Norske Sivilingeniørers Forening

NORTH SEA FLOW METERING WORKSHOP

Stavanger, 5 - 7 November 1985

Experience with gas chromatograph

3.2

Lecturer: Mr. Louis N. Cox
Daniel Industries Inc., USA

EXPERIENCE WITH GAS CHROMATOGRAPH

Louis N. Cox
Daniel Industries, Inc.
Post Office Box 19097
Houston, Texas 77224

METHODS AND PROBLEMS ASSOCIATED WITH ON-LINE CHROMATOGRAPHY

The on-line gas chromatographs available today are relatively maintenance free, due to a greater selection of separating column materials and advanced electronics - namely, the microprocessor based programmed controller. On-line chromatographs began with mechanical programmers which required continuous maintenance, but each generation of programmers has increased in reliability and accuracy, so that today's chromatographs can provide a BTU repeatability of ± .5 to 1 BTU/1000.

Installation of the chromatograph according to your manufacturer's recommendations is very essential.

A. Sample Probe

Should be installed one-third pipe diameter in the line. Pressure reduction, relief vent and sample line pressure gauge at the probe.

B. Sample Line

Sample line must not exceed 1/4", and should always be stainless steel tubing. If the sample line exceeds 50', reduce to 1/8" stainless steel tubing.

C. Installation

Install the chromatograph as near the sample point as possible. This will reduce transport problems. Some manufacturers state a temperature limit on their equipment, which may require some type of enclosure. If a temperature limit is not stated, install the chromatograph where morning or afternoon sun will not affect the chromatograph.

D. Calibration Gas

The calibration gas cylinder and gas are often not considered for ambient temperature limits. Special attention to the dew point of the gas must be given (low temperature). Consult your manufacturer for recommendations for calibration gas.

E. Liquid in Pipeline

If there is a possibility of liquid being carried through the pipeline (due to antifreeze operation, etc.), advise your manufacturer so filters or traps can be installed to collect this liquid.

F. Carrier Gas System

The carrier gas transports the sample through the chromatograph and, in some chromatographs, actuates the chromatograph valves. This eliminates the problems with compressed air.

Zero grade Helium (99.9999%) should be used for carrier gas. If zero grade is not available, chromatograph grade (99.95%) is acceptable.

The single most serious problem with the carrier gas system is changing the gas bottles. Dual gas bottle systems are available but most installations have one gas bottle with dual stage regulators. The objective is to keep air out of the system during bottle changes. Injection of air into the system plays havoc with the separation for several hours.

Install a tubing union and needle valve on outlet of dual state regulators. When changing bottles, close needle valve, trapping the Helium pressure in the chromatograph. Remove tubing union from regulator - remove regulator and install on full bottle, back off regulator pressure and place thumb over outlet, apply enough pressure so you can build up and release several times to "shake" the air from the regulator and gauges. Keep positive pressure on outlet, connect tubing union to regulator output, adjust to 100 Psi, open needle valve. The carrier gas bottle has been changed with no air entering the chromatograph.

If you do not know your supplier, as a safety precaution, installation of a carrier gas dryer might be advisable. These are available from your manufacturer.

G. Power Requirements

Power requirements vary with the manufacturer but are usually 120 VAC, 60 Hz, 150-200 watts. Areas that experience outages that cause nuisance shutdowns should consider uninterrupted power supply systems (UPS). Your manufacturer will have these available. If the microprocessor controller is mounted remote from the chromatograph, power must be on the same phase.

H. Chromatograph

The chromatograph contains the oven, separating columns, detector, valves, sample conditioning system and electronics, consisting of valve drivers, preamplifiers, decoder, temperature controller, etc.

Various manufacturers approach the component separation of C_1 - C_{6+} differently. Ideally, base line separation is desirable; i.e., each component returns to base line with no perpendicular drop or tangent skimming. The number of columns and chromatograph valves will determine the separation.

Figure 1 illustrates a one-column, one-valve separation for natural gas. The analysis time is extremely long (22 minutes). Also, due to diffusion in the column with time, the later eluting components will have very little detectability. Note: N_2, C_1, CO_2, C_2 not base line separated.

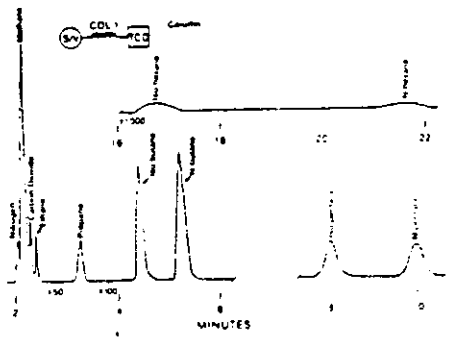

Figure 1

Figure 2 illustrates two-valve, two-column separation. The analysis time has been shortened; also, the sensitivity of the heavy components has been increased by grouping the C_{6+} components, the minimum detectable limit of the entire group becomes on the order of 20 parts per million.

Note: N_2, C_1, CO_2, C_2 are not base line separated.

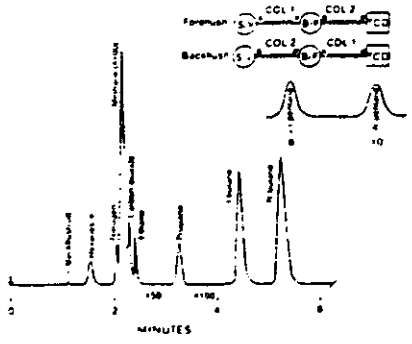

Figure 2

Figure 3 illustrates three-valve, three-column separation. The analysis time has been lengthened to twelve minutes but all components are base line separated for greater stability and accuracy.

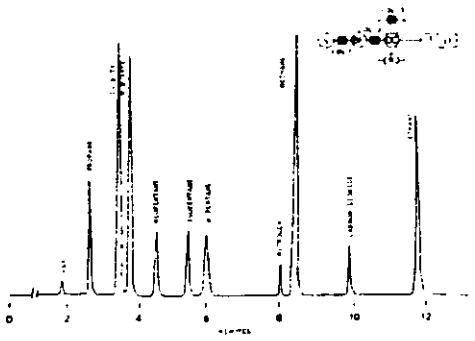

Figure 3

I. Detector

The thermal conducting detector is normally used for natural gas applications. Most manufacturers utilize the two element thermistor bead detector, which is rugged and long lasting. Loss of carrier gas does not destroy the detector.

J. Controller

The microprocessor-based controller controls the functions of the chromatograph: valve timing, peak identification, response factors, retention times, peak area or height measurement and computations. The microprocessor is an extremely reliable device and if left alone will operate for long periods of time.

There are various types of microprocessors available but all perform essentially the same functions. Most will self-check or troubleshoot all circuits and will alarm on a malfunction, indicating on a printer the the malfunction. Some features are:

1. Automatic calibration
2. 24-hour averages
3. Rolling averages
4. All component listing
5. BTU saturated or dry
6. Specific gracity
7. Compressibility
8. Long and short reports
9. RS-232 output
10. Analog outputs
11. Power failure - alarm - retain all data in memory via battery backup

K. Problems

Some problems can be readily identified with on-line chromatographs.

Sample conditioning system - A rotometer is installed on the inlet sample line with a needle valve. If the needle valve requires adjustment frequently to maintain the desired flow, indications are the in-line filter requires replacement.

Carrier gas regulator - If flow varies retention time will move, creating a retention time alarm.

Oven temperature varies - Increase in temperature decreases retention time about 5%/0° (temperature controller malfunction).

Sample size - A change in sample size will affect retention time. Check the sample valve for leaks, etc.

Prior to repairing a chromatograph, always run a chromatogram on the chart recorder. The chromatogram will indicate what is going on inside the chromatograph.

Conclusion

On-line chromatography is the most accurate, reliable device for component measurement on the market. Repeatability of BTU calculations are now as low as ± .5 BTU/1000 over a wide temperature span. You must be familiar with electronics and chromatography to fully understand the principle of measurement. The gas industry is rapidly becoming "high tech". Your manufacturers offer excellent training schools on their products. Take advantage of the opportunity to move into the "high tech" area of your company.

References

[1] Paper presented at the North Sea Flow Measurement Workshop, a workshop arranged by NFOGM & TUV-NEL

Note that this reference was not part of the original paper, but has been added subsequently to make the paper searchable in Google Scholar.