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Automatic hydrocarbon analyzer

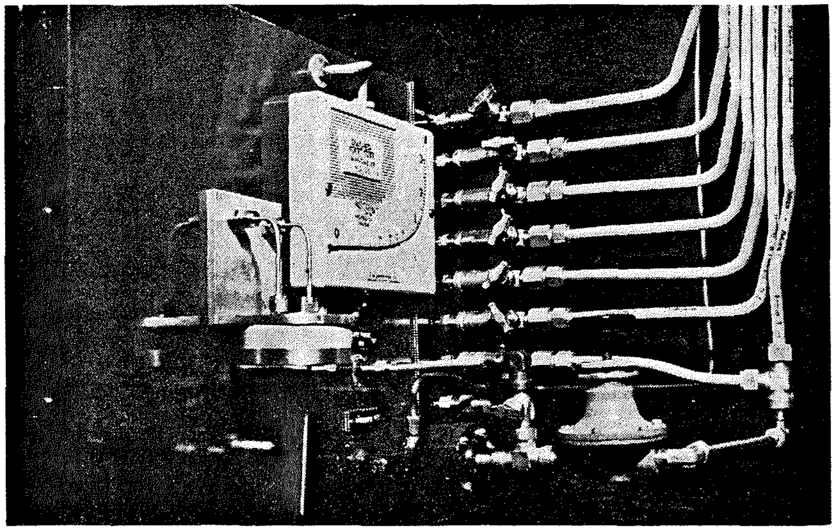
Initial data indicates that a hydrogen flame ionization detector will provide frequent and accurate checks of contamination level.

Analyzing various process streams at the Rohm & Haas Co. air plant in a rapid and relatively accurate manner has been under study to prevent dangerous concentrations of hydrocarbons. Although the original plant design incorporated all known safety devices such as Hopcalite filter, centrifugal air compressors, auxiliary vaporizer, etc., recent growth in the area has surrounded the plant with refineries and chemical plants. The increased air contamination has led to a study of the efficiency of the Hopcalite or catalytic filter, and also the degree of activation of the silica gel filters on the rich-liquid stream from the high pressure column.

Analytical methods

Originally an infrared analyzer was installed with continuous monitoring of the C_2H_2 in the O_2 separator. This never proved satisfactory and as a result better means of analyzing critical streams was sought. Gas chromatography appeared to be a partial answer in that separations could be made between the various hydrocarbons, using selected column packings. The usual chromatography unit, however, tends to pick up too many things when using a thermistor or thermal conductivity type detector and does not have good sensitivity. For instance, H_2O, CO_2; CO, and several other materials are troublesome with these types of detectors. Also, it is usually necessary to concentrate a sample to obtain a satisfactory response. This involves special techniques not readily adapted to routine plant operation.

Over a year ago we learned of a relatively new hydrogen flame ionization type detector which appeared to have great promise. It was said to be unaffected by H_2O, CO_2, and many other components when present in moderate quantities, and at the same time had very good sensitivity, particularly to hydrocarbons. A model of a detector made by a local manufacturer, Well Logging Equipment Mfg. Co., and used for monitoring the gas evolved from drilling mud, was adapted to analyzing process streams of the air plant. Initial observations showed that the instrument was basically sound and practical. The next step was to design a unit which would automatically analyze all of the critical streams desired.



Analyzer case showing sample connections, automatic hydrogen cut-off, and case pressure indicator.

Apparatus—a description

Figure 1 shows a schematic of the analyzer. For carrier air, a stream is withdrawn from the low pressure column several plates above the entrance of the rich liquid and gas stream from the high pressure column. At this point the gas has been scrubbed by the N_2 reflux and is relatively free from hydrocarbon contamination. The O_2 concentration is also sufficiently high to give a stable flame with H_2. It has been found advantageous to use a surge tank in the line to reduce fluctuations resulting from changes in pressure and O_2 composition. A Gelman diaphragm pump has been provided to increase the carrier air pressure if necessary. The chromatographic column consists of 8 ft. of ¼-in. aluminum tubing packed with 60-mesh activated silica gel. Column temperatures of 125°F to 145°F have been found satisfactory. Temperature control is not too critical since it affects only the column itself and is not multiplied by the effect on the detector. The detector or burner has been found to be stable and "flame-outs" are rare.

Continuous samples are taken from six different locations, Figure 2. Four of these are liquid and a sufficient sample is taken to cause frosting of the line several feet from the cold box. Excess gas is vented to atmosphere ahead of the rotary sample selector valve. This considerably reduces the possibilities of valve leakage and carry over from one sample to another. A programming device selects and injects a 15 cu. cm. sample into the column at the rate of 8/hr. Provisions have been made to inject a standard in place of sample No. 8 if desired. Lights indicate which sample is being analyzed. All lines are either stainless steel, aluminum, or Tygon with the exception of the H_2 line. This is to prevent formation of acetylides which might accumulate over a period of time.

Three hundred volts are impressed

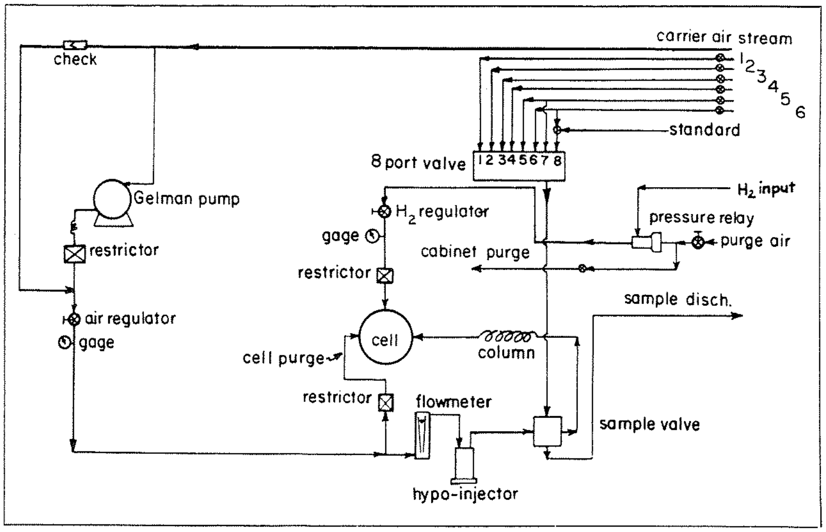


Figure 1. Schematic flow sheet of automatic hydrocarbon analyzer.

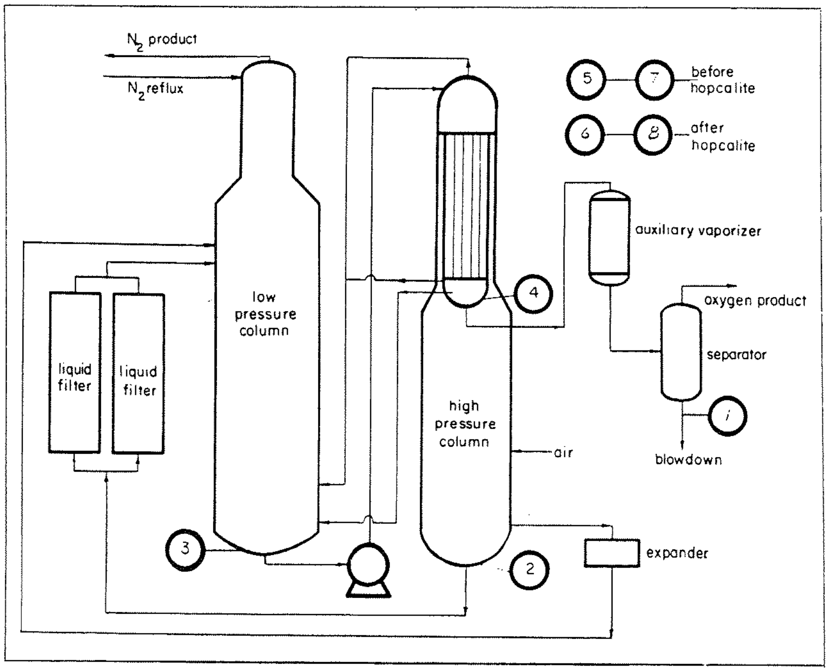


Figure 2. Schematic of air separation plant showing sample points.

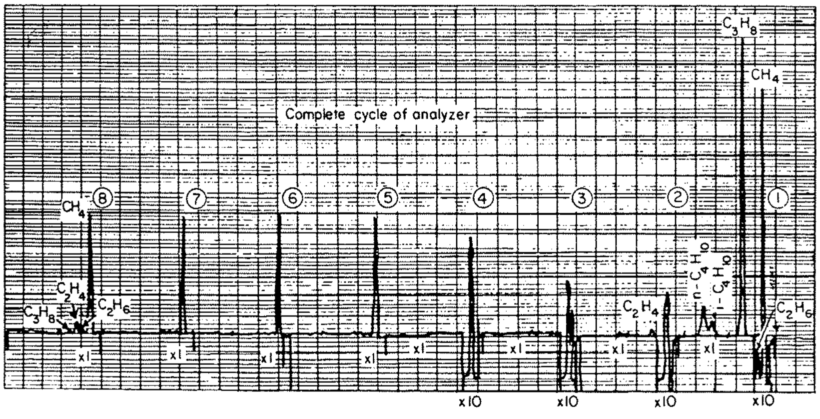


Figure 3. Typical recorder chart.

across the H_2 flame. When a hydrocarbon is introduced into the flame, ionization occurs with resultant flow of electrons. A d.c. amplifier is used to magnify this effect. The signal is then fed to a 0-1 mv recorder with a chart speed of 20 in./hr. Connected to the programmer is a timing cam which, if desired, allows automatic attenuation of the signal by a factor of 10 during the elution of CH_4 and C_2H_6. Manual attenuations of 2, 10, 50, 100, and 500 are also provided.

Calibration

A substantial quantity of standard gas is desirable to check the operation of the unit. Standards have been prepared by a previously described method (*1*) where a calibrated volume of gas is trapped between two valves and then flushed into a container or cylinder. Stainless steel valves and aluminum tubing have been substituted for glass. The cylinders used are 1.25 cu. ft. light weight steel, hydrostatically tested to 400 lb./sq. in. gauge. Filling pressure has been limited to 100 lb./sq. in. gauge. A ⅜-in. free-swinging steel ribbon 16-in. long tack-welded to the top cylinder valve allows the gases to be quickly and thoroughly mixed by simply rocking the top of the cylinder. No difficulties have been experienced in storing the standards when clean dry cylinders and gases are used.

Operation and analysis

The instrument as described has been in operation for a period of four months and time has not permitted collection of extensive data. Figure 3 shows a complete cycle of 8 samples starting with sample point No. 1 (liquid from O_2 separator) at the far right. This showed a CH_4 content of 35 ppm, 3.5 ppm C_2H_6, 2.8 ppm C_3H_8, 0.2 ppm *i*-butane, and 0.4 ppm *n*-butane. The next sample, No. 2, was taken from the bottom of the high pressure column. In addition to CH_4, 0.1 ppm of C_2H_4 was found. Ethylene could also be identified in samples 5, 6, 7, and 8. Analysis of a typical standard gas is shown in Figure 4. Each component has a mol concentration of 2.0 ppm. The instrument normally operates with sufficient gain to give a one inch peak for one ppm of C_2H_2.

Prior to the time the final instrument was installed, a pair of monitors (flame ionization type) was used to check the air before and after the Hopcalite catalytic filter in order to determine its efficiency. The temperature of the Hopcalite was 330°F at the time. Figure 5 shows a slug of contamination entering the air plant. The air before the filter reached a maximum of 100 ppm while downstream only 14 ppm showed. Comparison of the area under the curves indicated that 83% of the total carbon atoms present as hydrocarbons were converted to oxides of carbon. At this particular time the wind was blowing from an C_2H_2 plant. An analysis of the liquid from the high pressure column for C_2H_2 gave negative results, so it was concluded that the unreacted material was probably CH_4 and C_2H_6. Much of the contamination entering the air plant has been found to enter in slugs.

A series of curves, Figure 6, was drawn from data obtained with the chromatographic column and flame ionization detector during the deriming of the auxiliary vaporizer and O_2 separator following six months of continuous operation. The concentrations were such that it was felt that C_3H_8, *i*-butane, and *n*-butane had definitely frozen out and accumulated in these two pieces of equipment. No appreciable concentrations of these components were found during the deriming of the low pressure column or main vaporizer. This clearly shows the necessity of deriming these pieces regularly.

A similar graph, Figure 7, was made of a series of analyses during the derime of a rich-liquid filter. A small amount of CH_4 came out first, and as it was disappearing, C_2H_4 started to be evolved and reached over 300 ppm. After 300 min., it dropped sharply. During the time that the C_2H_4 was eluting, a small amount of C_3H_8, and an even smaller quantity of C_2H_2 were released from the bed. In this particular case no butanes could be identified, although in a more recent check of the same filter an appreciable amount of butanes were found. Knowing the rate of N_2 derime gas and the concentration of the contaminants, an estimate was made of the total contaminants held in the bed.

A similar series of analyses were made recently which confirms this particular graph. Very little, if any, hydrocarbons are evolved above 46°C although the bed was heated to approximately 70°C for several hours.

Sources of contamination

Aside from the more obvious sources found in refinery and oil and gas producing areas, units such as boiler houses and gas driven engines can be serious sources of saturated hydrocarbons, C_2H_4, and C_2H_2. For instance a boiler house located about 500 ft. from the air intake was found to contain up to 60 ppm C_2H_4, and 62 ppm C_2H_2. The exhaust from several four-cycle engines using natural gas as fuel contained 24 ppm C_2H_4 and 26 ppm C_2H_2.

Discussion and conclusions

Recorder charts may look quite formidable for the production operators or foremen to interpret. If it is remembered, however, that for all practical purposes at low concentrations, the peak height is a direct function of the mol or volume concentration (2), then peak heights can be measured in terms of concentration using a small scale. For further simplification, the gain can be adjusted to give, as an illustration, 10 divisions per ppm of the most critical component, C_2H_2. Under constant column conditions, each component elutes at a constant time from the injection. A standard tracing on a clear plastic sheet allows the operator to align the peaks and identify the component. After several weeks of observation and training, operators recognize the usual peaks without this aid.

Occasional checks, however, will continue to be made by the analytical laboratory. In addition to having a

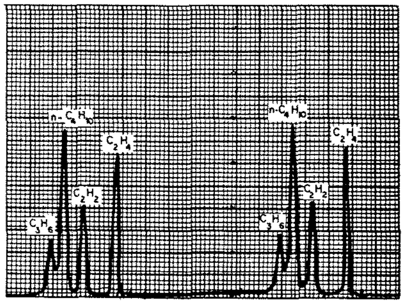


Figure 4. Two analyses of the same standard gas.

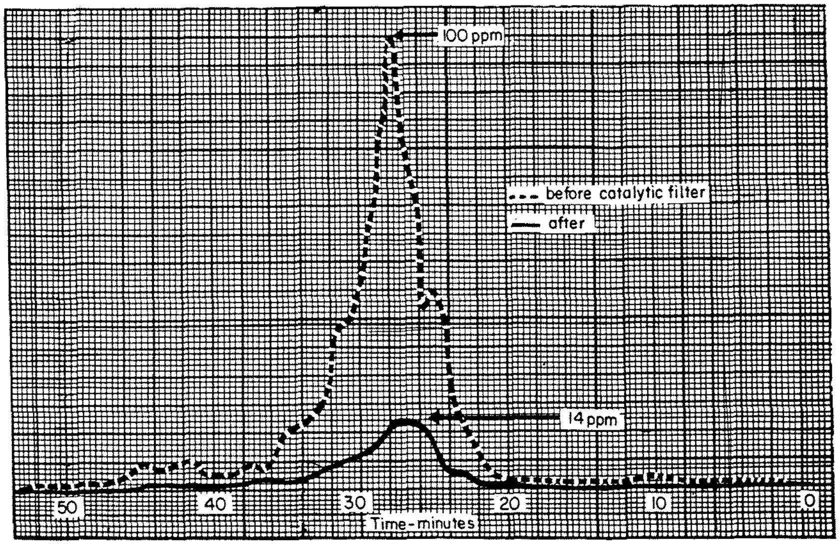


Figure 5. Typical slug of contamination entering air plant.

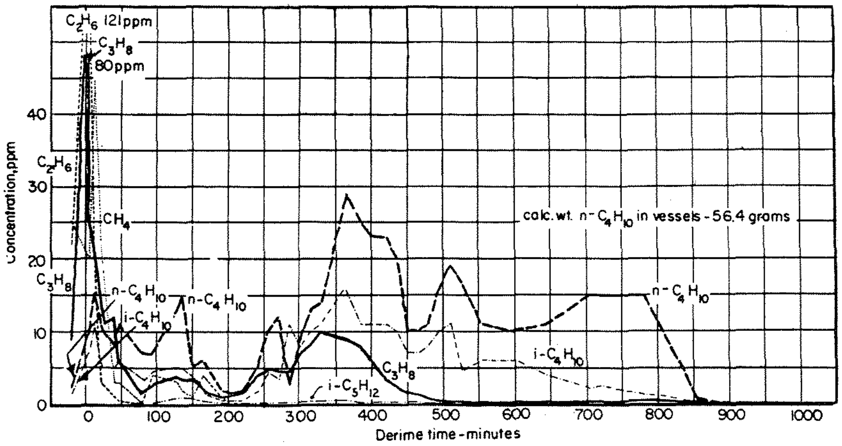


Figure 6. Derime of auxiliary vaporizer and oxygen separator after six months of operation.

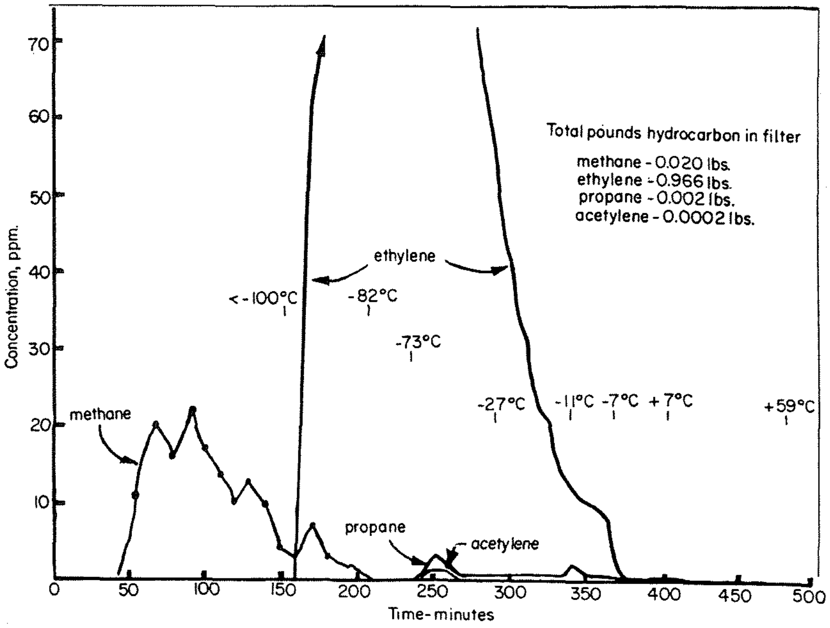


Figure 7. Reactivation of rich-liquid filter.

more frequent and accurate check on contamination levels, the instrument is expected to pay for itself in saving of analytical labor within the next two years.

ACKNOWLEDGMENT

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LITERATURE CITED

1. Gaulin, Michaelsen, Alexander, and Sauer, *Chem. Eng. Prog.*, *54*, No. 9, 49-53 (1958).
2. Andreatch, A. J., and R. Feinland, *Anal. Chem.* *32*, 1021 (1960).

Questions and answers

WEIGERS—American Cyanamid Co. New Orleans, La.: Do you use this instrument to determine your quanity of purge in your actual operating procedures?

COLEMAN: We have not as yet. This instrument was installed only recently and we are still working with it. We want to train the operators and prove it out before we use it as a guide for control of the plant. If we should find that the contaminants go up, I am sure we would increase the flowdown right now. So far we are just testing it. We hope to use it to operate the plant in a couple more weeks.

WEIGERS—American Cyanamid: Do you anticipate ever using this in lieu of the conventional C_2H_2 tests?

COLEMAN: Yes, we definitely hope so, both for C_2H_2 and for total hydrocarbons.

J. A. GLASS—Monsanto Chemical Co., Texas City, Texas: How long does it take to complete one cycle of the compounds illustrated?

COLEMAN: The way the instrument is set up right now, we complete a cycle each hour, or eight analyses in one hour.

P. C. MCELROY—Wyandotte Chemicals Corp., Geismar, La.: In your standard sample, you mentioned that you have C_2H_2 in there. How are you able to hold that concentration uniform?

COLEMAN: First of all, we use either steel, stainless, or aluminum equipment. We make up the standard in a dry steel cylinder and have found it to be stable. We have not had any particular trouble with the standard charging.

L. W. Coleman joined the Rohm & Haas organization in 1942 after obtaining a B.S. and M.S. in Ch.E. at Pennsylvania State Univ. During the next six years, he worked in the Development and Technical Service Div. in the manufacture of organic chemicals. When the Texas plant was under construction, he was transferred to Houston. Since that time he has served as Chief Chemical Engineer, Area Production Manager, and, more recently, as Special Problems Engineer.

WALTON—SunOlin Chem. Co., Claymont, Del.: Does this require a technician to operate?

COLEMAN: No, we hope that this will be just as automatic as a level recorder or flow controller. As a matter of fact, it is right now. Nothing more than the baseline adjustment is necessary and that is being done by a man in the control room.

R. W. SANDERS—Texaco Inc., Lockport, Ill.: Do you have any particular type of vaporizer for the liquid samples, or do you just let vaporizers in the line?

COLEMAN: We allow the liquid to vaporize in the line. A large purge is taken off each line continuously. The lines frost up quite some distance from the box, and we feel that by taking a large sample and allowing it to completely vaporize, we are getting very close, if not, the true analysis.

ANONYMOUS: You mentioned, I think, that this auxiliary vaporizer had been in service for six months. Is this your normal length of run between derimes of the auxiliary vaporizer?

COLEMAN: We were the victim of circumstances on that, I think. We just could not derime it without shutting the whole plant down. We had some leaking valves, and it was just impossible to do it.

ANONYMOUS: I asked the question because it has always been our feeling, and maybe we are in the conservative minority, that auxiliary vaporizers should be derimed more frequently than that.

COLEMAN: I agree with you wholeheartedly.

WALTON—SunOlin Chemical Co.: Someone reported in the questionnaire that they had devised a means of testing for oxides of nitrogen with a chromatograph. Would this be applicable to your setup also.

COLEMAN: It may be possible, and we probably will look into it a little later. We have not so far.

WALTON—SunOlin Chemical Co.: Would you like to make a statement as to the possibility of this setup being available commercially?

COLEMAN: Yes, I think it will be available commercially. We have had some inquiries due to occasional talks with various individuals in the Houston area. I think once this thing can be more or less systematized, or if instrument manufacturers see that the demands are such that they can make units on a larger scale, they will be glad to do it. I think all you have to do is contact them.