ANALYZING LIQUID O_2 FOR CONTAMINANTS

Infra-red method developed for identifying and measuring contaminants entering and concentrating in the oxygen plant

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This report is about an infra-red method for analyzing spot samples of liquid oxygen for nitrous oxide carbon dioxide, and a number of hydrocarbons. The method was developed as a part of our program to identify and measure contaminants entering and concentrating in the oxygen plant. It provided the clues which led to our assignment of the cause of our 1956 reboiler explosion to the deposition of co-crystals of nitrous oxide and acetylene in the liquid oxygen. All of the work leading to the conclusion has been published, but the details of the nitrous oxide (N_2O) method have not. We have described it in general terms as being a long path IR method. We used a Perkin-Elmer Model 21 infra-red spectrometer modified to accommodate a 10-meter path cell. This long path cell was selected because of its high resolution in the parts-per-million range and because it was not limited to analyzing for hydrocarbons alone.

How the system worked

An accurately known volume of liquid oxygen sample was isolated between two valves in a spiral coil immersed in liquid nitrogen. It was then admitted to a special sample receiver that had been previously evacuated to 10 microns absolute pressure and then cooled by immersion in liquid nitrogen. The sample container was then isolated, removed from the liquid nitrogen and allowed to warm to ambient temperature. The sample receiver then contained a vaporized liquid sample at pressures up to 1,800 lb./sq.in. gauge. The exact resultant pressure depended on the size of the spiral coil used and the composition of the sample.

The analyzer was prepared to receive the sample by first purging with pure nitrogen and evacuating to 10 microns absolute pressure. Since nitrogen was used as a carrier for calibrating the instrument, purging with nitrogen eliminated the atmospheric contaminants and put the sample results on a nitrogen-free basis.

The sample cylinder was attached to the 10-meter cell and the sample was admitted to bring the cell pressure up to 150 lb./sq.in. gauge thus placing a pressurized sample in the 10-meter path of the IR beam of the analyzer. The resultant scans were then compared to scans of calibrating gases of precisely known compositions to obtain the analysis of the sample.

The instrument was calibrated by analyzing synthetic samples of accurately known concentrations for each impurity identified in the process streams. The problems in obtaining reliable results were

Table 1. Limits of reliability of infra-red analyses.

Component	Minimum Detection Limit ppm by Wt.	Calibration Range ppm by Wt.	Accuracy
CO_2	0.08	0-135	± 5% relative or ± 0.2 ppm absolute, but no greater than 33.6 ppm absolute.
N_2O	0.15	0 -75	± 4% relative or ± 0.1 ppm absolute, but no greater than 1.2 ppm absolute.
		75-500	± 4% relative (estimated).
CH_4	0.48	0-350	± 4% relative or ± 0.6 ppm absolute, but no greater than 4.5 ppm absolute.
C_2H_4	0.10	0 -40	± 4% relative or ± 0.1 ppm absolute, but no greater than 1.2 ppm absolute.
C_2H_6	15.0	0-1000	± 4% relative or ± 6.0 ppm absolute, but no greater than 36.0 ppm absolute.
C_2H_2	0.02	0 - 1	± 4% relative or ± 0.04 ppm absolute, but no greater than 0.2 ppm absolute.
C_3H_8	25.0	15-450	± 4% relative or ± 12.0 ppm absolute, but no greater than 50.0 ppm absolute.

those associated with making very accurate dilutions of impurities to a concentration in the parts-per-million range and entering these gases into the 10-meter cell without contamination from the atmosphere. Multiple analysis of these synthetic samples were made to establish the analytical limits of reliability. The lower detection limits and the 95% confidence limits of the analyses obtained are given Table 1.

What the results were

The analyses of oxygen plant streams obtained by this method gave us enough information to make rough material balances which could be correlated with changes in the plant operating cycle. These rough material balances enabled us to determine the disposition of these contaminants in our system. The method is not good enough for continuous material balances because it requires two to three hours from the start of sampling to the completion of the analysis.

Two impurities in the liquid oxygen were of particular importance to us, carbon dioxide and nitrous oxide. Carbon dioxide has such a low solubility in liquid oxygen, we were not surprised to find out it occasionally exceeds its solubility limits but we were surprised to find it continuously present at about 2 ppm in the liquid oxygen. Nitrous oxide, while it only once exceeded its solubility limits, was generally present at a concentration level from 0.5 to 1.0 ppm.

The results we obtained strengthened some of our very early suspicions about the possible role of nitrous oxide in our explosion and helped us arrive at our explanation for the event. The methods, procedures, and practices developed for our study are generally applicable to process investigations involving analyses for trace impurities. Details on use of the method are given in the Appendix.

APPENDIX

Detailed Method for Infra-red Analysis of Liquid Oxygen in a 10-meter Cell.

Several problems were encountered in taking representative samples of liquid process streams. Since direct vapor sampling of a liquid stream would give a non-representative sample because of liquid fractionating, it was necessary to develop equipment and procedures for obtaining a representative liquid sample and then vaporizing it completely.

The apparatus developed, shown in figures 1 and 2, consists of a spiral coil of accurately known volume for collecting the liquid sample, a back-pressure device for the coil and a sample receiving cylinder. The back-pressure device is a surplus Air Corps oxygen tank equipped with a spring-loaded relief valve.

Figure 1. Apparatus for liquid sampling.

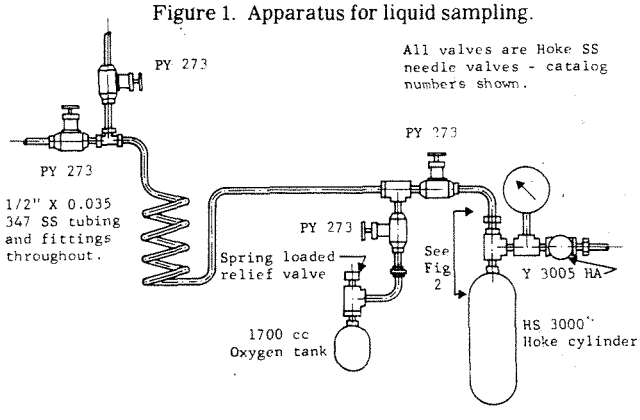
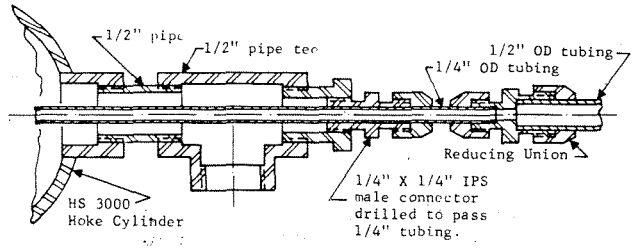


Figure 2. Details of liquid cylinder assembly.



All tubing, pipe and fittings are 347 SS.

The sample-receiving cylinder is evacuated to 10 microns pressure immediately before taking a sample. After the equipment is assembled as shown in Figure 1, the spiral coil is immersed in one container of liquid nitrogen and the back-pressure device and the sample-receiving cylinder are immersed in another container of liquid nitrogen. The sample line is purged, connected to the equipment, and the sample flow started. As soon as liquid flows from the relief valve on the Air Corps oxygen tank, the sample is isolated in the spiral coil, the evacuated sample receiver is opened, and the spiral coil removed from the liquid nitrogen. After defrosting at ambient temperature, the coil is heated with steam. The sample-receiving cylinder, then, is isolated, removed from the system, and the sample allowed to vaporize at ambient temperature.

The sample receiver will contain a vaporized liquid sample at up to 1800 lb./sq.in. gauge pressure. The exact resultant pressure depends on the size of the spiral coil used and the composition of the sample.

Analyzing

Follow the instructions below to obtain the most precise infra-red analysis of vaporized liquid samples from the oxygen plant.

A. Instrument Conditions

Speed	- 6 (next to slowest pulley)
Slit	- 0.984 (auto)
Gain	- 5.8
Response	- 1
Filter	- out
Auto. Suppr.	- 2
Intensity	- full (clockwise)
Balance	- full (clockwise)
Iris	- (ref. beam) - ½ closed - (set to have 80-85% trans - mittance at 4.0 u when cell is evacuated and instrument purged)
Scan	- 2.0 - 15.0 u
Purge	- 4-5 lb./sq.in.

Procedure

Refer to Figure 3 in connection with steps 4 thru 11.

1. Seal space between source and detection housing.
2. Purge instrument and between housing with CO_2 free air or Nitrogen.
3. Set instrument conditions.
4. Attach sample container to cell.
5. Evacuate cell and close valve E.

6. Evacuate connections between cell (valve E) and sample container (valve B).
7. Close valve C, crack and close valve B immediately to have positive pressure between valve B and C to prevent air from leaking into system.
8. Reopen valve E.
9. Scan from 4.0 - 4.5 u for CO_2 background correction. CO_2 background absorbance should not be greater than 0.100 absorbance units.
10. Close valve D, disconnect vacuum pump hose and open valve C fully.
11. Fill cell slowly to 150 lb./sq.in. gauge, controlling the flow with valve B.
12. Scan sample from 2.0 - 15 u. If absorbances are off scale for any component, rescan that region at a reduced pressure in steps of 25 lb./sq.in. gauge until it is on scale.
13. Measure absorbances at calibration wave lengths (see the respective calibration curve) and read ppm from calibration curve provided.
14. Apply corrections to answers when necessary.
15. Vent sample container and leave slight positive pressure to prevent diffusion of contaminates, before next sample is taken.

Safety Precautions

1. Remove vacuum hose from pump before entering sample. (Step 10)
2. Enter and remove sample from cell slowly. (step 11)
3. Leave sample container outside until it comes to ambient temperature.
4. Vent excess sample outside the room. (Step 15)
5. Keep cigarettes and oxidizable materials away from the area when entering or removing samples.
6. Use sample containers for oxygen plant samples only.
7. Never use hydrocarbons of any nature on sample container or cell.
8. Never exceed 155.0 psig on cell.
9. Remove sample from cell as soon as possible.
10. Before evacuating container for next sample purge with air or nitrogen.

Calculations

1. Corrected answers for samples — values from calibration curve xK.
   Where K is the approximate O_2/N_2 ratio.
   Examples are: Products (or 100% O) K — 0.8750
   Rich Air 50/50 K — 0.938
   Air K — 0.9750

2. Pressure broadening absorbance corrections for N_2O in rich air samples are as follows and should be subtracted from

Figure 3. Sample transfer to 10-meter IR cell.

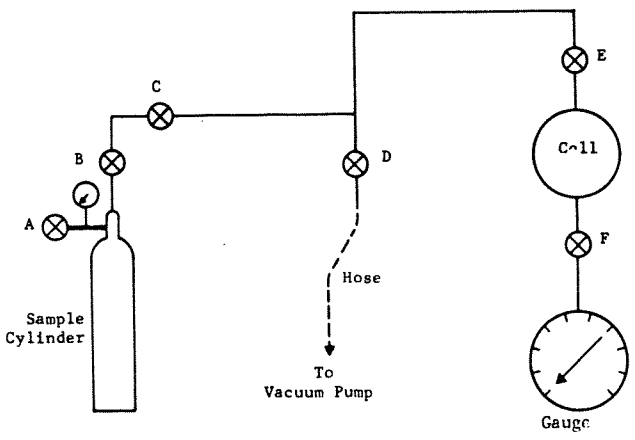
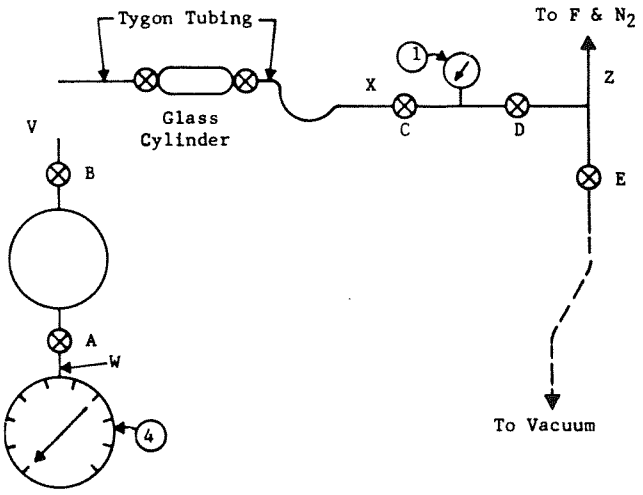


Figure 4. Introducing calibration mixture.



the observed N_2O absorbance:

150 lb./sq.in. gauge-.016
125 lb./sq.in. gauge-.012
100 lb./sq.in. gauge-.008
75 lb./sq.in. gauge-.005
50 lb./sq.in. gauge-.003
25 lb./sq.in. gauge-.001
0 lb./sq.in. gauge-.000

3. Make nitrous oxide correction for methane interference.

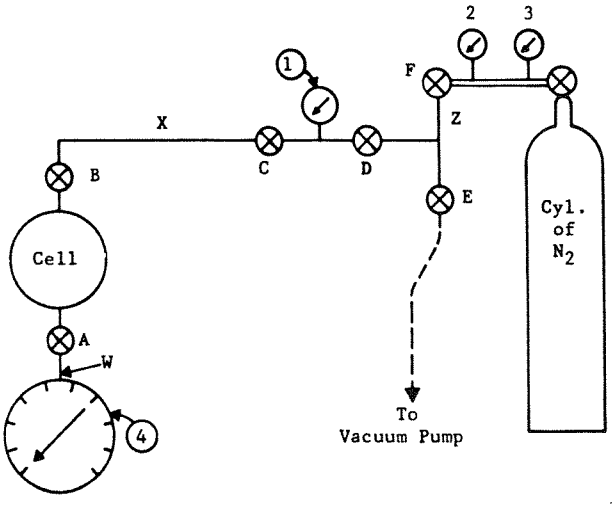
Calibrating

The problems of calibrating the 10-meter infrared (IR) cell were those associated with making very accurate dilutions of impurities to a concentration in the parts-per-million range.

The procedure used for making the dilutions is given below:

1. Prepare an accurately known mixture of the calibrating component and nitrogen in a high pressure nitrogen cylinder. (This is a common practice in the plant using pure components and very accurately measuring the pressure of each component and the total pressure in the cylinder.
2. Allow the cylinder to stand until diffusional mixing is complete –72 hours minimum.

Figure 5. Pressuring calibation mixture.



3. Enter a measurable amount of the calibrating mixture (10 mm Hg pressure or more) into a glass sample cylinder of known volume.

NOTE: Refer to Figures 4 and 5 for steps 4 through 18.

4. Evacuate the cell and cell gauge through line WXY with valve F closed.
5. Close valve A and B.
6. Disconnect line X from valve B.
7. Attach 1 in. to ¼ in. tubing line V to valve B.
8. Purge line V and one end of the glass sample cylinder with nitrogen. Use a hypodermic needle to introduce nitrogen into the dead ends.
9. Quickly attach purged end of sample cylinder to line V.
10. Purge other end of sample cylinder with nitrogen.
11. Reduce purge nitrogen pressure to 3 lb. sq.in. gauge.
12. Quickly attach line X to sample cylinder.
13. Open valve B and stopcocks on sample cylinder and purge synthetic into cell C; valve A should be closed.
14. Close valve B and attach line X to valve B.
15. Close valve D and set pressure at 150 lb./sq.in. gauge on gauge 2 with regulator F.
16. With valves B and C open, fully fill the cell with nitrogen to 150 lb./sq.in. gauge (red from gauge 1) controlling the flow with valve D.
17. Close valve B and open cell gauge valve A.
18. Record pressure of gauge 4 and adjust to 150 lb./sq.in. gauge.
19. Scan the calibration component(s) over the desired region, measure the absorbance and plot on a calibration curve.
20. Calculate the parts-per-million of the calibration component from PV — nRT, where R — 82.057, when P is in atmospheres and V is in cubic centimeters. The compressibility factor of N_2 is 1.0853 at 150 lb./sq.in. gauge. Volume of the cell — 5606 cu.cm and 1 mole of nitrogen — 22,404 cu.cm.

Mole weight N_2 = 28.016

ppm (wt.) = g sample / g N_2

gram sample = (mm of syn) (% of s in syn) (v of samp) (MW of s) / (760 mm) (82.057) (temp. K)

$$\text{gram } N_2 = \frac{5606 \text{ cu.cm.}}{\frac{1.0853}{\frac{\text{abs. gauge press.}}{14.69}}} \times \frac{22{,}404}{28.016}$$

NOTE: Above equation for grams of sample may not be valid for all samples. Best results will be obtained by using compressibility factor as used in equation for g N_2