

# CHROMATOGRAPHIC ANALYZER

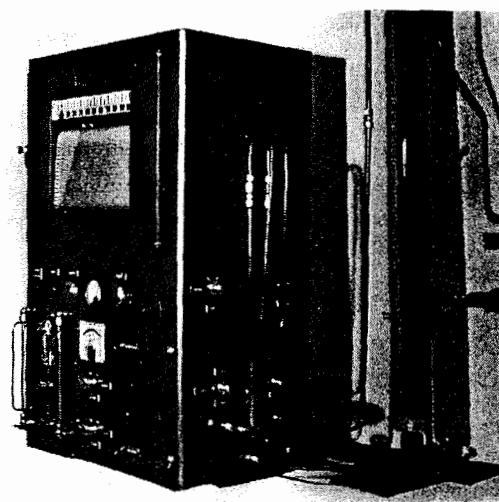
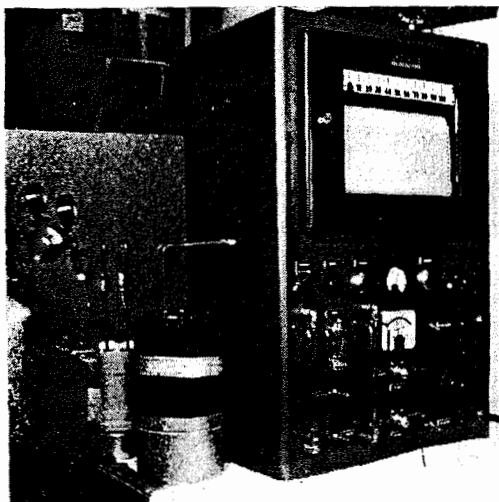
## For Determining Trace Hydro- Carbons In Air Separation Plants

The success of an analyzer in preventing explosions in liquid air plants—a detailed engineering study.

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Explosion hazards in liquid air plants have been attributed to the accumulation of hydrocarbons, particularly acetylene, in the air fractionating towers (3, 5, 6, 7). Trace amounts of acetylene are generally believed to provide the "trigger," and somewhat higher concentrations of other hydrocarbons the "fuel" in such explosions. Analysis for acetylene and other hydrocarbons in the liquid air to provide a basis for control is, therefore, of paramount importance. For this purpose a trace component gas chromatographic analyzer was developed and is in use at the ammonia

plant control laboratory of the Atlantic Refining Company in Philadelphia. In this plant by-product hydrogen from Catforming is combined with nitrogen separated from the atmosphere to produce ammonia (1, 2). The analyzer is used to monitor the hydrocarbon content of the liquid air in the rich air vaporizers as well as in the atmosphere surrounding the plant. Individual paraffinic and olefinic hydrocarbons ranging in molecular weight from  $C_2$  to  $C_5$ , including acetylene, are being determined on a routine basis at concentrations ranging from  
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Figures 1 and 2. Illustrate equipment details of analyzer

## Chromatographic analyzer

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less than 0.01 up to 40 p.p.m. in about one hour.

The analyzer is based on chromatographic techniques reported by Eggertsen and co-workers (4), of the Shell Development Company. The operating technique permits detection of hydrocarbon concentrations beyond the detectability range of presently available commercial instruments. Hydrocarbons are concentrated and separated from air by passing the sample through a packed U-tube immersed in liquid nitrogen. The trapped hydrocarbons are then flushed into a chromatographic column with helium carrier gas, where they are separated and then analyzed by passing through a thermal conductivity cell detector in the carrier gas stream. A permanent record of the analysis is obtained by transmitting electrical output from the detector cell to a strip chart recorder. Components of the sample are identified by their emergence times, and quantitatively determined by measuring peak heights or peak areas from the records obtained.

Three chromatographic columns, which may be operated at temperatures ranging from 0°C., or lower, up to about 175°C. are included in the analyzer. Any one of these columns may be selected for a given analysis by turning selector valves, and the columns can be readily changed to fit future needs.

The instrument has been used successfully by plant laboratory technicians for a period of five months.

### Description of analyzer

The analyzer is housed in a steel

cabinet proportioned for laboratory bench operation as shown by the photographs in Figures 1 and 2. Cabinet dimensions are approximately 23×15×35 in., and the whole installation requires a bench surface area of about 3×2 ft. The unit consists of five major components:

1. Three chromatographic columns contained in two constant temperature baths with appropriate selector valves.
2. Detector
3. Recorder
4. Carrier gas manifold and sampling system
5. Electrical power and measuring circuits.

The chromatographic columns are ¼-in. O.D. copper tubing filled with suitable packing and maintained at constant temperature. One column is contained in an ice bath to the left of the cabinet while the other two are held in a heated bath inside the cabinet.

The detector is a model TR2B, 4-filament, Gow-Mac thermal conductivity cell. Capillary glass tubes, 150 mm. long × 0.7 mm. I.D., are con-

nected to the exhaust from the reference and sample sides of the cell to provide a controlled pressure drop through the detector. The cell is operated with a current of 300 ma. and at a temperature of 210°F. A standard -0.05 to +1.05 mv. recorder measures detector output.

The carrier gas flow path (see Figure 3) provides concentration and introduction of the sample while maintaining regulated helium flow through the column and detector. A flow of 35 cc./min. is maintained through the sample side of the detector cell, and a flow of 5 cc./min. through the reference side. Carrier gas flow is controlled with needle valves and measured with rotameters. Helium supplied from a cylinder first passes through a U-tube immersed in liquid nitrogen to remove traces of hydrocarbons present as impurities. All manifold connections are sealed with Glyptal resin to prevent leaks, and Nordstrum No. 555 hydrocarbon insoluble grease is used to lubricate all analyzer valves.

The electrical system (Figure 4)

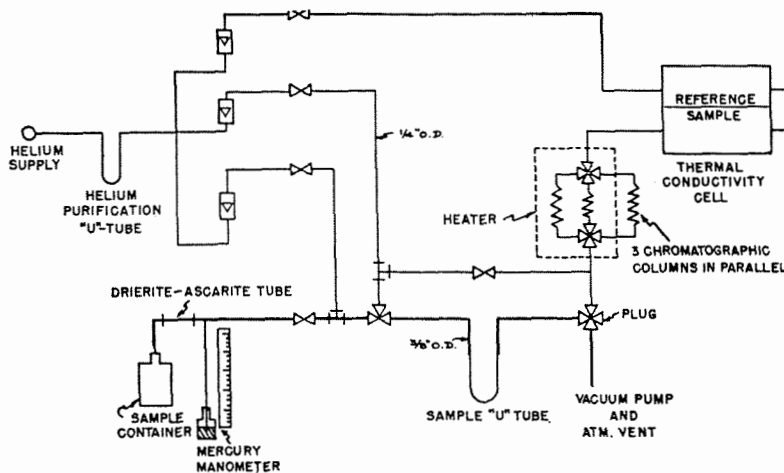


Figure 3. Analyzer flow diagram

consists of a measuring circuit and a 115-v. a.c. circuit which provides current for the recorder, column, and cell heaters. Manual temperature control of the heaters is used, since the sensitivity of the instrument is such that cycling heater control causes instability in the baseline of the chromatographic record. Current for the measuring circuit is supplied by two standard 12-v. automotive storage batteries which are alternated daily, so that one battery is being charged while the other is in use. Cell current is adjusted by means of a 25-ohm rheostat, while cell balance is accomplished by a system consisting of a 25-ohm potentiometer and a variable resistance shunted across the potentiometer to provide fine and coarse adjustments. The output from the cell can be attenuated in three steps: 100:1, 10:1 or 1:1 by means of a system of fixed resistances connected across the cell output terminals. Grounding of the cabinet and cell is essential for good instrument stability.

### Sampling procedure

Either gaseous or liquid-air samples may be analyzed. Gas samples are obtained in evacuated sample bottles or Orsat tubes of known volume, and the bottles, filled with sample at atmospheric pressure, are attached to the sample inlet of the analyzer with a mercury manometer. The sample U-tube is immersed in liquid nitrogen and the sample bottle evacuated through the U-tube to a pressure of about 100 mm. Hg. For gas samples up to one liter in volume, residual sample is flushed from the sample bottle by alternately filling the

partially evacuated bottles with helium from the manifold system followed by evacuating again through the sample U-tube. This procedure, which is carried out by turning the proper valves, is repeated twice. For samples larger than one liter, the volume of sample used is determined by calculation from the pressure remaining in the container.

Large samples of atmospheric air may be conveniently collected by immersing a sample bulb, Figure 5, in liquid nitrogen. Atmospheric air is drawn by condensation through the stopcock into the sample bulb at a rate of about 1.2 ml. of liquid or 1 liter of gas/min. Measured amounts of liquid sample also may be taken directly from the air plant into the sample bulb, which is immersed in liquid air of the same composition as the sample. When the Dewar flask is kept filled with liquid air, samples may be stored for several hours without a significant loss in volume. The sample bulb is attached with Tygon tubing to the sample line on the analyzer while still immersed in liquid air, and evacuation through the sample U-tube, which is immersed in liquid nitrogen, is begun. The Dewar flask around the sample bulb is then replaced by a glass tube wrapped with aluminum foil, precooled by filling to about 25 ml. with liquid nitrogen. Pumping is continued at a controlled rate so that a 25-ml. liquid air sample is completely evaporated in a minimum of 20 min., and to a pressure of 30 to 60 mm. Hg. If pressure surges occur during the evaporation, a small amount of liquid nitrogen is poured into the tube

around the sample holder. Residual gas sample is flushed from the sample holder by alternately filling with helium and evacuating. This flushing step is repeated twice, and the sample U-tube is purged to the atmosphere for 3 min., with helium at a rate of 800 cc./min. to remove excess air. The helium flow rate is then adjusted to 35 cc./min., the flow through the U-tube directed to the desired analytical column, and liquid nitrogen around the U-tube is replaced with a suitable heating bath to desorb the sample. For  $C_5$  and lighter hydrocarbons an ice bath is used for desorbing sample.

### Calibration and analysis for $C_5$ , lighter hydrocarbons

The column used for determining  
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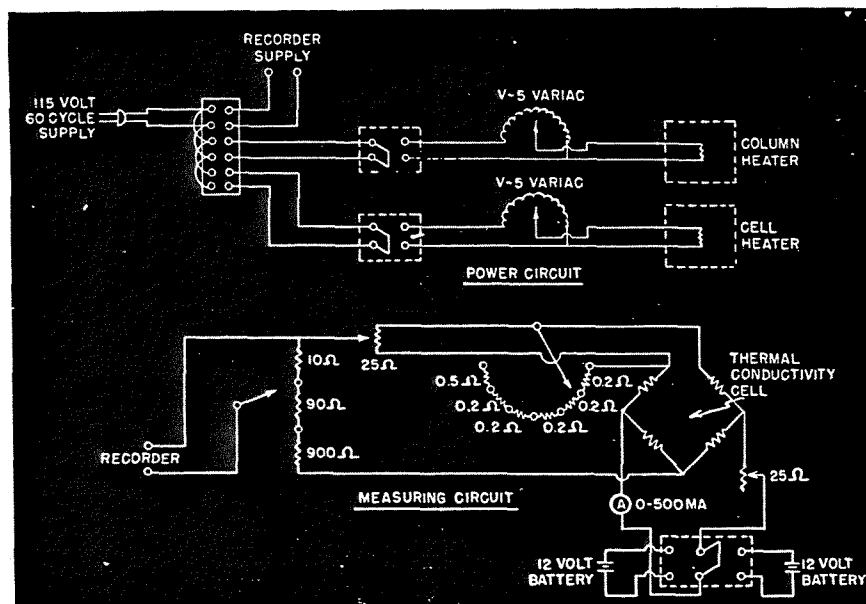


Figure 4. Analyzer circuit diagram

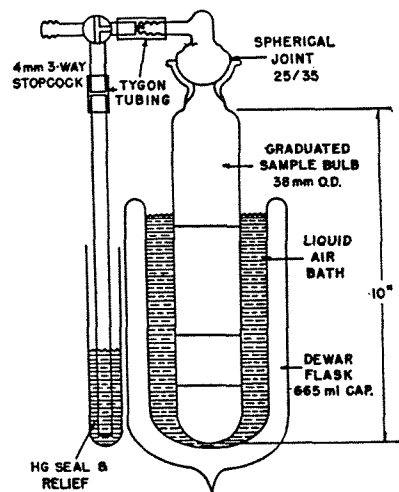


Figure 5. Sampling apparatus

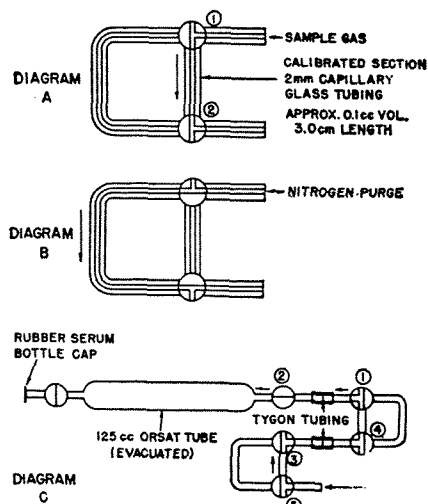


Figure 6. Use of gas pipets

# Chromatograph analyzer

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C<sub>5</sub> and lighter hydrocarbons is a 25-ft length of 1/4-in. O.D. copper tubing packed with 20-60 mesh C-22 firebrick (Columpak, Fisher Scientific Company) and impregnated with 20% by weight of 2, 4-dimethylsulfolane (Shell Chemical). The sorbent is packed into the column with a vibrator to a density of 3.4 g./ft. of column tubing. The column is coiled to fit into an ice bath contained in a 2-liter Dewar flask, and coupled to the analyzer with tubing unions. The sample U-tube and helium purifying U-tube are both packed with 6-in. of the same sorbent. In addition, a 15-in. length of 3/8-in. O.D. copper tubing is inserted in the sample train, packed one half with Drierite and one half with Ascarite as shown in Figure 3, to remove water and carbon dioxide from the sample. Carbon dioxide must be removed since it has the same retention time as propane. During continuous operation the Drierite and Ascarite are replaced each week.

For simplicity in rapid routine analysis of ammonia plant samples peak heights are used for determining concentration. Calibration is made with known mixtures containing propane and acetylene. The calibration curve for propane is used in calculating analyses for components with retention times through *n*-butane, and the acetylene curve is used for acetylene and other components with retention times through *n*-pentane.

Known mixtures of acetylene and propane are prepared by using calibrated gas pipets as shown in Figure 6. The pipets, about 0.1 cc. in volume are calibrated by weighing mercury

required to fill the calibrated section. One pipet is filled with acetylene and the other with propane, (diagram A, Figure 6), by flowing gas for one minute at a rate of about 100 cc./min. through the calibrated section. The stopcocks are then turned to the positions shown in diagram B to trap gas in the calibrated section at 1 atm. pressure, and the stopcocks are purged with nitrogen or air. The pipets are connected with Tygon tubing to an evacuated 125-cc. Orsat tube equipped at one end with a rubber serum bottle cap. Hydrocarbon free air is then allowed to flush the measured volumes of gas from the pipets into the Orsat tube to a pressure of one atmosphere by turning the stopcocks in the order shown in diagram C. Stopcock 2 is closed and the pipets disconnected. The gases in the Orsat tube are mixed by expanding and compressing with a 25-cc. hypodermic syringe inserted through the serum bottle cap. Aliquots of 1.0, 3.0, 5.0, and 10.0 cc. of this standard hydrocarbon mixture are then transferred by means of hypodermic syringes to other clean, evacuated 125-cc. Orsat tubes. The Orsat tubes are then connected separately to the analyzer sample line, and the known volumes of hydrocarbons flushed into the sample U-tube, as previously described, to obtain calibration curves in parts per million by volume as shown (Figure 7). Nordstrum No. 555 valve grease is used to lubricate the stopcocks, and starch-glycerine lubricant is used on the syringes.

In calculating analyses the concentration obtained from the calibration curve is multiplied by the appropriate sensitivity factor X1, X10, or X100, depending on the analyzer sensitivity setting used to keep the component peaks on scale.

Apparent retention times and rela-

Table 1. Retention Values of Hydrocarbons

Substrate: 2, 4-dimethylsulfolane  
Temperature: 0°C.  
Carrier: Helium at 35cc./min.

	Apparent retention time (min.)*	Relative retention volume
(Air)	(14.5)	....
Ethane	1.7	0.33
Ethylene	3.3	0.64
Propane	5.1	1.00
Propylene	9.3	1.81
<i>i</i> -Butane	10.8	2.12
<i>n</i> -Butane	17.3	3.39
Acetylene	24.0	4.71
Butene-1	29.4	5.76
Isobutylene	31.8	6.23
Isopentane & <i>trans</i> -Butene-2	39.8	7.81
<i>cis</i> -Butene-2	47.7	9.36
<i>n</i> -Pentane	51.7	10.01

\* Measured from the air peak

tive retention volumes for C<sub>5</sub> and lighter hydrocarbons are given in Table 1, and a typical chromatographic record for a 25-ml. liquid-air sample from the plant rich air vaporizers is shown in Figure 8. Sensitivity changes made during the analysis are indicated on the record.

Table 2 shows a comparison of analyses of a liquid air sample by this method and that of Quiram and Biller (8). The latter method involves concentration of hydrocarbons in a high vacuum manifold and subsequent analysis by mass spectrometer.

## Operation

The Atlantic instrument was intended for routine use in the ammonia plant control laboratory. Early in the design stage the complete set up was "breadboarded" to check the opera-

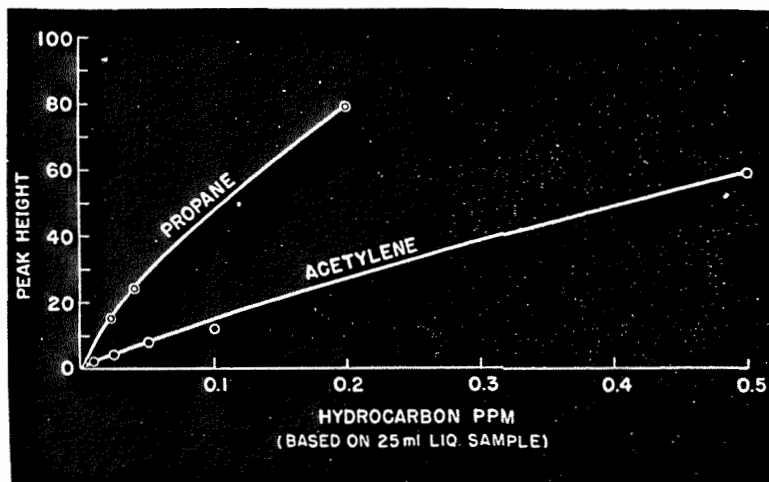


Figure 7. Chromatograph calibration (p.p.m.)

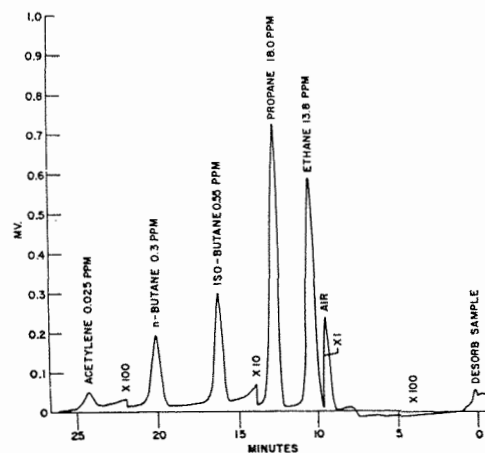


Figure 8. Chromatographic record—reboiler sample

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tion of the various components prior to construction. This procedure eliminated changes in the final unit.

Upon completion the instrument was tested and calibrated by technical personnel in the Research and Development Department. During this period, training in operation and maintenance of the unit was given to the plant laboratory technicians. In the plant the instrument was mounted on a laboratory bench on a sheet of sponge rubber to minimize vibration.

During the first two weeks of plant use, a minimum of technical help was required to overcome problems associated with plant operation. Some additional training in maintenance and operation was given the plant technicians on the site. Since its installation in December, 1957, the instrument has been operating on a satisfactory, routine basis, with all preventive maintenance in the hands of ammonia plant laboratory personnel and plant instrument mechanics.

### Other Applications

By proper selection of column packing and operating temperature the analyzer may be used for the analysis of other trace components. For example, higher boiling hydrocarbons up to about  $C_{12}$  in molecular weight can be determined by using columns operating at temperatures up to 150 or 180°C. Inorganic gases such as nitrogen, oxygen, and carbon monoxide might also be determined by using molecular sieves (Linde 5A) at temperatures ranging from room temperature to 100°C. For each specific application calibration is first obtained with known mixtures, and special consideration must be given to the nature of the sample U-tube required to separate the bulk of the sample from the trace components.

### ACKNOWLEDGMENT

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