

DOE/PC/89869--T12

DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

Contract DE-AC22-89PC89869

by

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Contract Objective

The objective of this contract is to examine the relationship between catalytic properties and the function of cobalt Fischer-Tropsch catalysts and to apply this fundamental knowledge to the development of a stable cobalt-based catalyst with a low methane-plus-ethane selectivity for use in slurry reactors.

Contract Tasks

- Task 1.0: Project Management Report
- Task 2.0: Reference Cobalt Catalyst
- Task 3.1: Modifier Role for Ruthenium
- Task 3.2: Particle Size Effects with Ruthenium
- Task 4.1: Identification of the Synergy between Cobalt and a Second Bimetallic Element, such as Ruthenium

- Task 4.2: Development of a Bimetallic Catalyst
Task 5.0: Demonstration of Stability

Experimental

The fixed bed pilot plant, the catalyst testing procedure, and the calculations for conversion and selectivities were previously described in the technical progress report covering the period of 3/16/88 to 6/16/88 for Contract No. DE-AC22-87PC79812. Conversions and hydrocarbon selectivities were calculated using data from an on-line gas chromatography (GC) analyzer. Alcohol selectivities were calculated using data from an on-line GC boiling point analyzer which analyzes the liquid product.

Catalysts were prepared via the steps of: impregnation, calcination and reduction. The catalyst preparation method was similar to one developed under a previous DOE contract (DE-AC22-84PC70028) to a division of Union Carbide which is now part of UOP. For the preparation of the support, a procedure similar to that developed in the previous work was used. Effect of differences in some of the operating parameters on the support properties are discussed below. One of the four new catalysts, No. 6531-194, contained the same levels of cobalt, manganese and zirconium as the one developed under the previous contract; the other three catalysts (No. 6531-196, -202, and -204) contained varying amounts of ruthenium in addition to the same levels of the three metals above. A pore-filling impregnation method with a special solvent was used. Following impregnation the catalysts were calcined for four hr at 450°C. After calcination the catalyst were mixed with a diluent (usually quartz sand) and loaded into the reactor where they were reduced with hydrogen for two hr at 350°C. Immediately afterwards the reactor was cooled to 211°C and 2 : 1 (molar) H₂ : CO feed was started. The diluent was added to facilitate removal of heat from the very exothermic reaction of H₂ with CO.

Catalyst loading was the same for all the runs in this report: 13 g of powdery calcined catalyst was loaded with 160 g of 60 to 80 mesh diluent. The first catalyst was screened by a three condition test (Table 1) wherein the initial condition (least strenuous) was the same as used for

the reference TC 211 catalyst developed under the previous contract (Run 65). The second and third conditions (higher temperature) provided higher conversions which were similar to the conversion observed with the more active catalyst TC 211 (Run 65). This allowed selectivity comparisons at similar conversions. For cobalt catalysts methane selectivity changes with conversion, and it is generally lower at higher conversions. A goal of the current work is to develop high activity catalysts which exhibit low methane selectivity. The three ruthenium-containing catalysts (No. 6531-196, -202, and -204) were more active; conversions at the first condition were high enough so that conditions 2 and 3 were not investigated.

For the catalyst testing runs discussed in this report, run summary plots of conversions and selectivities versus hours-on-stream are attached in Appendix A. Catalyst compositions are shown in Table 2 and summary performance data are shown in Tables 3 and 4.

Scope of Work During Reporting Period

Four new catalysts (No. 6531-194, -196, -202, and -204) were prepared using steamed, acid-washed Y-zeolite as support. Two batches of support were used, each prepared by extensive acid-washing of the steamed Y-zeolite. X-ray analysis (Table 2) of the acid-washed supports suggests that crystallinity of the steamed Y-zeolite is destroyed during the acid washing. These supports can be best described as amorphous silica. Three of the four catalysts (No. 6531-196, -202, and -204) contained ruthenium in addition to the usual cobalt, manganese and zirconium. An important objective of this contract is to determine whether small amounts of ruthenium can enhance the properties of cobalt Fischer-Tropsch catalysts.

Results and Discussion

Run 89

The catalyst used in Run 89, No. 6531-194, contained cobalt, manganese and zirconium (Table 2). The performance data for Run 89 are summarized in Tables 3 and 4. The

conversions and selectivities as a function of the hours-on-stream are summarized in Figures A-1 to A-7. The carbon monoxide conversion at the initial condition was about 18%, quite a bit lower than that from the reference catalyst. The run was too short to assess catalyst stability. Since both catalysts (Catalyst TC-211 and 6531-194) contained about the same levels of the three metals and were prepared in the same way, it is most likely that this activity difference resulted from the different supports used. The reference catalyst was prepared on a steamed, acid-washed Y zeolite which had not been as extensively acid-washed and, therefore, retained the Y zeolite crystallinity. Condition 2 for catalyst 6531-194 provided a carbon monoxide conversion of 85%, significantly higher than that of the reference catalyst at condition 1 (see Table 3). Also, the selectivity of the reference catalyst for methane (7%) was slightly better than that of catalyst 6531-194 (8.5%).

Run 91

The catalyst used in this run, No. 6531-196, contained cobalt, manganese, zirconium and ruthenium (Table 2). The conversions and selectivities vs. hours-on-stream data are summarized in Figures A-8 to A-14. This catalyst was more active than the similar but ruthenium-free catalyst No. 6531-194 (tested in Run 89). However, as opposed to Run 89, there was a notable activity loss during the short run. At the end of Run 91, the initial conditions were restored and the catalyst performance appeared to have stabilized at about 59% carbon monoxide conversion, a conversion still considerably higher than the 18% carbon monoxide conversion observed in Run 89. The reason for the activity loss is under investigation.

At the end of Run 91, the CO conversion was the same as that of the reference catalyst (Run 65) under similar conditions; however, there were differences in selectivities. The selectivity to light products was higher with catalyst 6531-196. Furthermore, the selectivity to ethanol was also higher (Table 4). The ethanol selectivity appeared to increase as the catalyst aged.

The level of ruthenium on the catalyst 6531-196 was relatively high (1.2 wt%). Two catalysts were prepared with lower levels of ruthenium and tested in Run 92 and 93.

Runs 92 and 93

The catalysts, 6531-202 and 6531-204, evaluated in Runs 92 and 93 were prepared on separate batches of the same support that was used in the preparation of catalyst 6531-196. These catalysts contained, respectively, 0.3 and 0.07 wt% ruthenium. During Runs 92 and 93, only one condition change was made: a lowering of the space velocity from 4.9 to 2.45 NL/hr/g Co at 70 hours-on-stream. Selectivities and conversions for Run 92 and Run 93 are summarized in Figures A-15 to A-23 and Figures A-24 to A-30, respectively.

Performance of catalysts 6531-202 and 6531-204 was similar to that of catalyst 6531-196. All of these three catalysts were more active initially than the ruthenium-free catalyst 6531-194. Catalyst 6531-204, containing 0.07 wt% ruthenium appeared to lose activity slightly faster than catalyst 6531-202 which contains 0.3 wt% ruthenium. This is illustrated by the observed CO conversion of 80% at 120 hours-on-stream in Run 92 (for catalyst 6531-202) compared to 70% in Run 93 (for catalyst 6531-204). This two catalysts exhibited similar selectivity to various products.

Summary and Implications for Further Work

Unlike the cobalt-ruthenium catalyst 6531-175, tested in Run 78, (Technical Progress Report No. 11), wherein no increase in activity was noted due to ruthenium, three new cobalt-ruthenium catalysts (No. 6531-196, -202, and -204) have shown more activity than a similar but ruthenium-free catalyst (No. 6531-194). These three catalysts lost activity over a short run, whereas catalyst 6531-194 did not. However, the rate of loss of activity of the three catalysts had slowed significantly by the end of the run, and at this point they were still much more active than the ruthenium-free catalyst. All catalysts were prepared on amorphous silica supports resulting from acid-washing of steamed Y zeolite. Making an amorphous silica support is not

desirable; however, such supports were obtained because of the acid-washing which was inadvertently too extensive.

All three ruthenium-containing catalysts, No. 6531-196, -202, and -204, were of similar initial activity even though the amount of ruthenium varied from 1.2 to 0.07 wt%. Among the two lower ruthenium catalysts, No. 6531-202 and -204, the rate of loss of activity seemed greater with the catalyst 6531-204 containing 0.07 wt% ruthenium.

The ruthenium-free catalyst (No. 6531-194) was not as active as the ruthenium-free reference catalyst (TC 211) prepared under the previous DOE-Union Carbide contract (No. DE-AC22-84PC70028) even though the amounts of metals, the calcination and the reduction were similar. It is possible that the difference in activity of these two catalysts was due to the supports being different. The reference catalyst was prepared on a less extensively acid-washed material which retained most of the crystallinity of the steamed Y zeolite. Future catalysts will be prepared on less extensively acid-washed supports. Such material should retain most of the crystallinity of the steamed Y zeolite and also have accessible 50-100Å pores within the crystal structure. Hopefully more active and less methane selective (stable) catalysts will result.

Table 1
Key Operating Variables for the Three Condition Test

	Condition 1	Condition 2	Condition 3
Pressure, psig	287	287	287
Temperature, °C	211	231	231
Feed rate, (NL/hr/g Co)	4.9	4.9	2.5

Table 2
Support Properties and Catalyst Composition

Support Properties					Catalyst No.	Run No.	Metals, AAS, wt-%			
Treatments	SA ¹	PV ²	Al ³	X-ray			Co	Mn	Zr	Ru
Steamed/ HCl ⁴	143	0.45	0.35	Amorphous ⁵	6531-194	89	11.1	1.1	1.5	
					6531-196	91	9.8	1.2	0.6	1.2
Steamed/ HCl ⁴	145	0.47	0.35	Amorphous ⁵	6531-202	92	8.5	1.7	0.5	0.3
					6531-204	93	9.1	1.8	0.5	0.07

¹ Surface area in m²/g
² Pore volume in cc/g
³ wt-%
⁴ Wash 72 hr With 4M HCl
⁵ X-ray showed only broad peaks indicative of an amorphous structure

Table 3
Activity and Hydrocarbon Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Hydrocarbon Selectivity, %				
			C ₁	C ₂	C ₂ ⁻	C ₃	C ₃ ⁻
65	1	58	7	0.6	0	1.7	2.0
89	1	18	15	0.9	0	2.0	6.0
	2	85	8.5	0.9	0	1.7	1.8
	3	90	6.5	0.9	0	1.5	1.6
91	1(initial)	90 → 82	11	1.6	0	3.0	2→3
	1(end of run)	59	15	1.7	0	3.7	4
92	1	92 → 78	10→12	1.5→2	0	2.5→3	2.5→4
93	1	90 → 80	9→10	1→1.8	0	2→2.9	2→3.5

Table 4
Activity and Alcohol Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Alcohol Selectivity, %		
			C ₂	C ₃	C ₄
65	1	58	0.5	0.6	2.0
89	1	18	3.7	1.0	0.8
	2	85	0.2	0.2	0.2
	3	90	0	0.1	0.2
91	1 (initial)	90 → 82	0.7	0.3	0.5
	1 (end of run)	59	4.0	0.8	1.5
92	1	92 → 78	1.3	0.7	2.0
93	1	90 → 80	1.5	0.8	1.8

APPENDIX A
CATALYST PERFORMANCE DATA
RUN SUMMARY

FIGURE A-1

PLT 700A RUN 89 Co, Mn, Zr on HCl washed Y
6531-194 w/11.1% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

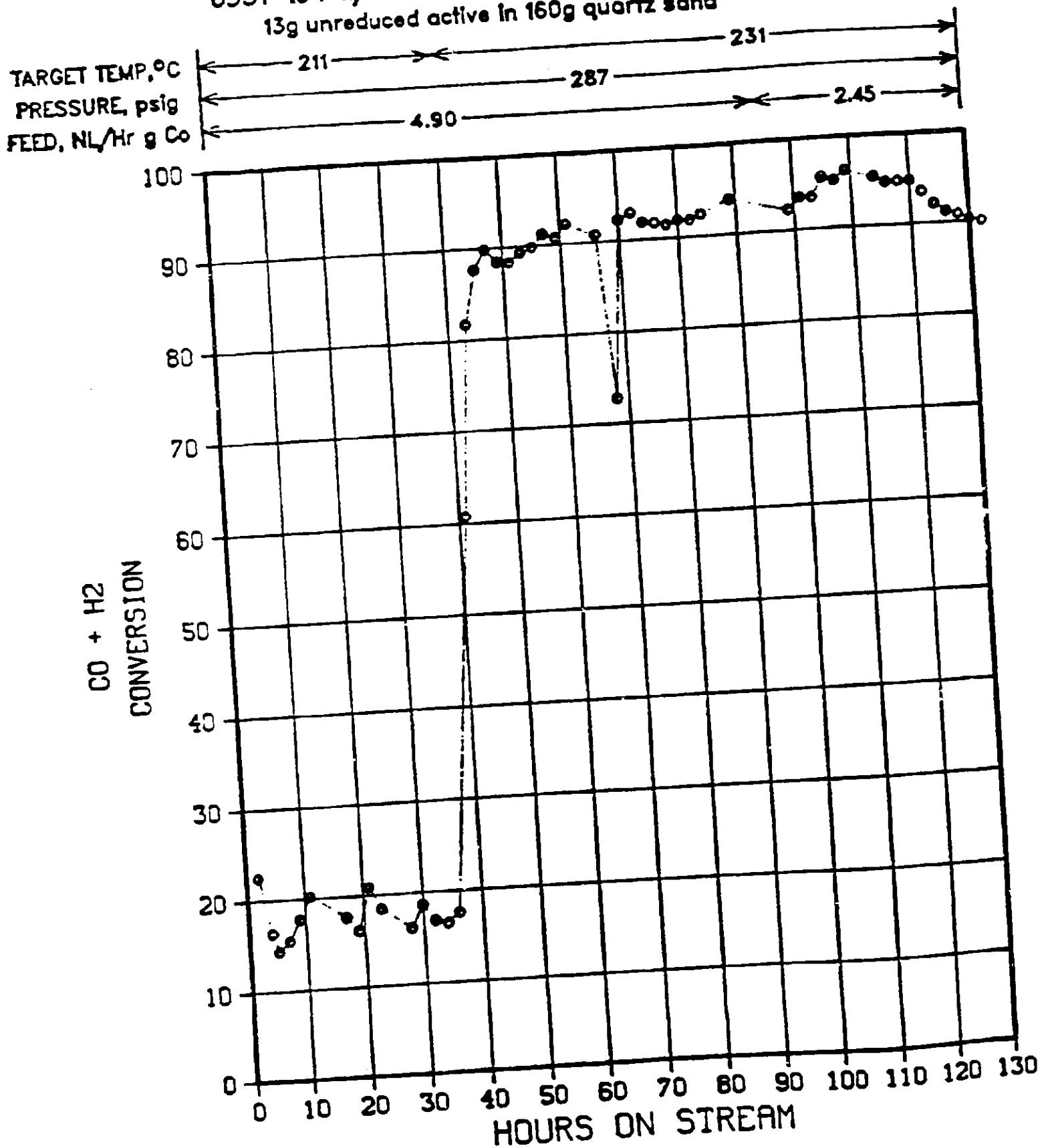


FIGURE A-2

PLT 700A RUN 89 Co, Mn, Zr on HCl washed Y
 6531-194 w/11.1% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

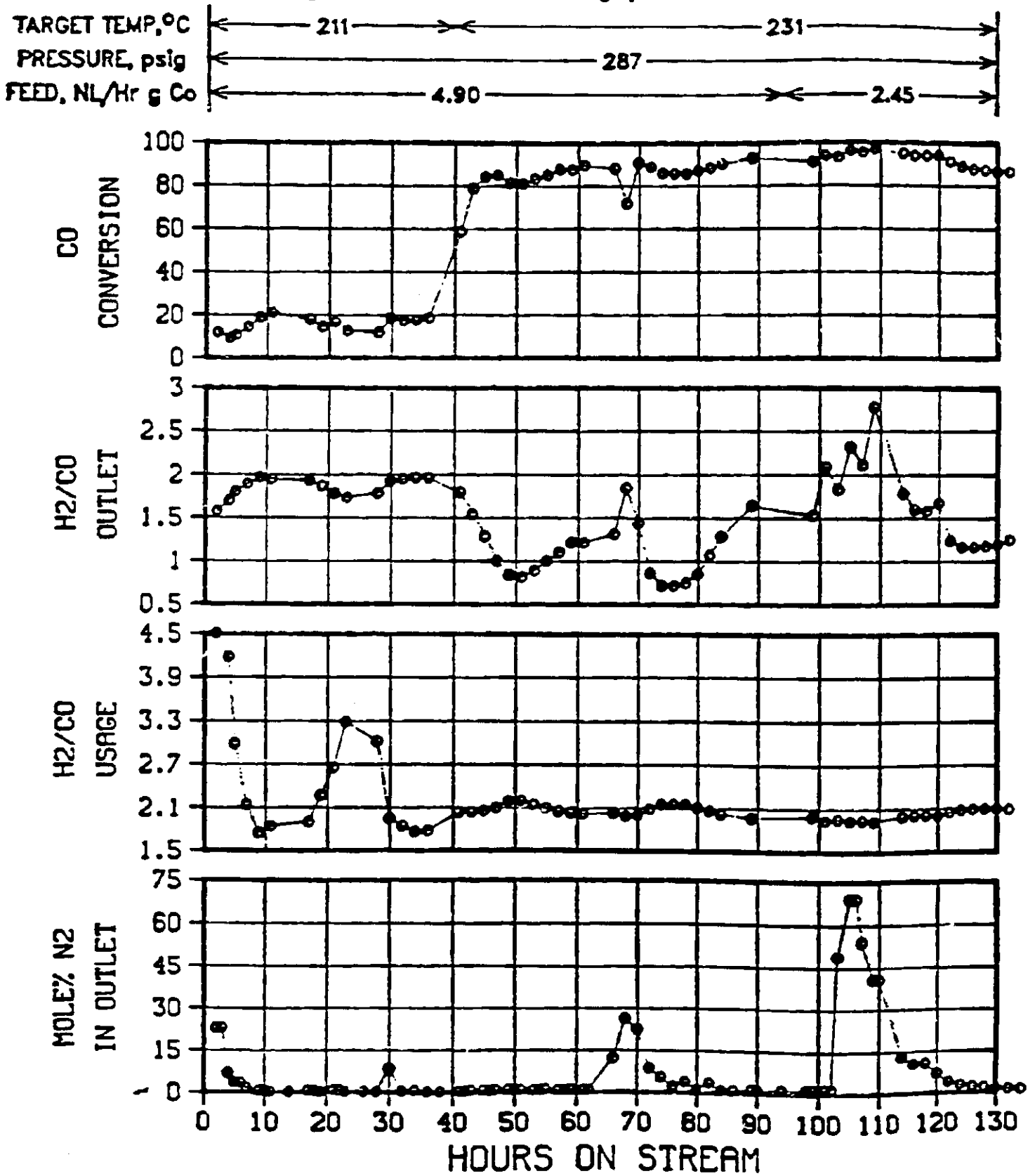


FIGURE A-3

PLT 700A RUN 89 Co, Mn, Zr on HCl washed Y
6531-194 w/11.1% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

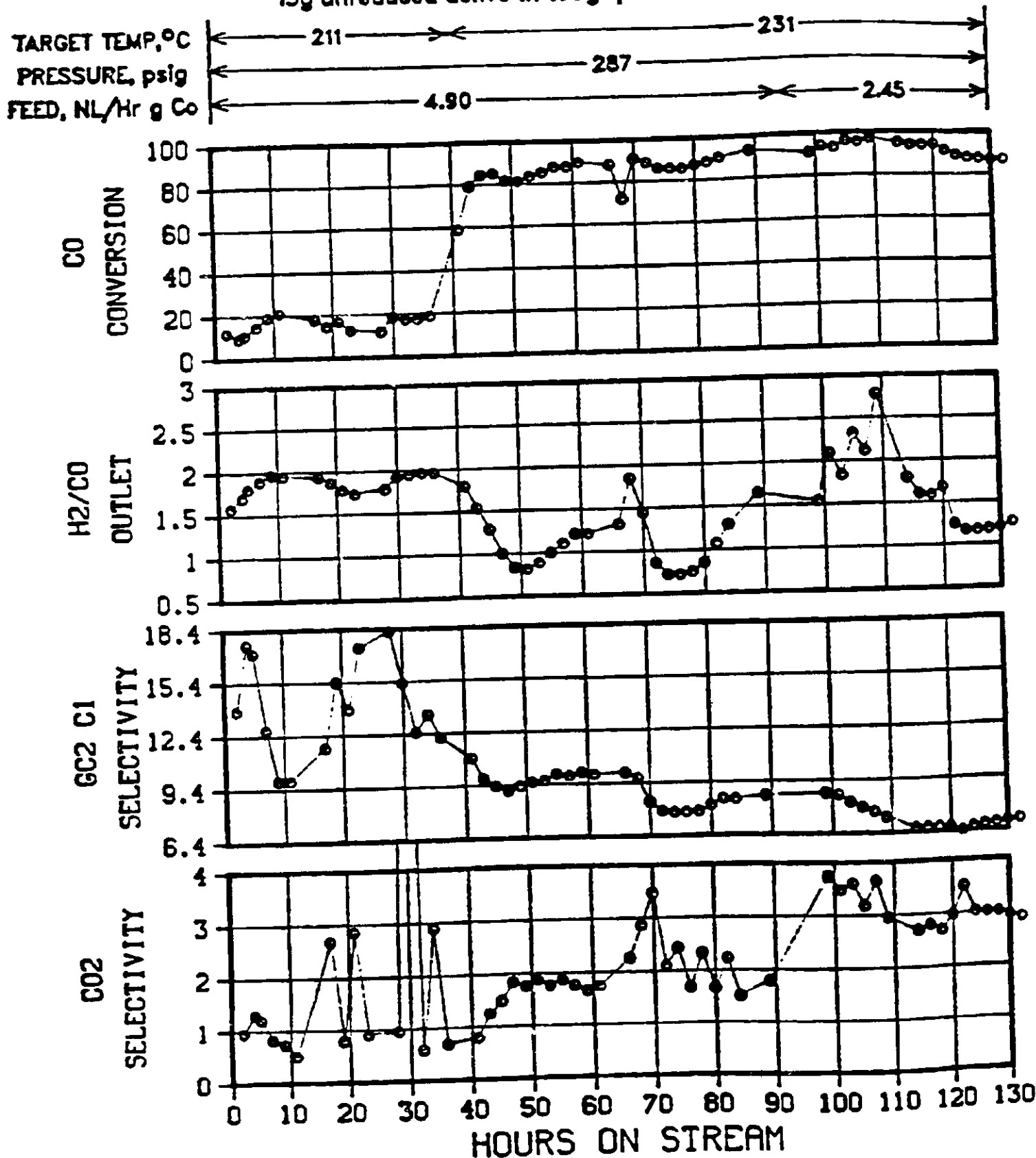


FIGURE A-4
PLT 700A RUN 89 Co,Mn,Zr on HCl washed Y
6531-194 w/11.1 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

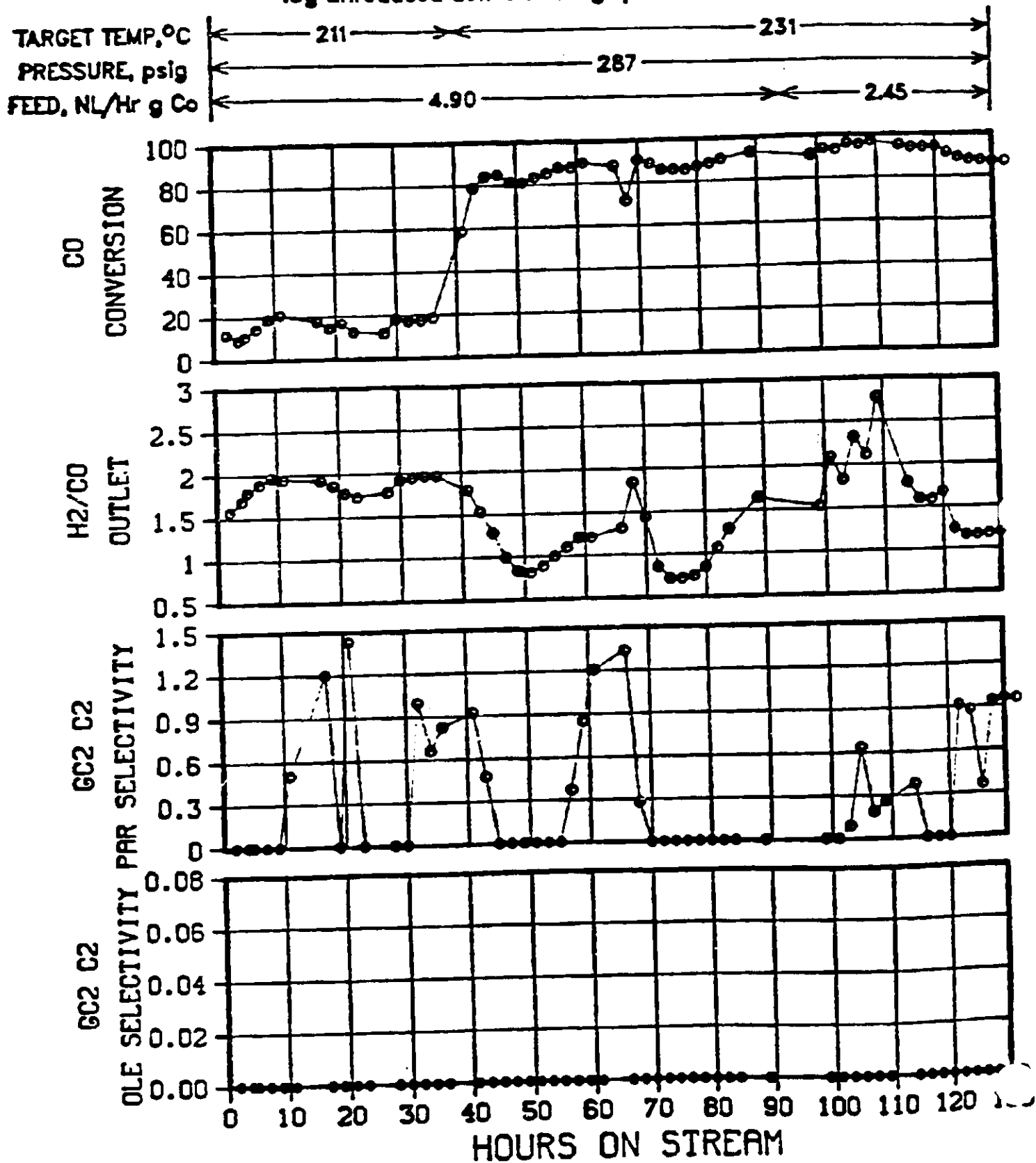


FIGURE A-5

PLT 700A RUN 89 Co, Mn, Zr on HCl washed Y

6531-194 w/11.1% Co via eth-glycol pore fill

13g unreduced active in 160g quartz sand

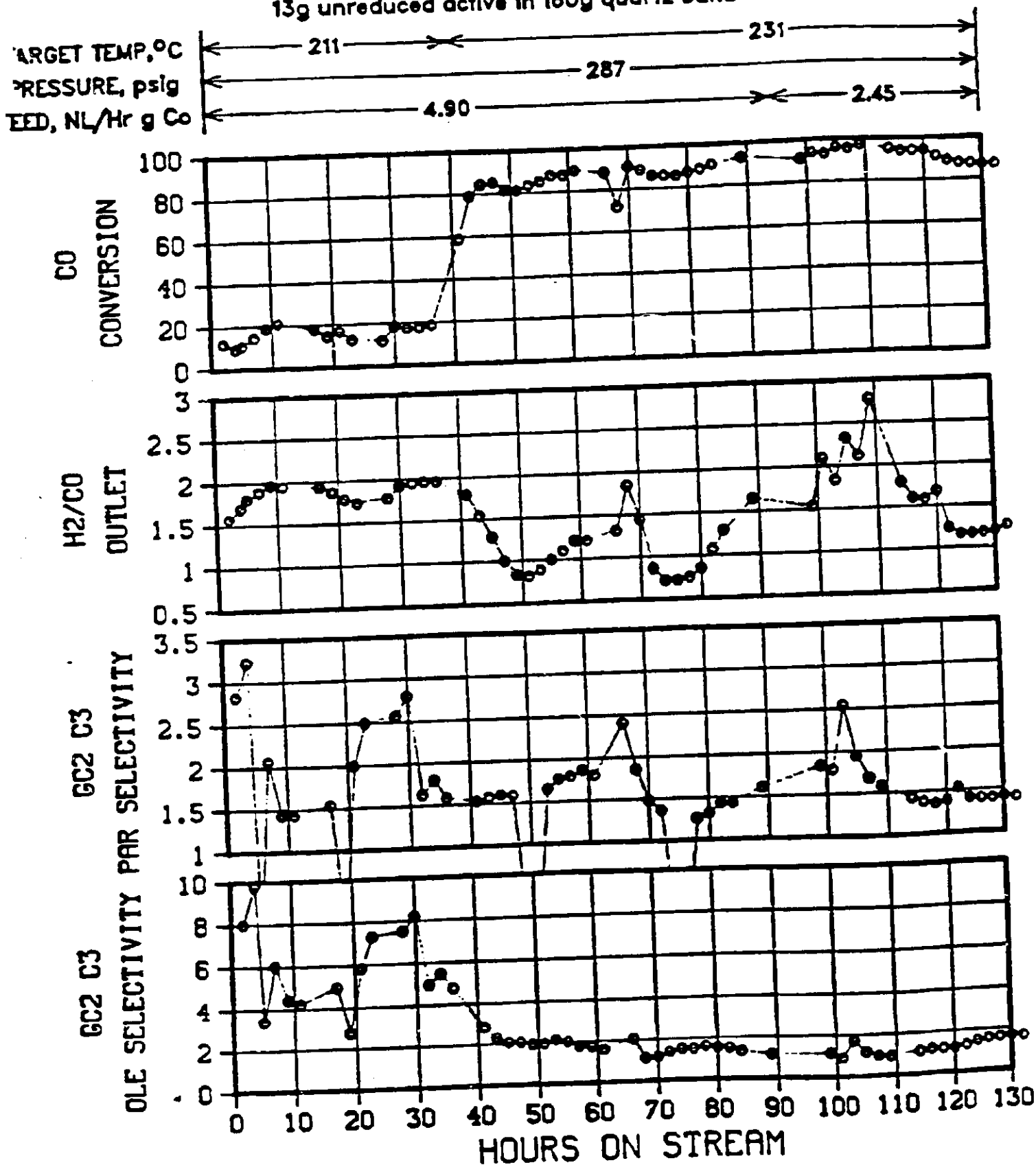


FIGURE A-6
PLT 700A RUN 89 Co,Mn,Zr on HCl washed Y
6531-194 w/11.1 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

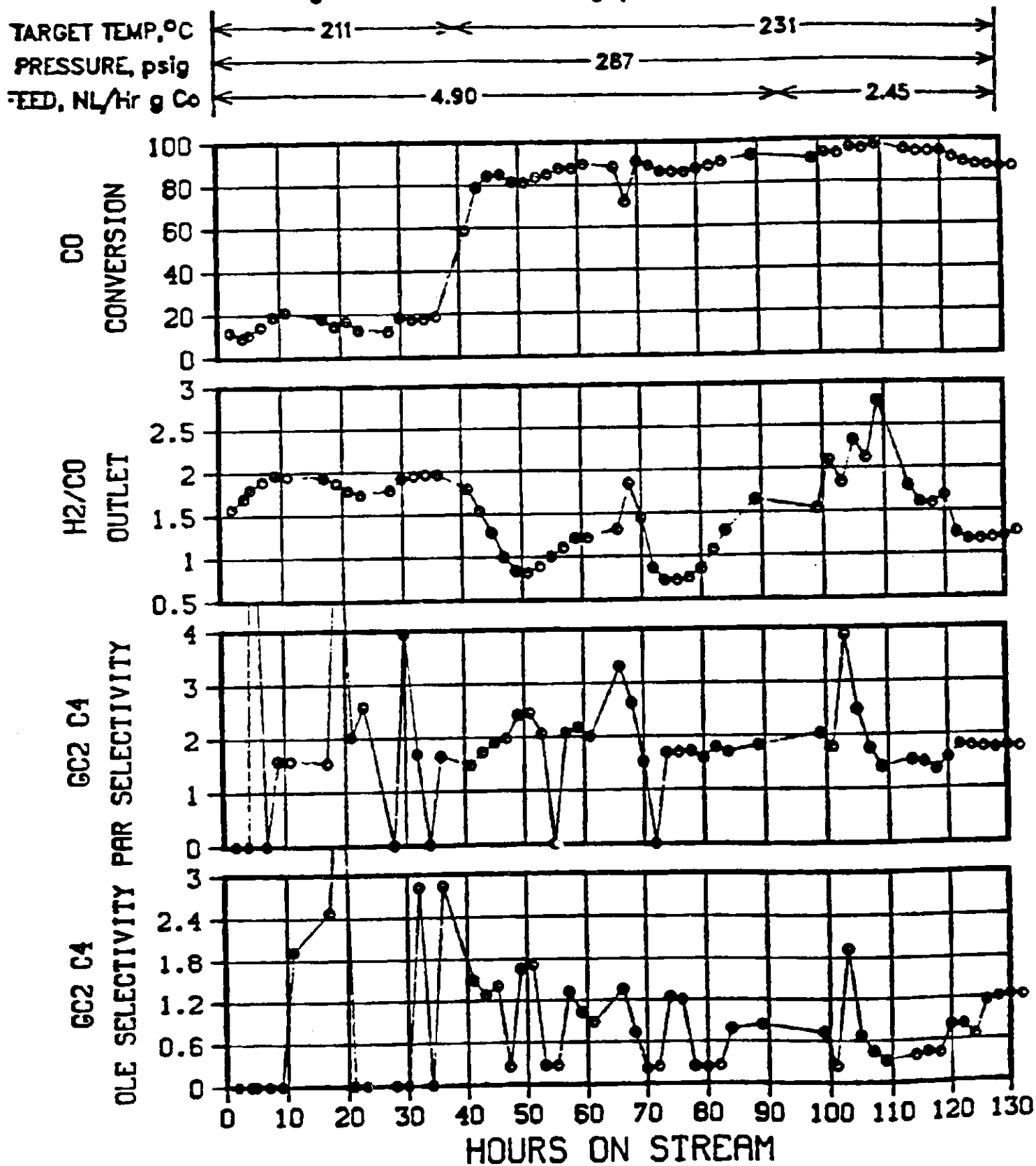


FIGURE A-7
PLT 700A RUN 89 Co, Mn, Zr on HCl washed Y
6531-194 w/11.1% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

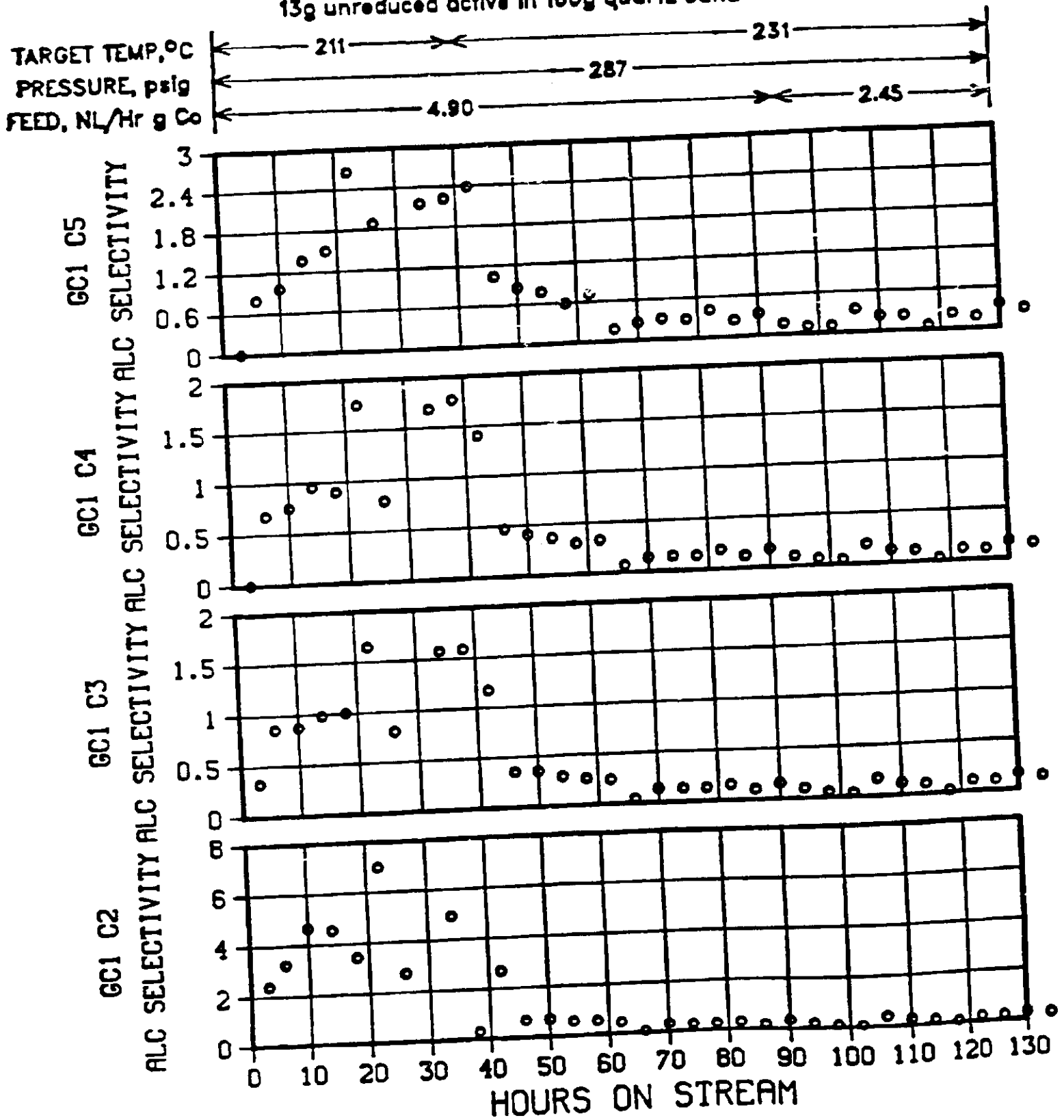


FIGURE A-8
PLT 700A RUN 91 Co,Mn,Zr,Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

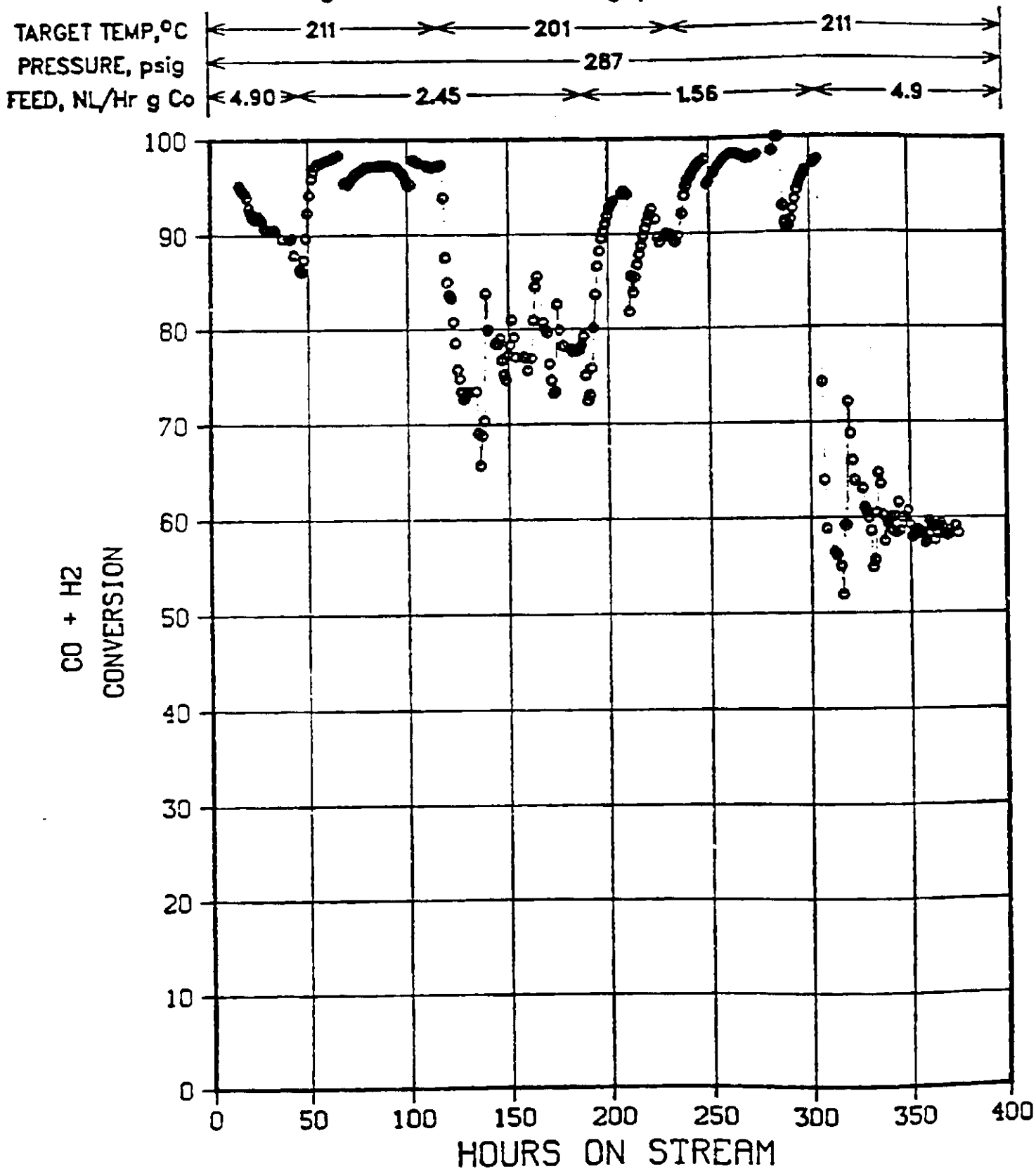


FIGURE A-9
PLT 700A RUN 91 Co, Mn, Zr, Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

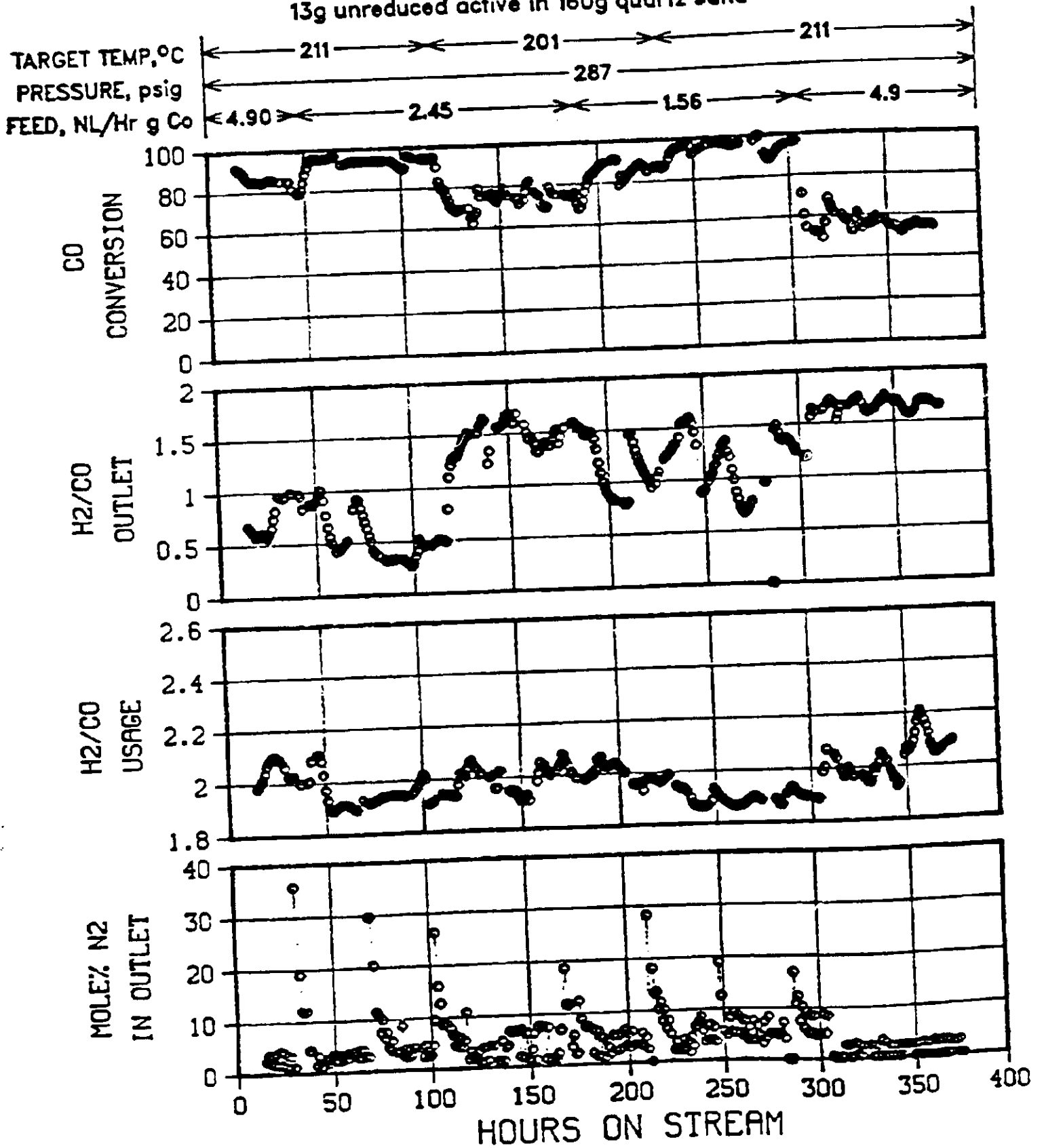


FIGURE A-10
PLT 700A RUN 91 Co,Mn,Zr,Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

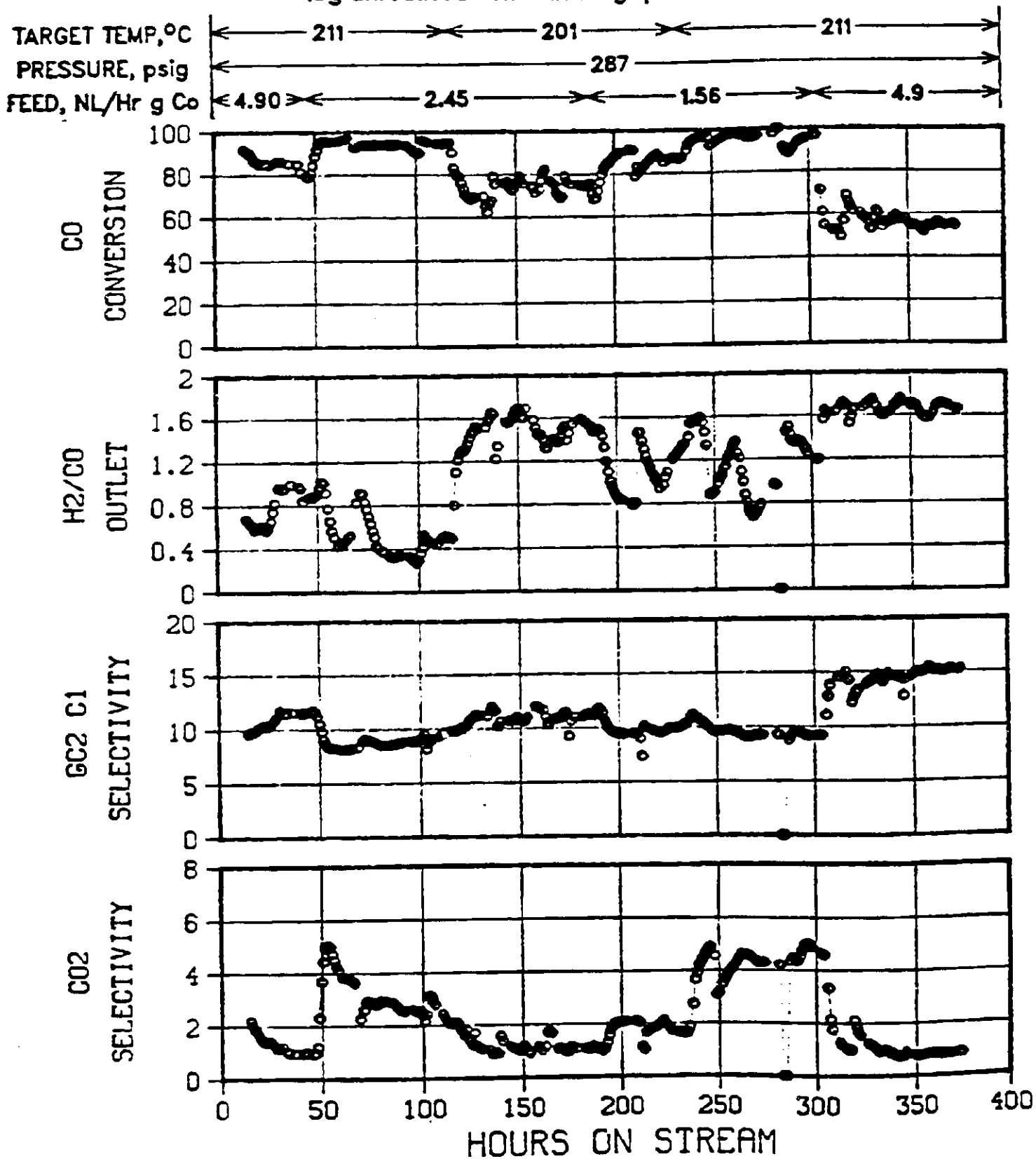


FIGURE A-11

PLT 700A RUN 91 Co,Mn,Zr,Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

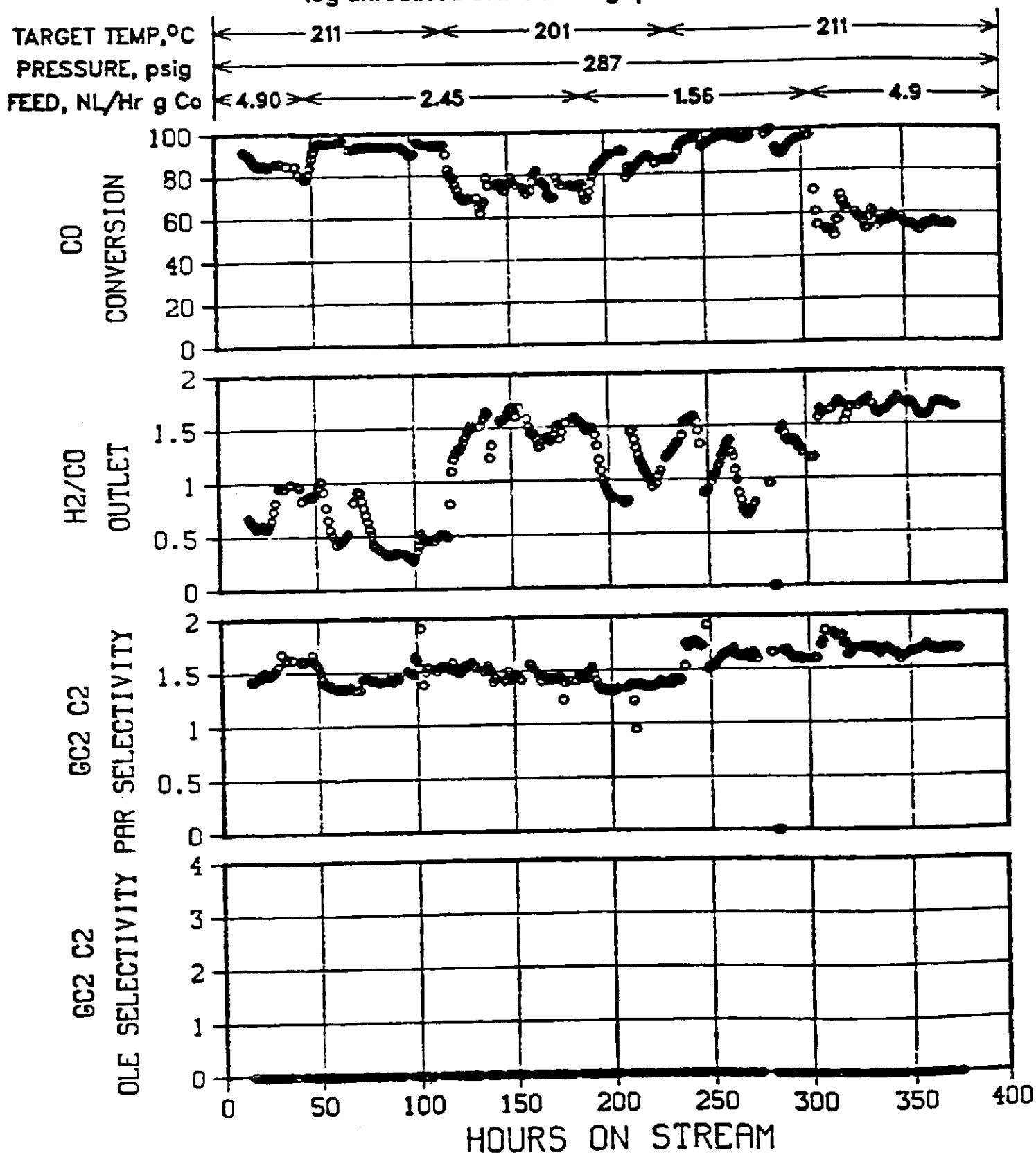


FIGURE A-12

PLT 700A RUN 91 Co,Mn,Zr,Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

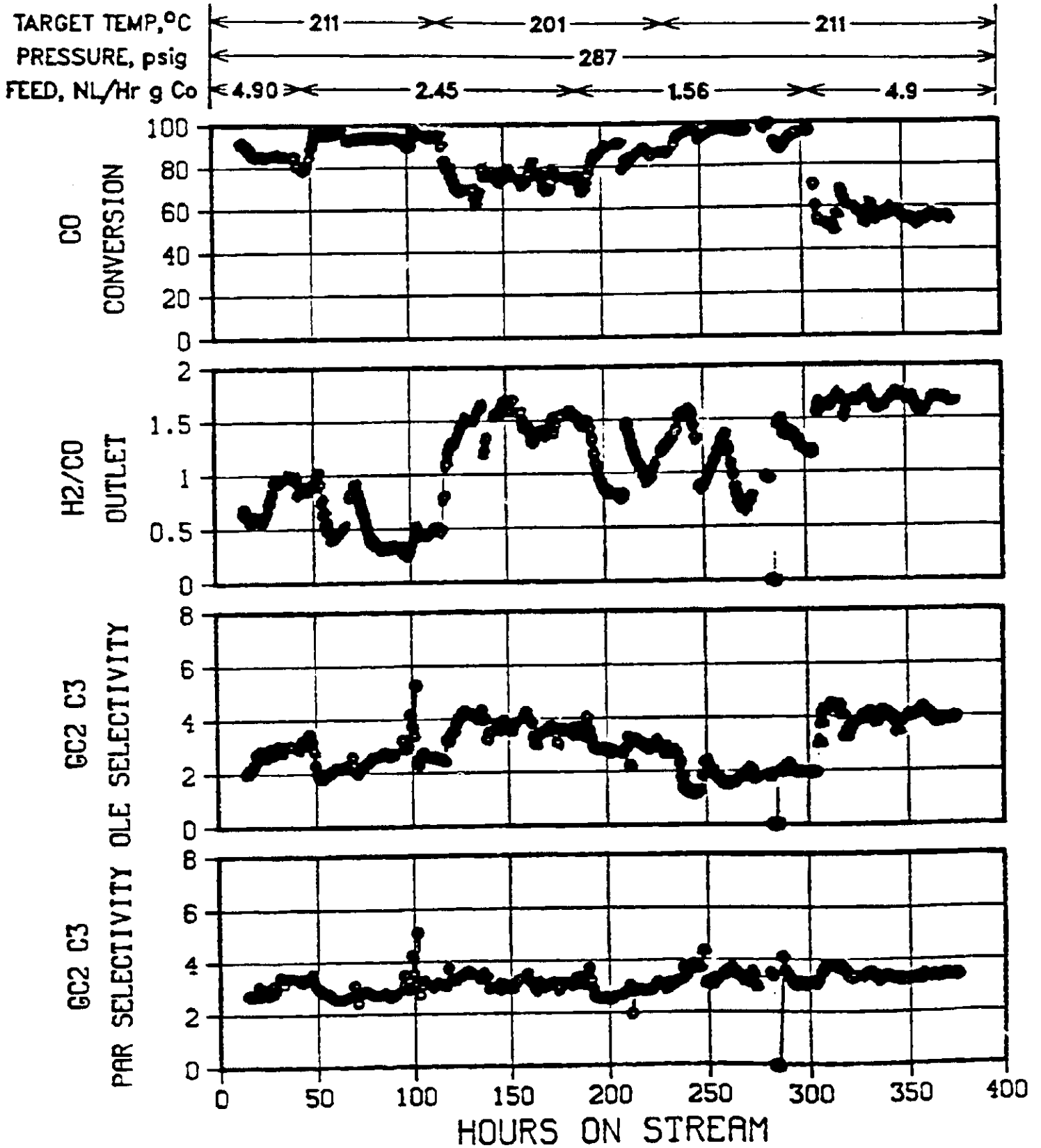


FIGURE A-13
PLT 700A RUN 91 Co,Mn,Zr,Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

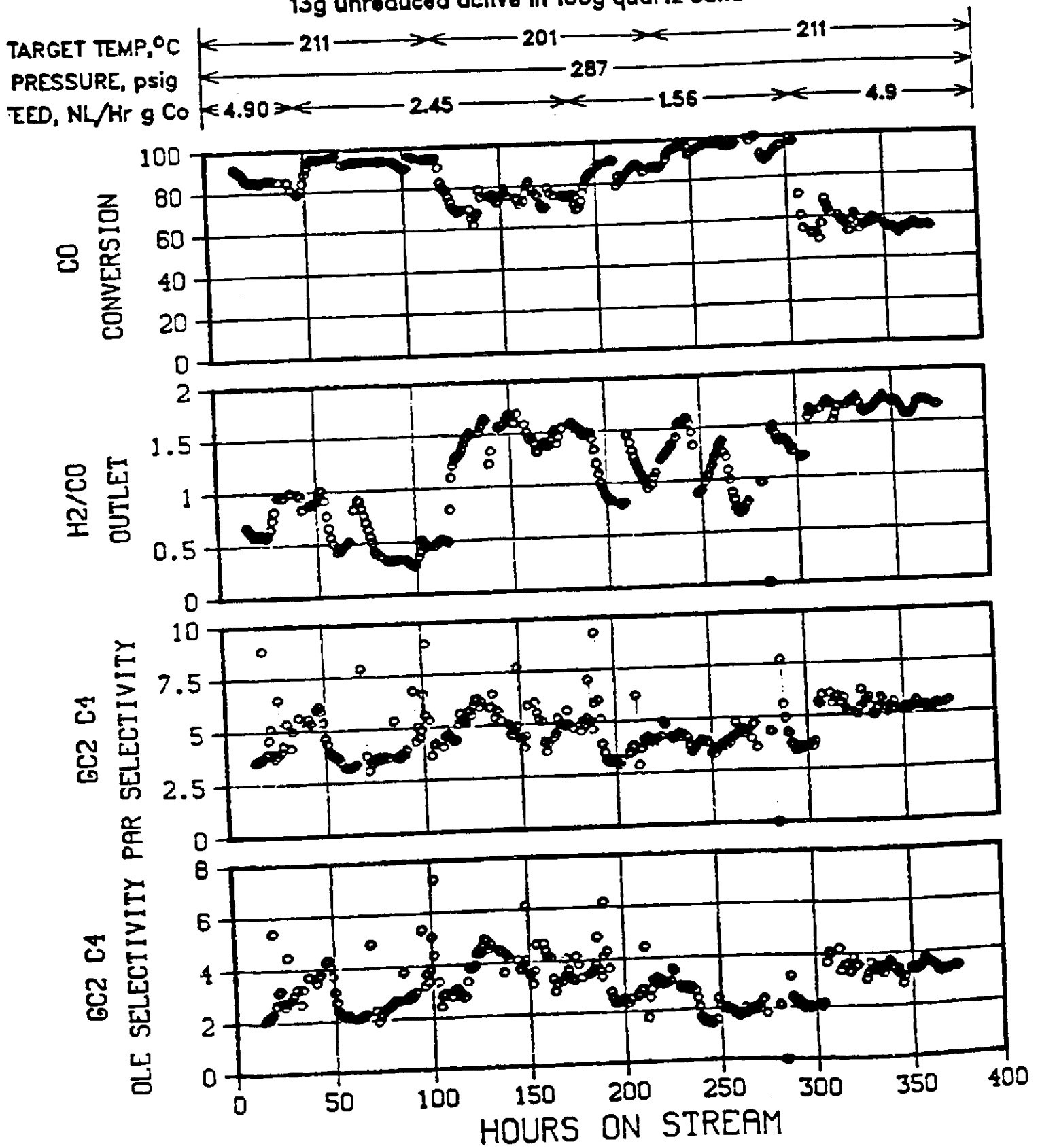


FIGURE A-14
PLT 700A RUN 91 Co,Mn,Zr,Ru on HCl washed Y
6531-196 w/9.76 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

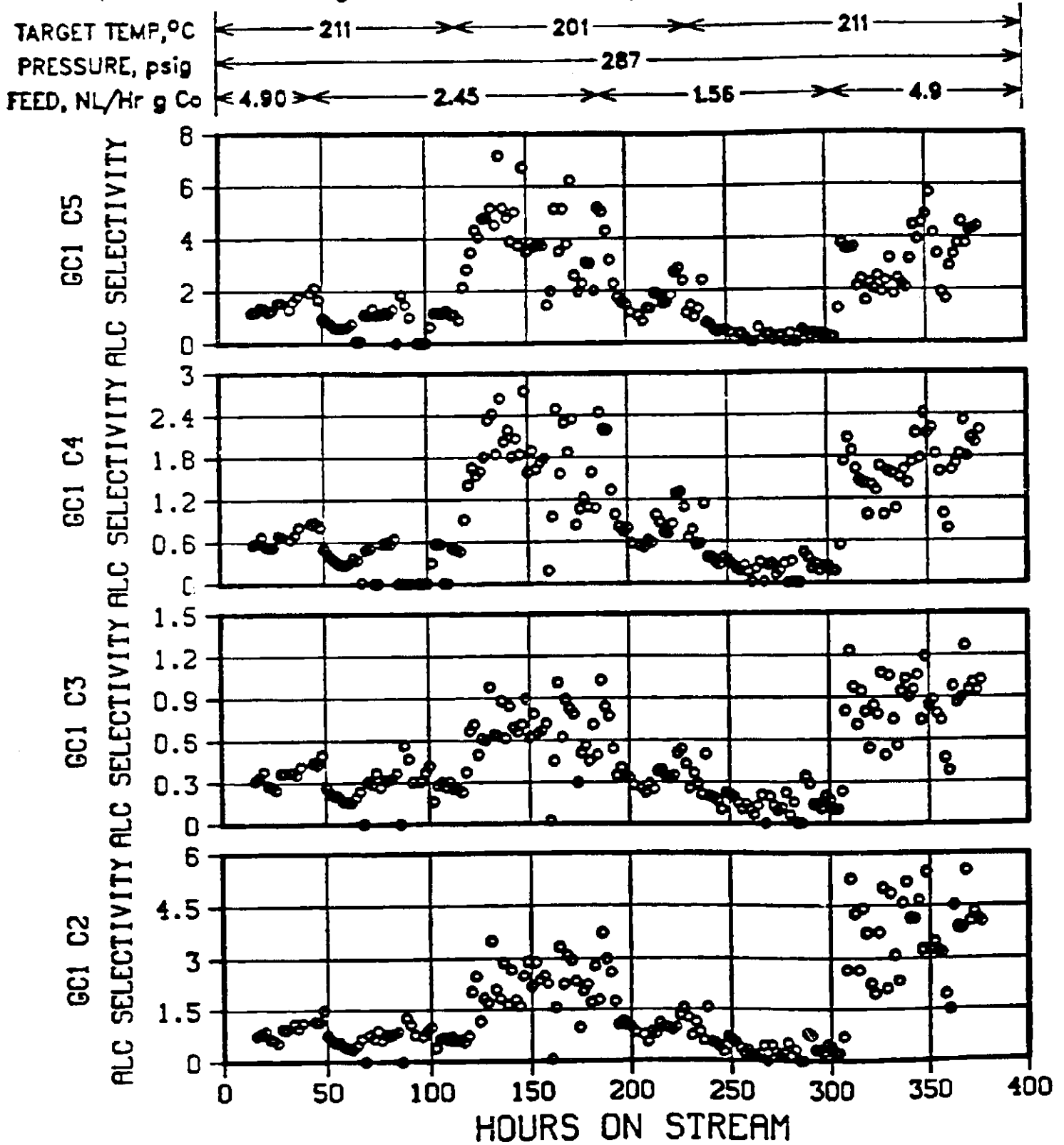


FIGURE A-15
PLT 700A RUN 92 Co,Mn,Zr,Ru on HCl Washed Y
 6531-202 w/8.51 % Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

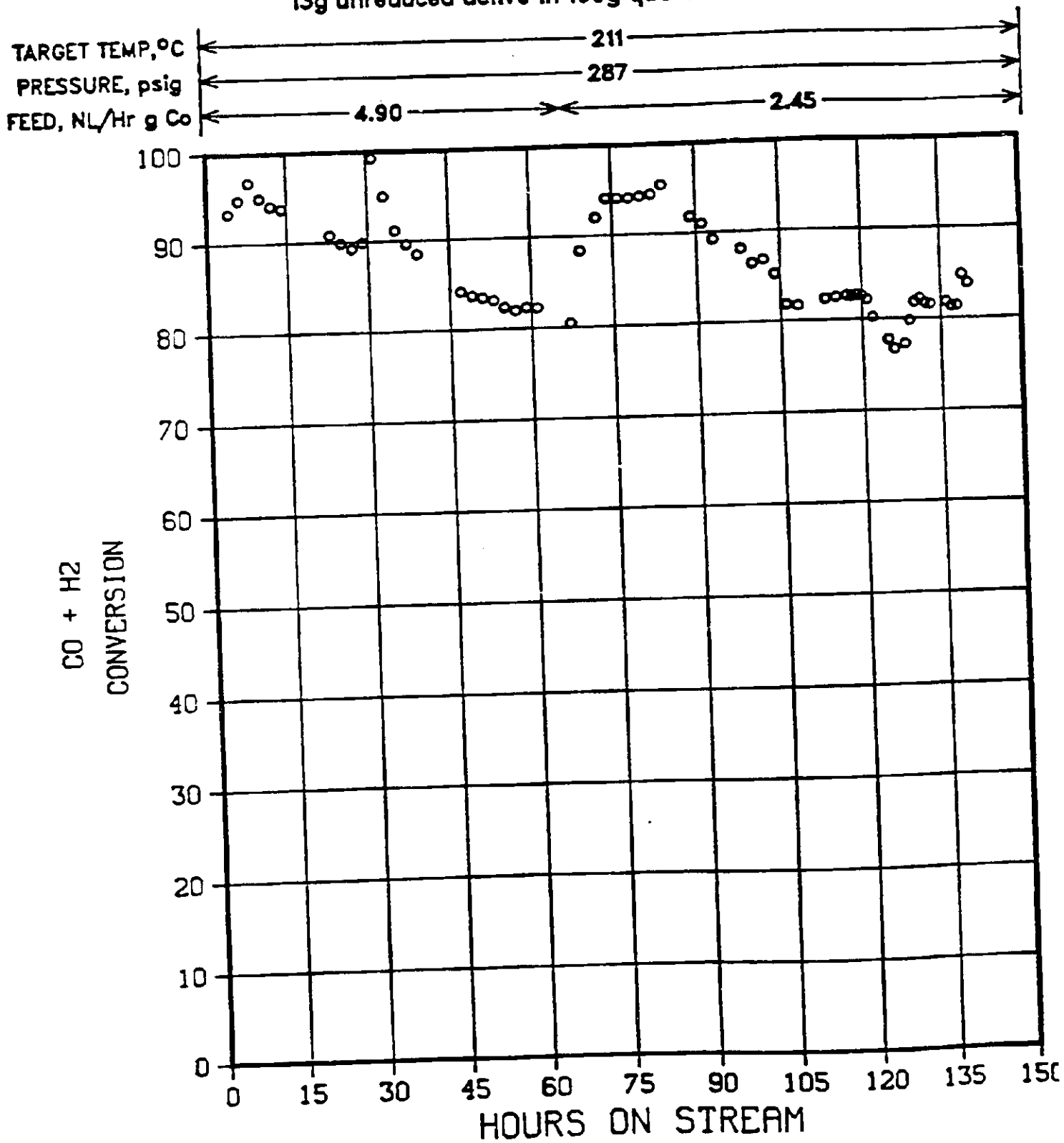


FIGURE A-16
PLT 700A RUN 92 Co,Mn,Zr,Ru on HCl Washed Y
 6531-202 w/B.51% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

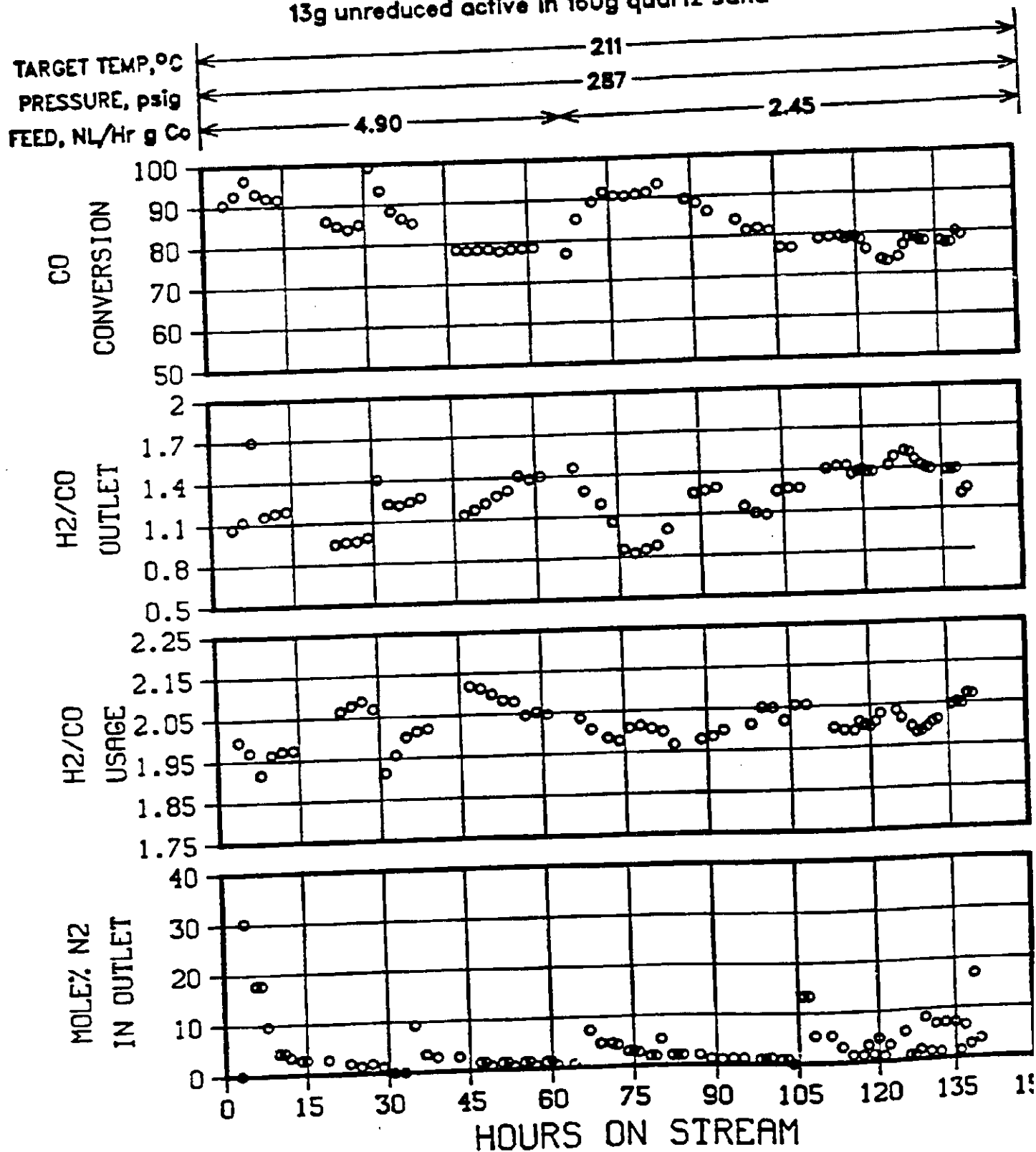


FIGURE A-17
PLT 700A RUN 92 Co,Mn,Zr,Ru on HCl Washed Y
 S531-202 w/8.51 % Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

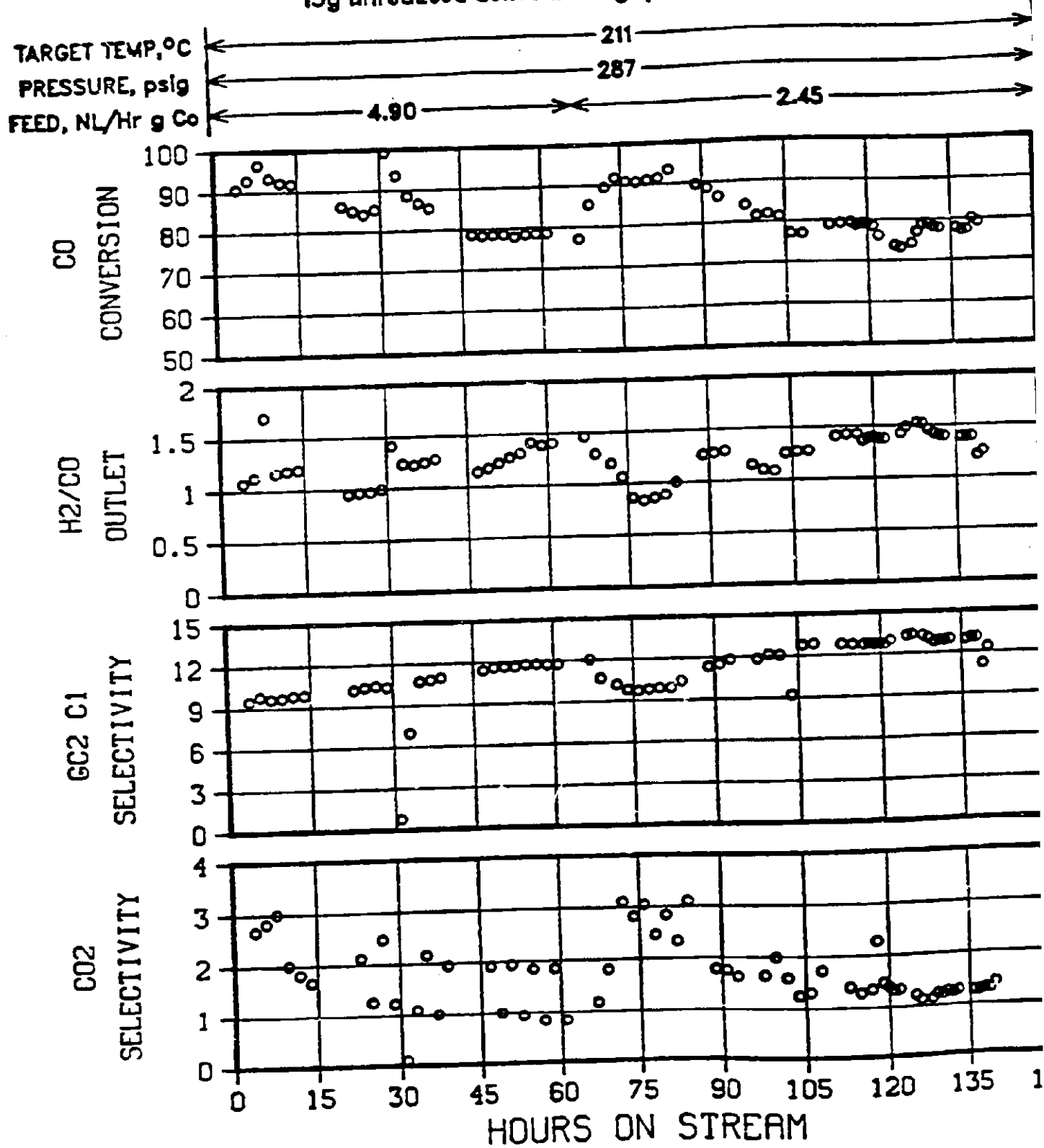


FIGURE A-18
PLT 700A RUN 92 Co, Mn, Zr, Ru on HCl Washed Y
 6531-202 w/8.51% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

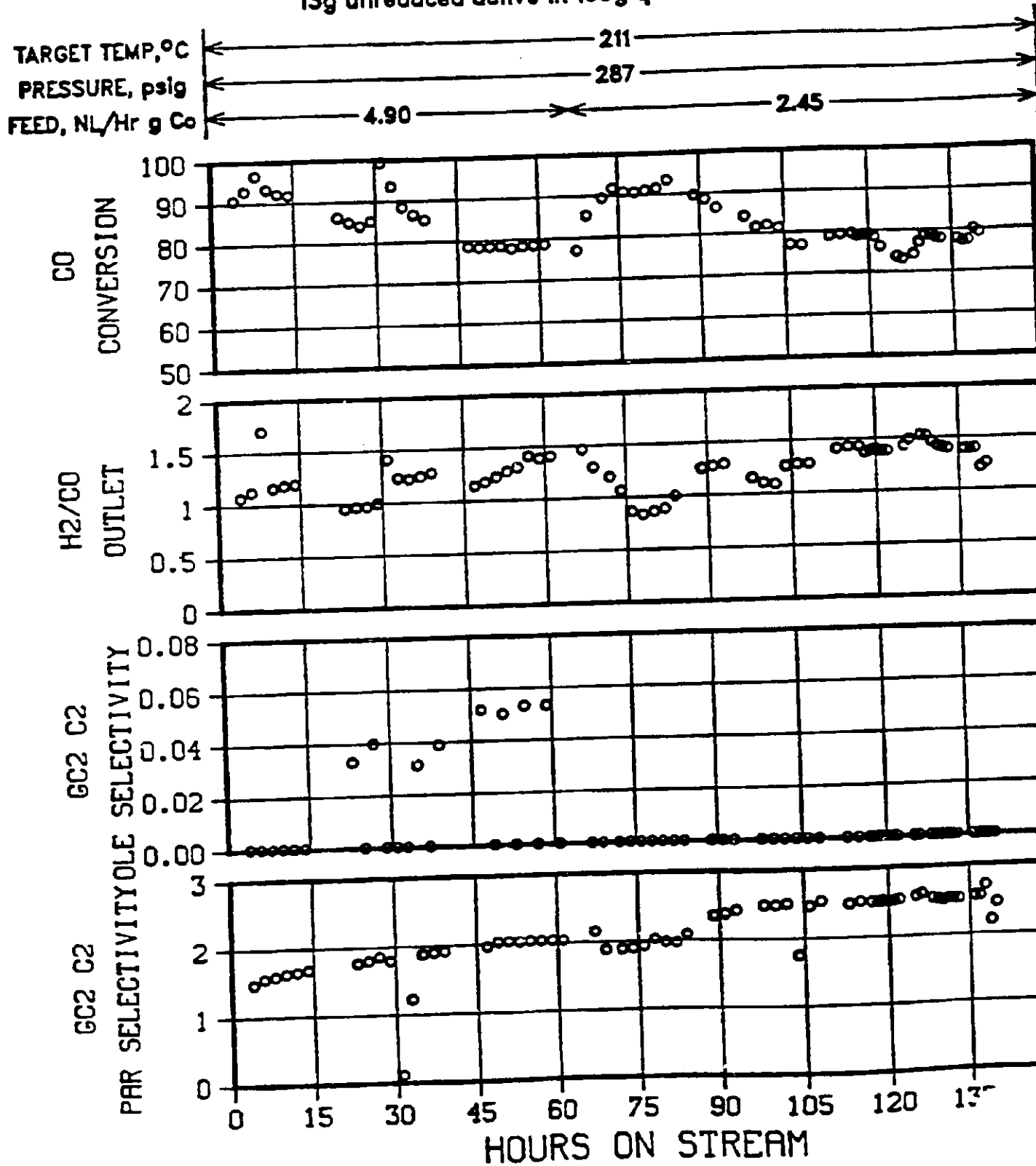


FIGURE A-21
PLT 700A RUN 92 Co,Mn,Zr,Ru on HCl Washed Y
 6531-202 w/8.51 % Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

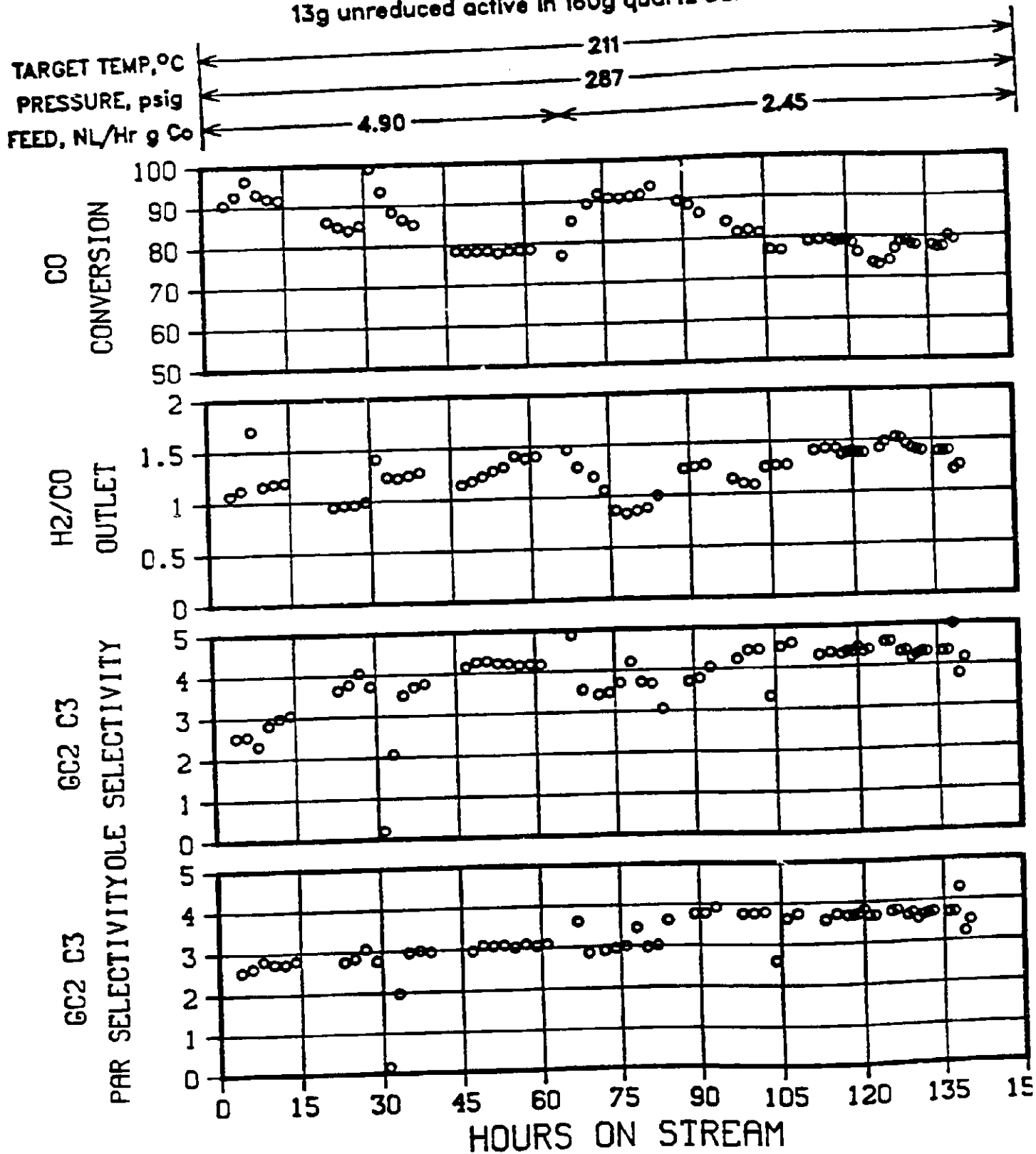


FIGURE A-22
PLT 700A RUN 92 Co,Mn,Zr,Ru on HCl Washed Y
 6531-202 w/8.51 % Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

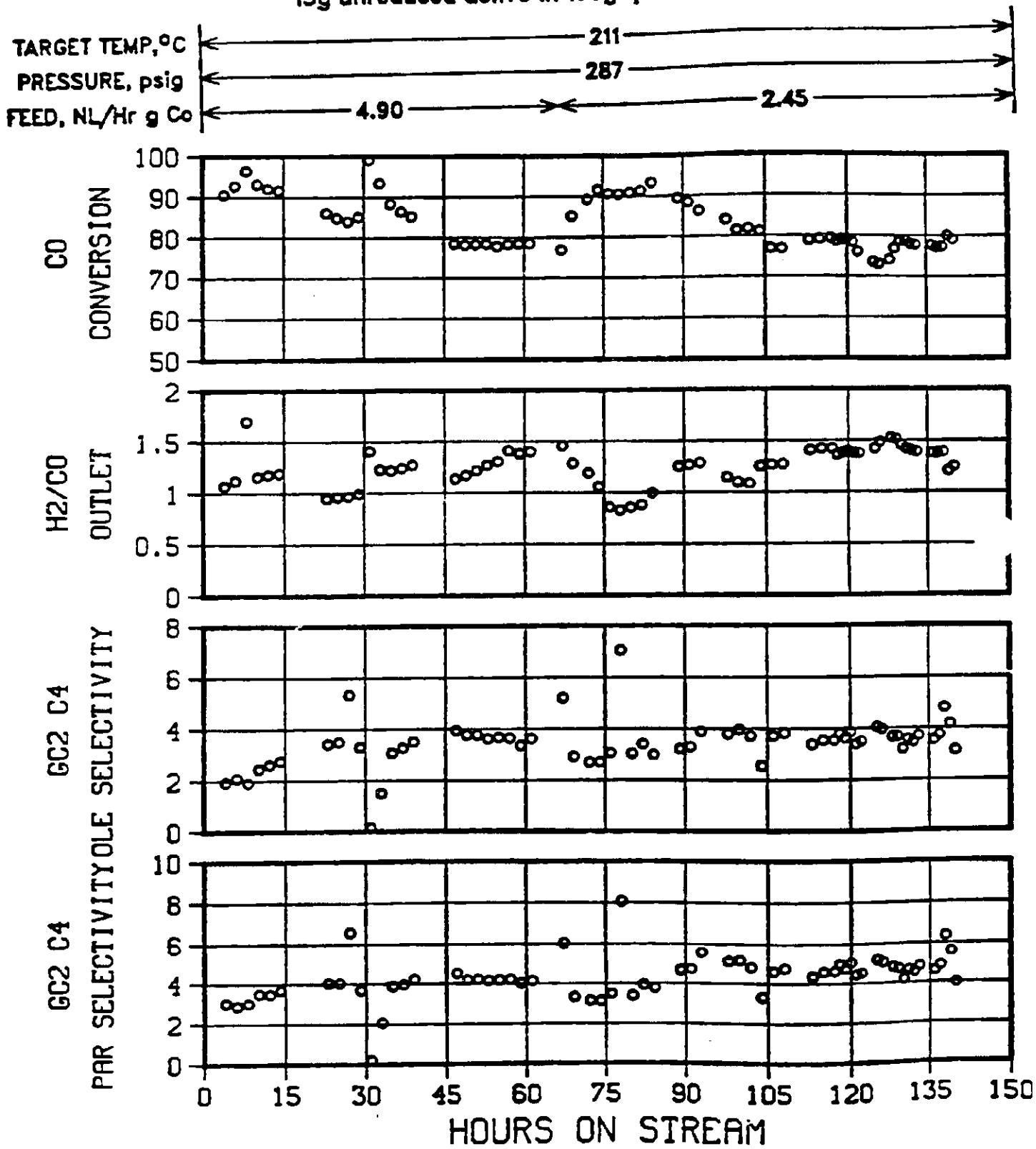


FIGURE A-23
PLT 700A RUN 92 Co, Mn, Zr, Ru on HCl Washed Y
 6531-202 w/8.51% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

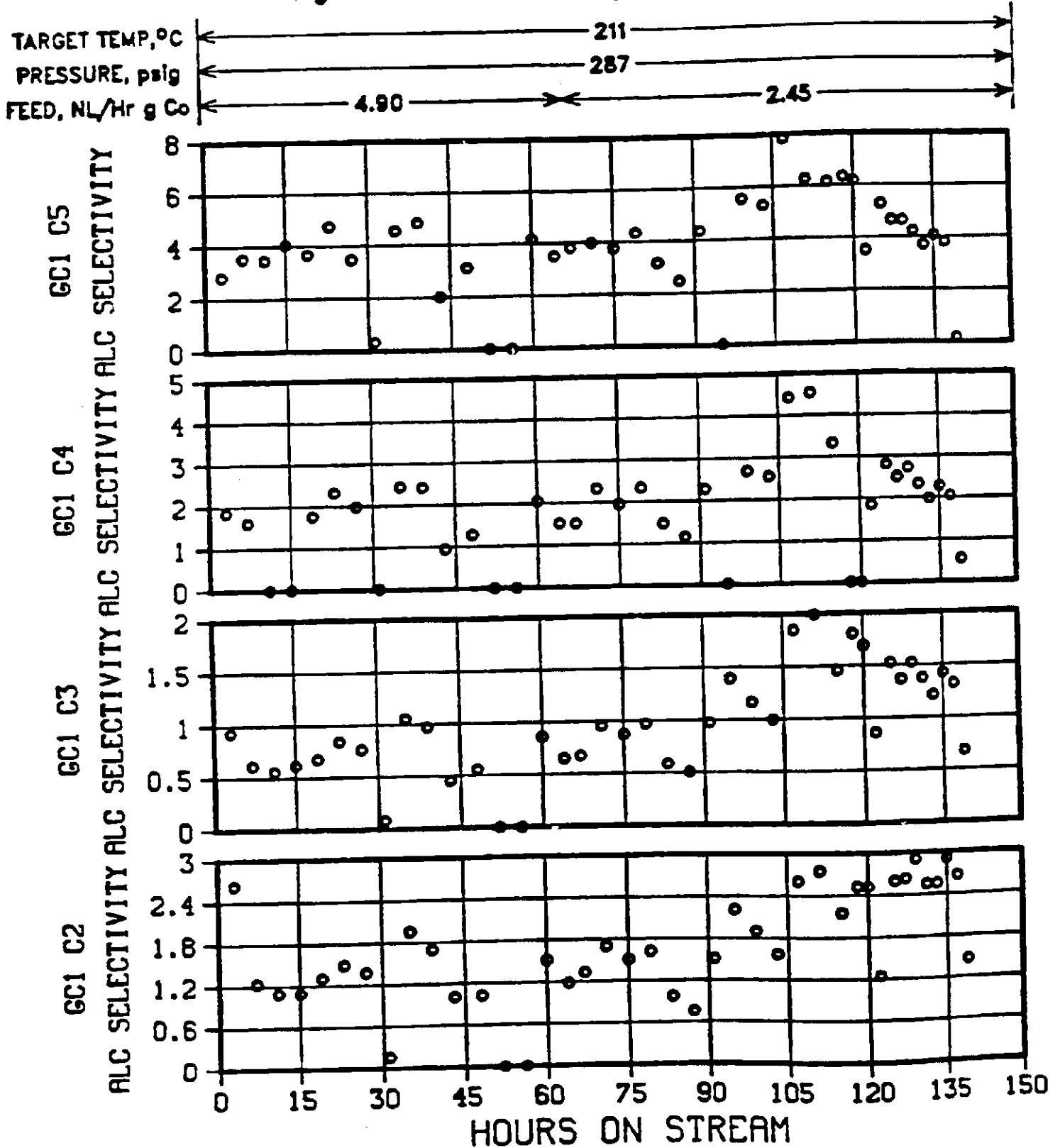


FIGURE A-24

PLT 700A RUN 93 Co,Mn,Zr,Ru on HCl Washed Y

6531-204 w/9.1% Co via eth-glycol pore fill

13g unreduced active in 160g quartz sand

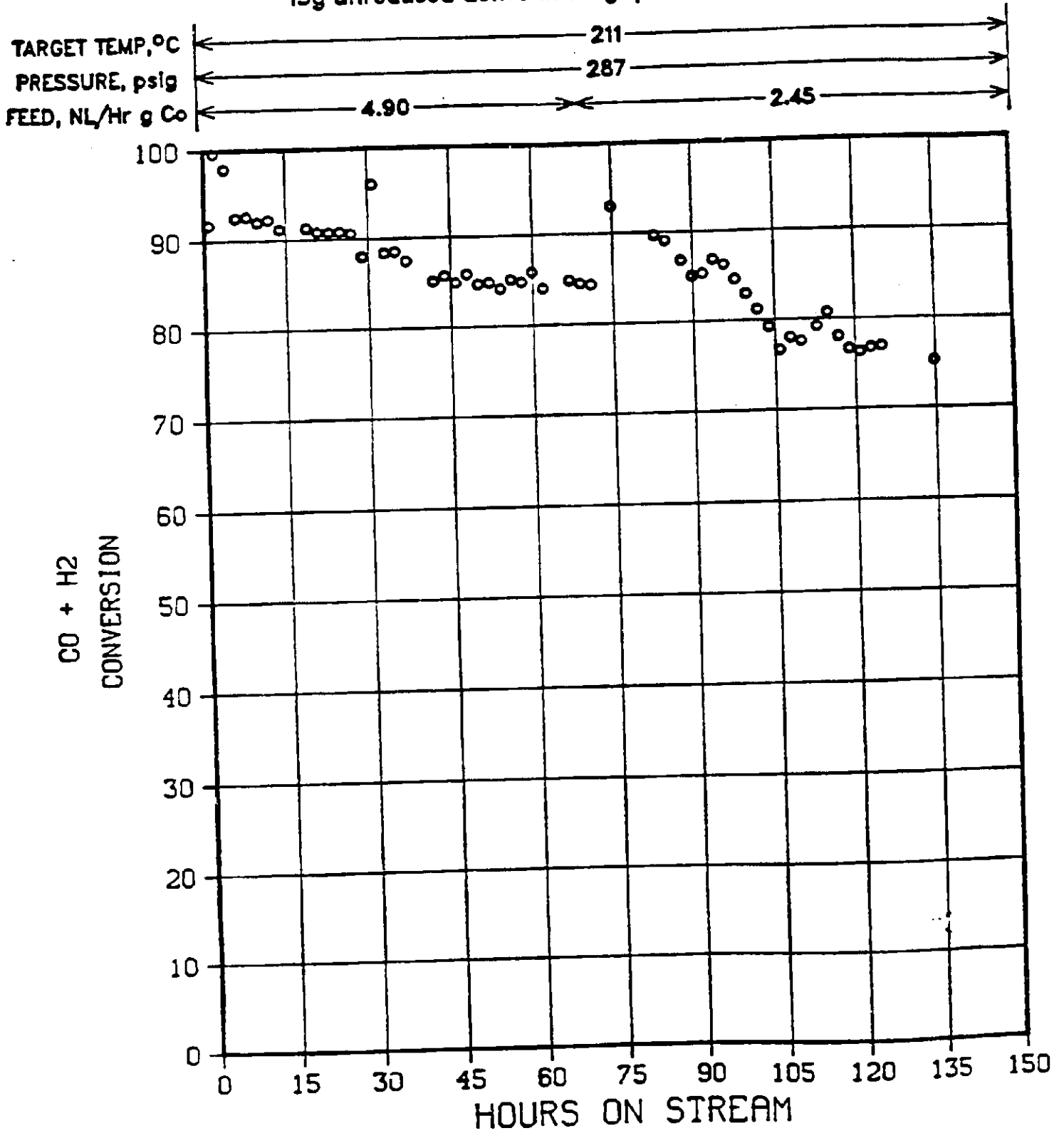


FIGURE A-25
PLT 700A RUN 93 Co,Mn,Zr,Ru on HCl Washed Y
 6531-204 w/9.1% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

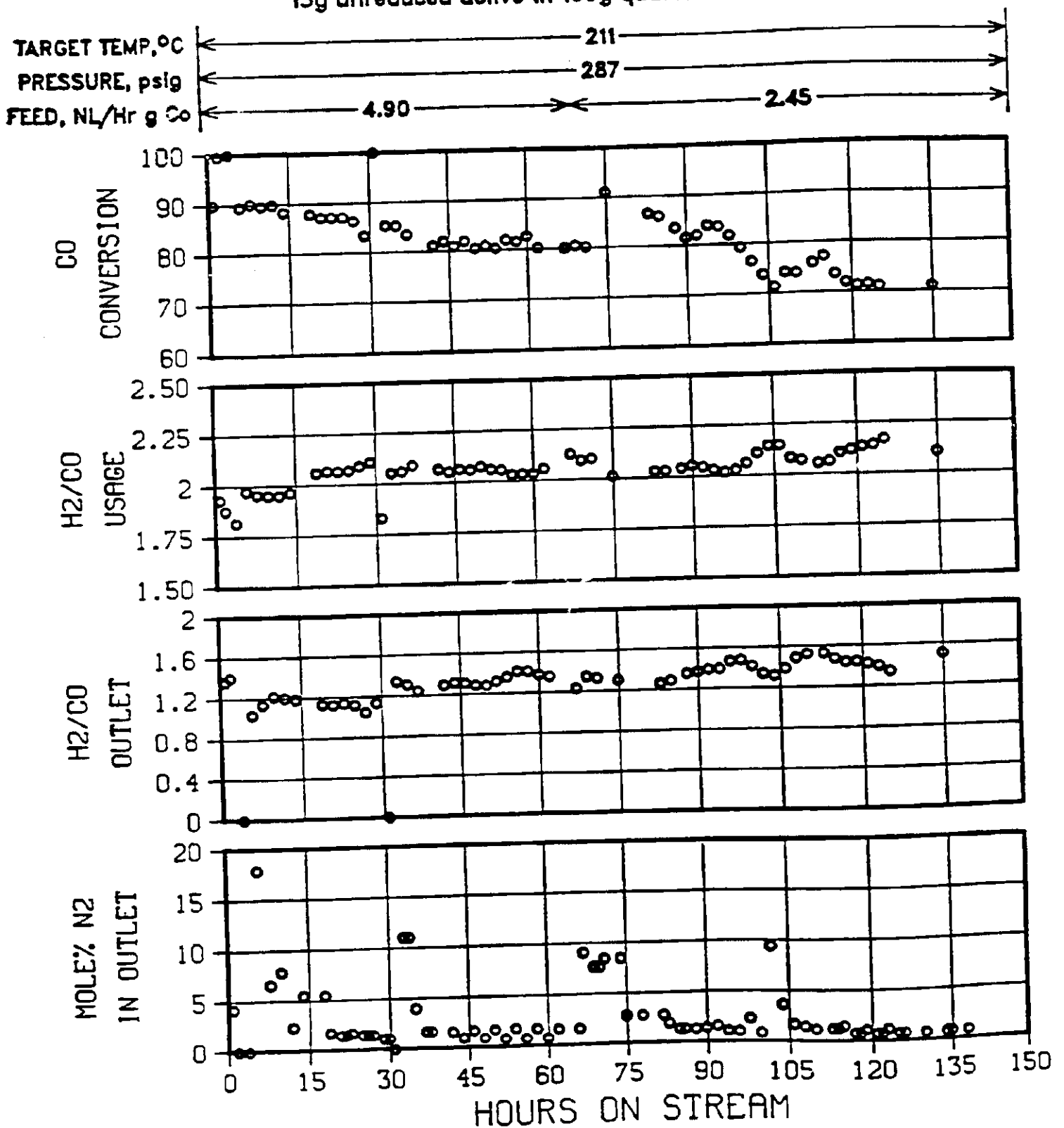


FIGURE A-26
PLT 700A RUN 93 Co,Mn,Zr,Ru on HCl Washed Y
 6531-204 w/9.1% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

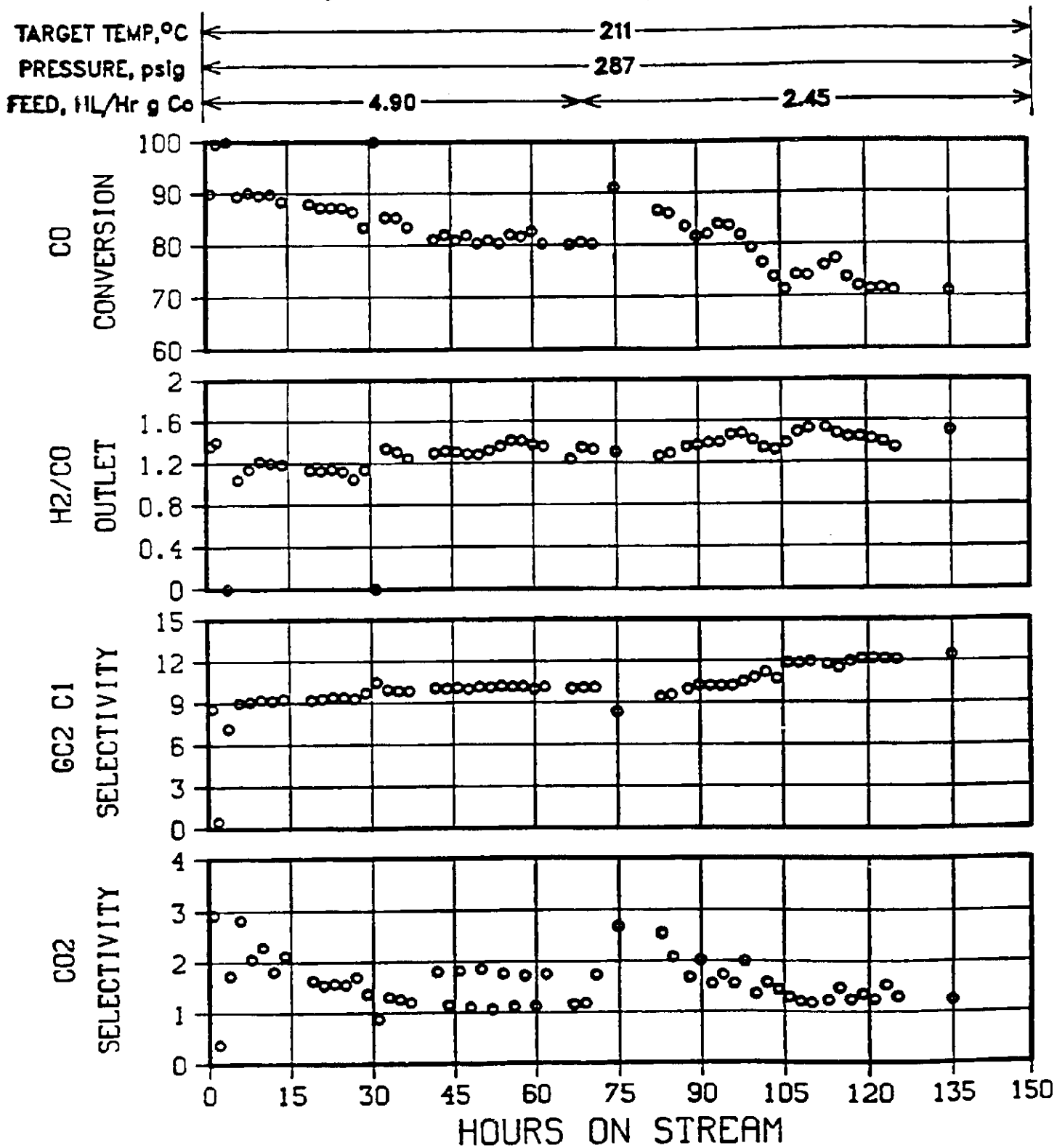


FIGURE A-27
PLT 700A RUN 93 Co,Mn,Zr,Ru on HCl Washed Y
 6531-204 w/9.1% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

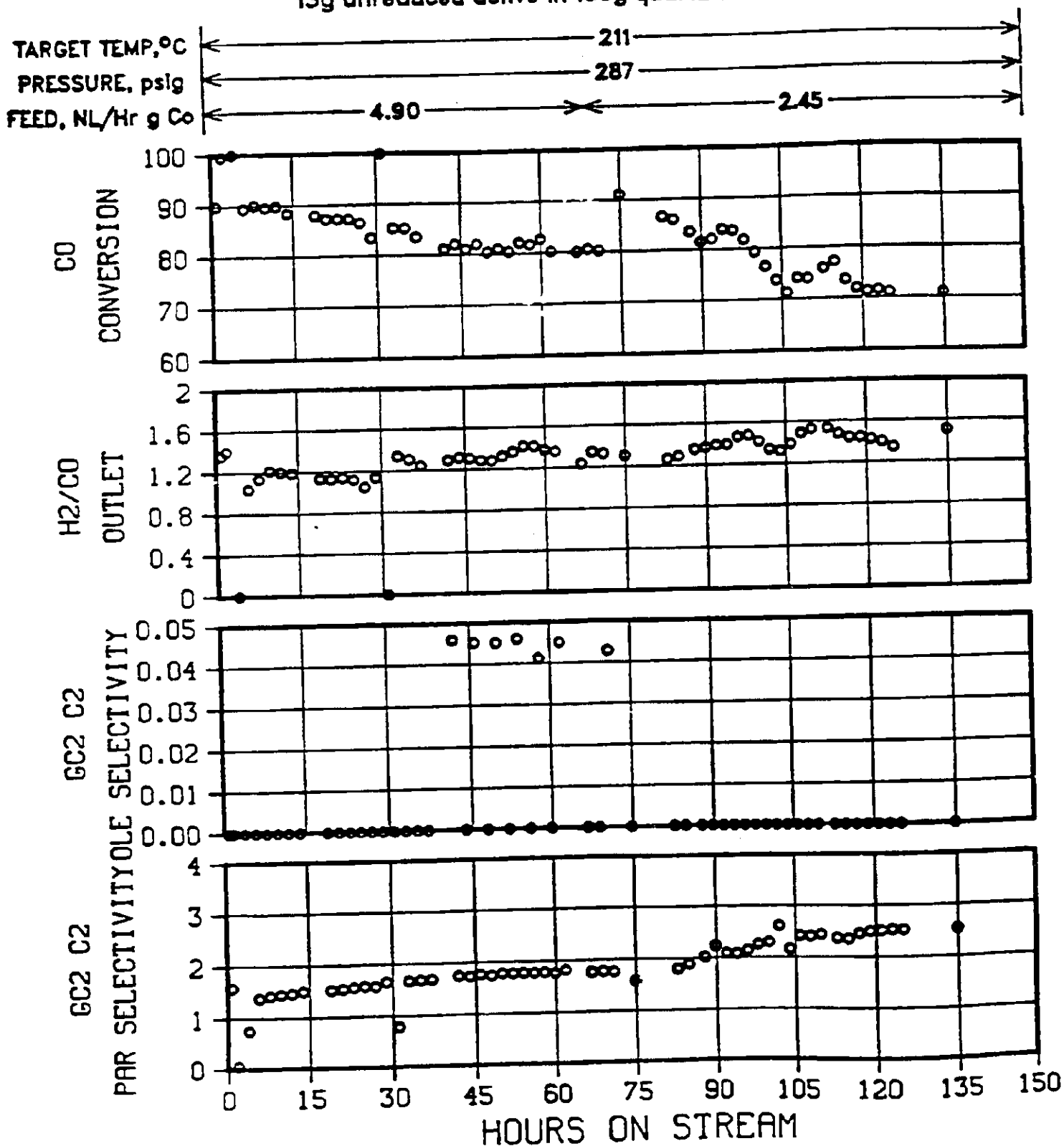


FIGURE A-28
PLT 700A RUN 93 Co,Mn,Zr,Ru on HCl Washed Y
 6531-204 w/9.1% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

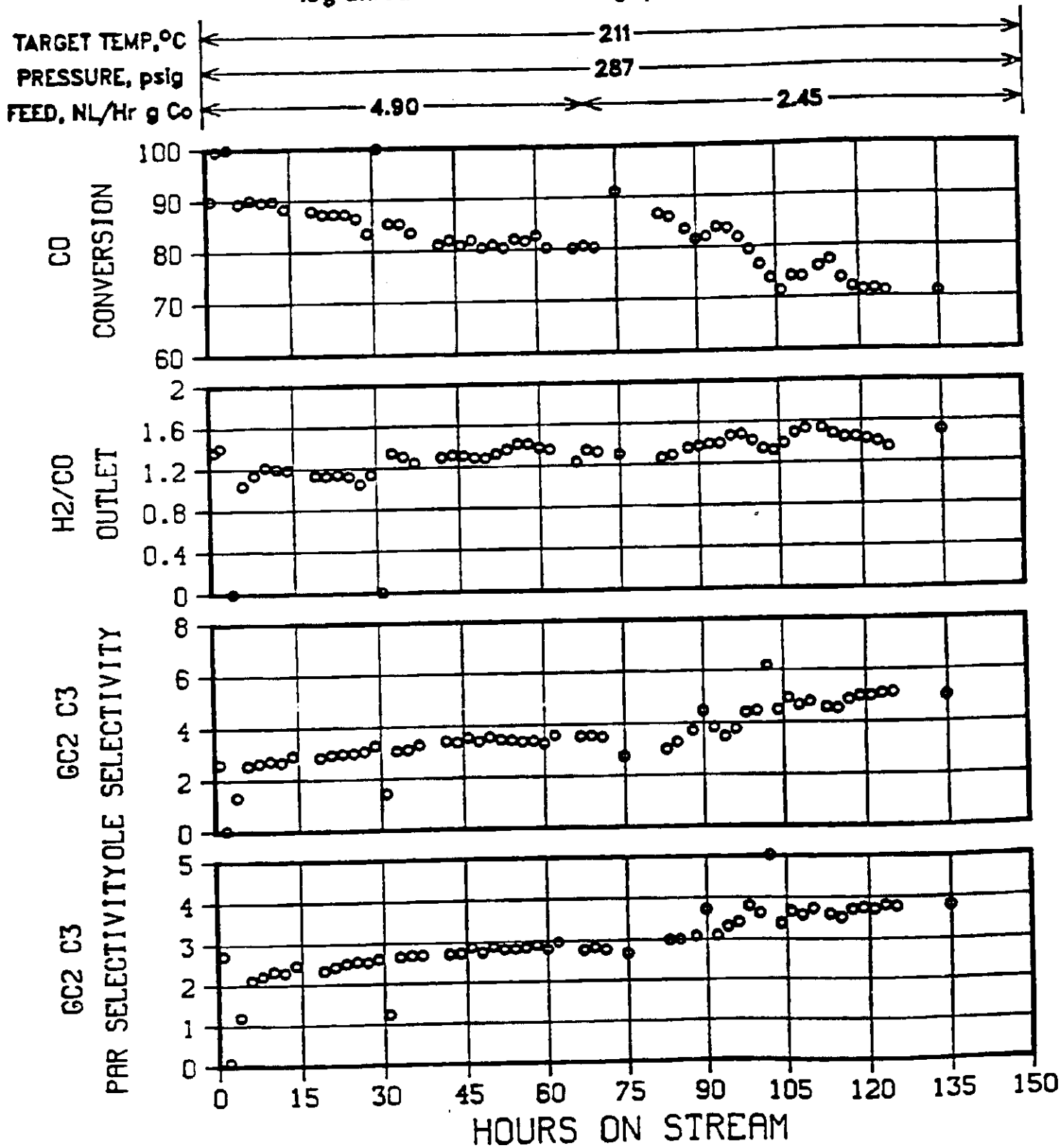


FIGURE A-29

PLT 700A RUN 93 Co,Mn,Zr,Ru on HCl Washed Y

6531-204 w/9.1% Co via eth-glycol pore fill

13g unreduced active in 160g quartz sand

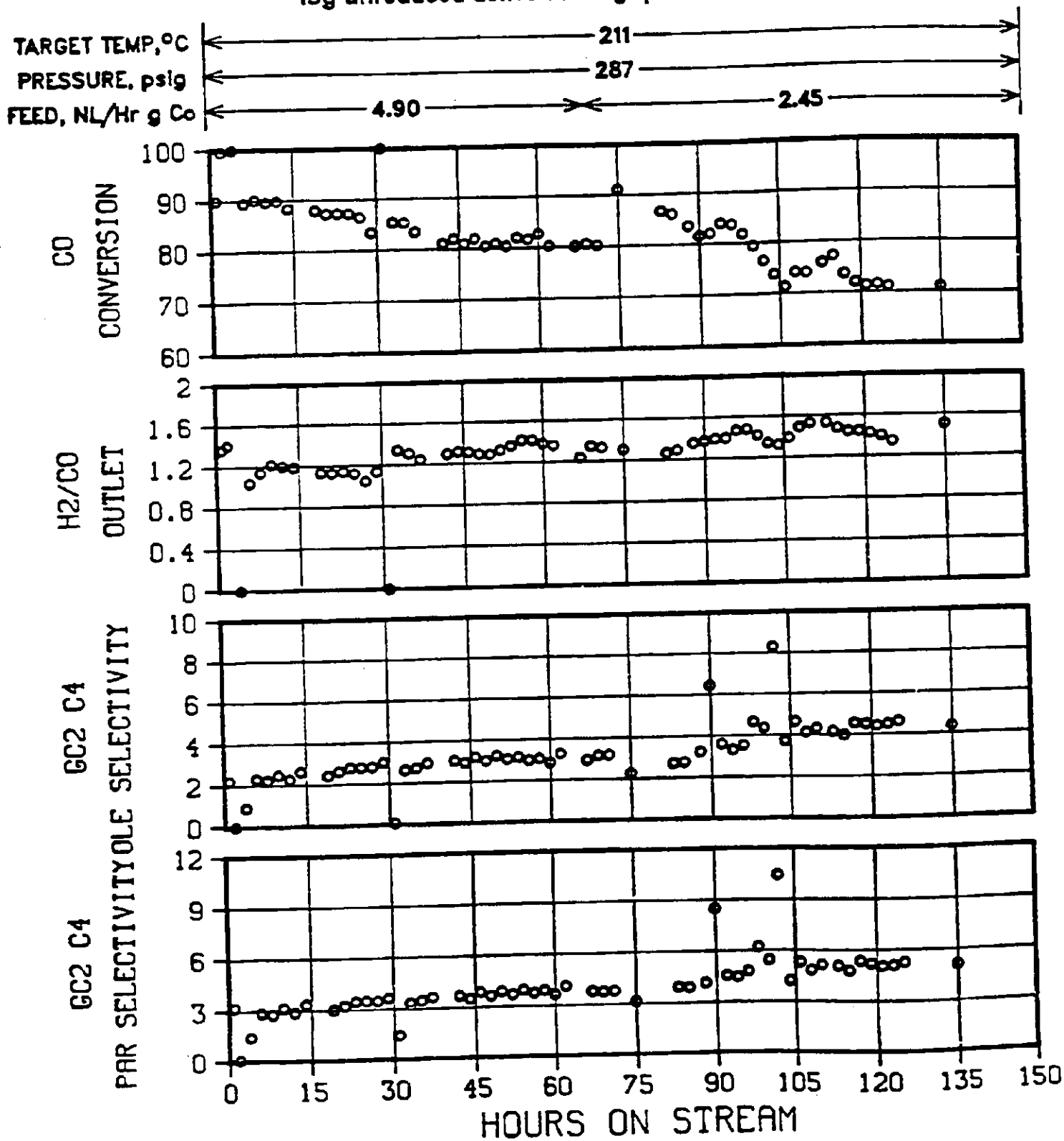


FIGURE A-30
PLT 700A RUN 93 Co, Mn, Zr, Ru on HCl Washed Y
 6531-204 w/9.1% Co via eth-glycol pore fill
 13g unreduced active in 160g quartz sand

