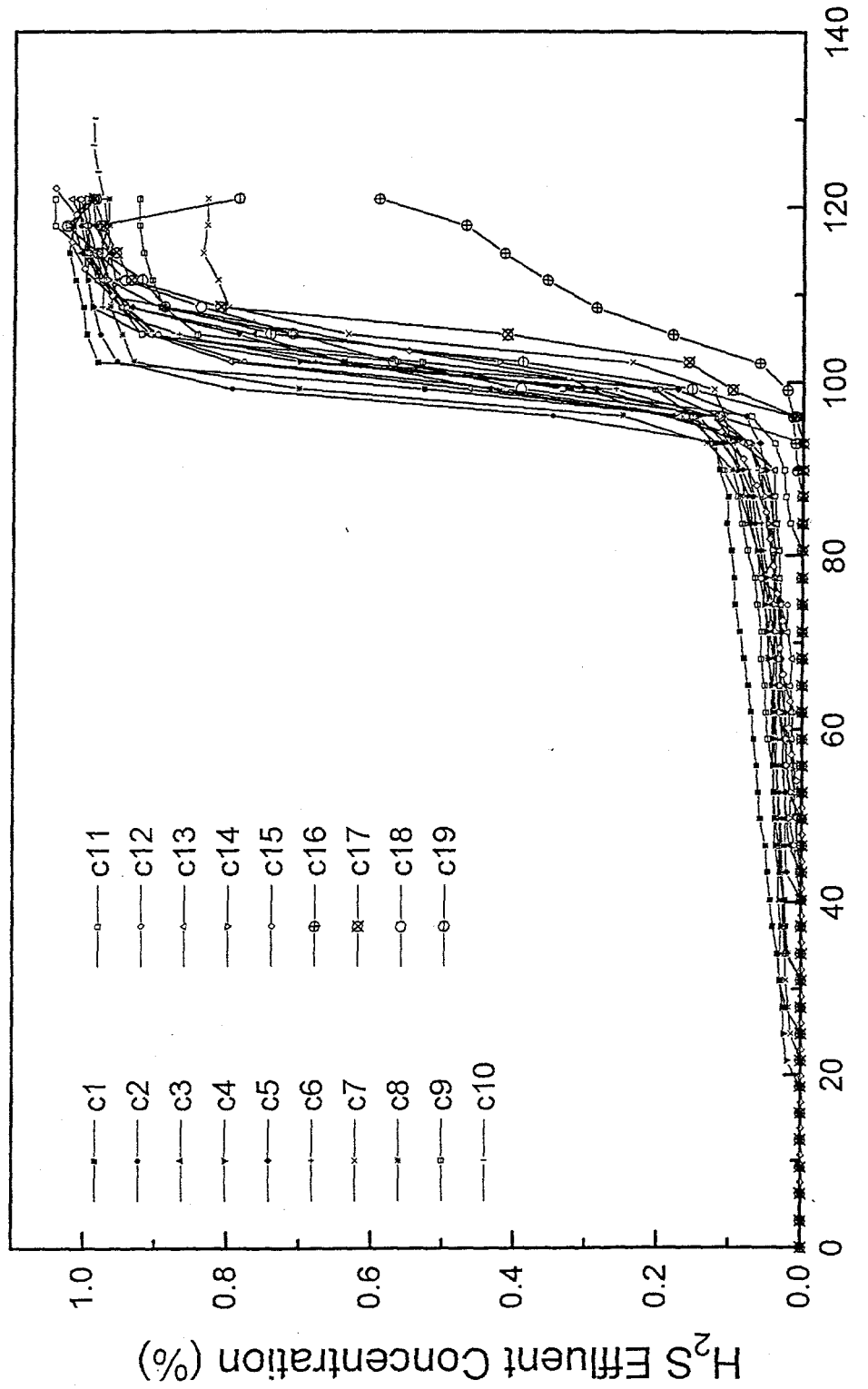


Figure 9. H_2S Breakthrough Curves Through Nineteen Cycles

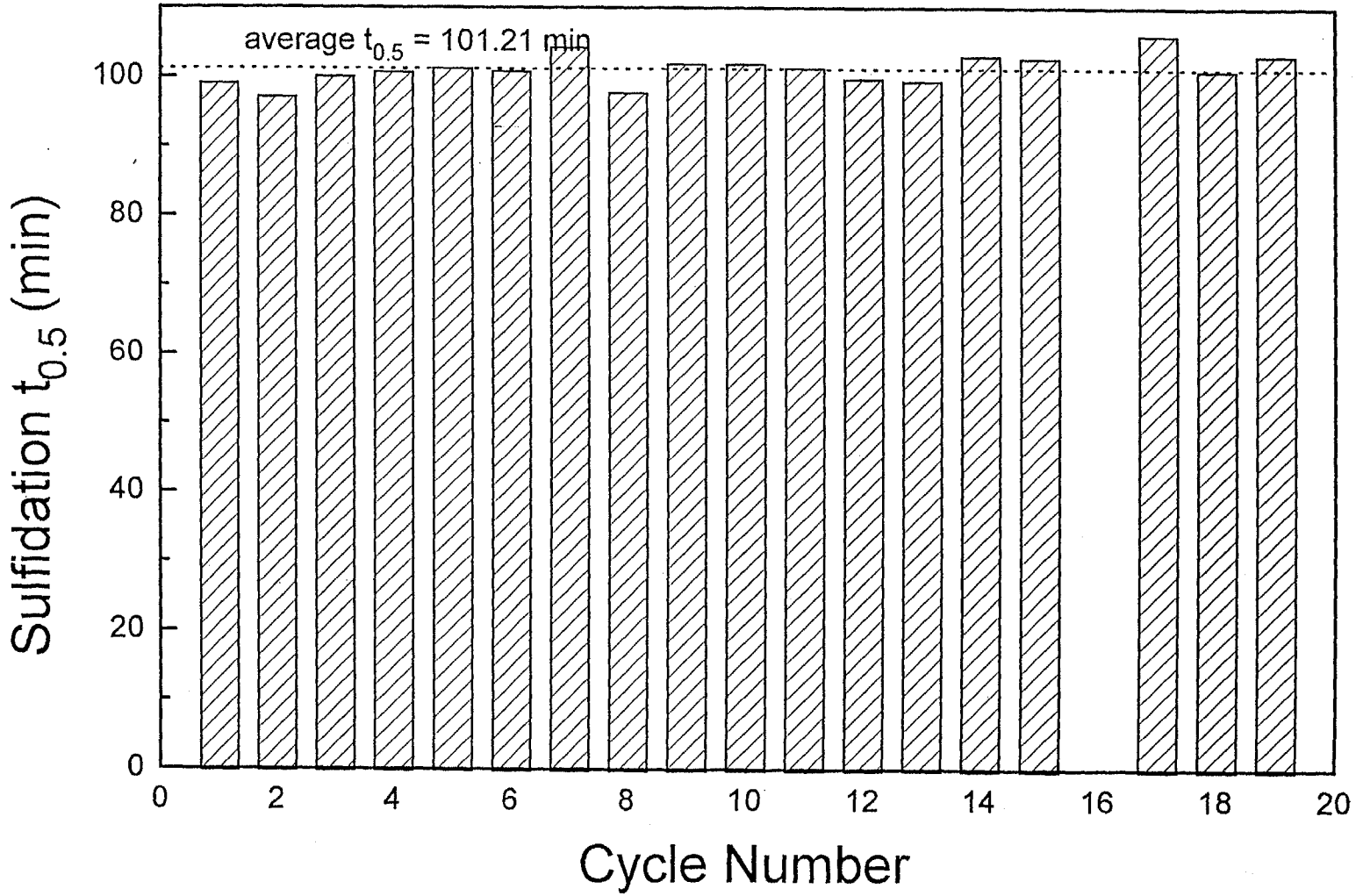


Figure 10. Time Required for Product H_2S concentration to Reach 50% of Feed Concentration

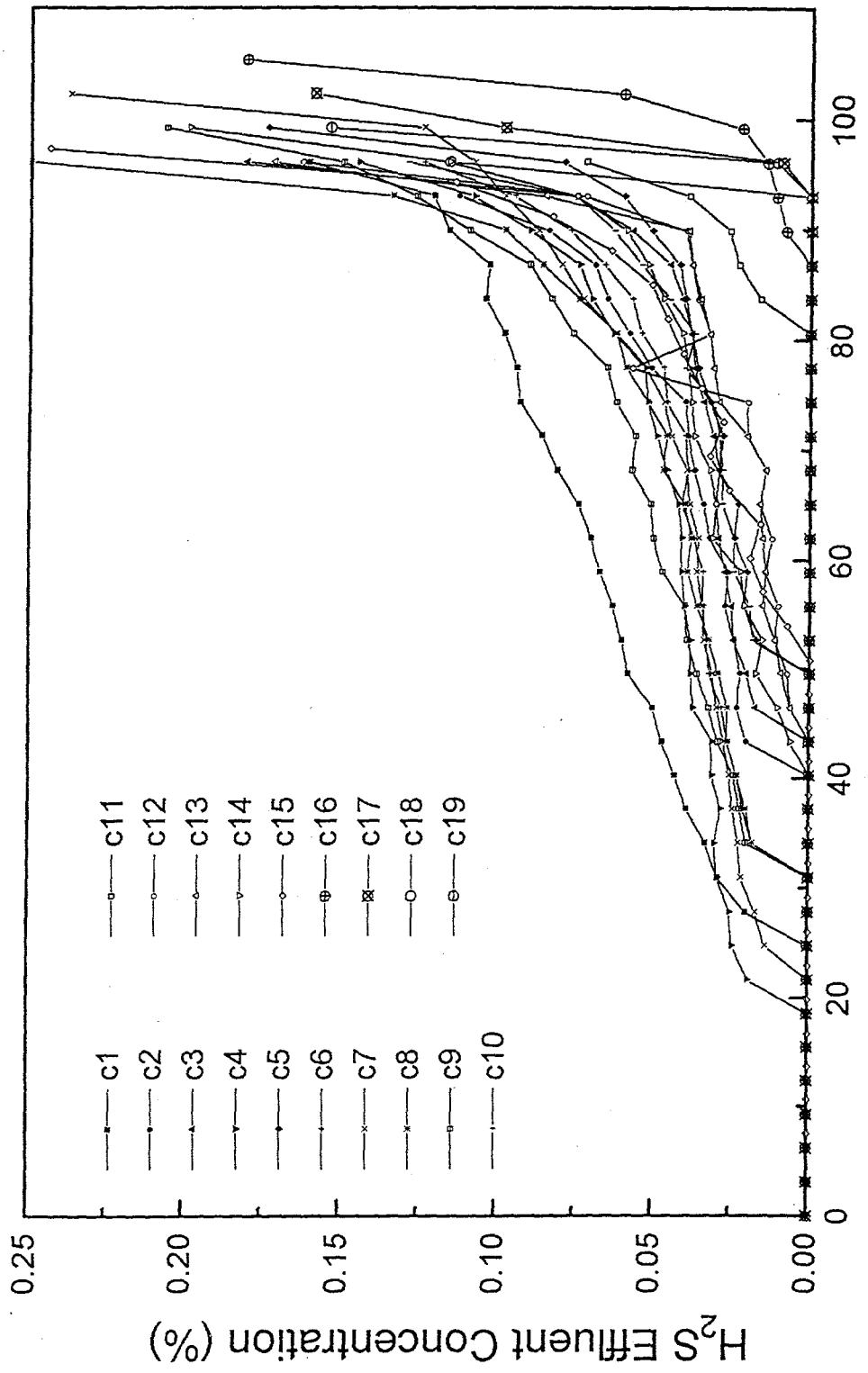


Figure 11. Prebreakthrough H_2S Concentrations Through Nineteen Cycles

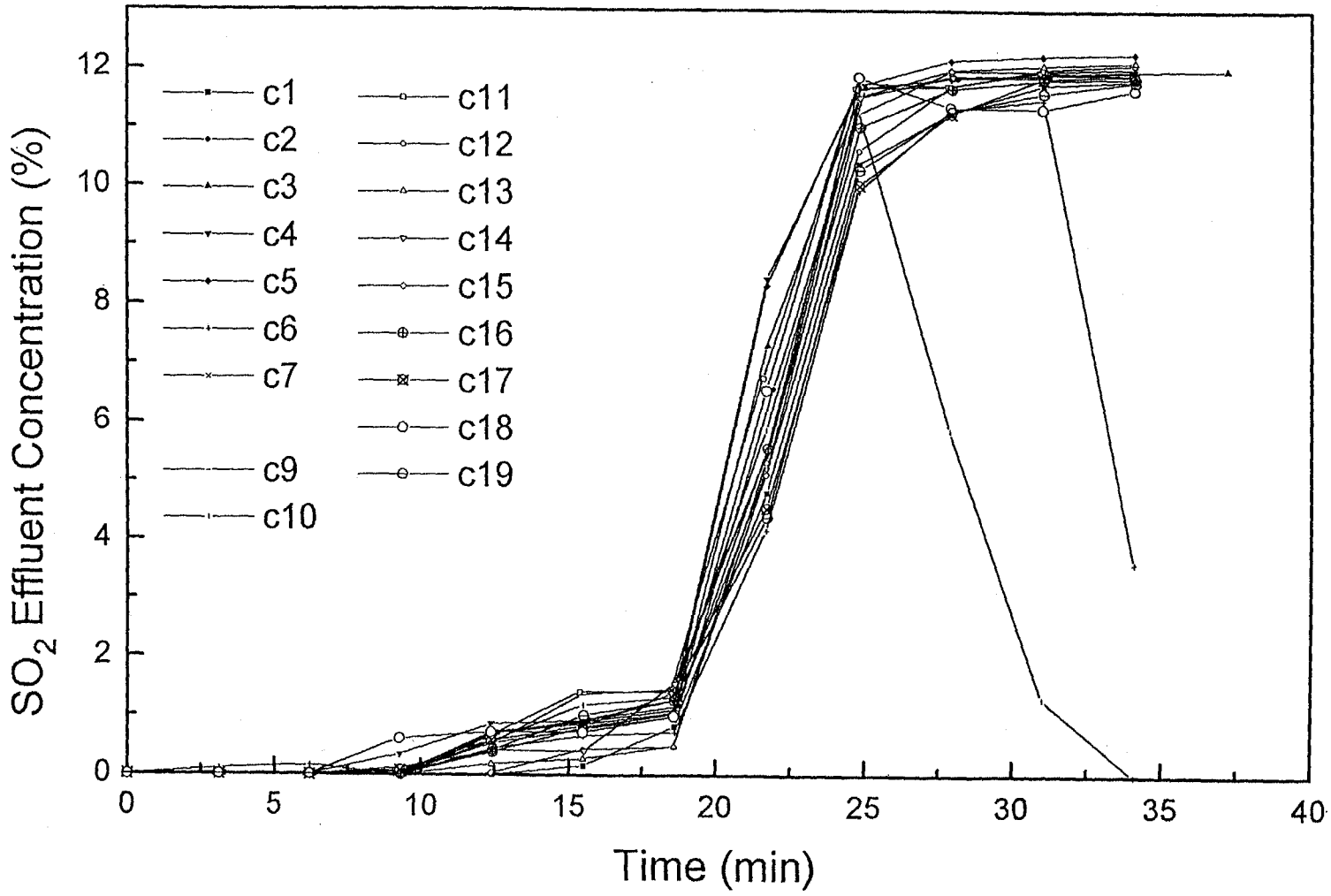


Figure 12. SO_2 Breakthrough Curves Through Nineteen Cycles

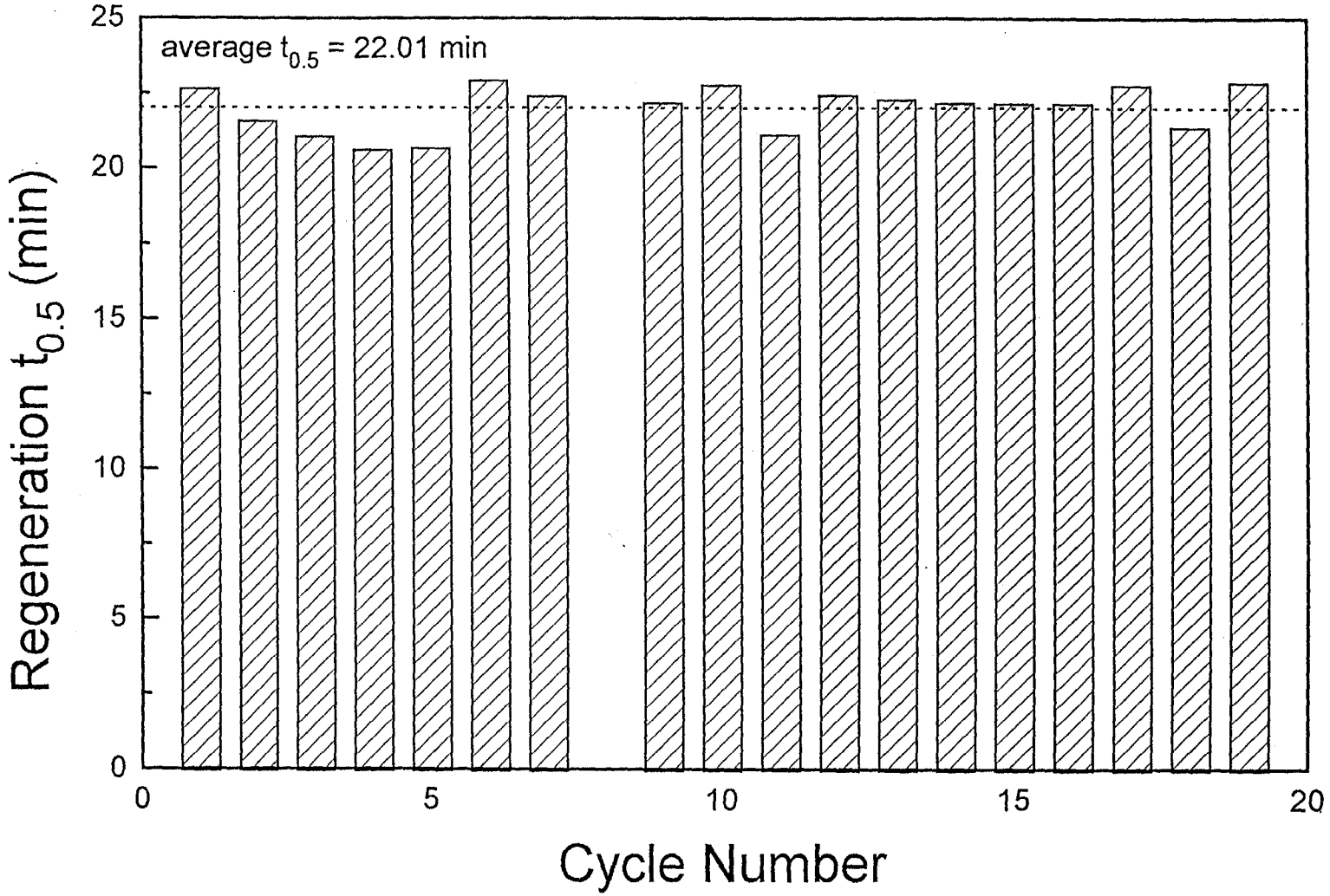


Figure 13. Time Required for the Product SO_2 Concentration to Reach 50% of Feed Concentration

DOE F1332.3
APPROVED
(11-84)

U.S. DEPARTMENT OF ENERGY
MILESTONE SCHEDULE ☐ PLAN ☐ STATUS REPORT

FORM

OMB NO. 1901-1400

1. TITLE	2. REPORTING PERIOD	3. IDENTIFICATION NUMBER
Advanced Sulfur Control Concepts for Hot Gas Desulfurization	October-December 1997	DE-AC21-94MC30012

4. PARTICIPANT NAME AND ADDRESS	5. START DATE	6. COMPLETION DATE
Department of Chemical Engineering Louisiana State University Baton Rouge, LA 70803	March 1994	March 1998

7. ELEMENT CODE	8. REPORTING ELEMENT	9. DURATION																						FY	FY	10. PERCENT COMPLETE	
		1997												1998												a. Plan	b. Actual
		O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M								
Task 1.1	Preliminary Assessment	Completed in FY 94																								100	100
Task 1.2	Select Approaches	Completed in FY 94																								100	100
Task 2.1	Evaluate Concepts	Completed in FY 94																								100	100
Task 2.2	Concept Eval. Rpt.	Completed in FY 94																								100	100
Task 3.1	Project Plan	Completed in FY 95																								100	100
Task 3.2	Laboratory Development																									100	100
Task 3.3	Lab. Devel. Report																									100	100
Task 4.1	HTHP Test Plan																									100	100
Task 4.2	Bench-Scale Testing																									100	50
Task 4.3	Bench-Scale Test Report																									50	0
Task 5.1	Proc. Model Devel.																									95	100
Task 5.2	Economic Analysis																									75	100

11. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER AND DATE