

# Continuous monitoring of HYDROCARBON CONTAMINANTS in low temperature air separation plants

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To insure safe operation of an air plant it is necessary to frequently measure the concentration of contaminants in process streams. Considerable attention has been paid to such explosion initiators as ozone and acetylene, but it is also imperative to keep the quantity of hydrocarbon fuel within safe limits.

IN RECENT YEARS there has been an increasing demand for large quantities of high purity oxygen and nitrogen. To meet this demand, many new low temperature air separation plants have been built. A large number of these new plants are located in industrial areas near chemical plants, oil refineries, and steel mills, where atmospheric pollution can be a serious problem. Because some of the contaminants present in industrial atmospheres are potential safety hazards when concentrated in liquid oxygen, there has been considerable emphasis on safe design and safe operation of air plants.

Several articles have been published recently (1, 2) which discuss principles of safe design and operation. A safe design is only the beginning of a safe plant. In addition, the plant must be operated in the safest possible manner. Two of the most important principles of safe operation are:

1. Keep the quantity of contaminants entering the plant to a minimum.

2. Prevent contaminants which enter from accumulating in the plant.

For an explosion to occur in an air plant, both oxygen and a fuel must be present, plus some means of initiation. Since oxygen must be present by the nature of the process, only the fuel and means of initiation can be controlled. All initiators or suspected initiators, such as acetylene, ozone, and oxides of nitrogen, should be kept at very low levels. However, it is also imperative to keep the quantity of fuel within safe limits since all possible means of initiation may not be known. To control only the concentration of initiators such as acetylene and to ignore the concentration of hydrocarbon fuel is fundamentally un-

sound. This attitude overlooks the existence of unsuspected initiators. If a large quantity of fuel is present, there is the remote possibility that it may be detonated by some unsuspected means of initiation even though no acetylene is present. For effective elimination of explosion hazard, it is necessary to control the concentration of both hydrocarbon fuel and all known or suspected initiators.

To insure safe operation of an air plant, it is necessary to frequently measure the concentration of contaminants in various process streams. For many years operators had to rely entirely on intermittent chemical testing, which was both time consuming and expensive and which resulted in considerable delay before the results were known. With recent advances in instrumentation, it is now possible to monitor all hydrocarbon fuels and some initiators on a continuous basis.

One of the most important developments has been the use of nondispersive infrared analyzers for measuring hydrocarbons at very low concentra-

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#### ACKNOWLEDGMENT

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Figures 1, 2 & 3. In Figure 1 a simplified flow diagram of a Sun Oil Company Air Plant shows the exact location of hydrocarbon analyzers. Figure 2 is an infrared analyzer and related sampling equipment for measuring total hydrocarbon concentration in four process streams. Figure 3 shows catalytic oxidation chambers used to convert hydrocarbon contaminants to carbon dioxide which is determined by the infrared analyzer.

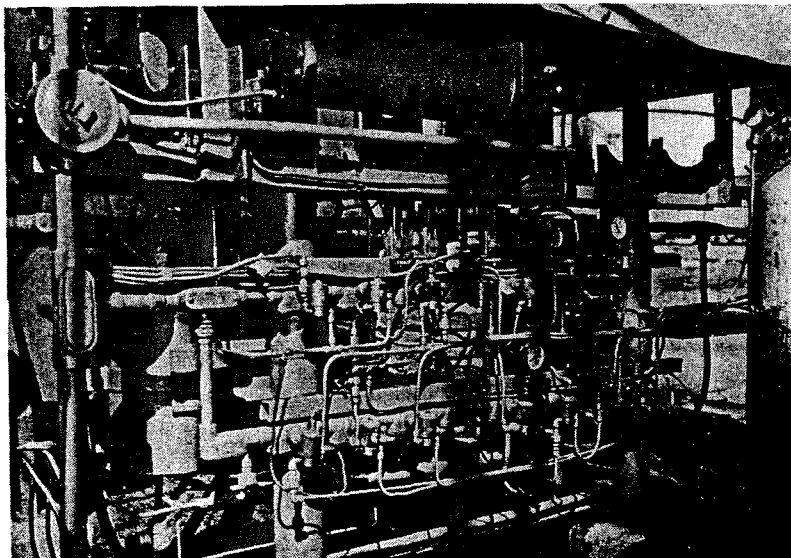


Figure 2

tions. These infrared analyzers can be used to determine a particular hydrocarbon, such as acetylene, or to determine total hydrocarbons. There are two methods for determining total hydrocarbons. One is to sensitize an analyzer to a representative mixture of hydrocarbons. The other is to catalytically oxidize the hydrocarbons and monitor the resultant carbon dioxide.

The reading of an analyzer sensitized to a mixture of hydrocarbons is only approximately proportional to the concentration of the hydrocarbons present. The relative proportions of the various hydrocarbons in the sample will affect the scale reading to some extent. Catalytic oxidation of the hydrocarbons to carbon dioxide has the advantage of giving readings which are proportional to the weight of hydrocarbons present. It is also a more sensitive method since carbon dioxide is a much stronger absorber of infrared radiation than hydrocarbons, and since each mol of hydrocarbon heavier than methane produces two or more mols of carbon dioxide. If a sample stream contains a few parts per million of carbon dioxide before oxidation, it can be compensated by passing a portion of the unoxidized sample through a reference cell in the analyzer. In this way, only the increase in carbon dioxide concentration resulting from oxidation is measured.

A total hydrocarbon analyzer is not effective for controlling acetylene contamination in an air plant. Since dangerous acetylene concentrations are several orders of magnitude lower than total hydrocarbon concentrations, an acetylene build-up cannot be detected

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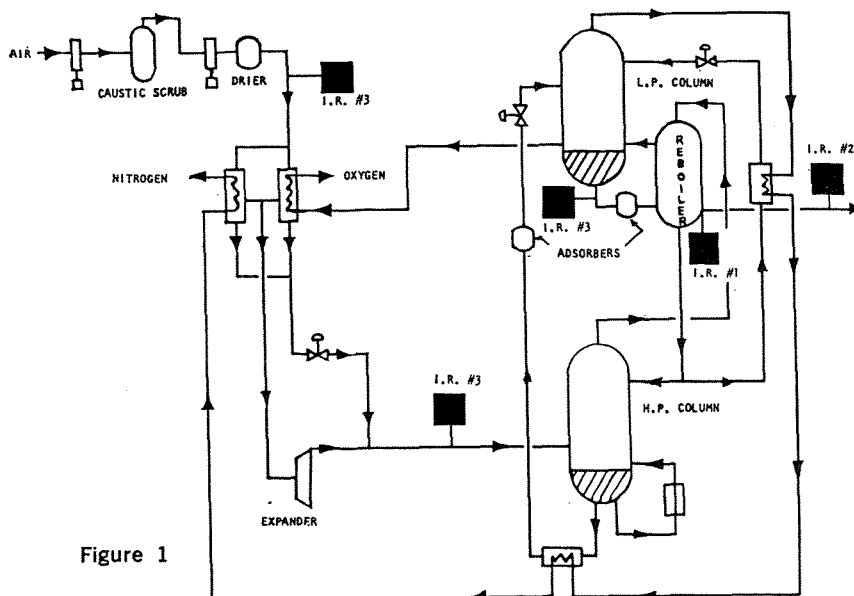


Figure 1

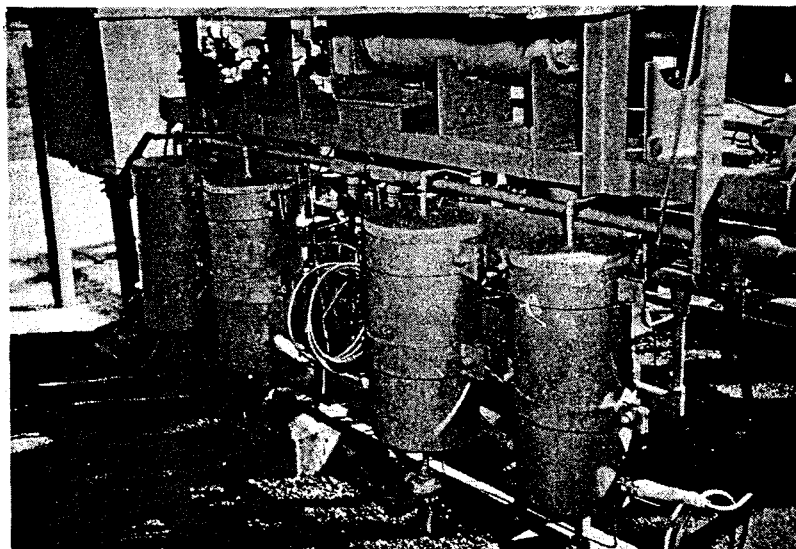


Figure 3

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by a hydrocarbon analyzer. In most areas frequent laboratory testing is satisfactory for determining the acetylene concentration in the liquid oxygen. However, in areas with significant quantities of acetylene in the atmosphere, a continuous acetylene analyzer should be considered.

### Sun Oil Installation

At the Sun Oil Company air plant at Marcus Hook, Pennsylvania, extensive use of infrared analyzers is made to monitor total hydrocarbons in various process streams. The air plant produces about 290 tons/day of high purity nitrogen for ammonia synthesis and 90 tons/day of gaseous 95% oxygen.

Figure 1 is a simplified flow diagram of the air plant showing the location of the infrared analyzer sampling points. Three analyzers are used to monitor five different process streams. Analyzer No. 1 continuously monitors the hydrocarbons in the feed air. Analyzer No. 2 monitors the liquid withdrawn from the plant. The third analyzer can monitor streams from any one of several sampling points, including the high pressure column feed, low pressure column bottoms, and the liquid oxygen in the reboiler-condenser. Analyzers Nos. 1 and 3 measure the carbon dioxide formed by catalytically oxidizing the sample streams. Analyzer No. 2 measures total hydrocarbons directly.

Figures 2 and 3 are photographs of analyzer No. 3 with its sampling system and catalytic oxidation chambers. This analyzer, which is sensitized to carbon dioxide, is a standard Liston-Becker Model 21, supplied by Beckman Instruments, Inc. The analyzer is enclosed in an explosion-proof housing since it is located in the plant

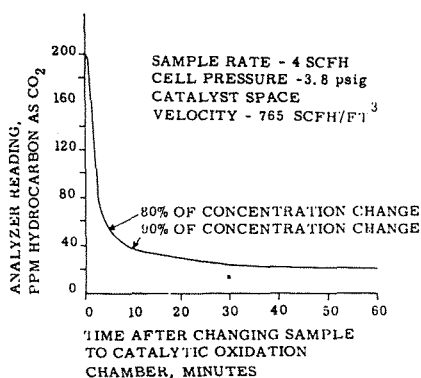


Figure 5. Response of a catalytic oxidation chamber and infrared analyzer to a change in sample stream. The same catalytic oxidation chamber being used for both samples.

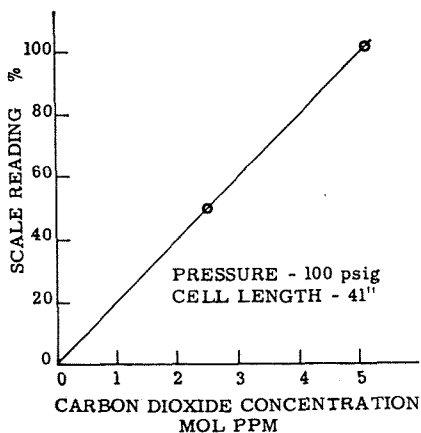


Figure 4. Calibration curve for an infrared analyzer.

area. The absorption cell, which can be pressurized up to 600 lb./sq. in. gauge, is 13½ in. long and has sapphire windows which transmit to about 6 $\mu$ . The reference cell is sealed with a filling of nitrogen. The detector output is amplified, rectified, and then recorded.

Analyzer No. 1 is similar to No. 3 with the exception that its cells are 41 in. long for greater sensitivity. In addition, the reference cell has been modified so that a flowing reference sample can be passed through it to compensate for the residual carbon dioxide present (1-2 p.p.m.) in the feed air. Analyzer No. 2 has a 35-in. sample cell with a 5-in. carbon dioxide filter cell and is sensitized to a mixture of hydrocarbons, eliminating the need for oxidation of the sample stream.

Each sample which requires catalytic oxidation has its own oxidation chamber. These chambers are constructed of Inconel to eliminate carbon dioxide contamination which results from the use of steel. They are filled with about 9 cu. in. of Baker Platinum Division (Engelhard Industries) Type F pelleted catalyst. The oxidation chambers are maintained at about 900°F. with special nickel-plated heaters coiled around the chambers. These heaters can safely operate in Class I, Group D, Division 2 areas. The catalyst chambers are insulated with 4 in. of high temperature insulation covered with sheet metal. An iron-constantan thermocouple in each catalyst bed is used to measure the temperature.

The sampling systems for the analyzers were carefully designed to insure minimum lag time with maximum flexibility and simplicity of operation. The sampling points for the liquid streams are located as close to the outside of the cold box as

possible to keep the length of the sample lines to a minimum. To further reduce lag time, the liquid samples are vaporized as soon as they leave the cold box. Two types of vaporizers have been used successfully. The simplest type consists of a coil of ¼-in. tubing immersed in a bath of boiling water. The second type consists of a small electrically heated stainless steel vessel. By maintaining a large excess heat input, the walls of the vessel are kept hot enough to completely vaporize the liquid as it enters the vessel.

The multipoint analyzer has a specially designed, versatile sampling manifold. The flows of the sample streams and calibrating gases to the analyzer are controlled by solenoid valves operated from the control room. The sample streams continuously flow through their individual oxidation chambers, with only the sample being monitored passing through the analyzer. Those oxidized streams which are not flowing through the analyzer are vented directly to the atmosphere. All sample lines to the analyzers contain sintered steel filters with 20- $\mu$  porosity.

### Evaluation of the analyzers and oxidation catalyst

Infrared analyzers Nos. 1 and 3 have been calibrated over a range of carbon dioxide concentrations using reference mixtures whose compositions were known from chemical analysis. The full-scale ranges of the analyzers are varied by changing the sample pressure or amplifier gain setting. With a 41-in. cell at a pressure of 100 lb./sq. in. gauge, the full-scale chart reading corresponds to 5 p.p.m. carbon dioxide and the calibration curve is linear. (See Figure 4.) The limit of detectability is about 0.2

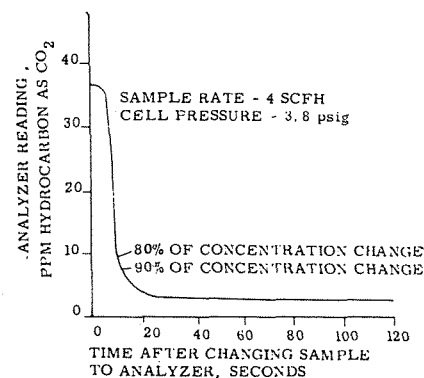


Figure 6. Response of infrared analyzer #3 to a change in sample stream. Each stream passing through a separate catalytic oxidation chamber.

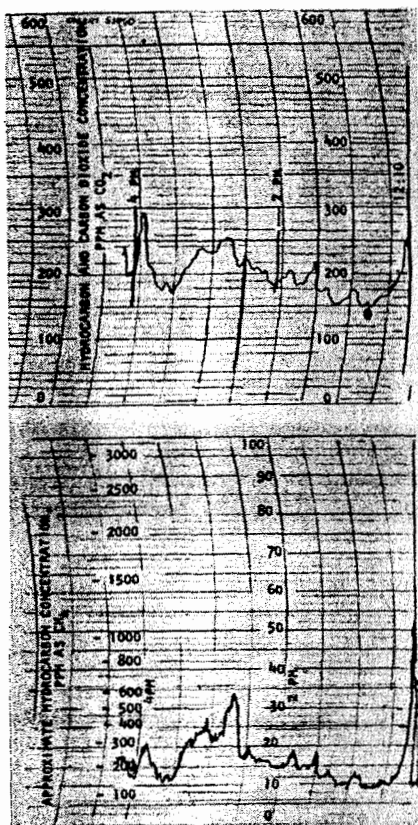


Figure 7. Comparison of the response of an infrared analyzer sensitized to hydrocarbons with the response of a catalytic oxidation chamber and infrared analyzer sensitized to carbon dioxide.

p.p.m. At atmospheric pressure, full-scale readings of 50 to 200 p.p.m. can be obtained with linear calibration curves. At higher concentrations the calibration curve becomes nonlinear because of excessive absorption. Since it was desired to use analyzer No. 3 for samples containing up to 500 p.p.m., a standard 13½-in. cell was used. This cell gives good linearity over full-scale ranges of 60 to 600 p.p.m.

Analyzer No. 2 is calibrated using a mixture of methane in nitrogen. The full-scale reading is 3000 ppm. methane and the calibration curve is nonlinear. A linear calibration curve could be obtained by shortening the cell length.

The effectiveness of the oxidation catalyst was studied by passing known mixtures of methane in carbon dioxide-free air over the catalyst and through an infrared analyzer. Methane was used because it is the most difficult of all light hydrocarbons to oxidize. A comparison of the methane concentrations in the blends as determined by gas chromatography and the analyzer readings showed excellent agreement.

Table A

METHANE IN BLEND, P.P.M. CH <sub>4</sub>	ANALYZER READING, P.P.M. CO <sub>2</sub>
24	24
30	32
30	31
50	51
87	88

To determine whether there was an upper limit to the concentration of methane which could be oxidized by the catalyst, a mixture containing approximately 6000 p.p.m. was passed over the catalyst under normal conditions. The concentration of methane in

the exit gas, as determined by gas chromatography, was less than 1 p.p.m.

To learn whether lubricating oil would deactivate the catalyst, some oil in a gas stream was introduced into the catalyst chamber for a short period of time. The expected formation of large concentrations of carbon dioxide occurred for a while, but there was no indication of any loss of catalytic activity.

During early work with the oxidation catalyst and infrared analyzer, it was found that the catalyst is an excellent adsorbent for carbon dioxide. Fresh catalyst, when placed in a chamber at a temperature of about 950°F. and purged with pure oxygen, gives off several hundred parts per million of carbon dioxide for nearly a week before the blank valve drops to zero. After subsequent exposures to the atmosphere, the catalyst again shows high carbon dioxide values on purging, although for a shorter period of time than for the initial clean-up.

Another indication of the adsorbent properties of the catalyst was noted. A known mixture of methane was passed over the catalyst at 950°F. long enough to give a constant carbon dioxide value. When the catalyst temperature was dropped by about 50°F., the apparent carbon dioxide content of the exit gas first dropped to zero. As the temperature was held constant, the carbon dioxide reading returned to its original value. When the temperature was raised 50°F., the carbon dioxide reading first increased and then returned to the original value at the higher temperature. It seems clear that an equilibrium is established at each temperature between the carbon dioxide in the gas stream

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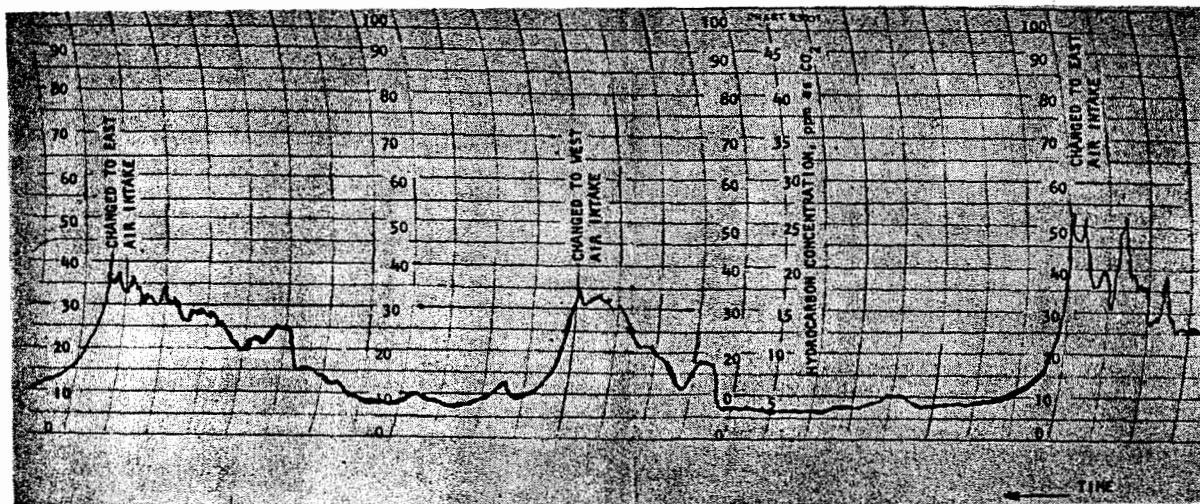


Figure 8. Illustration of how feed air infrared analyzer is used to minimize hydrocarbon concentration in feed air entering cold box.

... the operator is warned that the plant is unsafe to operate and must be shut down and dumped.

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and that adsorbed on the catalyst. For this reason the oxidation temperature is held within fairly narrow limits ( $\pm 10^\circ\text{F.}$ ) although the exact value is not important.

Measurements have been made to determine the time required for carbon dioxide in a sample to reach equilibrium with that on the catalyst. A sample stream of known methane concentration was passed over the oxidation catalyst for several hours to be certain that equilibrium was achieved. The sample was then replaced by another stream of known concentration and the time required to reach equilibrium was measured. Figure 5 shows the results of these experiments. Since the time required to achieve 90% of the change is almost 10 min., it is undesirable to use one catalytic oxidation chamber for more than one sample. If, however, each sample stream has its own oxidation chamber, the lag time when changing samples is reduced to only that time required to purge the analyzer sample cell. Figure 6 shows a lag time of considerably less than one minute when separate oxidation chambers are used.

The response time of the catalyst to changes in hydrocarbon concentrations in a sample stream has also been studied. Part of a sample stream containing some carbon dioxide and about 200 p.p.m. hydrocarbons was passed over catalyst and through an analyzer sensitized to carbon dioxide. Another part of the same stream was simultaneously passed directly to the analyzer sensitized to hydrocarbons. Figure 7 shows a comparison of the response of the two methods of determination. Adsorption of carbon dioxide on the catalyst delayed the appearance of the hydrocarbon peaks several minutes. In addition, adsorption rounded off sharp peaks which were detected by the hydrocarbon analyzer. If desired, the response time can be improved by using less catalyst or using a higher sample flow rate. Using too little catalyst, however, can result in incomplete oxidation and may require more frequent catalyst changes. The maximum space velocity for fresh catalyst was found to be about 6000 std. cu. ft./ (hr.) (cu. ft.).

### **Analyzer performance in the plant**

During the first two years of oper-

ation, there has been no serious maintenance problem on any of the analyzers. Almost all of the maintenance which has been required has been related to the infrared source assembly. The most frequent trouble has been dirty contacts which are easily cleaned. Several of the chopper motors and bearings have also required some attention. Dirt in the sample stream has caused some trouble, requiring cleaning of the sample cells and filters on two occasions. Only a few hours a month of servicing are required to keep the analyzers in good working condition. By well-planned preventive maintenance and by stocking important spare parts, it has been possible to almost entirely eliminate instrument failures.

In addition to maintenance, the zero and full-scale span of each analyzer are checked three times a week. These checks take about one hour per week for each analyzer. Both the zero and span drift have been less than the maximum guaranteed by the manufacturer. Any large or erratic changes in the zero or gain settings indicate trouble, which is immediately investigated. Once a month the catalyst activity of each of the chambers is checked using a standard methane blend. This check requires about an hour for each chamber. No catalyst deactivation has been detected.

### **Value of infrared analyzers**

The value of infrared analyzers as aids to safe operation of air plants is immeasurable. They warn an operator of potentially hazardous conditions and enable him to take quick corrective action. The operator can observe the effectiveness of the corrective action and he knows when the potential hazard has passed. If the corrective action is ineffective and the hydrocarbon concentration continues to increase, the operator is warned that the plant is unsafe to operate and must be shut down and dumped.

Figure 8 illustrates how an analyzer can be used to keep the quantity of hydrocarbons entering the plant to a minimum. The hydrocarbon concentration at each of the two air intakes is affected by the wind direction. As the wind direction changes, the air intake which gives the lowest concentration of hydrocarbons is used. The figure shows three actual instances when the hydrocarbon concentration in the feed air was reduced about 75% by using the proper air

intake as indicated by the infrared analyzer.

Infrared analyzers are also necessary for obtaining the most efficient utilization of the safety features in a plant. For instance, the rate of liquid oxygen withdrawn from the reboiler-condenser can normally be controlled to maintain a reasonable hydrocarbon level in the reboiler. Since any liquid withdrawn represents a loss of refrigeration, it is desirable to keep the rate of withdrawal at the lowest level that is consistent with safe operation. Only by use of continuous infrared analysis in conjunction with laboratory testing can this be done.

In the Sun Oil plant, every phase of operation is dependent on the concentration of hydrocarbons and initiators in various process streams as determined by the infrared analyzers and laboratory testing. The analyzer readings are tangible evidence that no hydrocarbons are accumulating in the plant. As a result of many months of continuous, almost trouble-free operation, the operators place great confidence in the analyzers.

The infrared analyzer readings are always supplemented by laboratory testing. Acetylene and nitrogen oxides are determined one or two times a day. Total oxidants (ozone) are measured twice a week. Complete hydrocarbon analyses by carbon number of various streams are made three times a week. The methods used are gas chromatography for methane and a combination of low temperature freeze-out and mass spectrometry for ethane and heavier.

The hydrocarbon analyzers are also valuable research tools for studying such problems as distribution of hydrocarbons in an air plant, effectiveness of hydrocarbon removal facilities, optimum regeneration temperature for silica gel adsorbers, and measuring the quantity of hydrocarbons removed when defrosting a plant. They are also valuable in locating sources of hydrocarbon contamination and in choosing air intake locations.

### **Conclusion**

Total hydrocarbon analyzers, when complemented with laboratory testing for known or suspected initiators, have proven their value as aids to safe operation of air plants. They are dependable, versatile, and almost completely trouble-free. They should be seriously considered for any air plant located in an industrial area.

### **LITERATURE CITED**

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2. McKinley, C. and F. Himmelberger, *Chem. Eng. Progr.* 53, No. 3, pp. 112-21 (March, 1957).