

HYDROCARBON SHIFFER PROGRAM FOR MAFLA OCS RIG MONITORING

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## A. Redesign

The AMOCO sniffer and auxillary equipment and an extensive parts box were received in good condition. The AMOCO sniffer was incapable of water analyses for specific hydrocarbons and it was therefore redesigned to permit gas chromatographic-like analyses for trace amounts of specific light hydrocarbons. The redesigned unit is shown in Figure 1.

The system is designed to permit the scrubbing collection of hydrocarbons from 10 to 50 ℓ of sea water or more, if necessary. Provision has also been made for batch analysis of up to 250 ml of sea water using the system shown in Figure 2. This modification can be used if very high concentrations of hydrocarbons are encountered.

The water scrubbing section of the unit was retained from the old AMOCO equipment. Helium gas was used as part of the scrubbing gas and also as a carrier for the hydrocarbons removed from the water samples. The sample gas stream is passed through a drying tube and into a liquid nitrogen-cooled U-trap which collects all of the hydrocarbons. The trapped gases are then analyzed by a flame ionization detector (FID)(Perkin-Elmer) as they evolve from the heated U-trap. The analysis obtained is similar to a programmed temperature gas chromatographic analysis and a typical standard analysis pattern is shown in Figure 3.

## B. Construction

The light hydrocarbon analyzer (LHA) was constructed using the frame and much of the original equipment from the old AMOCO unit. The AMOCO unit was shock mounted and then designed for more rugged field use. Since the filter chambers had been leaking, a new gasket sealing compound had to be

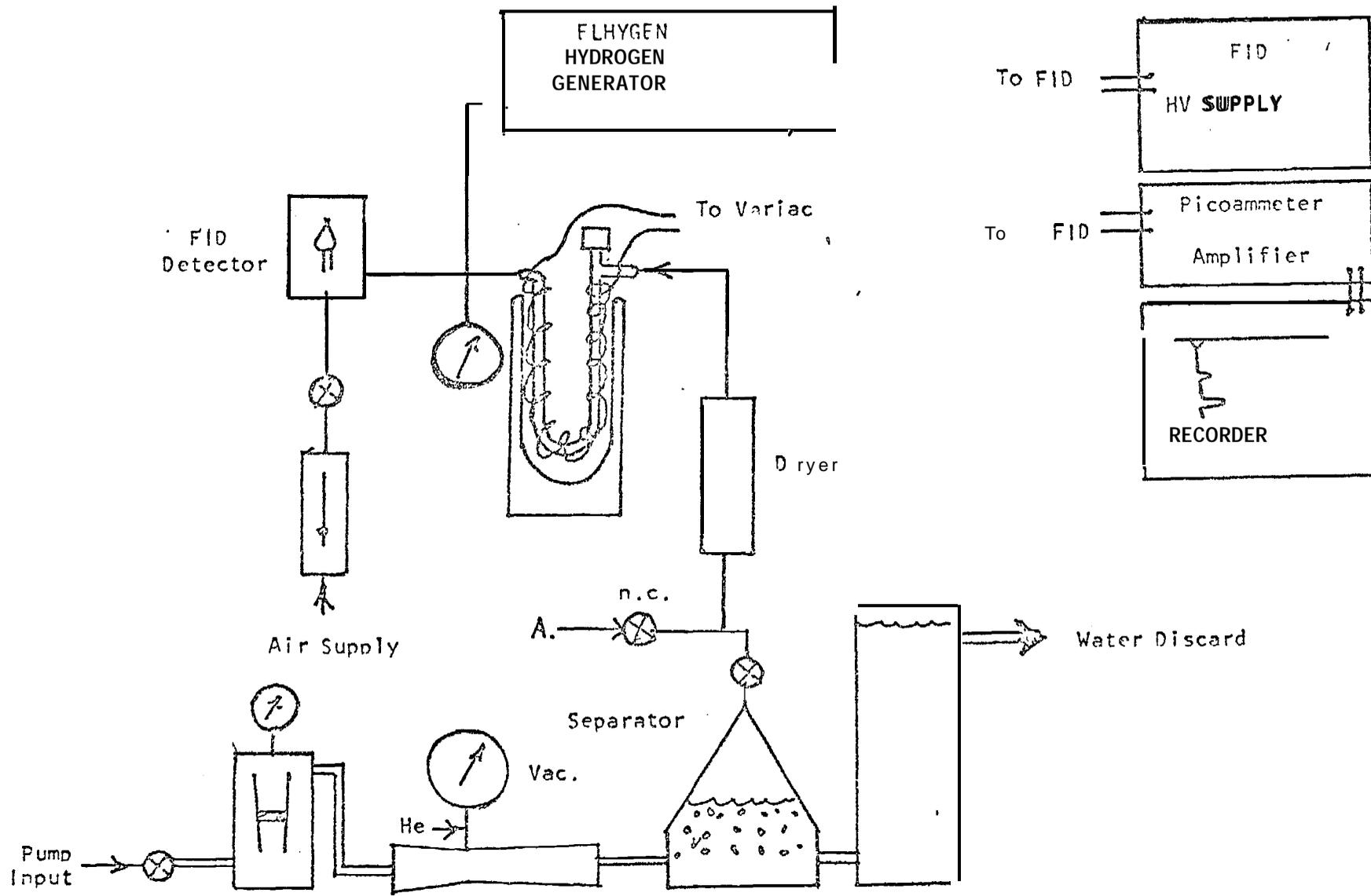


FIGURE I Apparatus Arrangement for LHA Unit

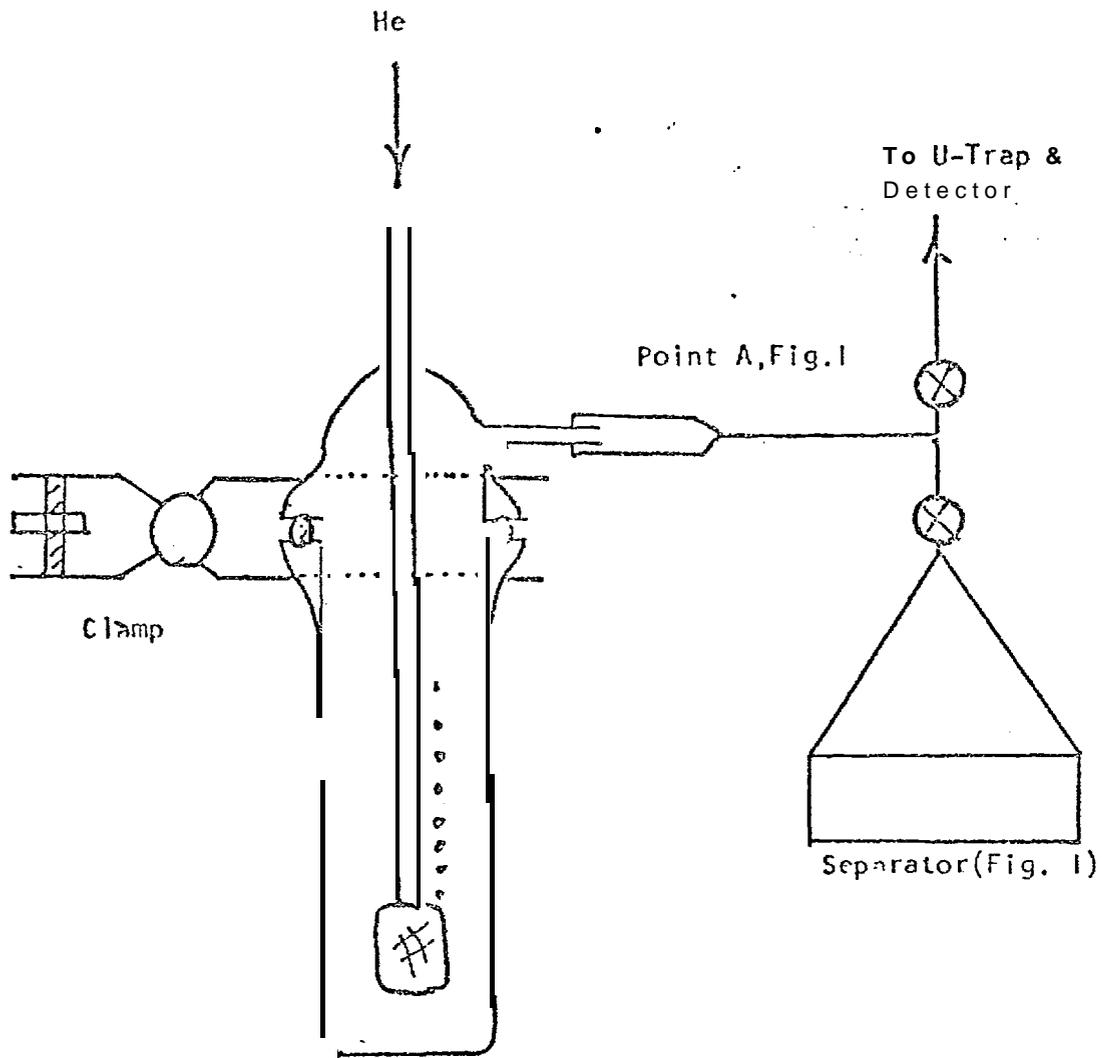


FIGURE 2 Batchwise Water Scrubbing System-Connection to LHA Unit

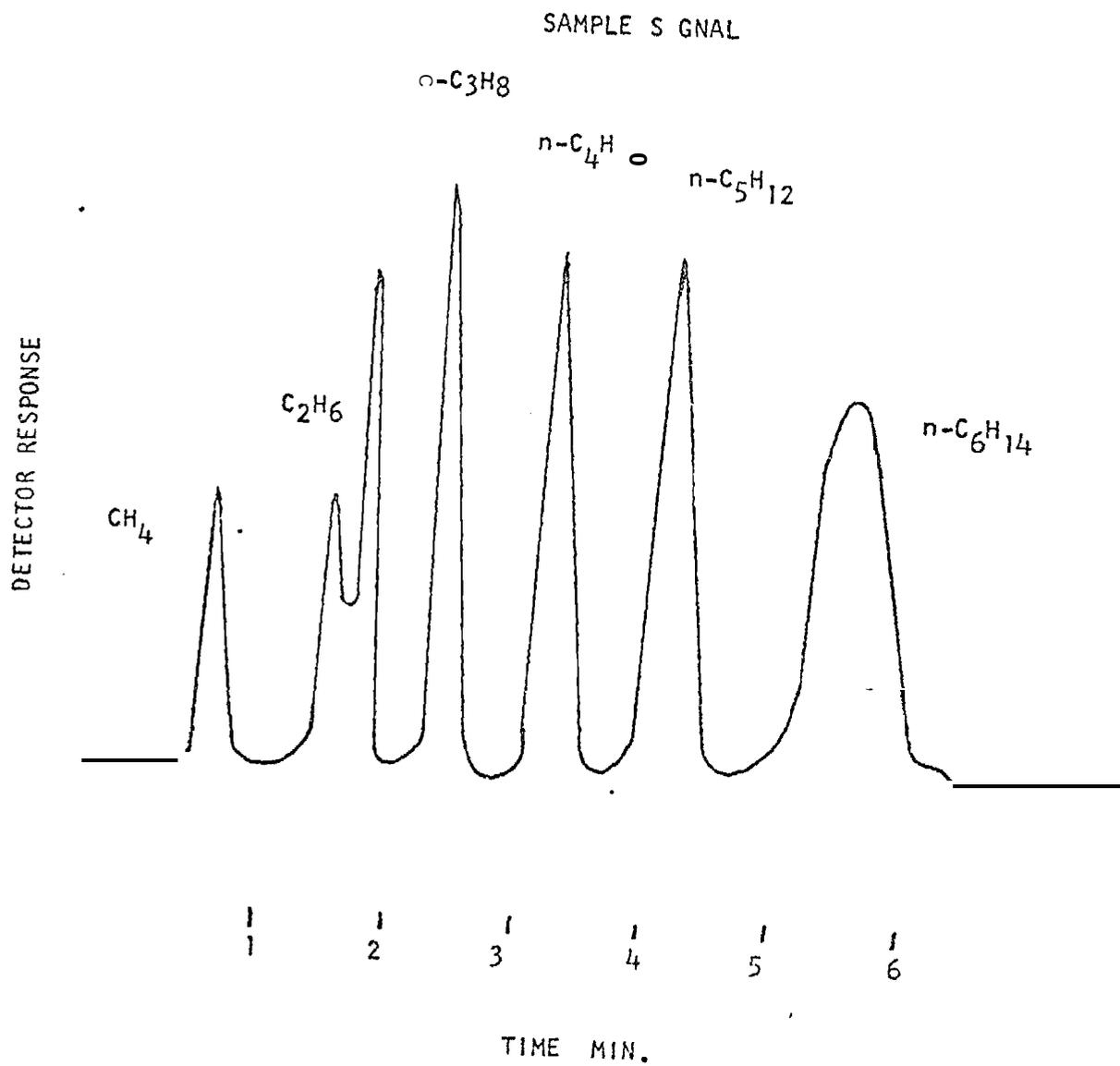


Figure 3

sample <etector response

used to replace the unsatisfactory silicon material previously used by AMOCO. Other problems encountered included elimination of leaks and, plugged lines, simplifying the carrier gas system and mounting the U-trap in the instrument. The most serious problem was an amplifier failure during a sea trial but this amplifier was replaced with a new solid state FET transistor input stage amplifier (Kiethley Model 414S) and after the Rust Rack recorder was replaced by a new integrating strip chart recorder (Linear Instruments Corp. ) no other data collection problems were encountered.

### C. Laboratory Testing

Laboratory testing, redesign and construction were an interrelated part of this project. The experimental parameters of carrier gas flow rate, hydrogen gas and air feed rates to the detector, and sample gas flow rate had to be adjusted to obtain maximum sensitivity, maximum separation of components and minimum separation time. This was done along the way as modifications were made in the equipment. Analysis time was reduced to less than five minutes per sample.

Standardization of the detector response was found to be easily accomplished using a standard 1000 ppm mix of  $C_1$  to  $C_6$  normal alkanes in nitrogen gas (Mircycl calibration gas, MG technical products, Kearny, N. J.). Samples of 20 to 500  $\mu\ell$  were injected directly onto the liquid nitrogen cooled U-trap through an injection port. The limit of detection for hydrocarbons was found to be less than 0.1 n $\ell$ /sample. This was well below the needed limit of detection for sea water analysis even when working at open ocean ambient concentrations (about 50 n $\ell$ / $\ell$ ).

The efficiency of the water scrubbing system was tested using a

100 ℓ hold tank, as shown in Figure 4. The efficiency had to be known to relate the standardized detector response to light hydrocarbon concentrations in water. The scrubbing factor was found to be an exponential expression and is discussed later in this report. In the scrubbing efficiency experiments amounts of hydrocarbons were placed in 100 ℓ of water. The LHA continuously scrubbed these hydrocarbons from the tank as a function of time and returned the partially degassed water to the holding tank. Periodically two minute collections were acquired and analysed. To assure that the scrubbing process was monitored as a continuous function of time, the pump was temporarily halted during the analysis cycle. Figure 5 summarizes the results of a typical scrubbing experiment.

The scrubbing versus flow rate experiments were accomplished in an analogous manner. The instrument's flow gauge was calibrated in liters per minute of water flow and the scrubbing experiments were repeated at various flow rates. The results of these experiments are represented in Figure 6.

Data in Figure 6 indicates that control must be maintained over sample flow rate. Calibrations of the system for scrubbing factor upon which quantitative results depend must be made at the actual sampling flow rate. The k factor is not a highly sensitive function of flow rate, a 10% change in sample flow rate will cause a 10% change in results. Sample flow rate control was found to require careful observation of the flow meter during operation and occasional changing of filters in the sample pump system. During operations flow control was maintained to within  $\pm 5\%$  relative of the calibration flow rate. Since flow rate is

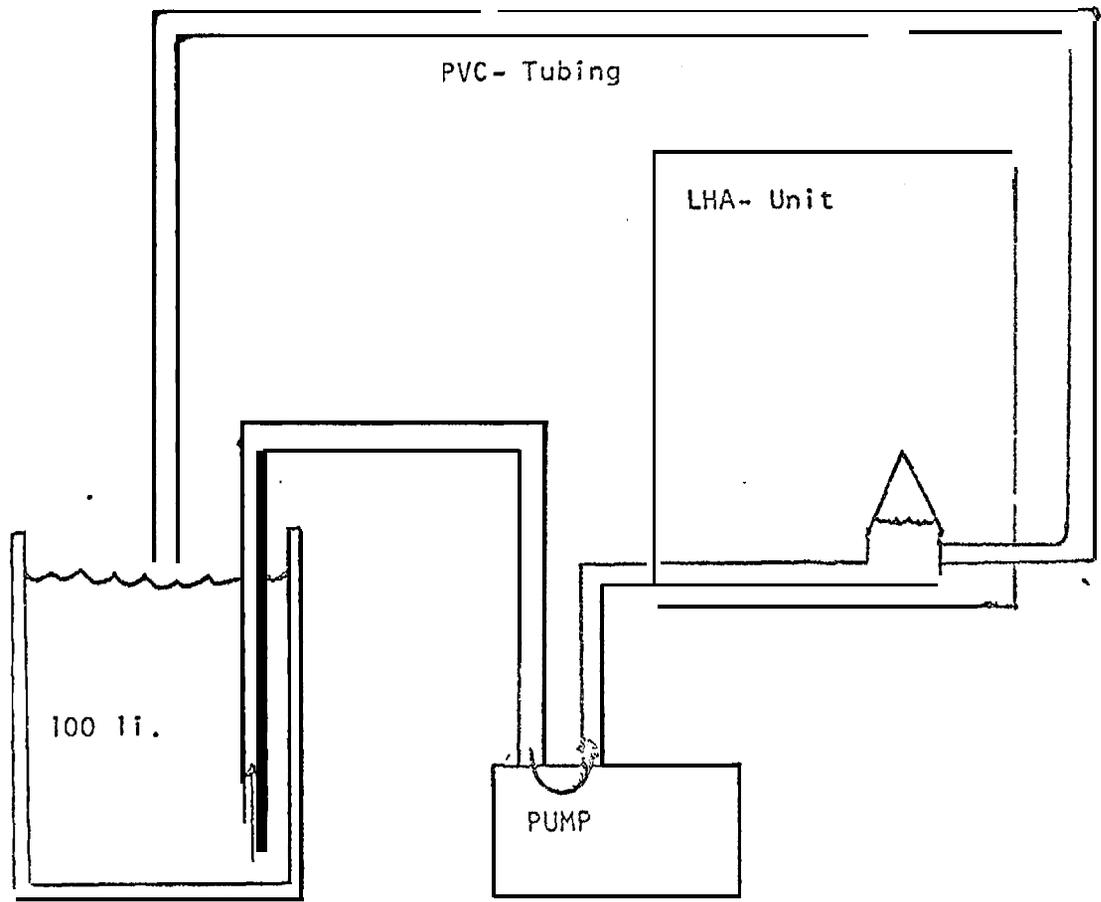
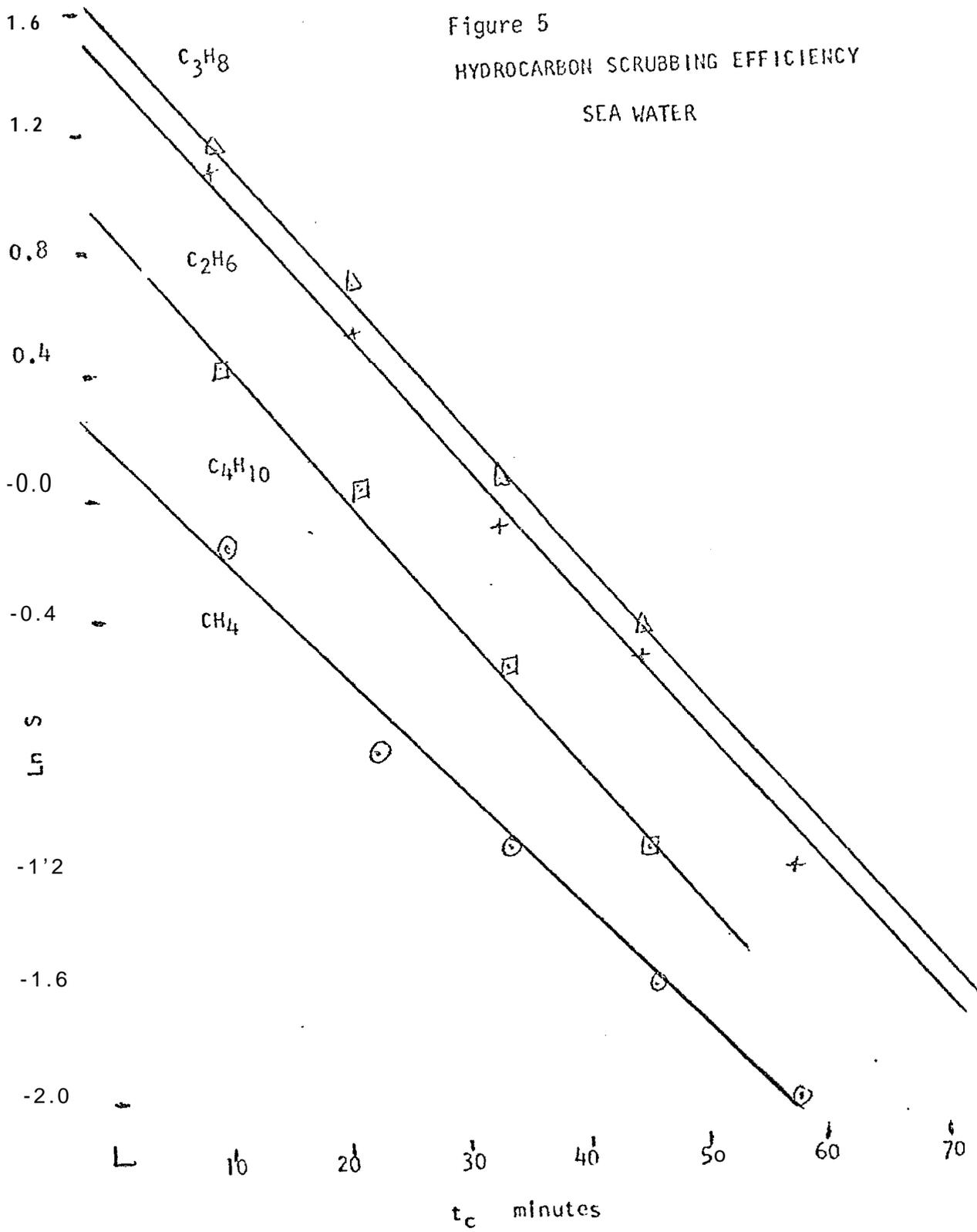


Figure 4 Apparatus Arrangement for Scrubbing Efficiency Experiments

Figure 5  
HYDROCARBON SCRUBBING EFFICIENCY  
SEA WATER



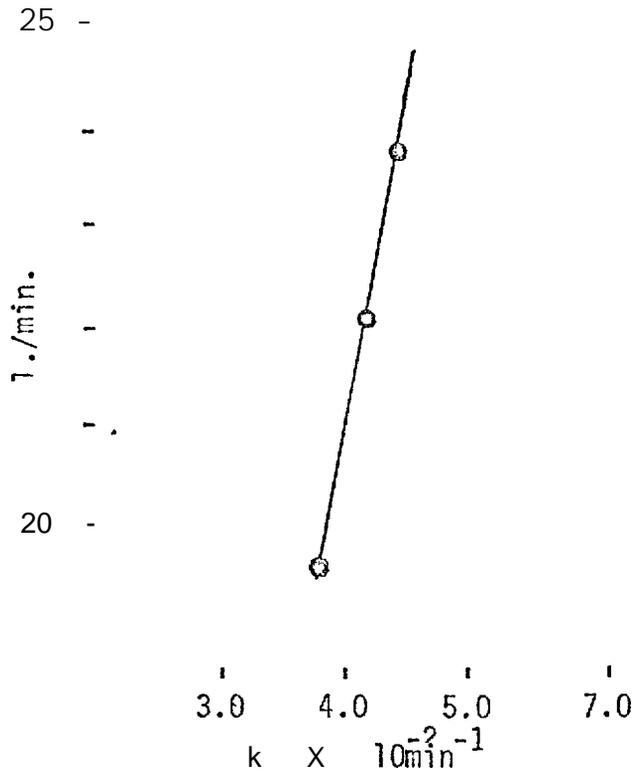


Figure 6 Flow vs. k (CH<sub>4</sub>)

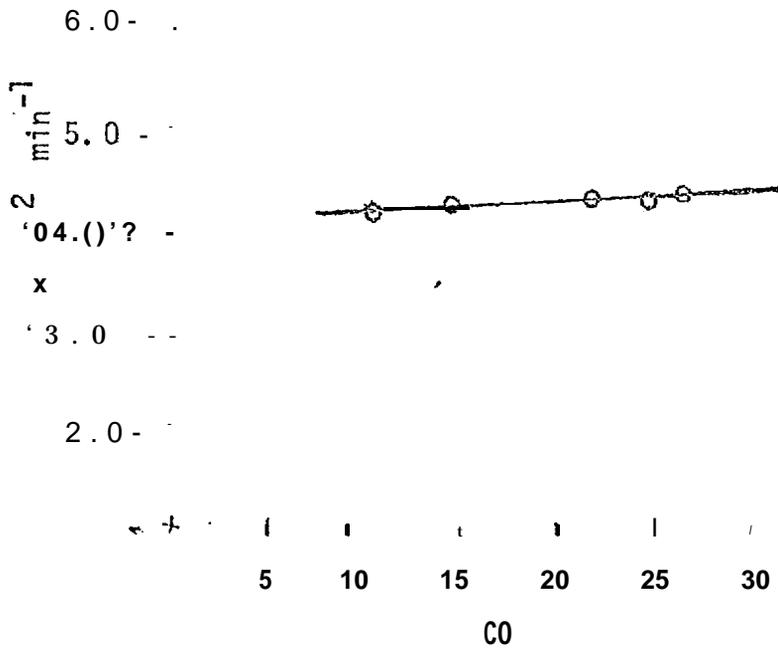


Figure 7 k vs. Temp. (CH<sub>4</sub>)

the major source of error compared to others (temperature, calibrations, etc.) ,  $\pm 5\%$  is a good estimate of the data precision of the system.

Scrubbing as a function of temperature experiments were done in the 100 l Dewar tank. The temperature was adjusted before the analysis began and maintained by the addition of small amounts of ice. Low temperature experiments were terminated before any appreciable dilution error occurred. The results of these experiments are shown in Figure 7.

Temperature has little effect *on* the k factor for methane over a wide range. Failure to calibrate at each operating temperature should result in errors on the order of  $2\%$  relative.

#### D. Scrubbing Theory

The theory of exponential dilution has been investigated by Ritter and Adams\*. The rate  $(-dC_L/dt)$  at which the hydrocarbons are eluted from the LHA is proportional to the concentration of hydrocarbons in the sample. Thus;

$$(1) \quad dC_L/dt = kC_L$$

where  $k$  is a constant characteristic for the LHA and  $C_L$  is the concentration,  $n\ell/\ell$ , of hydrocarbon in the aqueous sample. If  $X_t$  is the amount,  $n\ell$ , of hydrocarbons that has been scrubbed out after time  $t$ ,  $[W_0]$  the concentration,  $n\ell/\ell$ , of the hydrocarbon in the water sample before scrubbing and  $V$  the volume,  $\ell$ , of water scrubbed then equation (1) becomes;

$$(2) \quad dC_L/dt = -k((V[W_0] - X_t)/V).$$

Since  $C_L = (V[W_0] - X_t)/V$  it follows that  $dC_L/dt = -dX_t/Vdt$  and equation (2) can be expressed as;

$$(3) \quad -1/V(dx_t/dt) = -k((V[W_0] - X_t)/V)$$

which can be simplified to

$$(4) \quad dX_t/dt = k(V[W_0] - X_t).$$

Rearranging equation (4) gives a familiar differential equation;

$$(5) \quad dX_t / (V[W_0] - X_t) = k dt$$

and integration of (5) gives;

$$(6) \quad -\ln(V[W_0] - X_t) = kt + C_1.$$

At  $t=0$ ,  $X_t$  becomes zero and the integration constant can be evaluated and equation (6) becomes;

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\*Ritter, Adams, Anal. Chem 612 (1976).

$$(7) \ln(V[W_0]/(V[W_0] - X_t)) = kt.$$

Equation (7) can be expressed as;

$$(8) V[W_0]/(V[W_0] - X_t) = \exp(kt)$$

and then rearranged to give;

$$(9) X_t = V[W_0] (1 - \exp(-kt)).$$

Differentiation of (9) gives;

$$(10) \frac{dX_t}{dt} = V[W_0]k \exp(-kt).$$

Taking the  $\ln$  of equation (10) gives;

$$(11) \ln \frac{dX_t}{dt} = \ln(V[W_0]k) - kt$$

and a plot of  $\ln \frac{dX_t}{dt}$  vs  $t$  will give a line with slope  $k$ , the scrubbing factor for the analyzer. Once  $k$  has been obtained equation (9) can be used to evaluate the  $[W_0]$  for environmental samples taken.

Since the scrubbed hydrocarbons are collected over a constant time interval,  $\Delta t$ , the signal that is actually recorded by the LHA is not the differential of  $X_t$  with respect to time but is in fact the increment in  $X_t$  with respect to delta time. It is necessary, therefore, to show that a plot of the increment in  $X_t$  vs time will also result in the evaluation of  $k$ .

The amount of hydrocarbon released after scrubbing for time,  $t$ , is expressed by equation (9). Thus the amount released after scrubbing,  $t + \Delta t$ , is given by;

$$(12) X_{t + \Delta t} = V[W_0] (1 - \exp(-k(t + \Delta t))).$$

The amount,  $(X_{t + \Delta t} - X_t)$  collected over the time interval  $\Delta t$  is the difference between equation (9) and equation (12) and can be represented as;

$$(13) \Delta X = (V[W_0] \exp(-kt)) (1 - \exp(-k\Delta t)).$$

Expressing  $\exp(-k\Delta t)$  as a series and neglecting the second order terms gives;

$$(14) \exp(-k\Delta t) = 1 - k\Delta t$$

and the substitution of equation (14) into (13) gives;

$$(15) \Delta X = (V[W_0] \exp(-kt)) (k\Delta t)$$

which can easily be represented as;

$$(16) \Delta X/\Delta t = V[W_0]k \exp(-kt).$$

The error involved in expanding  $\exp(-k\Delta t)$  to the first order term is five parts in 1000 when  $k\Delta t$  has a value of 0.1 and decreases as the value of  $k\Delta t$  decreases. Since  $k$  is equal to  $(\ln 2)/\tau_{1/2}$ , where  $\tau_{1/2}$  is the half life of the scrubbing experiment, the expansion of  $\exp(-k\Delta t)$  introduces an error of less than five parts in 1000 when the collection time,  $\Delta t$ , is less than 0.144 of  $\tau_{1/2}$ . Therefore equation (16) is an excellent approximation of equation (10) when  $\Delta t$  is less than 14.4% of  $\tau_{1/2}$  and equation (16) can be utilized to evaluate the scrubbing factor,  $k$ .

## E. Preliminary Field Testing

Field tests were made on two fresh water lakes. These were not overly successful because the high organic content of the lake water overloaded the detection system. The pumping and filtering systems were also overtaxed and no modifications for fresh water work were attempted. However, the batch analysis method, (see Figure 2), could be used in situations like this. A successful at-sea field test of the LHA unit was made in October 1975. The two sampling methods, as well as alternative water collection methods, were investigated and only minor correctable problem were encountered. In general, the sea trial showed that the equipment would operate on the R/V Bellows and provided a much needed training exercise for all project personnel.

## F. Rig Monitoring

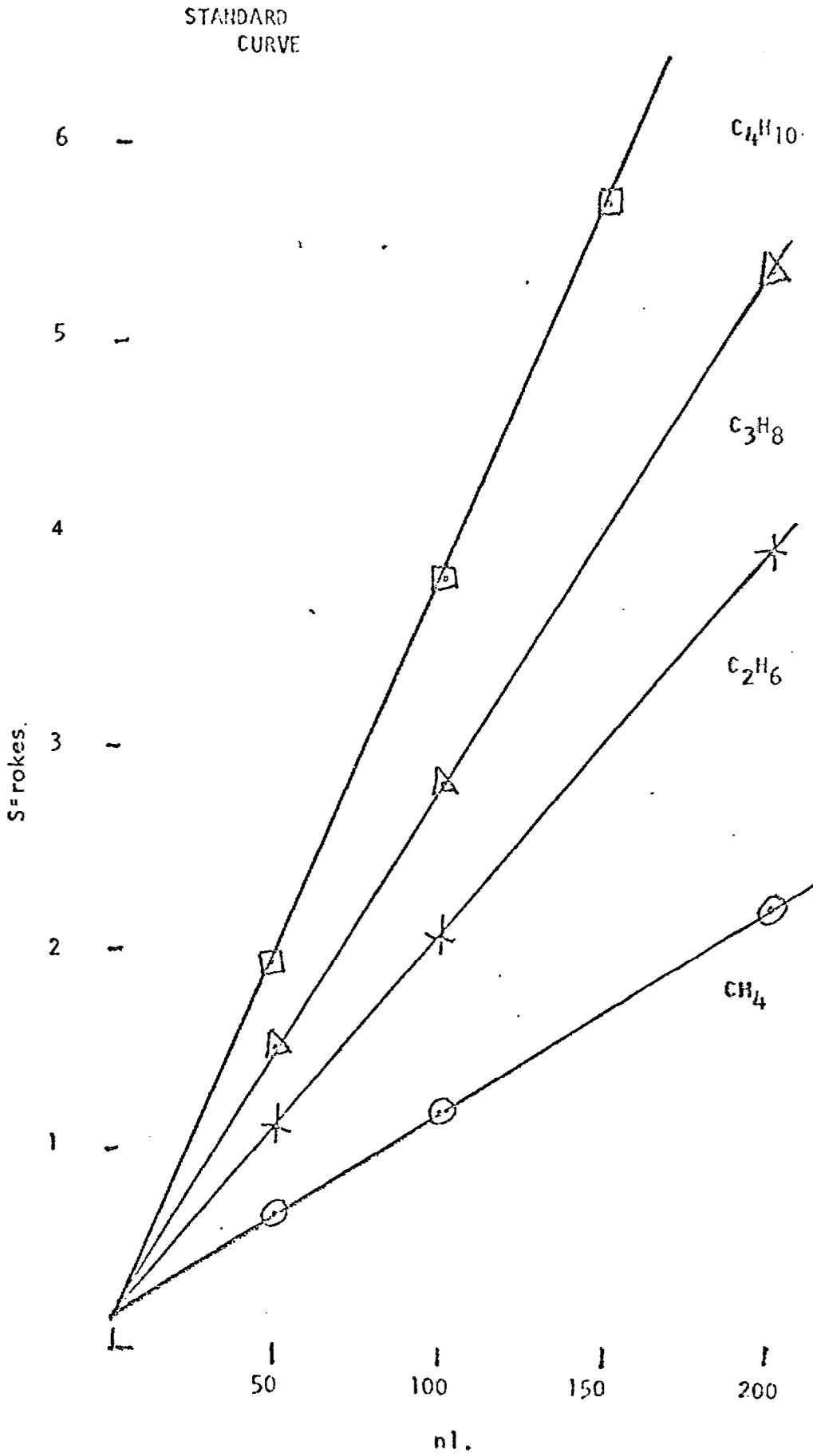
### 1. Calibration of Detector

Selected amounts of methane, ethane, Propane and butane were drawn into a microliter syringe (Unimetrics) and then injected onto the cold trap. Corresponding detector response areas were plotted against injected gas volumes (Figure 8) and this data is also summarized in Appendix A. Periodic laboratory calibration checks were conducted and a calibration check was performed at each rig monitoring site.

### 2. On Site Sampling

The light hydrocarbon analyzer as described was employed in all operations. Water sampling was done through the ship's sampling pump systems during the first cruise period and by means of a towed tube

Figure 8



and pump system during all subsequent operations. During all field operations the flow rate was kept constant. The analysis procedure consisted of cold trapping for two minutes of scrubbing time while underway. Trapped, scrubbed gases were then analyzed for a period of approximately three to five minutes and the analysis cycle repeated. The analysis system therefore analyzed a composite sample of water obtained while the ship was underway and presented the average water quality for the distance traveled in the two minute period.

Scrubbing experiments, as described in section C, were conducted at sea to determine the value of the scrubbing factor. Linear regression analysis was employed to determine the slopes of lines obtained from the experimental data. These values of the scrubbing factor,  $k$ , are presented in Appendix A. Excellent correlation between experimental data and scrubbing theory was obtained and in all experiments conducted the collection time, two minutes, was less than  $0.144 \tau_{1/2}$ .

### 3. Data Discussion

The drilling rig site near Port Aransas, Texas was surveyed prior to drilling on December 1-2, 1975. Data presented in Appendix A indicated that there is a detectable amount of methane present. The methane values are in accord with the findings of others. An interesting feature of the data is that the methane values decreased as the sampling point became further removed from the ship channel outlet to the Gulf. No particular pattern of hydrocarbons was noted in the test area.

Because of the termination of drilling operations prior to being able to survey the site near Port Aransas, Texas a second time, it was decided to survey a drilling operation at latitude  $27^{\circ}37'13.87''N$ ,

longitude 96°57'55.17"W, near Port O' Conner, Texas. The survey was done on January 23, 1976, and no general light hydrocarbon contamination was observed in the area. One of the samples obtained showed a substantial amount of light hydrocarbons, nevertheless, we believe it was caused by a single bubble of natural gas seepage and must be a solitary event since any substantial continual seepage or leakage from drilling would contaminate the entire area surveyed.

During the January 2-6 cruise period the towed sampling system was tested in the Corpus Christi ship channel. Results demonstrated the ability of the analyzer to detect light hydrocarbons in polluted waters. Nearby refineries were likely the source of C<sub>2</sub> to C<sub>6</sub> hydrocarbons found in the turning basin in the urban area of Corpus Christi. Waters decreased in hydrocarbon concentration as the more open areas of Corpus Christi bay were crossed and further yet as the ship channel approached the open Gulf. Data shown in Appendix A includes some results of air analyses of the port area.

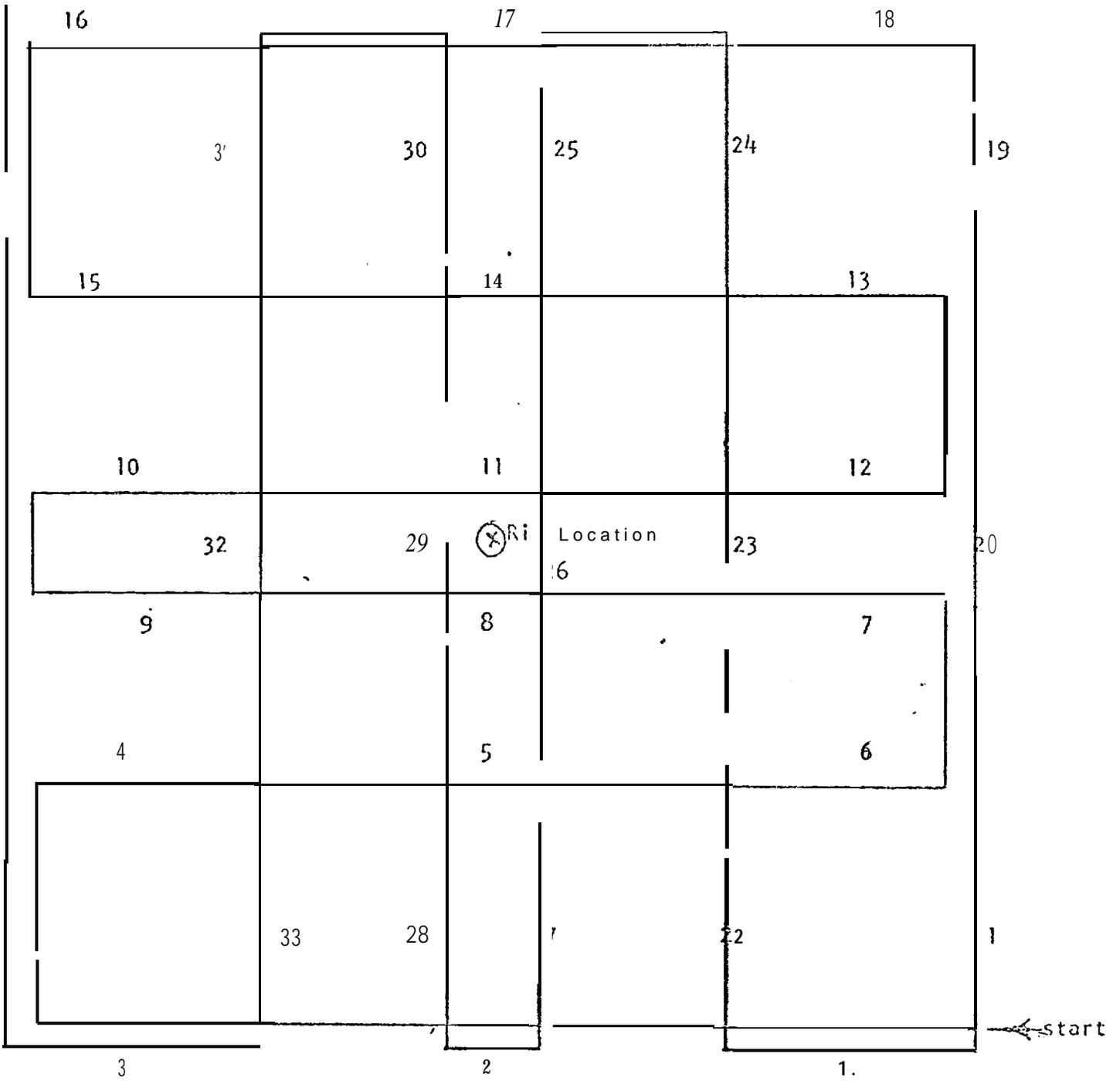
APPENDIX A

TABLE I

## LHA SURVEY PRIOR TO DRILLING

sample No.	nℓ/ℓ			
	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	
0-1	390	8.6	14	
0-2	290	3.8	9*5	
0-3	250	4.2	10	
1	170	6.7	1	3
2	110	6.3	6.7	
3	64	3.8	9.2	
4	54	6.9	9.2	
5	31	4.2	9.0	
6	9	6.1	9.5	
7	56	7.1	12	
8	35	4.4	9.5	
9	30		9.2	
10	85	5.9	10	
11	38	5.5	11	
12	36	7.1	14	
13	103	7.1	16	
14	31	8.4	14	
15	39	4.8	11	
16	16	5.0	8.6	
17	34	5*3	9.9	
18	38	1.0	6.7	
19	40	5.5	13	
20	36	6.7	10	
21	28	5.5	8.2	
22	39	4.6	9.8	
23	35	2.7	7.4	
24	31	9.0	16	
25	57		-	
26	48	3.6	3.8	
27	28	4.0	4	8
28	36	8.0	13	
29	25	5.3	11	
30	26	6.1	-	
31	34	2.9	6.7	
32	25	3.2	7.8	
33	28	2.5	2.7	
34	43	7.8	12	
35	48	11	16	
36	47	8.6	14	

end



RIG MONITORING SAMPLING GRID-SHIP TRACK  
(location of samples-approx.)

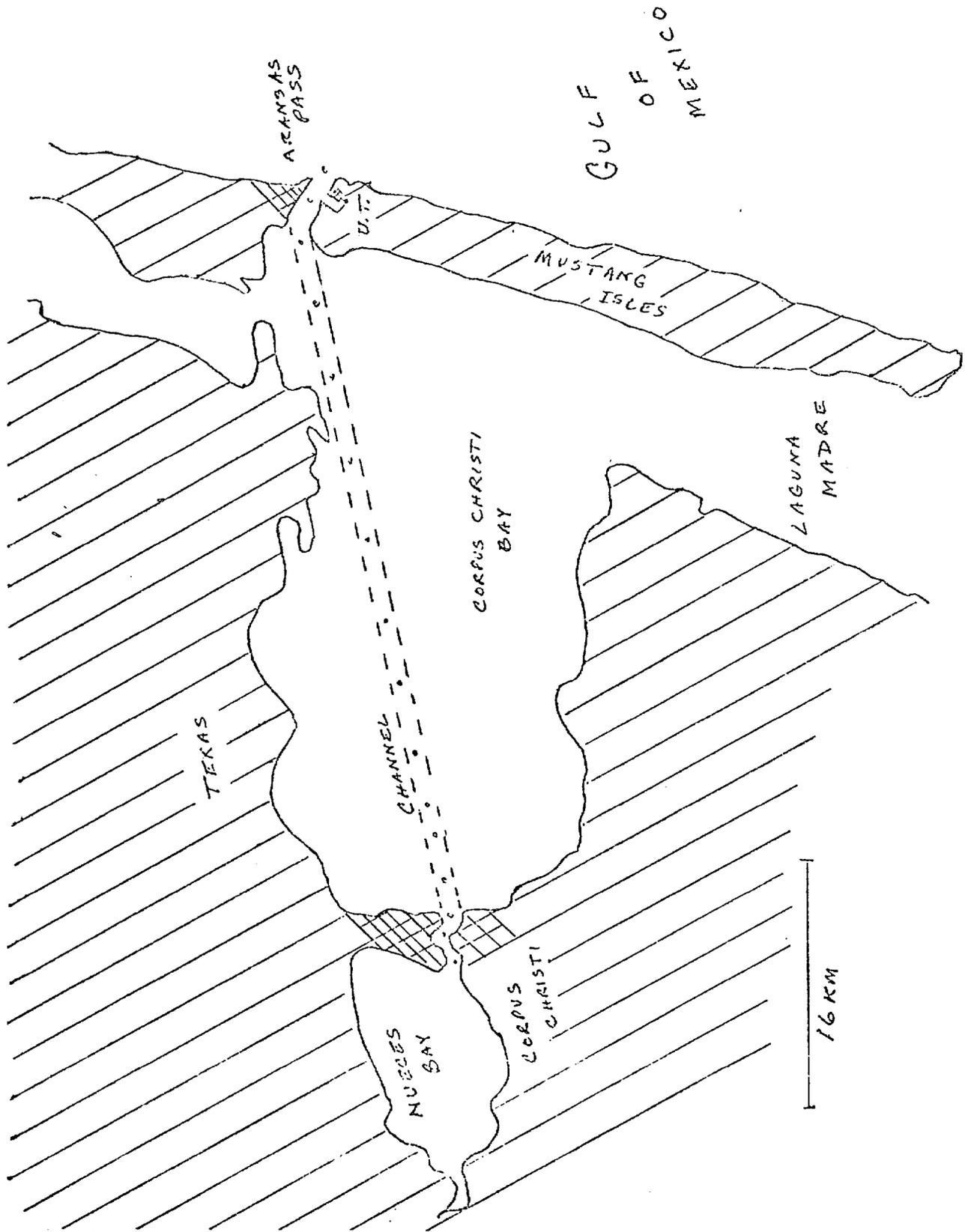


TABLE 2

## SURVEY OF CORPUS CHRISTI SHIP CHANNEL

sample No.	nℓ/ℓ				
	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>14</sub>
W-1	940	16	340	230	97
W-2	lost		200	120	65
W-3	940	36	200	140	67
W-4	840	10	180	170	65
W-5	660	2.3	23	13	11
W-6	470	2.3	6.2	13	
W-7	450	2.3	11	16	10
W-8	lost	2.7	6.5	8.2	
W-9	380	3.4	5.7	6.9	1.9
W-14	270	6.1			
W-15	220	1.3			
W-16	80	-			

Locations: W-1 to W-3 interior port of C. Christi

W-4 to W-9 Nueces bay towards Gulf

W-14 - W-15 Outer ship channel

W-16 At jetty near open gulf

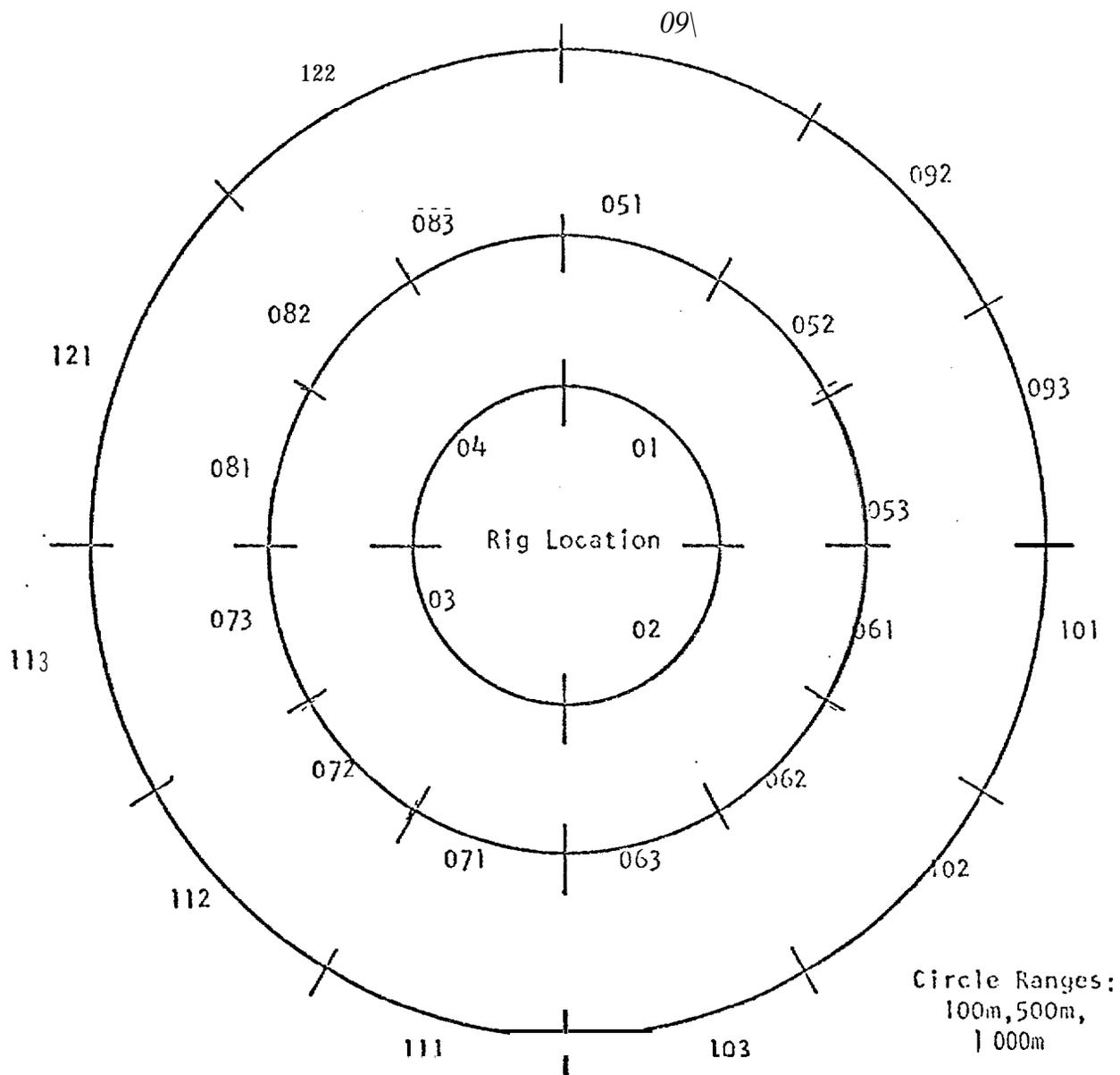
TABLE 3. LHA- Unit Air Analysis Of Corpus Christi Ship Channel

Sample No.	$\mu\text{l/l}$		
	$\text{C}_1\text{H}_4$	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$
A-7	0.11	17	0.3
A-6	0.02	6.7	0.4
A-5	0.02	4.9	
A-4	0.03	5.7	
A-3	0.03	6.4	0.9
A-2	0.03	7.3	0.4
A-1	0.03	9.5	

Note locations:

A-7 to A-5 interior port of Corpus Christi

A-4 to A-1 Nueces bay towards Gulf



RIG MONITORING SAMPLING GRID - SHIP TRACK  
(drilling operation underway)

TABLE 4

## RIG MONITORING, DRILLING UNDERWAY

nl/l

Sample No.	C H <sub>1</sub>	Remarks
R- 1	300	4025 m from rig
R-2	170	2816 m from rig
R-3	200	1770 m from rig
R-4	200	965 m from rig
<b>100 m Circle</b>		
0-1	<b>260</b>	
0-2	220	
0-3	220	
0 - 4	220	
<b>500 m Circle</b>		
051	<b>230</b>	
052	200	
053	190	
061	210	
062	105	
063	200	
071	200	
072	320	
073	180	
081	150	
082	100	
083	240	
<b>1000 m Circle</b>		
091	880	
092	330	C <sub>2</sub>
093	<b>260</b>	
101	140	
102	280	
103	250	
111	290	
112	250	
113	200	
121	220	
122	180	
		C <sub>3</sub> 40 C <sub>4</sub> 100

Table 5

## Regression Analysis for Scrubbing Factor

flow 17ℓ/min

T C*	k x 10 <sup>-2</sup>	s.d. x 10 <sup>-2</sup>	corr.	alkane
11.5	4.07	0.48	0.997	CH <sub>4</sub>
14.0	4.68	0.36	0.982	CH <sub>4</sub>
<b>22.0</b>	3.58	1.2	<b>0.978</b>	CH <sub>4</sub>
<b>25.2</b>	4.25	0.56	0.985	CH <sub>4</sub>
<b>25.2</b>	3.96	0.27	0.985	C <sub>2</sub> H <sub>6</sub>
<b>25.2</b>	<b>2.95</b>	0.24	0.977	C <sub>3</sub> H <sub>8</sub>
<b>22.0</b>	4.05	0.74	0.992	C <sub>2</sub> H <sub>6</sub>
<b>22.0</b>	4.25	0.62	0.980	C <sub>3</sub> H <sub>6</sub>