

## MEASUREMENT OF BENZENE IN AIR

### EASTERN METROPOLITAN SUBURBAN AREA SERVICE STATION 1

#### COMPANY B

#### DISCUSSION

The Company B Service Station 1 was located in a large eastern metropolitan suburban area approximately 1000 meters from a turnpike. The terrain is very hilly with a major rush hour thoroughfare passing by the station. The self-service station is surrounded by a residential area and has a competitive brand self-service station 200 meters to the west of the station on the same side of the highway, a restaurant across the highway approximately 100 meters to the east, and another service station across the highway and 300 meters to the east. The station operated 24 hours a day with peak hours from 8:00 p.m. to 12:00 midnight. There are an average of 2000 gallons pumped per day and 63,000 gallons per month. On the sampling date 655 gallons of unleaded gasoline and 1,478 gallons of regular gasoline were pumped for a total of 2,133 gallons. A delivery occurred at 5:30 a.m. The benzene content of the gasoline is shown in Table B-3.

The weather data are shown in Table B-4. The winds were in the SW to WSW direction and varied from calm to 12 miles per hour in the early afternoon hours. The temperature ranged from a low of 49°F degrees at 3:30 a.m. to a high of 74°F at 3:30 p.m. The humidity ranged from 33% to 63%. Skies were partly cloudy to clear and sunny. The barometric pressure varied from 30.06 to 30.20.

The samples were collected over a 24-hour period around the perimeter of the service station. Three eight-hour samples were collected on 600 mg charcoal tubes at each of the seven sampling sites. The sites are shown on Figure B-2 and the benzene analyses are shown on Table B-5. The upwind location were sample sites 5 and 6 and were located near a competitive brand self-serve station approximately 200 meters from Company B station. The benzene concentration averaged 5 ppb during the A sampling period, 9.5 ppb during the B shift, and 13 ppb during the C sampling period. The downwind location was sampling site 2, approximately 200 meters from the station, with an average of trace levels of benzene to 10 ppb over the C sampling shift. The perimeter averages ranged from 8.5 ppb to 30 ppb during the 24-hour samples. Group A results included the evening rush hour traffic and Group C included the morning rush hour traffic and a gasoline delivery. The car traffic contributed to the benzene content in the atmosphere.

TABLE B-4  
 WEATHER DATA FOR JUNE 21-22, 1977  
 Company B SELF-SERVICE STATION 1

| DATE    | TIME        | TEMPERATURE<br>°F | RELATIVE<br>HUMIDITY<br>% | BAROMETER | WINDS       | SKIES      |
|---------|-------------|-------------------|---------------------------|-----------|-------------|------------|
| 6-21-77 | 12:30 PM    | 68                | 44                        | 30.06     | SW 10       | Sunny      |
|         | 1:30        | 72                | 39                        | 30.06     | SW 12       | Sunny      |
|         | 2:30        | 73                | 35                        | 30.06     | WSW 14      | Pt. Cloudy |
|         | 3:30        | 74                | 34                        | 30.06     | WSW 12      | Pt. Cloudy |
|         | 4:30        | 74                | 33                        | 30.07     | WSW 12      | Pt. Cloudy |
|         | 5:30        | 72                | 33                        | 30.07     | Light SW 12 | Sunny      |
|         | 6:30        | 72                | 34                        | 30.07     | Light SW 12 | Sunny      |
|         | 7:30        | 70                | 36                        | 30.08     | Light SW 12 | Clear      |
|         | 8:30        | 68                | 42                        | 30.08     | Calm        | Clear      |
|         | 9:30        | 61                | 45                        | 30.11     | Calm        | Clear      |
|         | 12 Midnight | 56                | 49                        | 30.13     | Calm        | Clear      |
| 6-22-77 | 2:30 AM     | 50                | 58                        | 30.13     | Calm        | Clear      |
|         | 3:30        | 49                | 60                        | 30.14     | Calm        | Clear      |
|         | 4:30        | 49                | 63                        | 30.14     | Calm        | Clear      |
|         | 7:30        | 51                | 63                        | 30.15     | Calm        | Hazy       |
|         | 8:30        | 58                | 63                        | 30.17     | Calm        | Clear      |
|         | 9:30        | 62                | 55                        | 30.18     | Calm        | Clear      |
|         | 10:30       | 62                | 48                        | 30.20     | Light SW    | Clear      |
|         | 11:30       | 70                | 42                        | 30.20     | Light SW    | Clear      |

TABLE B-3

BENZENE CONCENTRATIONS IN GASOLINE AT COMPANY B SERVICE STATION 1

|          | <u>Volume %</u> |
|----------|-----------------|
| Regular  | 0.8             |
| Unleaded | 0.6             |

TABLE B-5

BENZENE CONCENTRATIONS SUBURBAN EASTERN SERVICE STATION 1COMPANY B

| <u>Location</u>               | <u>Distance from<br/>Serv. Station<br/>Meters</u> | <u>A</u>                         |            | <u>B</u>                         |            | <u>C</u>                          |            |
|-------------------------------|---------------------------------------------------|----------------------------------|------------|----------------------------------|------------|-----------------------------------|------------|
|                               |                                                   | <u>12:30 p.m.-<br/>8:30 p.m.</u> |            | <u>8:30 p.m.<br/>- 4:30 a.m.</u> |            | <u>4:30 a.m.<br/>- 12:30 p.m.</u> |            |
|                               |                                                   | <u>MCM</u>                       | <u>ppb</u> | <u>MCM</u>                       | <u>ppb</u> | <u>MCM</u>                        | <u>ppb</u> |
| 1                             | 40                                                | 32                               | 10         | BDL                              | BDL        | 127                               | 40         |
| 2                             | 85                                                | TR                               | TR         | TR                               | TR         | 32                                | 10         |
| 5                             | 175                                               | TR                               | TR         | 29                               | 9          | 45                                | 14         |
| 6                             | 160                                               | 32                               | 10         | 32                               | 10         | 37                                | 12         |
| 7                             | 25                                                | 24                               | 7          | 96                               | 30         | 64                                | 20         |
| Upwind Avg.<br>(sites 5,6)    |                                                   | 16                               | 5          | 30                               | 9.5        | 41                                | 13         |
| Downwind Avg.<br>(site 2)     |                                                   | TR                               | TR         | TR                               | TR         | 32                                | 10         |
| Perimeter Avg.<br>(sites 1,7) |                                                   | 27                               | 8.5        | 48                               | 15         | 95                                | 30 -       |

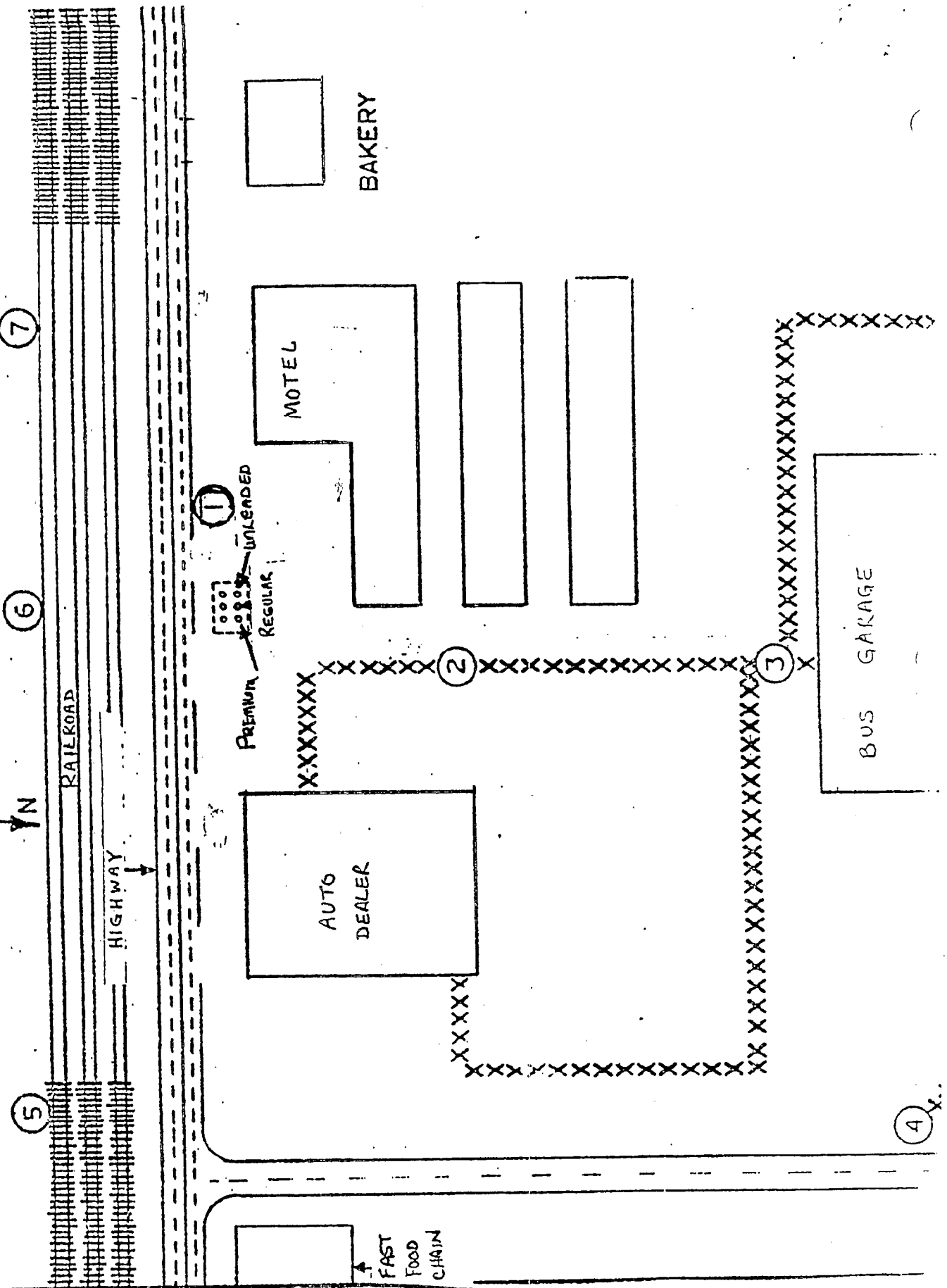
TR = Trace

BDL = Below Detection Limits

Sample 3 spilled during analysis -- pump was 30 meters from station

Sample 4 pump failed; benzene content on tube was 0.014 mg. Pump was  
55 meters from station.

FIGURE B-3  
SUBURBAN EASTERN COMPANY B SERVICE STATION 2



## MEASUREMENT OF BENZENE IN AIR

### EASTERN METROPOLITAN SUBURBAN AREA SERVICE STATION 2

#### COMPANY B

#### DISCUSSION

The Company B service station 2 was located in a large eastern metropolitan suburban area approximately 1000 meters from a turnpike. The terrain is very hilly with a major rush hour thoroughfare passing by the station. The self-service station is in a commercial strip with a fast food chain, auto dealer, motel, and bakery in the immediate vicinity. The station operated 16 hours during the day from 7:00 a.m. to 11:00 p.m. with peak hours from 5:00 to 11:00 p.m. The station pumps an average of 2500 gallons per day and 75,000 gallons per month. On the date of sampling, there were 415 gallons of premium sold, 850 gallons of unleaded sold, and 1,690 gallons of regular sold for a total 2,955 gallons sold. The benzene content is shown in Table B-6.

The weather as seen in Table B-7 was clear and sunny with a temperature ranging from 56°F at 7:30 a.m. to 77°F at 3:30 p.m. The relative humidity ranged from 30% to 59% with barometric readings from 30.10 to 30.20. The winds were light and variable from four to five mph.

The samples were collected at the seven sampling sites on 600 mg charcoal tubes. The samples were collected in an integrated manner with eight hours of collection during the 16-hour period. The pumps were on two hours and off two hours during the sampling period.

The results of the benzene sampling is shown in Table B-8. Sampling sites 1,2,3,4 ranged from 10 ppb to 50 ppb in the commercial strip. The 50 ppb level was located on the highway. Pump 5 was vandalized and pumps 6 and 7 were located on the railroad tracks. Pump 6 had trace levels and pump 7 had 10 ppb levels. The levels were higher in the commercial strip and on the highway showing the automobile influence. The winds were light and variable which did not contribute to upwind and downwind averages.

TABLE B-7  
 WEATHER DATA FOR JUNE 23, 1977  
 Company B SELF-SERVICE STATION 2

| DATE    | TIME    | TEMPERATURE<br>°F | RELATIVE<br>HUMIDITY<br>% | BAROMETER | WINDS        | SKIES |
|---------|---------|-------------------|---------------------------|-----------|--------------|-------|
| 6-23-77 | 7:30 AM | 56                | 59                        | 30.20     | NE 6         | Clear |
|         | 9:30    | 59                | 53                        | 30.20     | E 5          | Clear |
|         | 10:30   | 63                | 50                        | 30.10     | Calm         | Clear |
|         | 11:30   | 68                | 42                        | 30.10     | NE 4         | Clear |
|         | 1:30 PM | 72                | 33                        | 30.10     | WSW 4        | Clear |
|         | 2:30    | 74                | 31                        | 30.13     | NE 4         | Clear |
|         | 3:30    | 77                | 30                        | 30.14     | Light Breeze | Clear |
|         | 4:30    | 76                | 30                        | 30.12     | Light Breeze | Clear |
|         | 5:30    | 73                | 33                        | 30.12     | Light Breeze | Clear |
|         | 6:30    | 73                | 35                        | 30.11     | Light Breeze | Clear |
|         | 8:30    | 73                | 36                        | 30.11     | Light Breeze | Clear |
|         | 9:30    | 69                | 37                        | 30.11     | Light Breeze | Clear |
|         | 10:30   | 68                | 39                        | 30.11     | Light Breeze | Clear |

TABLE B-6

BENZENE CONCENTRATIONS IN GASOLINE AT SERVICE STATION 2COMPANY B

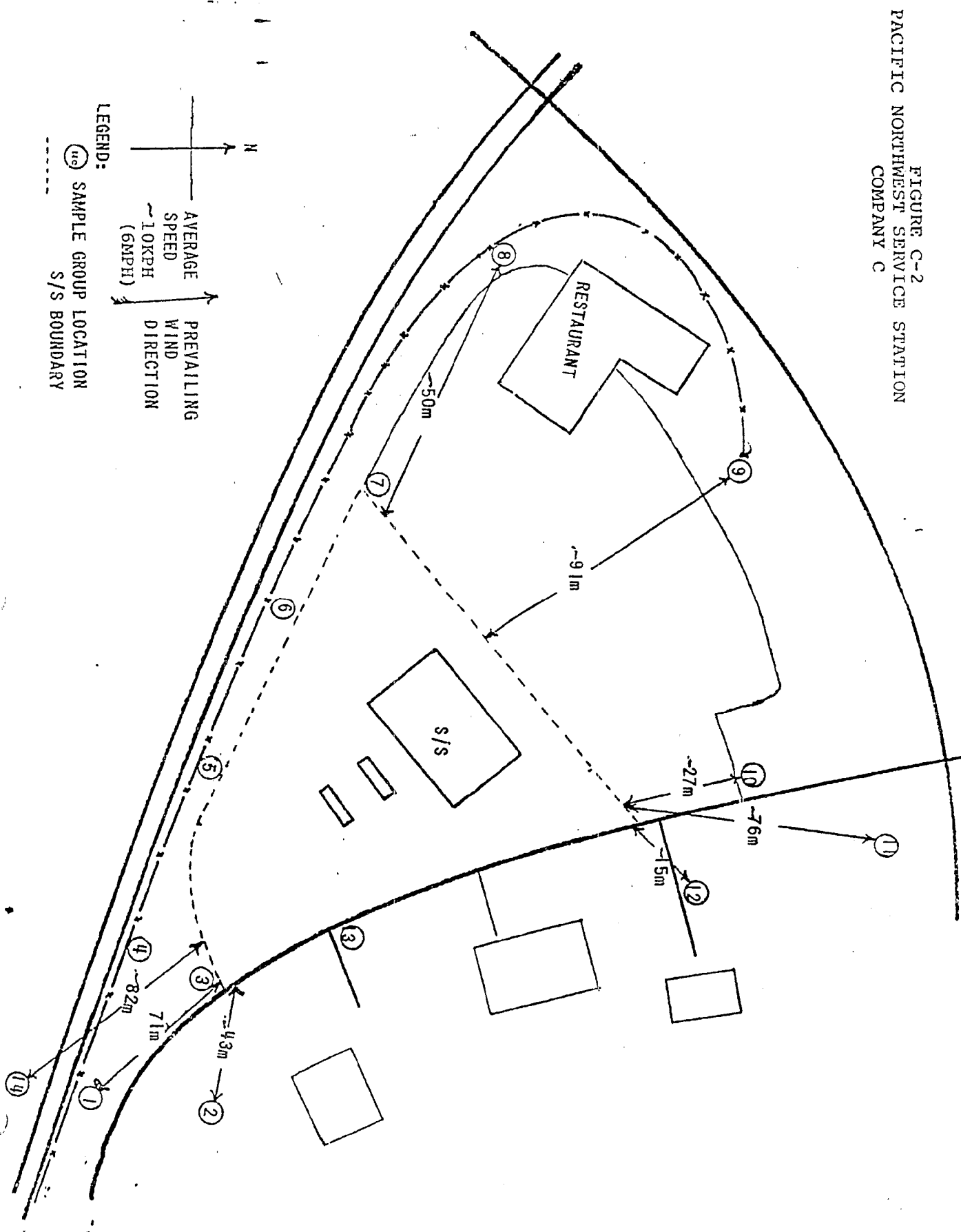
|          | <u>Volume %</u> |
|----------|-----------------|
| Regular  | 0.9             |
| Unleaded | 0.6             |
| Premium  | 0.7             |

TABLE B-8

BENZENE CONCENTRATIONS SUBURBAN EASTERN SERVICE STATION 2COMPANY B

| <u>Location</u> | <u>Distance from<br/>Service Station</u> | <u>Benzene</u> |            |
|-----------------|------------------------------------------|----------------|------------|
|                 |                                          | <u>MCM</u>     | <u>ppb</u> |
| 1               | 0                                        | 159            | 50         |
| 2               | 50 m                                     | 64             | 20         |
| 3               | 100 m                                    | 32             | 10         |
| 4               | 150 m                                    | 64             | 20         |
| 5               | 130 m                                    | Vandalized     |            |
| 6               | 50 m                                     | Trace          | Trace      |
| 7               | 80 m                                     | 32             | 10         |

FIGURE C-2  
PACIFIC NORTHWEST SERVICE STATION  
COMPANY C



## PACIFIC NORTHWEST SERVICE STATION

### COMPANY C

#### DISCUSSION

The Pacific Northwest service station is a 24-hour station located in a rural area at an intersection with an interstate highway. It is a combination full and self-service station. The land around the service station was fairly level with the exception of the ramp system at the intersection. A motorcycle sales/service shop and private homes were located upwind and across the interstate highway from the service station. Several houses and a restaurant were adjacent to the service station. The remaining land was used primarily for farming.

The weather was clear during the 24-hour period although an extremely heavy dew covered the ground during the early morning hours (a relative humidity of 95% was observed). The prevailing wind was from a south to a southeasterly direction at an average speed range of 4.7 to 7.1 mph.

Sampling pumps equipped with 1000 mg charcoal tubes were set up on a north-south axis along the interstate highway. Sampling at 1 liter/minute was continued for eight hours. Sample tubes were replaced every eight hours for the 24-hour test period.

Product thruput at the service station was 1,600 gallons. Benzene contents of the gasolines are as follows: Premium, 1.1 vol.%; Regular, 0.9 vol.%; Unleaded at 1.1 vol.%. -

Analyses of the samples show that there was relatively little variation in ambient benzene level between upwind, downwind, and perimeter samples. Higher average benzene concentrations were observed during the 4:00 a.m. to 12:00 noon monitoring period. We are unable to account for this increase since no unusual operating conditions were observed and no deliveries were made to the service station during the monitoring period. Overall the average benzene concentration was 4 ppb, individual readings ranging from Nil to 16 ppb were observed.

TABLE C-4

BENZENE LEVELS AROUND PACIFIC NORTHWEST SERVICE STATION

| <u>Sampling Location</u>       | <u>Distance from Station meter</u> | <u>COMPANY C</u>               |                         |                               |                         |                                |                         |
|--------------------------------|------------------------------------|--------------------------------|-------------------------|-------------------------------|-------------------------|--------------------------------|-------------------------|
|                                |                                    | <u>12:00 Noon to 8:00 p.m.</u> |                         | <u>8:00 p.m. to 4:00 a.m.</u> |                         | <u>4:00 a.m. to 12:00 Noon</u> |                         |
|                                |                                    | <u>ppb</u>                     | <u>µg/m<sup>3</sup></u> | <u>ppb</u>                    | <u>µg/m<sup>3</sup></u> | <u>ppb</u>                     | <u>µg/m<sup>3</sup></u> |
| 1                              | 71                                 | 1                              | 4                       | 1                             | 4                       | 3                              | 9                       |
| 2                              | 43                                 | 1                              | 2                       | 2                             | 5                       | 6                              | 17                      |
| 3                              | 0                                  | 3                              | 10                      | Nil                           | Nil                     | 6                              | 17                      |
| 4                              | 0                                  | 3                              | 8                       | 3                             | 4                       | 1                              | 4                       |
| 5                              | 0                                  | 2                              | 6                       | 3                             | 4                       | 1                              | 2                       |
| 6                              | 0                                  | 3                              | 9                       | 4                             | 11                      | 5                              | 16                      |
| 7                              | 0                                  | 4                              | 11                      | 3                             | 10                      | 8                              | 23                      |
| 8                              | 50                                 | 1                              | 2                       | 2                             | 6                       | 2                              | 7                       |
| 9                              | 91                                 | 4                              | 11                      | 4                             | 11                      | 5                              | 16                      |
| 10                             | 27                                 | 3                              | 9                       | 4                             | 11                      | 16                             | 47                      |
| 11                             | 76                                 | 2                              | 6                       | 3                             | 8                       | 10                             | 29                      |
| 12                             | 15                                 | 3                              | 9                       | Nil                           | Nil                     | 3                              | 10                      |
| 13                             | 0                                  | 3                              | 8                       | 1                             | 4                       | 1                              | 4                       |
| 14                             | 82                                 | 4                              | 11                      | 1                             | 4                       | 7                              | 21                      |
| Average                        |                                    | 3                              |                         | 2                             |                         | 5                              |                         |
| Avg. Upwind Samples (1,2,14)   |                                    | 2                              |                         | 1                             |                         | 5                              |                         |
| Avg. Perimeter Samples         |                                    | 3                              |                         | 2                             |                         | 4                              |                         |
| Avg. Downwind Samples (8,9,10) |                                    | 3                              |                         | 3                             |                         | 8                              |                         |

TABLE C-3

WEATHER DATA FOR JULY 20-21, 1977PACIFIC NORTHWEST SERVICE STATION

| <u>Time</u>               | <u>Temperature<br/>OF</u> | <u>Relative<br/>Humidity %</u> | <u>COMPANY C</u> |                  | <u>General<br/>Weather<br/>Conditions</u> |
|---------------------------|---------------------------|--------------------------------|------------------|------------------|-------------------------------------------|
|                           |                           |                                | <u>Wind</u>      | <u>Speed</u>     |                                           |
|                           |                           |                                | <u>Direction</u> | <u>kph (mph)</u> |                                           |
| 12:15 p.m.<br>- 8:15 p.m. | 80                        | 55                             | S                | 7.5 (4.7)        | Clear                                     |
| 8:15 p.m.<br>- 4:15 p.m.  | 68                        | 70                             | SE               | 11.4 (7.1)       | Clear, Heavy<br>Dew                       |
| 4:15 a.m.<br>- 12:15 p.m. | 54                        | 95                             | S                | 10.2 (6.4)       | Cloudy, Heavy<br>Dew                      |

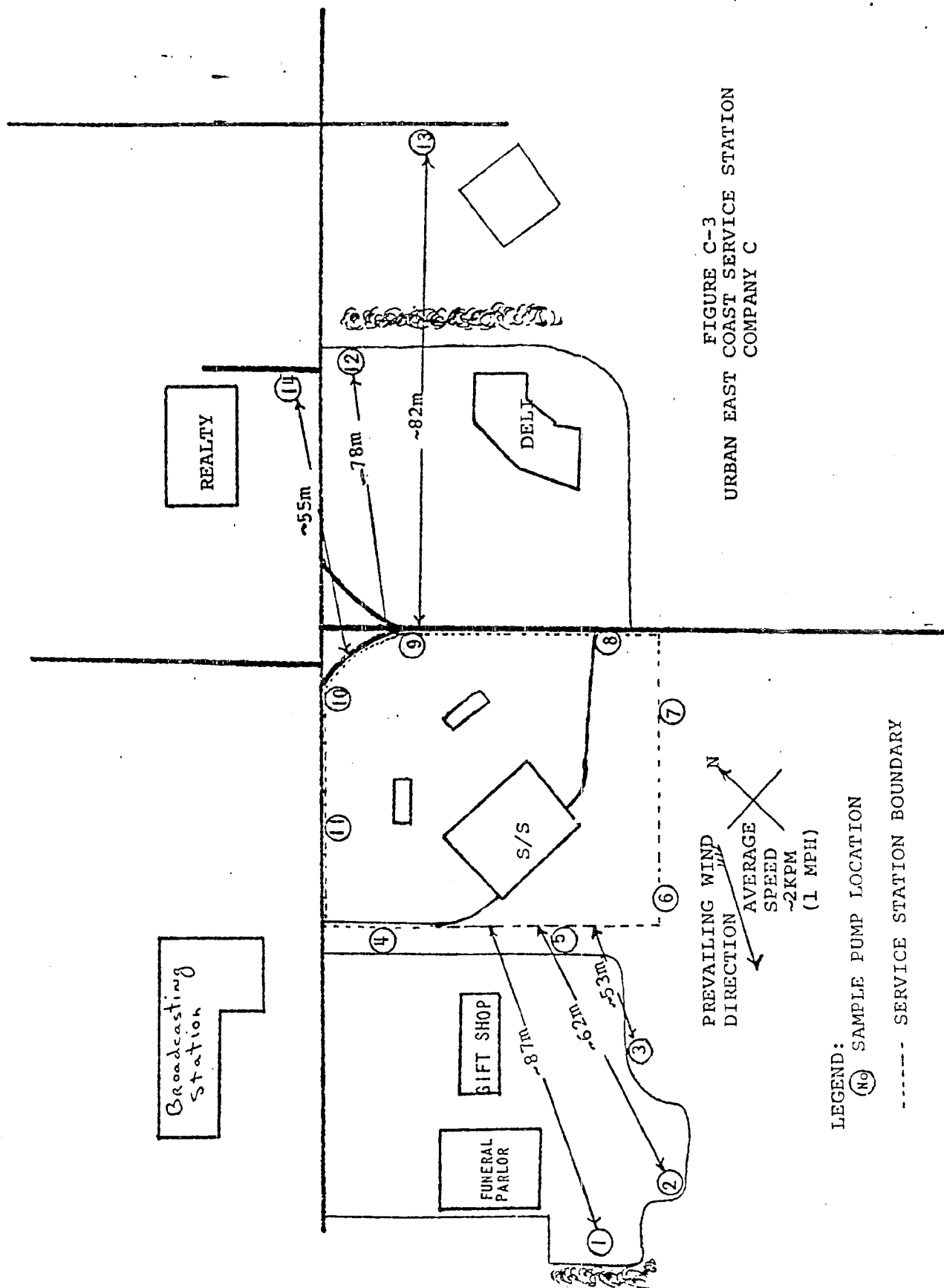


FIGURE C-3  
URBAN EAST COAST SERVICE STATION  
COMPANY C

LEGEND:  
 (N) SAMPLE PUMP LOCATION  
 ---- SERVICE STATION BOUNDARY

## URBAN EAST COAST SERVICE STATION

### COMPANY C

#### DISCUSSION

Company C's urban East Coast service station is a full service station located in a relatively level section of rolling terrain in an East Coast city. Except as noted in Figure C-3, the property surrounding the service station is used primarily for private one-family housing.

The weather was clear throughout testing. A high prevailing northeast wind was blowing at an average of 0.3 to 2.3 mph. The temperature ranged from 66 -80°F with a relative humidity of 34%-88%.

Sampling pumps were set up on a northeast by southwest axis at the intersection of two city streets. A moderate flow of traffic passed through the intersection during the day. Samples were collected using 600 mg charcoal tubes at a flow rate of 1 liter/minute. Continuous eight-hour sampling was done throughout the 24 hours of monitoring.

The service station was open from 7:30 a.m. to 10:00 p.m. No deliveries were received during monitoring. Throughput at the service station during the 24-hour test was 900 gallons. Benzene contents of the gasolines are as follows: Premium, 1.2 vol.%; Regular, 1.0 vol.%; and Unleaded, 0.4 vol.%.

The overall average ambient benzene concentration was 4 ppb with a range of 1-19 ppb. Sample analyses show that during one eight-hour period the average downwind benzene concentration reached 10 ppb during the 8:30 p.m.-4:30 a.m. period. The perimeter samples taken on the downwind side of the service station during the same period do not reflect the slightly higher observed downwind concentrations.

TABLE C-6

BENZENE LEVELS AROUND URBAN EAST COAST SERVICE STATIONCOMPANY C

| <u>Sampling Location</u>       | <u>Distance from Station Meters</u> | <u>12:30 p.m. - 8:30 p.m.</u> |                                            | <u>8:30 p.m. - 4:30 a.m.</u> |                                            | <u>4:30 a.m. - 12:30 p.m.</u> |                                            |
|--------------------------------|-------------------------------------|-------------------------------|--------------------------------------------|------------------------------|--------------------------------------------|-------------------------------|--------------------------------------------|
|                                |                                     | <u>ppb</u>                    | <u><math>\mu\text{g}/\text{m}^3</math></u> | <u>ppb</u>                   | <u><math>\mu\text{g}/\text{m}^3</math></u> | <u>ppb</u>                    | <u><math>\mu\text{g}/\text{m}^3</math></u> |
| 1                              | 87                                  | 3                             | 8                                          | 13                           | 38                                         | 2                             | 6                                          |
| 2                              | 62                                  | 4                             | 13                                         | 7                            | 20                                         | 2                             | 7                                          |
| 3                              | 53                                  | 4                             | 11                                         | 12                           | 36                                         | 2                             | 6                                          |
| 4                              | 0                                   | 3                             | 9                                          | 5                            | 14                                         | 1                             | 2                                          |
| 5                              | 0                                   | 2                             | 6                                          | 1                            | 4                                          | 1                             | 4                                          |
| 6                              | 0                                   | 3                             | 8                                          | 7                            | 20                                         | 1                             | 2                                          |
| 7                              | 0                                   | 2                             | 7                                          | 4                            | 11                                         | 3                             | 8                                          |
| 8                              | 0                                   | 6                             | 18                                         | 4                            | 12                                         | 1                             | 2                                          |
| 9                              | 0                                   | 6                             | 18                                         | 3                            | 10                                         | 3                             | 10                                         |
| 10                             | 0                                   | 5                             | 14                                         | 2                            | 7                                          | 1                             | 4                                          |
| 11                             | 0                                   | 8                             | 23                                         | 19                           | 59                                         | 2                             | 6                                          |
| 12                             | 78                                  | Missing                       |                                            | 5                            | 14                                         | 3                             | 9                                          |
| 13                             | 82                                  | 4                             | 13                                         | 9                            | 27                                         | 2                             | 5                                          |
| 14                             | 55                                  | 5                             | 14                                         | 5                            | 14                                         | 3                             | 9                                          |
| Average                        |                                     | 4                             |                                            | 7                            |                                            | 2                             |                                            |
| Avg. Upwind Samples (12,13,14) |                                     | 4                             |                                            | 6                            |                                            | 3                             |                                            |
| Avg. Perimeter Samples         |                                     | 4                             |                                            | 6                            |                                            | 2                             |                                            |
| Avg. Downwind Samples (1,2,3)  |                                     | 4                             |                                            | 10                           |                                            | 2                             |                                            |

TABLE C-5

WEATHER DATA FOR AUGUST 15-16, 1977URBAN EAST COAST SERVICE STATION

| <u>Time</u>              | <u>Temperature</u><br><u>°F</u> | <u>Relative</u><br><u>Humidity %</u> | <u>COMPANY C</u><br><u>Wind</u> |                                  | <u>General</u><br><u>Weather</u><br><u>Conditions</u> |
|--------------------------|---------------------------------|--------------------------------------|---------------------------------|----------------------------------|-------------------------------------------------------|
|                          |                                 |                                      | <u>Direction</u>                | <u>Speed</u><br><u>kph (mph)</u> |                                                       |
| 12:30 p.m.-<br>8:30 p.m. | 88                              | 34                                   | NE                              | 2.7 (1.7)                        | Clear                                                 |
| 8:30 p.m.-<br>4:30 a.m.  | 66                              | 88                                   | N                               | 0.4 (0.3)                        | Clear,<br>Moderate Dew                                |
| 4:30 a.m.-<br>12:30 p.m. | 79                              | 68                                   | NE                              | 3.7 (2.3)                        | Cloudy                                                |

The benzene air concentrations are listed in Table D-9 in parts per billion V/V and in micrograms per cubic meter. There was no breakthrough of benzene or toluene on any sample within the limits of detectability reported by the laboratory. Therefore, no problems were created by use of 150- rather than 600-milligram charcoal tubes.

Series C levels, collected when the station was closed and traffic was very light, were about the same at all locations sampled. The results suggest that sources from the busy highway west of the station outweigh contributions from the station operation.

## MEASUREMENT OF BENZENE IN AIR

### SUBURBAN MOUNTAIN STATION

#### COMPANY D

#### PURPOSE

Measure benzene levels in the air around a service station.

#### SCOPE

Round-the-clock sampling at up to 16 sites around the station perimeter and at locations upwind and downwind up to 300' away.

#### PROCEDURE

The benzene was analyzed using ASTM D-3606 (1977) in the procedure in Appendix A. However, 150-milligram charcoal tubes were used. The toluene peaks in the chromatographs were also analyzed to confirm whether any breakthrough of the front charcoal layer had occurred.

#### DISCUSSION

The area around the station is flat in all directions at an elevation of about 4200' above sea level. There is a drop-off of about six feet at the east and south perimeter of the station. A large-scale grading operation was in progress during the sampling. The grading is for a large shopping center to be built to the east of the station, beyond the eastern-most sampling sites used in the survey. Diesel-fueled scrapers and dozers, in use from 0700-1600 hours each day, were parked overnight and at noon in the area directly south of the station. Highway traffic was heavy during the day, moderate in the early evening and light during the night.

Wind readings at the station and weather readings from an airport about three miles northeast are listed in Table D-6. Winds around the station were occasional, light and variable in direction. The sampling sites were selected in anticipation of westerly winds, which were predicted for the area. However, no significant consistent upwind/downwind pattern developed during the survey.

The volume and benzene content of the gasoline pumped during the sampling are shown in Table D-7. No gasoline deliveries were made to the station underground product tanks during the sampling period. This station does not have a vapor recovery system and there are no breather valves on the product storage tanks.

The sampling sites are shown in Figure D-2 and are described in Table D-8. The sensitivity or lowest level of detectability for benzene in the eight-hour samples was found to be 0.3 micrograms.

TABLE D-6  
SUBURBAN MOUNTAIN STATION WEATHER DATA  
COMPANY D

A. Source: Direct Measurements at Station

| <u>Time</u><br><u>(2400 Hour)</u> | <u>Wind Speed Range</u><br><u>(MPH)</u> | <u>Visual Estimate of</u><br><u>Wind Direction</u><br><u>From</u> |
|-----------------------------------|-----------------------------------------|-------------------------------------------------------------------|
| <u>July 13, 1977:</u> 0712        | 0-1                                     | W                                                                 |
| 0720                              | 1-3                                     | S                                                                 |
| 0818                              | 0-2                                     | E                                                                 |
| 1130                              | 2-5                                     | W                                                                 |
| 1230                              | 0-5                                     | SW                                                                |
| 1510                              | 0-2                                     | NE                                                                |
| 1700                              | 0-5                                     | Variable                                                          |
| 1930                              | 0-5                                     | Variable                                                          |
| 2200                              | Nil                                     | -                                                                 |
| 2243                              | 0-1                                     | Variable                                                          |
| <u>July 14, 1977:</u> 0110        | Nil                                     | -                                                                 |
| 0319                              | Nil                                     | -                                                                 |
| 0642                              | Nil                                     | -                                                                 |
| 0751                              | Nil                                     | -                                                                 |
| 0952                              | Nil                                     | -                                                                 |
| 1151                              | Nil                                     | -                                                                 |
| 1320                              | 0-8                                     | Variable                                                          |
| 1504                              | 0-5                                     | Variable                                                          |

B. Source: Airport, about 3 miles Northeast of Station

| <u>Time</u><br><u>(2400 Hour)</u> | <u>Temperature</u><br><u>(°F)</u> | <u>% Relative</u><br><u>Humidity</u> | <u>Barometric</u><br><u>Pressure</u> |
|-----------------------------------|-----------------------------------|--------------------------------------|--------------------------------------|
| <u>July 13, 1977:</u> 0720        | 57                                | 45                                   | 30.09                                |
| 0800                              | 62                                | 40                                   | 30.10                                |
| 1200                              | 82                                | 20                                   | 30.07                                |
| 1400                              | 86                                | 15                                   | 30.04                                |
| 1600                              | 89                                | 15                                   | 30.02                                |
| 1800                              | 90                                | 15                                   | 29.99                                |
| 2130                              | 78                                | 20                                   | 30.05                                |
| <u>July 14, 1977:</u> 0330        | 51                                | 60                                   | 30.10                                |
| 0630                              | 50                                | 60                                   | 30.13                                |
| 1000                              | 75                                | 27                                   | 30.13                                |
| 1200                              | 83                                | 18                                   | 30.10                                |
| 1500                              | 93                                | 13                                   | 30.04                                |

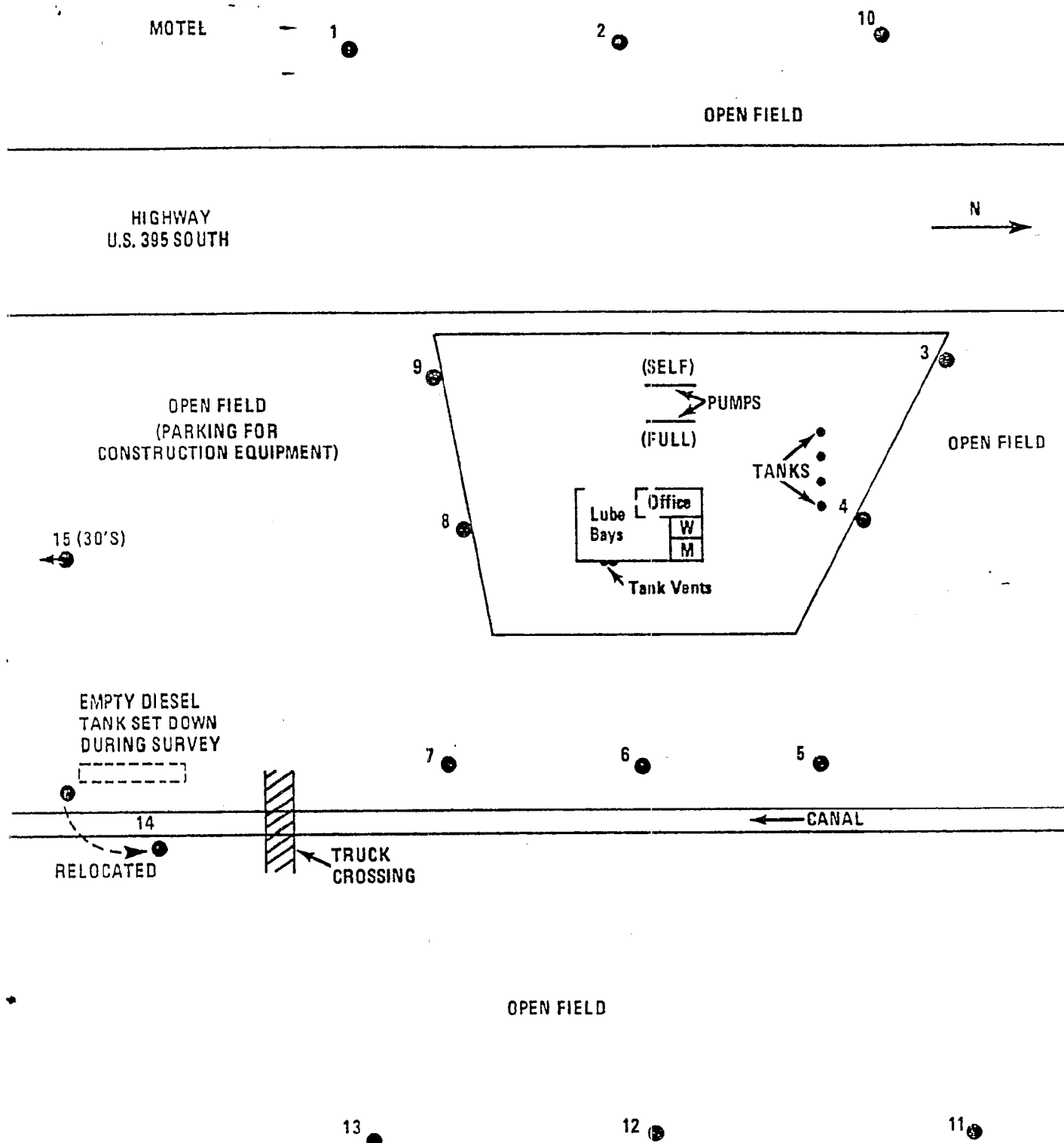


FIGURE D-2

SUBURBAN MOUNTAIN STATION

Scale: 1" = 50'  
7-25-77

TABLE D-8  
SAMPLING SITES AT SUBURBAN MOUNTAIN STATION  
COMPANY D

SITE

- 1 180' West of pump islands across Highway.
- 2 150' West of the pump island across Highway --- in large open area.
- 3 115' North of pump islands at the station fence near Highway ---.
- 4 100' Northeast of pump islands at station fence opposite restrooms.
- 5 150' East-northeast of pump islands about 70' east of the station fence in open area.
- 6 140' East of pump islands in rear of station building in open area.
- 7 160' Southeast of pump islands in open area.
- 8 80' Southwest of pump islands at fence opposite lube bays.
- 9 70' South of pump island at fence near Highway ---.
- 10 140' Northwest of pump islands across Highway --- at fence north of open area.
- 11 310' East-northeast of pump islands in open field.
- 12 260' South of pump islands in open field.
- 13 310' East-southeast of pump islands in open field.
- 14 270' South-southeast of pump islands at edge of canal near truck cross-over.
- 15 240' South of pump island at edge of mound of dirt at far side of open area adjacent to the station.

TABLE D-7

## GALLONS OF GASOLINE PUMPED AT SUBURBAN MOUNTAIN STATION

## COMPANY D

|                         | <u>Premium</u> | <u>Regular</u> | <u>Unleaded</u> | <u>Total</u> |
|-------------------------|----------------|----------------|-----------------|--------------|
| <u>Percent Benzene</u>  | 1.3            | 1.1            | 1.5             | NA           |
| SERIES A                |                |                |                 |              |
| 0700-1400               |                |                |                 |              |
| <u>July 13, 1977</u>    |                |                |                 |              |
| Self-Serve              | 81             | 416            | 133             | 630          |
| Full-Serve              | <u>130</u>     | <u>258</u>     | <u>312</u>      | <u>700</u>   |
| TOTAL                   | 211            | 674            | 445             | 1330         |
| SERIES B                |                |                |                 |              |
| 1430-2200               |                |                |                 |              |
| <u>July 13, 1977</u>    |                |                |                 |              |
| Self-Serve              | 53             | 294            | 69              | 416          |
| Full-Serve              | <u>38</u>      | <u>180</u>     | <u>84</u>       | <u>302</u>   |
| TOTAL                   | 91             | 474            | 153             | 718          |
| SERIES C                |                |                |                 |              |
| 2200-0700               |                |                |                 |              |
| <u>July 13-14, 1977</u> |                |                |                 |              |
| TOTAL                   | None           | None           | None            | None         |
| SERIES D                |                |                |                 |              |
| 0700-1430               |                |                |                 |              |
| <u>July 14, 1977</u>    |                |                |                 |              |
| Self-Serve              | 114            | 491            | 131             | 736          |
| Full-Serve              | <u>163</u>     | <u>338</u>     | <u>193</u>      | <u>694</u>   |
| TOTAL                   | 277            | 829            | 329             | 1430         |

TABLE D-9  
BENZENE LEVELS AROUND SUBURBAN MOUNTAIN STATION

COMPANY D

| <u>Sample Series</u>       | <u>A</u>             |              | <u>B</u>             |            | <u>C</u>                |            | <u>D</u>             |            |
|----------------------------|----------------------|--------------|----------------------|------------|-------------------------|------------|----------------------|------------|
| <u>Time</u><br><u>Date</u> | 0700-1430<br>7/13/77 |              | 1430-2200<br>7/13/77 |            | 2200-0700<br>7/13-14/77 |            | 0700-1430<br>7/14/77 |            |
| <u>SITE</u>                | <u>PPB*</u>          | <u>MCM**</u> | <u>PPB</u>           | <u>MCM</u> | <u>PPB</u>              | <u>MCM</u> | <u>PPB</u>           | <u>MCM</u> |
| 1                          | 3                    | 10           | 2                    | 7          | 1                       | 4          | 4                    | 12         |
| 2                          | 3                    | 8            | 2                    | 5          | 2                       | 6          | 2                    | 6          |
| 3                          | 2                    | 8            | 4                    | 12         |                         |            | 3                    | 11         |
| 4                          | 2                    | 6            | 3                    | 8          |                         |            | 3                    | 11         |
| 5                          | nil                  | 1            | 2                    | 6          | 2                       | 5          | 1                    | 3          |
| 6                          | 1                    | 2            | 1                    | 5          |                         |            | 1                    | 3          |
| 7                          | 1                    | 3            | 2                    | 6          |                         |            | 1                    | 4          |
| 8                          | 2                    | 5            | 3                    | 9          | 2                       | 6          | 1                    | 4          |
| 9                          | 2                    | 5            | 4                    | 12         |                         |            | 4                    | 12         |
| 10                         | 3                    | 9            | 2                    | 5          |                         |            | 2                    | 7          |
| 11                         | nil                  | 1            | 1                    | 5          |                         |            | 1                    | 3          |
| 12                         | nil                  | 1            | 1                    | 4          |                         |            | nil                  | 1          |
| 13                         | 1                    | 3            | 1                    | 3          |                         |            | 1                    | 4          |
| 14                         | 1                    | 3            | 2                    | 5          | 2                       | 5          | 1                    | 4          |
| 15                         | 1                    | 4            | 2                    | 6          |                         |            | 1                    | 3          |

\* Parts per billion of Benzene, volume/volume

\*\* Micrograms of Benzene per cubic meter of air

is not considered to be a breakthrough problem. This conclusion is supported by the toluene results which showed less than 0.1 microgram on the "back" charcoal in 8 of the same 10 samples. In the remaining two samples, B14 and B16, the toluene found on the "back" charcoal was only 10% of the amount found on the "front" charcoal. Even if the "back" charcoal benzene had been added to the "front" charcoal benzene before preparing Table V, it would not have significantly changed the levels shown in Table D-13; i.e., the reported ppb benzene would be increased by only 1 ppb for each of 10 samples and would not have changed for the remaining 46 samples.

The Series C benzene levels, sampled when the station was closed and traffic was no more than a few cars per hour, were similar at all locations and comparable to the lowest Series A, B and D results. Site 10 in the center of a busy supermarket parking lot and Sites 14, 15 and 16 nearest the freeway showed somewhat higher Series A, B and D benzene levels. Sites 2, 3, 4, and 5, closest to the pump islands, showed the highest Series A, B and D benzene levels. All levels were very low. However, measured benzene levels were marginally higher close to the pump islands, at the parking lot and near the freeway.

MEASUREMENTS OF BENZENE IN AIR  
RURAL WEST COAST SERVICE STATION  
COMPANY D

PURPOSE

Measure benzene levels in the air around a service station.

SCOPE

Round-the-clock sampling at up to 16 sites around the station perimeter and at locations upwind and downwind up to 300' away.

PROCEDURE

The benzene was then analyzed using ASTM D-3606 (1977) in the procedure in Appendix A. The toluene peaks in the chromatographs were also analyzed to confirm whether any breakthrough of the first charcoal layer had occurred.

DISCUSSION

The area around the station is flat, about 200 feet above sea level. Upslopes start on the east side of Old Highway and beyond northernmost sampling sites. The traffic on Main Street was heavy during the day starting at 0500 and tapering off around 1900. There was very little traffic after dark. The traffic on Old Highway was very light at all times. Freeway traffic was light to moderate during the day and very light at night.

Weather readings taken at the station are listed in Table D-10. There were continuous light gusting winds, variable in direction. No consistent upwind/downwind pattern persisted during the survey period. There was fog with light misting at the start of Series A, during Series C and intermittently at the start of Series D.

The gallons of gasoline pumped during the survey are shown with their benzene content in Table D-11. No gasoline deliveries were made to the station underground product tanks during the sampling period. This station does not have a vapor recovery system and there are no breather valves on the product storage tanks. The sampling sites are shown on Figure D-3 and are described in Table D-12.

The benzene air concentrations are listed in Table D-13 in parts per billion V/V of benzene and in micrograms per cubic meter.

The benzene found on the "back" charcoal appeared to exceed 25% of the amount found on the "front" charcoal for 10 of the 56 samples. None of these back charcoal samples contained more than one microgram of benzene. Since the sensitivity for benzene was 1.5 micrograms, this

TABLE D-10  
 WEATHER DATA TAKEN AT RURAL WEST COAST STATION  
 COMPANY D

| <u>Time</u><br><u>2400 Hour</u> | <u>Temperature</u><br><u>°F</u> | <u>% Relative</u><br><u>Humidity</u> | <u>Visibility</u> | <u>Wind</u> |                  |
|---------------------------------|---------------------------------|--------------------------------------|-------------------|-------------|------------------|
|                                 |                                 |                                      |                   | <u>MPH</u>  | <u>Direction</u> |
| <u>July 27, 1977</u>            |                                 |                                      |                   |             |                  |
| 0530                            | 55                              | 88                                   | Fog               | 0-2         | NW               |
| 0730                            | 56                              | 85                                   | Fog               | Nil         | -                |
| 0930                            | 56                              | 88                                   | Clearing          | 4           | SW               |
| 1130                            | 57                              | 82                                   | Sun               | 1-2         | SW               |
| 1300                            | 66                              | 72                                   | Sun               | 0-2         | NNW              |
| 1500                            | 64                              | 70                                   | Sun               | 3-7         | W                |
| 1800                            | 66                              | 66                                   | Sun               | 2-4         | WNW/WSW          |
| 2000                            | 64                              | 70                                   | Sun               | 2-4         | WSW              |
| 2100                            | 58                              | 88                                   | Fog               | 0-1         | Variable         |
| 2300                            | 55                              | 94                                   | Fog               | 0-1         | Variable         |
| <u>July 28, 1977</u>            |                                 |                                      |                   |             |                  |
| 0130                            | 54                              | 94                                   | Fog               | 0-1         | Variable         |
| 0300                            | 54                              | 94                                   | Fog               | Nil         | -                |
| 0500                            | 53                              | 88                                   | Fog               | Nil         | -                |
| 0730                            | 57                              | 88                                   | Clearing          | 2-4         | SSW              |
| 0930                            | 66                              | 80                                   | Clearing          | 2           | SSW              |
| 1050                            | 62                              | 84                                   | Sun               | 2-4         | W                |
| 1115                            | 63                              | 80                                   | Sun               | 3-5         | WNW              |
| 1230                            | 65                              | 80                                   | Sun               | 2-4         | W                |

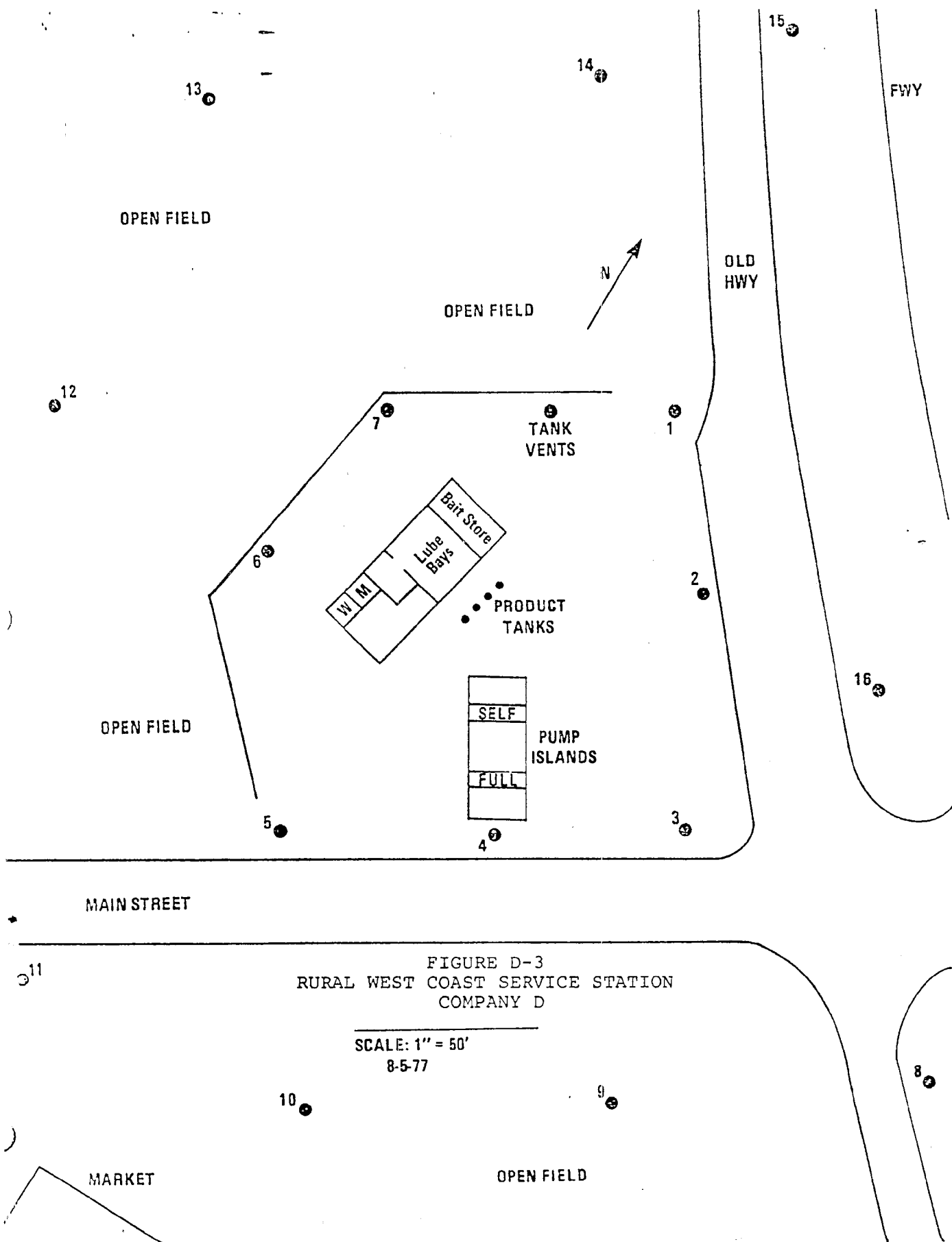


FIGURE D-3  
RURAL WEST COAST SERVICE STATION  
COMPANY D

SCALE: 1" = 50'  
8-5-77

TABLE D-12  
SAMPLING SITES AT RURAL WEST COAST STATION  
COMPANY D

SITE

- 1 160' NNE of pump islands at sidewalk edge of planter in north corner of station.
- 2 125' NE of pump islands at sidewalk edge of planter in center of Old Highway --- side of station.
- 3 80' E of pump islands at station edge of planter in east corner of station.
- 4 40' SE of south pump island at station edge of planter in center of Main Street side of station.
- 5 100' SW of pump islands at station edge of planter in south corner of station.
- 6 125' W of pump islands near station fence in planter in southwest corner of station.
- 7 150' NNW of pump islands near station fence in planter in northwest corner of station.
- 8 230' E of pump islands near tip of gore across Main Street between Old Highway --- and the on-ramp south for freeway ---.
- 9 160' SE of pump islands in vacant lot across Main Street between Bait Shop and Saunder's store parking lot.
- 10 180' SSE of pump islands in planter in Saunder's store parking lot near east end.
- 11 225' SW of pump islands in planter in the NW corner of Saunder's store parking lot.
- 12 260' W of pump islands in open field west of station.
- 13 300' NNW of pump islands in open field north of station.
- 14 280' NNE of pump islands in open field north of station.
- 15 330' NE of pump islands across Old Highway --- next to chain link fence for freeway --- southbound off-ramp.
- 16 160' E of pump islands across Old Highway --- next to chain link fence for freeway --- southbound off-ramp.

TABLE D-11

## GALLONS OF GASOLINE PUMPED AT RURAL WEST COAST STATION

COMPANY D

|                         | <u>Premium</u> | <u>Regular</u> | <u>Unleaded</u> | <u>Total</u> |
|-------------------------|----------------|----------------|-----------------|--------------|
| <u>Percent Benzene</u>  | 2.0            | 1.7            | 2.3             | N/A          |
| SERIES A                |                |                |                 |              |
| 0500-1300               |                |                |                 |              |
| <u>July 27, 1977</u>    |                |                |                 |              |
| Self-Serve              | 222            | 795            | 219             | 1236         |
| Full-Serve              | <u>94</u>      | <u>439</u>     | <u>203</u>      | <u>736</u>   |
| Total                   | 316            | 1234           | 422             | 1972         |
| SERIES B                |                |                |                 |              |
| 1300-2100               |                |                |                 |              |
| <u>July 27, 1977</u>    |                |                |                 |              |
| Self-Serve              | 318            | 799            | 206             | 1323         |
| Full-Serve              | <u>139</u>     | <u>342</u>     | <u>133</u>      | <u>614</u>   |
| Total                   | 457            | 1141           | 339             | 1937         |
| SERIES C                |                |                |                 |              |
| 2100-0500               |                |                |                 |              |
| <u>July 27-28, 1977</u> |                |                |                 |              |
| Total                   | None           | None           | None            | None         |
| SERIES D                |                |                |                 |              |
| 0500-1300               |                |                |                 |              |
| <u>July 28, 1977</u>    |                |                |                 |              |
| Self-Serve              | 327            | 812            | 148             | 1287         |
| Full-Serve              | <u>188</u>     | <u>434</u>     | <u>116</u>      | <u>738</u>   |
| Total                   | 515            | 1246           | 264             | 2025         |

TABLE D-13

## BENZENE LEVELS AROUND RURAL WEST COAST SERVICE STATION

## COMPANY D

| Sample Series | A                          |       | B                          |     | C                             |     | D                          |     |
|---------------|----------------------------|-------|----------------------------|-----|-------------------------------|-----|----------------------------|-----|
|               | 0500-1300<br>July 27, 1977 |       | 1300-2100<br>July 27, 1977 |     | 2100-0500<br>July 27-28, 1977 |     | 0500-1300<br>July 28, 1977 |     |
| Site          | PPB*                       | MCM** | PPB                        | MCM | PPB                           | MCM | PPB                        | MCM |
| 1             | 1                          | 4     | 2                          | 8   |                               |     | 1                          | 4   |
| 2             | 3                          | 8     | 1                          | 3   | 2                             | 6   | 4                          | 11  |
| 3             | 1                          | 2     | 2                          | 8   |                               |     | 3                          | 10  |
| 4             | N11                        | 1     | 4                          | 12  | N11                           | 1   | 7                          | 22  |
| 5             | N11                        | N11   | 1                          | 4   |                               |     | 2                          | 6   |
| 6             | N11                        | N11   | 1                          | 2   | 1                             | 4   | 1                          | 5   |
| 7             | N11                        | 1     | 1                          | 2   | 1                             | 4   | 1                          | 3   |
| 8             | N11                        | N11   | 1                          | 4   | 1                             | 4   | 1                          | 2   |
| 9             | N11                        | N11   | 1                          | 4   |                               |     | 1                          | 2   |
| 10            | 1                          | 4     | 1                          | 3   |                               |     | 1                          | 4   |
| 11            | N11                        | N11   | N11                        | N11 | 1                             | 2   | 1                          | 2   |
| 12            | N11                        | N11   | 1                          | 2   | 1                             | 3   | 1                          | 2   |
| 13            | N11                        | N11   | 1                          | 2   |                               |     | N11                        | 1   |
| 14            | N11                        | N11   | 2                          | 7   | 1                             | 2   | 1                          | 2   |
| 15            | 1                          | 2     | 1                          | 4   |                               |     | 1                          | 3   |
| 16            | 1                          | 2     | 2                          | 6   |                               |     | 1                          | 3   |

\* Parts per billion of benzene, volume/volume

\*\* Micrograms of benzene per cubic meter

APPENDIX A

PROPOSED MINIMUM PARAMETERS FOR 24-HOUR RANGE SETTING STUDY

| Samples                                                                         | Service Stations                                                                                                                 | Refinerics                                                                                   |
|---------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| Operation                                                                       | 11                                                                                                                               | 11                                                                                           |
| Background                                                                      | 3                                                                                                                                | 3                                                                                            |
| Grab                                                                            | 0                                                                                                                                | 0                                                                                            |
| Elevation                                                                       | 5 ft.                                                                                                                            | 5 ft.                                                                                        |
| Meteorology<br>(single location<br>on down wind side once<br>per 8 hour period) | Temperature<br>Wind Speed<br>Wind Direction<br>Humidity - wet/dry bulb                                                           | same                                                                                         |
| Sample method                                                                   | 1 ltr/min with<br>150 mg charcoal                                                                                                | same                                                                                         |
| Operating Parameters                                                            | No deliveries of fuel<br>Gals pumped per 24 hrs.<br>Sample all grades of gas<br>Actual hrs. of operation<br>Drawing of each site | Rated capacity<br>Normality of operations<br>Benzene unit in plant<br>Type of bulk transfers |
| Weather Conditions                                                              | No rain<br>No sampling with wind<br>> 20 mph at any time                                                                         | same                                                                                         |

6/27/77

**Gulf Science and Technology Company**

MEDICAL AND HEALTH RESOURCES DIVISION

P O Box 3240  
Pittsburgh PA 15230

September 12, 1977

Re: AN11-50-05  
(MR02-02-00)

Mr. W. L. Wascher, Jr.  
Mobil Oil Corporation  
Products Department 633-27  
150 East 42nd Street  
New York, NY 10017

Dear Bill:

I recommend that the attached "Tentative Method for Determination of Benzene in Ambient Air (Integrated Sampling)" be transmitted to EPA as part of our presentation on September 13, 1977. This text has been reviewed and agreed upon by the other participating API members and Mr. John Margeson of the EPA Office of Air Quality Planning and Standards.

The 600 mg charcoal tubes containing a known level of benzene have just been sent to the participants for their analysis. The Gulf Industrial Hygiene Laboratory has already completed its analysis and found that the accuracy of their work is in agreement with those statements contained in Section 4.0, "Precision and Accuracy". Once the results are received from the other laboratories, we will have confirmation of stated accuracies (see Section 4.2) or make appropriate adjustments accordingly. Although the above is a technical detail, it nonetheless must be done.

We expect that the final results will be available no later than October 28, 1977.

Very truly yours,

*H. E. Runion*

H. E. Runion

HER:az  
Attachment

cc w/att.: Members of Ad Hoc Task Force on Benzene  
B. A. McCrodden  
A. G. Smith  
R. K. Stone  
W. C. Streets  
W. C. Sussky  
S. L. Zwicker  
E. P. Crockett (API Staff)



TENTATIVE METHOD FOR DETERMINATION OF  
BENZENE IN AMBIENT AIR (INTEGRATED SAMPLING)

This method has been drafted from available information and is still being evaluated in the laboratory. The evaluation has not been completed and, therefore, the method is subject to further revision when additional information becomes available.

GULF SCIENCE AND TECHNOLOGY COMPANY  
GULF OIL CORPORATION  
INDUSTRIAL HYGIENE LABORATORY  
PITTSBURGH, PENNSYLVANIA 15230

SEPTEMBER 1977

indicate the following relative standard deviation of the analytical method:  $58 \pm 4$  ppb and  $350 \pm 20$  ppb.<sup>2</sup> Further experiments are in progress and should be forthcoming in the near future.

4.2 The statements presented below on precision and accuracy were established for the 150 mg charcoal tube and it is believed that the same or similar values would be reflected with the 600 mg charcoal tubes as shown above.

4.2.1 The mean relative standard deviation of the analytical method is 8% (see section 4.2).

4.2.2 The mean relative standard deviation of the analytical method plus field sampling using a personal sampling pump is 10% (see section 4.2).

4.2.3 The accuracy of the overall sampling and analytical method is 10% when the personal sampling pump is calibrated with a charcoal tube in the line (see section 4.2).

## 5. Apparatus

### 5.1 Sampling<sup>1</sup>

5.1.1 Charcoal tubes. Glass tube with both ends flame sealed, 11 cm long with a 8-mm O.D. and a 6-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 5-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 400 mg of charcoal, the backup section 200 mg. A 5-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. Tubes with approximately these specifications are presently available from SKC Incorporated, Pittsburgh, Pennsylvania 15220 and MSA Corporation, Pittsburgh, Pennsylvania 15116.

5.1.2 Charcoal tube caps. For capping charcoal adsorption tubes as supplied.

5.1.3 Sampling pump. A calibrated sampling pump whose flow can be determined accurately at 1 liter per minute.

5.1.4 Air flow meter. Rotameter or other type of device for measuring air flow rate, 0 to 3 lpm range.

SEPTEMBER 1977

TENTATIVE METHOD FOR DETERMINATION OF  
BENZENE IN AMBIENT AIR (INTEGRATED SAMPLING)<sup>1</sup>

1. Principle and Applicability

1.1 Benzene in ambient air is adsorbed onto activated coconut shell charcoal. The benzene is then desorbed with carbon disulfide and analyzed by gas liquid chromatography using a flame ionization detector.

1.2 The method is applicable to integrated sampling in the vicinity (near the fence line) of benzene sources and return of the collected samples to the laboratory for analysis.

2. Lower Detectable Limit and Range

The lower limit of detection is estimated to be  $3 \mu\text{g}/\text{m}^3$  (1 ppb) assuming a 480 liter air sample. The range of the method is 3 to  $480 \mu\text{g}/\text{m}^3$  (1-150 ppb) and can be extended to high values with shorter sampling periods.<sup>2</sup>

3. Interferences<sup>1</sup>

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Experimental evidence indicates that high humidity decreases the breakthrough volume, although it has been verified that 95% RH does not interfere with the method described herein.<sup>2</sup>

3.2 It must be emphasized that any compound which has the same retention time as benzene at the conditions described in this method is an interference. For this reason, it is important that a sample of the bulk material(s) be submitted at the same time so that identity(ies) can be established by other means where necessary. This is particularly important where non-hydrocarbon materials are in the area(s) of interest.

4. Precision and Accuracy<sup>1</sup>

4.1 Preliminary experiments involving five 600 mg charcoal tubes

## 6.1 Sampling

6.1.1 Charcoal tubes. Commercially available as discussed in Section 5.1.1.

## 6.2 Analysis

6.2.1 Nitrogen or helium for chromatographic carrier gas.

6.2.2 Combustion air. Containing less than  $1.3 \text{ mg/m}^3$  hydrocarbons (2 ppm as methane). To operate flame ionization detector.

## 6.3 Calibration

6.3.1 Benzene. See Section 11 for safety considerations.

## 7. Procedure

### 7.1 Sampling

7.1.1 Sampler location. Ideally, the charcoal tube should be located at the breathing level - 4 to 6 feet above ground level. However, the tube should be high enough above ground to eliminate contact of the incoming air with vegetation or physical obstructions.

#### 7.1.2 Eight-hour sampling.

7.1.2.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one half the internal diameter of the tube (3mm).

7.1.2.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

7.1.2.3 The charcoal tube is connected to the sampling pump with an appropriate length of tubing.

7.1.2.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

7.1.2.5 The flow, time, and/or volume must be measured as accurately as possible at the initiation and termination of sampling. The sample should be acquired at a flow rate of 1 lpm to attain the total sample volume required.

7.1.2.6 The charcoal tubes should be sealed with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

5.1.5 Tubing. Rubber or tyeon tubing of sufficient length to connect the charcoal tube to the sampling pump.

5.1.6 Calibration kit. Calibrated wet test meter or soap bubble flow meter for calibration of sampling pumps.

## 5.2 Analysis

5.2.1 Gas chromatograph. With flame ionization detector.

5.2.2 A mechanical or electronic integrator or a recorder and some method for determining peak area.

5.2.3 Chromatographic columns. For confirmation and analysis. If columns other than those listed below are utilized, they must be capable of performing the required separations and this documentation should be noted.

5.2.3.1 Three meter stainless steel column, 1/8" O.D., packed with 10% 1,2,3-tris (2-cyanoethoxy) propane on stationary phase.<sup>3</sup>

5.2.3.2 Sixty meter glass capillary column (0.3 mm I.D.) with SF 96 as the liquid phase.<sup>4</sup>

5.2.3.3 Column system as specified in ASTM D-3606 (1977).<sup>5</sup>

5.2.4 Hamilton syringes: 10 µl, and convenient sizes for making standards.

5.2.5 Pipets: 5 ml delivery pipets and 1.0 ml gas tight hypodermic syringe.

5.2.6 Wheaton serum vials and crimper: 5 ml septum Teflon-lined securing flange type caps.

5.2.7 Optional autosampler vials: septum Teflon-lined sealing caps - size is dependent upon autosampler manufacturer but usually 1 or 2 ml.

5.2.8 SKC charcoal developer: electric agitator to assist desorption.

## 6. Reagents

Unless otherwise indicated, it is intended that all reagents be chromatographic grade or conform to the specifications established by the Committee of Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use best available grade.

and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2  $\mu$ l to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then inserted through the desorption vial septum and immersed in the sample. A 5- $\mu$ l aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

7.2.3.2 Automatic. Utilization of autosampling accessories can be of significant assistance in performing the analysis of benzene. It permits 24-hour chromatograph operation and provides increased accuracy and greater consistency of injection volumes. Desorption vials described in Section 5.2.6 can be directly loaded into the injection tray or a sample aliquot can be transferred to an appropriate vial for tray loading. Specific operating parameters for autosamplers are detailed by the manufacturer, however, at least three solvent syringe flushes should be included for each injection.

7.2.4 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

7.2.5 Confirmation. Confirm the presence of benzene in collected samples by determining its relative retention on a second column in Section 5.2.3. It is also necessary that quantitative separation of benzene for both the analytical and confirmation columns be demonstrated. This can be accomplished by spiking appropriate aliquots of actual field samples. In addition, this is particularly important when sampling in a situation where interference from other organics or solvents may exist.

7.2.6 Gas chromatograph conditions. Operating parameters for the gas chromatograph are dependent upon the analytical column of choice (see Section 5.2.3).

7.1.2.7 One tube should be handled in the same manner as the sample tube (break, seal and transport), except that no air is sampled through this tube. This tube should be labeled as the field blank.

7.1.3 Greater than eight-hour sampling. If a sampling time greater than eight hours is desired, e.g., 24 hours, this can be obtained by three successive eight-hour samplings.

7.2.1 Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a vial as described in 5.2.6 and sealed with Teflon-lined septum caps. The separating section of foam is removed and discarded; the second section is transferred to another vial and also capped. These two sections are analyzed separately. The addition of carbon disulfide to the adsorbent as described in the following section results in an exothermic reaction. Utilization of capped vials will eliminate the loss of benzene due to volatilization.

7.2.2 Desorption of samples. Exactly 1.0 ml of carbon disulfide is syringe injected through the septum into each vial. (All work with carbon disulfide should be performed in a hood because of its toxicological properties). Desorption is complete in 30 minutes if the vial is agitated occasionally during this period. The utilization of an electric agitator such as described in Section 5.2.8 is recommended, as its use for 30 minutes further standardizes this procedure. Also, it eliminates a possible variable that hand agitation could introduce.

7.2.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. Two methods of choice are available depending upon chromatographic instrumentation. The first method is for manual sample injection and the second is automatic and requires an automatic injection accessory.

7.2.3.1 Manual. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and

used to calibrate the pump. Calibration charts are prepared by plotting actual flow rate (Soap bubble meter) in lpm versus pump rotameter reading, digital count, etc. Wet test meters and mass flow monitors can be used for calibration as well, however, all devices must be periodically calibrated themselves to insure volume integrity.

8.2 Analytical System. It is convenient to express concentration of benzene standards in terms of mg/1.0 ml CS<sub>2</sub> because samples are desorbed in this amount of CS<sub>2</sub>. To minimize error due to the volatility of carbon disulfide, one can inject 10 times the weight into 5 ml of CS<sub>2</sub> and utilize sealed vials with Teflon-lined septum caps. For example, to prepare a 0.3 mg/1.0 ml standard, one would inject 1.5 mg into exactly 5 ml of CS<sub>2</sub>. The density of benzene (0.874 at 25°C) is used to convert 1.5 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

## 9. Calculations

9.1 Uncorrected volume. The volume of air sample is not corrected to S.T.P., because of the uncertainty associated with 24-hour average temperature and pressure values. Determine the air sample volume taken for an eight-hour sampling.

$$V_m = \frac{F_1 + F_2}{2} \times T \times 10^{-3},$$

where:

- $V_m$  - The volume of gas sampled (uncorrected), m<sup>3</sup>
- $F_1$  - The measured flow rate before sampling, l/min.
- $F_2$  - The measured flow rate after sampling, l/min.
- $T$  - The sampling time, min.

### 7.3 Determination of Desorption Efficiency

7.3.1 Importance of determination. The desorption efficiency of benzene can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the benzene that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

7.3.2 Procedure for determining desorption efficiency. Unused charcoal tubes from the same batch as the collected samples are selected at random. The sealed ends are broken as described in Section 7.1.2.1. A known amount of the benzene is injected directly into the activated charcoal with a microliter syringe, and the tube is capped. The amount injected is usually equivalent to that present in a 480-liter sample at a concentration equal to 0.05 ppm. At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of benzene onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are prepared, desorbed and analyzed in exactly the same manner as the sampling tube described in Section 7.2. Two or three standards are prepared by injecting the same volume of benzene into 1.0 ml of CS<sub>2</sub> with the same syringe used in the preparation of the sample. These are analyzed with the samples. The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{Desorption Efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

### 8. Calibration and standards.<sup>1</sup>

8.1 Sampling pump. Each sampling pump must be calibrated with a representative charcoal tube in the line. Also, the length of tubing connecting the charcoal tube with the sampling pump should be the same length as used during sample acquisition. This will minimize errors associated with uncertainties in the sample volume collected. Soap bubble flow meters capable of accurately measuring 1 lpm are usually

Benzene on Charcoal] to validate this procedure as well as to verify an in-house "control standard" can be very advantageous.

### 13. References

1. Several sections of this method are either direct quotes or reflective of the NIOSH P&CAM No. 127, "Organic Solvents in Air". In each instance, such sections are indicated with reference number 1.
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4. Kinzer, G. W. and Neher, M.B., "Sampling and Analysis of Selected Toxic Substances". Third Quarterly Progress Report - Battelle Columbus. January 19, 1977.
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7. Federal Register 43(85), 22516 - 22529, May 3, 1977
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9. Quality Assurance Handbook for Air Pollution Measurements Systems: Volume 1, Principles. EPA-600/9-76-005, March, 1976.
10. Industrial Hygiene Service Laboratory Quality Control Manual, Technical Report No. 78. HEW NIOSH Cincinnati, Ohio, 1974.
11. Quality Control For The Industrial Hygiene Laboratory. American Industrial Hygiene Association, Akron, Ohio, July, 1975.

NOTE: For successive eight-hour samples,  $V_m$  becomes the sum of individual eight-hour values.

9.2 Calculate the benzene concentration as  $\mu\text{g}/\text{m}^3$ . From the calibration curve, select the value of  $W_{\text{BZ}}$  that corresponds to the measured sample peak area.

$$C_{\text{BZ}} = \frac{W_{\text{BZ}}}{V_m \times \text{DE}}$$

where:

- $C_{\text{BZ}}$  - The concentration of benzene in the air sample,  $\mu\text{g}/\text{m}^3$ .
- $W_{\text{BZ}}$  - The quantity of benzene measured,  $\mu\text{g}$ , desorbed from the charcoal adsorbent.
- $V_m$  - The air volume,  $\text{m}^3$ .
- DE - Desorption Efficiency.

#### 10. Sample storage and shipping conditions

10.1 It is not necessary to use refrigeration to store the charcoal tubes after sampling. Hot environments such as can be experienced in automobile trunks during warmer months are to be avoided.

10.2 If samples cannot be carried to the laboratory following sample collection, then the capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping. Samples of the suspected benzene containing bulk materials should be submitted to the laboratory. These liquid bulk samples should not be transported in the same container as the samples or blank tubes.

#### 11. Safety

Benzene and carbon disulfide are toxic. Repeated exposure to high concentrations should be avoided.<sup>6,7,8</sup>

#### 12. Quality Control

A multi-faceted quality control program must be employed to insure the integrity of all benzene results. Examples of acceptable programs are available from EPA<sup>9</sup>, NIOSH<sup>10</sup> and AIHA<sup>11</sup>. The use of NBS SRM 2661

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memo

From: Leslie G. Polgar *LP* December 30, 1977

To: Martha Beauchamp

SUMMARY OF PROPOSED RESEARCH ON BENZENE

Regulatory agencies have expressed increasing concern regarding possible risks to humans exposed to benzene in both the workplace environment and the ambient air. A reliable scientific evaluation of these risks requires specific knowledge about the magnitude and distribution of benzene concentrations. Unfortunately, such data are quite limited, especially background data for the general ambient air.

The American Petroleum Institute, following an evaluation of competing proposals from major environmental monitoring firms, has recently awarded a contract for the purpose of measuring ambient benzene concentrations at a wide variety of locations in the United States.

The monitoring program is designed to provide an initial representation of the range of benzene concentrations as a function of (1) region and (2) degree of influence ascribable to human activity. The regional variability will be incorporated by taking data in six major areas: Pacific Northwest, Southern California, Gulf Coast, East Coast, Midwest, and Southeast. These areas span most of the major climatological categories found in the U. S. The second major variable--proximity to human activity--will be represented by three categories: (1) urban/suburban, (2) rural, and (3) remote areas in each of the six regions.

The focus of this program is the general ambient air, as opposed to ambient air immediately adjacent to specific sources. Hence, the new program complements the purpose of a recent petroleum industry study whose emphasis was on the ambient concentrations of benzene in the immediate vicinity of petroleum refineries and gasoline service stations.

The new study calls for monitoring for 21 consecutive 8-hour periods at each site. An asymmetric factorial design is utilized with 3 urban/suburban, 1 rural, and 2 remote sites in each of the six regions. The asymmetry reflects the fact that urban/suburban sites represent the air to which most of the U.S. population is exposed and the assumption that remote areas exhibit the lowest benzene levels.

The monitoring will be carried out during the winter (early 1978). Preliminary consideration is being given to repeating the study during the summer of 1978 in order to account for seasonal variables.