ANALYSIS OF HYDROCARBON IMPURITIES IN OXYGEN PLANT STREAMS BY GAS CHROMATOGRAPHY

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Hydrocarbons in general, and acetylene in particular, present a very special hazard when present as impurities at the parts-per-million level in liquid oxygen plant streams. For this reason some type of automatic, continuous process instrumentation was desired which would serve as a hydrocarbon monitor. Acetylene analysis was assigned the highest priority while the monitoring of other light hydrocarbons was of interest provided they could be reliably obtained.

Two instrument types, process infrared and process gas chromatography with a high sensitivity detector, appeared adequate for such an analysis. At the time active study began on this application considerable work had been done by various instrument companies in upgrading process infrared analyzers to such a degree that the desired reliability and acetylene detection limit could be obtained. With all the work that had been done, the best obtainable infrared analyzer was considered marginal at best for the proposed application.

Process chromatography with a high sensitivity type ionization detector was just becoming available as the study began. Detectors of this type were performing quite satisfactorily in laboratory type chromatographs but unattended continuous process type instrument applications were both quite new and few in number. However, increased sensitivity and the ability to monitor more than a single component were two factors favoring chromatography over infrared analysis. When a commercial process chromatograph with a hydrogen flame detector became available on a consignment basis the decision to use chromatography, as opposed to infrared, was made.

Instrument and analysis

The instrument as received was a standard Beckman Model 320 Process Chromatograph with a hydrogen flame type ionization detection system and a 1 mv, 1 second response L & N Model G recorder. The initial laboratory check out revealed that only a few minor modifications and adjustments were needed before reliable instrument operation was obtained. The only major modification was the addition of an automatic re-ignition circuit which would automatically relight the burner within less than one minute after it went out. This was considered necessary for unattended operation both for continuity of analyses and for preventing accumulation of hydrogen inside the burner housing and vent line.

Two columns, connected in series, have proven adequate for separating the desired components. The column configuration is shown in Figure 1 with the columns being 40 ft. of Drapex 4.4 on Chromosorb P followed by 5 ft. of Carbowax 400 on Chromosorb P. Using this column system, ethane and ethylene were eluted first as a single peak, followed by acetylene, propane, and n-butane. These were the components displayed in the anaylsis. Table 1 gives the full scale calibration based on peak height for each component present in the two sample streams. Any shorter column length results in insufficient separation between components and any longer length only adds to the 15 minute analysis time.

As seen from the table, the acetylene calibration for the reboiler oxygen analysis is 0.5 ppm full scale. At this sensitivity the baseline noise level was approximately 1% of full scale or 1 division on the recorder chart paper, and the minimum acetylene detection limit is about 0.005 ppm or 5 parts per billion. Due to this extreme sensitivity of the acetylene calibration it was decided to have the recorder chart drive run and thus scan during the elution and presentation of this peak. This was done so that any baseline drift could be seen and would not be mistaken as a false indication of the presence of acetylene. The other three components in the analysis were presented on the recorder in bargraph form as the reduced sensitivity settings needed for their respective full scale calibrations resulted in such a small amount of baseline drift that it could be adequately compensated for by automatic zeroing of the instrument twice during each sample cycle. The instrument was zeroed once just before the sample was injected and again just prior to the elution of the n-butane peak. Figure 2 shows a section of a recorder chart with several complete analyses displayed.

Burner vent system inadequate

Operation of the analyzer in the lab showed that the burner vent system was inadequate for removing the water formed as a combustion product of the hydrogen flame. Buildup of water in the vent line caused irregular back pressure on the burner which in turn caused a very noisy and erratic instrument base line. Changing the vent line so that it came directly out of the bottom of the analyzer, rather than the side, corrected the problem. After the instrument was moved to the plant, the vent coming out of the bottom of the analyzer was connected to a small metal cylinder which served
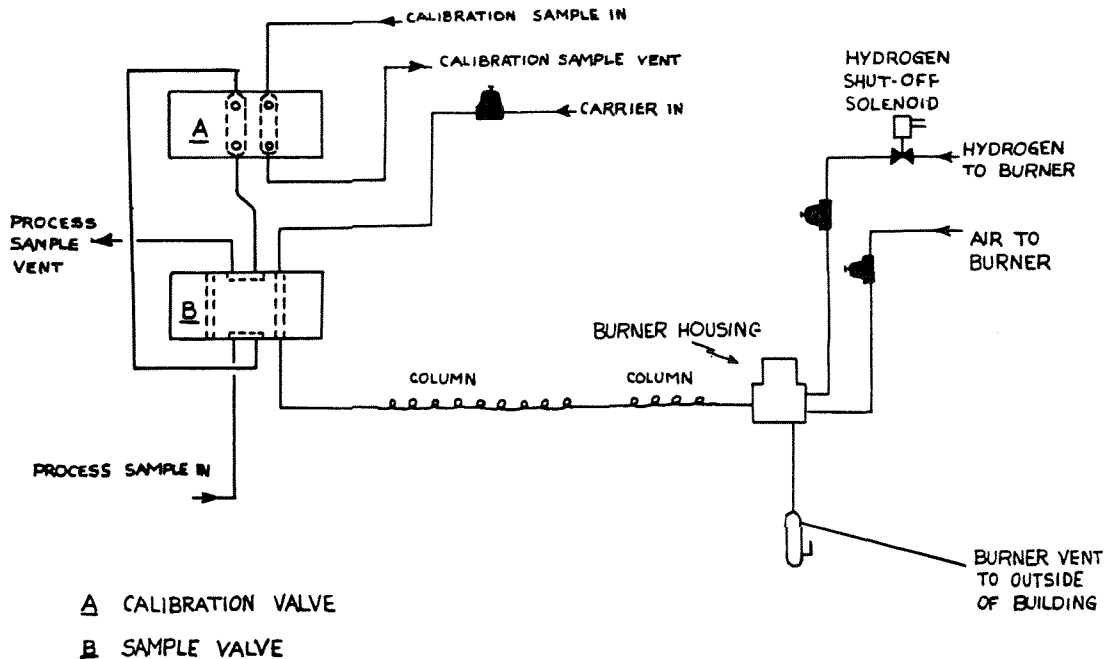
A CALIBRATION VALVE

B SAMPLE VALVE

Figure 1. Column configuration for separating desired components.

TABLE NO. 1
Full-Scale Calibration Peak

Component	Reboiler Oxygen Sample	Fresh Air Feed Sample
Ethane plus ethylene	0-100 ppm	0-2 ppm
Acetylene	0-0.5 ppm	0-2 ppm
Propane	0-100 ppm	0-2 ppm
n-butane	0-2 ppm	0-2 ppm

both as a knock-out trap for the water and also as a water seal which prevented the vent gases from escaping to the immediate area around the analyzer. A 3/8 in. stainless steel tube running from this cylinder up to a small vent hood outside the building was to be used to carry off these gases. Water build-up in this line presented the same problem as was encountered initially in the lab. To correct this a 3/8 in. tube was run, sloping downward, directly from the knock-out cylinder to the outside of the building. By doing this any water which condensed out in the tube ran on out and did not cause back pressure. A small sheet metal hood was placed over the outside end of the tubing to prevent any wind from blowing directly on the tubing end as this also would show up as back pressure noise in the instrument.

As low parts-per-million synthetic standard samples are difficult to prepare with any degree of accuracy, and when prepared do not exhibit good long term stability, calibration of the analyzer was achieved by dilution of standard samples containing percent rather than parts-per-million concentrations of the desired components. The internal volume of the calibration value shown in Figure 1 is a known fraction of the analyzer sample volume. As an example of how this dilution technique works assume the volume ratio to be 1 to 5,000. In this case a prepared sample containing 1% of a certain component, when introduced from the small volume will result in the same output signal as would be obtained from 2 ppm of the same component introduced from the larger analyzer sample volume. This internal dilution calibration procedure was described in detail in a paper presented earlier
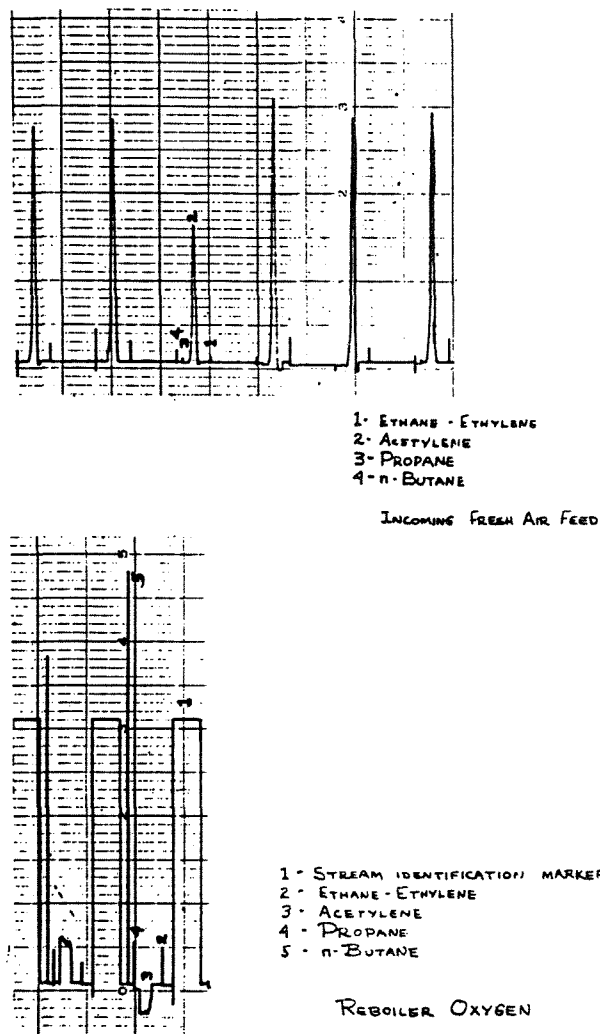

1- Ethane - Ethylene
2- Acetylene
3- Propane
4- n-Butane

Incoming Fresh Air Feed

1 - Stream identification marker
2 - Ethane - Ethylene
3 - Acetylene
4 - Propane
5 - n-Butane

Reboiler Oxygen

Figure 2. Section of recorder chart with several complete analyses shown.

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this year, and is presently available from the published proceedings of that meeting. (1)

Sample systems

As stated, the two samples of primary interest were the fresh air feed to the plant and the liquid oxygen product, both being piped directly to the analyzer. Provisions were also made in the sample system so both of the main samples could be either blocked off or bypassed around the analyzer and samples taken anywhere in the plant by means of evacuated sample cylinders could be injected and analyzed. This feature has been quite useful for periodic spot checks of various plant streams where the hydrocarbon content is of interest.

The fresh air feed sample shown in Figure 3 presented no problems as the sample pressure was more than adequate to maintain a constant, regulated flow at rates sufficient to give a response, or sample lag time of less than 1 minute. The only impurity present in addition to the hydrocarbons was water. As a hydrogen flame detector does not respond to water, no special provisions were required to remove it prior to the sample entering the analyzer. All of the sample system components were cleaned with de-greasing solvent after installation to prevent possible sample contamination.

Also shown in Figure 3 are the vent systems, inlet connections for samples collected in evacuated cylinders, and the inlet connection for standard gases used for instrument calibration. Separate vents for the process samples and the calibration samples were found to be necessary due to memory effects from the percentage concentration of hydrocarbons present in the calibration gases. The solenoids on the incoming sample lines are part of the automatic sample switching equipment.
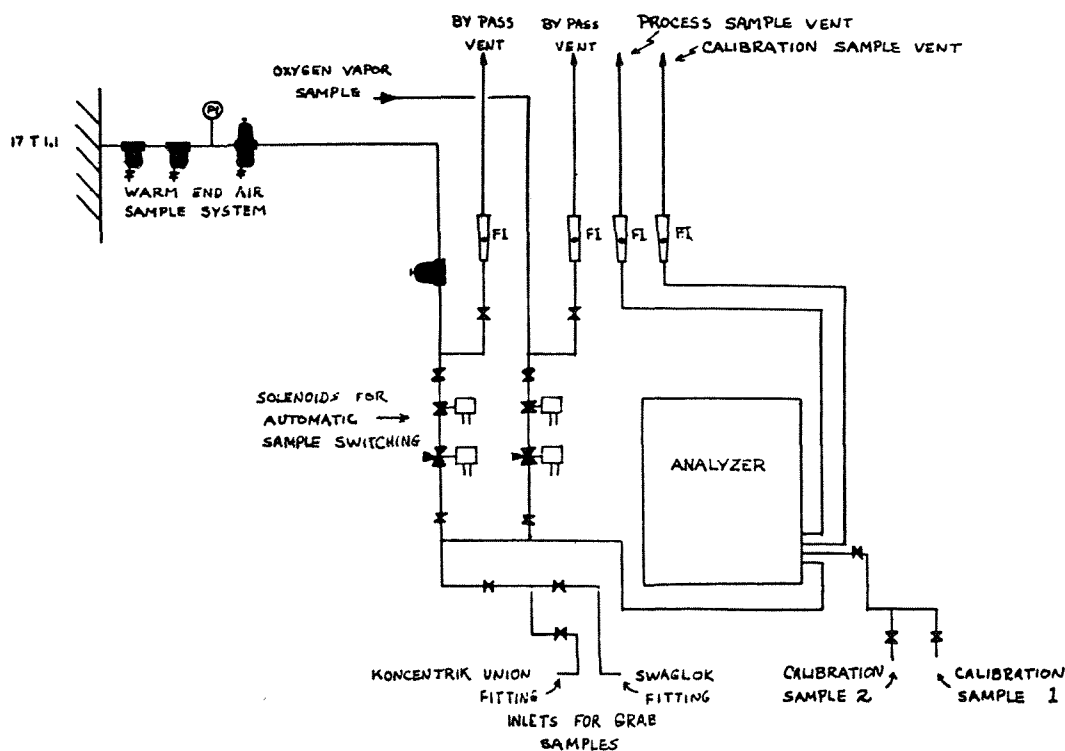
Taking samples & problem

Representative sampling of the liquid oxygen presented a formidable problem. The analyzer was not equipped to handle samples in the liquid state so the oxygen had to be vaporized before reaching the analyzer. In order that a representative sample would be obtained, the liquid oxygen had to be flash vaporized. If slow boiling, rather than flash vaporization was used, then concentration of the hydrocarbon impurities would take place in the boiling chamber. Along with a non-representative sample, this would also create a serious safety hazard. With these requirements in mind, the vaporizer shown in Figure 4 was developed. The capillary lead in tube enable a fine jet of liquid oxygen to be directed upon the heated aluminum plate and at the same time acted as a flow restrictor which prevented enough liquid from entering to flood the vaporizer and start concentration of impurities.

The vaporizer was thoroughly lab tested using liquid nitrogen as a sample and is now working quite satisfactorily in the field. The only problem encountered in the field was vapor locking which was corrected by eliminating all heat leaks in the insulation. The vaporizer has been pulled out of service and inspected for accumulation of any foreign matter in the vaporizing chamber twice since it was installed; and on both occasions, it has been found to be completely clean.

The over-all liquid oxygen sample system is shown in Figure 5. The steam to the vaporizer is alarmed for both high and low pressure; thus, if the steam supply is shut off or if the vaporizer should freeze up and block off the steam, a warning is given. The temperature indicator on the exit vapor line gives a visual indication of the oxygen vapor sample temperature as it leaves the vaporizer, and the relief valve on this same line prevents excessive pressure build-up

Figure 3. Fresh air feed sample system.
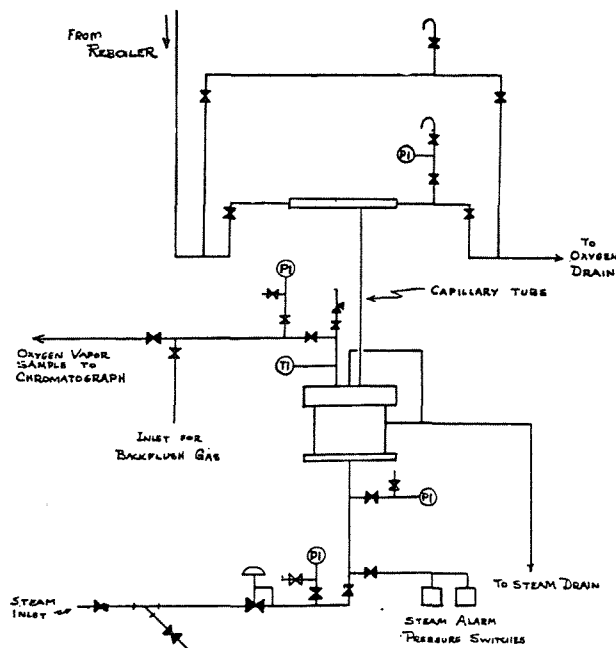
LIQUID OXYGEN SAMPLE SYSTEM

Figure 4. Vaporizer developed for system eliminated sampling problems.

in case of the sample line plugging. All tubing coming in contact with the oxygen is stainless steel, thoroughly de-greased as it was installed. All tubing fittings were back welded as a double safe guard against leakage.

During normal operation both samples flow continuously, with one going to the analyzer and the other being bypassed to a vent.
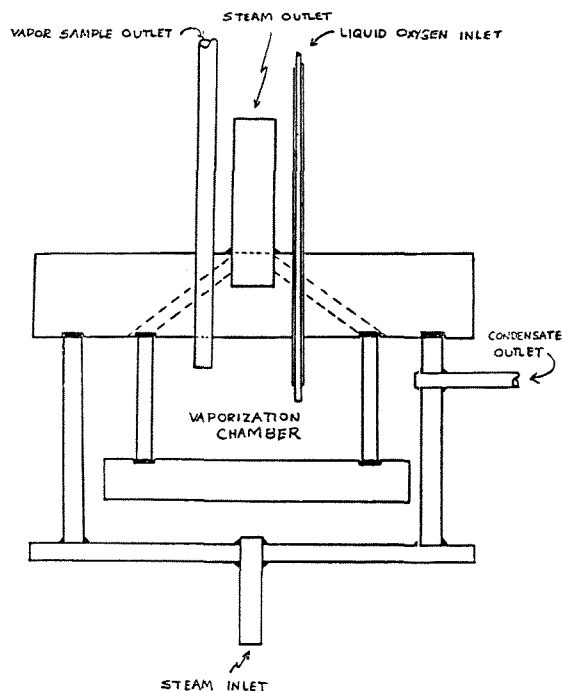

Figure 5. Over-all liquid oxygen sample system.

Analyzer operation

The analyzer completes one analysis every 15 minutes. The sample is automatically alternated between liquid oxygen and fresh air feed samples every 60 minutes so that current data concerning the hydrocarbon impurity level of each stream is always available. The same switching circuit which alternates the samples also switches the attenuation circuits in the analyzer programmer so that the calibration is always in the correct range for the sample being analyzed. All of this circuitry and sample switching was added to the instrument after it was received from the manufacturer. The instrument was installed in the plant control room with the recorder mounted in the control panel and the analyzer and programmer placed behind the control panel. This arrangement has proven quite satisfactory. Maintenance requirements have been low with the onstream time exceeding 95%.

Conclusions

Process gas chromatography with hydrogen flame detection has proven to be a very successful and trouble-free method for the monitoring of hydrocarbons in oxygen plant streams. It has proven to be a definite aid in normal day by day plant operation while at the same time adding greatly to safe plant operation. The analyses have proven quite accurate and are available immediately for use by the plant operating personnel.

Literature cited

1. Parks, J. C. and Hinkle, E. A. "A New Calibration Method for Process Gas Chromatography," ISA 8th Annual Symposium on Instrumental Methods of Analysis, Charleston, W. Va., April 30—May 2, 1962.

Questions and answers

Q. Where do you locate the vaporizer?

PARKS—It comes off of a blowdown line on the auxiliary reboiler—the vaporizer itself is mounted on ground level where it can be conveniently worked on.

Q. You cannot control it outside of the box?

PARKS —Yes. It is out in the area, but not inside the box.

Q. First, do you use an independent source of air to maintain your flame or do you use your sample to maintain your flame? Secondly, if you use an independent source of air, how do you assure yourself that it's clean?

PARKS —We use bottled air for air to the flame.

Q. Have you had any difficulties with the purity of the hydrogen?

PARKS —No. We've used electrolytic grade hydrogen and the background level from the flame changes every time we change hydrogen cylinders out. It's a small change but we just learned to live with and expect it and everytime we have to change hydrogen cylinders because the old ones are empty, we just sit there with it and

watch until a new background level is obtained from the new hydrogen.

Q. I see. You have not then tried to maintain your flame with your sample stream.

PARKS —No.

Q. I was wondering if you ever had any trouble with false high indications from the analyzer, due to contamination of the sample, or in some of the tubing to it, or anything like that. Has this been a problem at all?

PARKS —No. We never experienced this.

Q. The maintenance requirements you said were low— do you have any estimate of how much time per day, or week, or month is spent on the analyzer by maintenance people.

PARKS—Maintenance requirements have averaged approximately 5 hours per week.

Q. I have a question concerning your liquid sampling lines. Are these liquid nitrogen jacketed—are they all inside the box up to which point?

PARKS —The lines are 1/4 inch stainless steel, with 4 inches of urethane insulation around it and they are all right outside.

Q. Do you drain liquid oxygen all the time, other than through the capillary?

PARKS— Yes, to insure a good sample at the capillary.

NORMAN WACKS—Dupont. Is there any particular reason for maintaining the condensate level in the vaporizer?

PARKS—No. In our research lab the steam pressure is quite low and condensate built up during the lab tests so the drain was added to safeguard against this occurence. However, after plant installation where we had a good high pressure steam source, the drain has not been needed.

Q. Well, I was wondering why the condensate wasn't permitted to drain out the bottom and have the steam come in on the side?

PARKS —The thinking on that was to have the steam coming in shooting directly against the aluminum plate which was the vaporizing plate.

Q. How frequently do you check or recalibrate your column?

PARKS —This is normally done once a week, I believe. Unless there is a time when it looks like the levels are going up and you begin to question the thing. There are times when the instrument is more important to you than others.

GIBSON—Atlantic Refining Co. We had an interesting experience one time. We have two instruments. One instrument showed all components except acetylene. When we switched to the other instrument, acetylene was detected. Apparently our column became poisoned to acetylene while all others showed normal.

SEFTON—Ontario Research Foundation. What type of valves did you use in the analyzer? In particular, the selector valves, were they of Teflon?

PARKS—In the analyzer the sample valve was a Beckman LG valve as they call them, which is Teflon and metal, with the Teflon sliding against metal. The calibration valve was one that we make ourselves. We have since gone to making all of our own valves which are, again, the Teflon to metal sliding plate type, but differs in the configuration from the Beckman valve.