

Various methods can be used to Verify GC Data at a Custody Meter Station

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Most “On-line” gas chromatographs operate for long periods of time without developing biased or even outright unacceptable measurement. Therefore, most users undertake system-wide performance testing infrequently. But as rising gas prices demand increased scrutiny on measurement data – flow volume, energy content, and often hydrocarbon dewpoint analysis -- many measurement staffs may search for better performance testing of GC’s, often for the first time. Others may already have adequate performance testing in place but want to review it for completeness. The following points out various factors to be considered.

GC-data Validation

GC data are generally validated in one or two of these formats:

1. Off-site data scrutiny
2. Periodic (*typically monthly*) operational inspection of the on-line GC
3. Periodic performance testing using external standards (*typically annual or bi-annual*).

The following examines methods to aid measurement personnel in effectively evaluating and undertaking measurement quality assurance campaigns for any of these situations..

Questionable data originates in either of two ways. (1) It may occur immediately following an event such as hardware malfunction or a faulty clerical entry into the application program. (2) Periodic drift or subtle change may occur that escapes any but intense scrutiny. Malfunctions or faulty clerical entry account for discrepancies more often than drift. Whatever the cause, the same examinations will prove effective in uncovering errors. The following courses of action have proved helpful.

Off site data scrutiny:

Examine data logs both aboard the GC as well as logs recorded in off-site archives. Do key events coincide with the origins of the measurement discrepancies? Some such events may include the change of calibration cylinders, the return to service of a GC following maintenance, sample system components faulty or improperly set, or a change in the GC application program.

Perform field inspections.

Examine the sample system – including its basic design -- to assure proper sample flow rate, routing through the GC sample system and proper sample phase. Beware of design shortcomings such as oversized tubing or improperly located sample probes.

Is a probe in place? Properly placed probe regulators are the first line defense against improper liquid sampling. Probe regulators use a stem and seat located inside the line to avoid the condensation of heavier components. Additionally, some probes employ in-line membranes that remove liquid at line conditions.

Is the sample system heated? Recent API (API 14.1) requirements establish temperature ranges to which samples must be heated.

Is the sample system properly adjusted? Check to assure that throughput of streams and calibration gas are equal. Also, check the bypass flow rate to verify that the sample lag is sufficient to exchange the sample system volume twice or more per analysis.

Examine the carrier flow consumption rate. Leaks in the carrier system can cause measurement errors.

Measure performance

Examine the chromatogram. The chromatogram is a most useful tool in determining measurement quality. It should exhibit a stable baseline, clear separation of components, and proper integration of peaks. It will also be helpful to compare current chromatograms to chromatograms that were taken during intervals free of discrepancies.

Measured repeatability should always be checked. Run an analysis using calibration gas as the sample. Compare results with the certified components of the cal gas and with each other. At least three cycles should be run. Repeatability of a GC best reflects its degree of uncertainty and linearity without attaching external standings. Manufacturers' repeatability specifications vary. Measurement departments should not expect limits of repeatability better than the manufacturer's specification.

External standards are seldom useful; other means of verification will usually prove more valuable.

GC calibration must be current. GC's used in custody measurement should be calibrated daily. But if malfunctioning or if the daily automatic calibration is turned off, then the technician should verify GC calibration. Results of an analysis using cal gas as the unknown should match composition certified for the cal gas. This can be part of the repeatability tests above.

Response factors should be "logical". The process known as "Fidelity Plotting," frequently used to verify GC calibration in a laboratory, is a plot of the logarithmic relationship between molecular weight and the response factor. However, fidelity plotting of response factors may not be practical in the field. In most cases it will suffice for technicians to simply check for *orderly ascension* according to Thermal Conductivity Index from C₁ to C₆₊. See Figure 1.

#	Component	Usr/Std	Det ID	Ret Time	Resp Factor	Fxd/Var	Calib Conc	Anly Meth	RT Sec Dev	RT Upd Meth	Resp Fact %
1	C6+ 47/35/17	Std	1	30.2	2013490	Var	0.0289%	Area	2	Cal	10
2	PROPANE	Std	1	50.2	1316330	Var	1%	Area	2	Cal	10
3	iBUTANE	Std	1	65.7	1520820	Var	0.3%	Area	2	Cal	10
4	n-BUTANE	Std	1	73.6	1545350	Var	0.3%	Area	2	Cal	10
5	NEOPENTANE	Std	1	86.3	1651260	Var	0.1%	Area	3	Cal	10
6	iPENTANE	Std	1	109.4	1715050	Var	0.0993%	Area	4	Cal	10
7	n-PENTANE	Std	1	121.6	1793230	Var	0.0999%	Area	4	Cal	10
8	NITROGEN	Std	1	149.5	782820	Var	2.5%	Area	2	Cal	10
9	METHANE	Std	1	153.1	637330	Var	89.5719%	Area	3	Cal	10
10	CARBON DIOXIDE	Std	1	179.2	953088	Var	1%	Area	4	Cal	10
11	ETHANE	Std	1	200.6	1060440	Var	5%	Area	5	Cal	10

Figure 1 -- Various pertinent values for components are shown in this screen, including Response Factors – which should show an orderly progressive increase in value from the lightest component (methane) to the heaviest.

Ranking of response factors is based upon thermal conductivity difference between pure helium and the thermal conductivity of given molecules that yield response factors progressing as molecular weight varies from the mole weight of helium. The heavier a component's mole weight, the larger its Response Factor.

Deviation of response factors can be caused by various factors, including:

- Carrier or cal-gas improperly purged
- Unstable baseline
- Column valve actuation timing
- Leaking carrier or cal-gas
- Retention time not properly set.

Figure 2. This checklist can help technicians validate GC data.

Characteristic	OK Y/N?	Needs Correction	Action taken -- Results	Operator/Date
Offsite Correlation Is there correlation of measurement discrepancies with known events?				
Sample System Appropriately sized tubing? Proper size, design, and location of sample probes? Sample system heated per API 14.1? Bypass rate sufficient for two volume exchange per analytical cycle ? Cal-gas pressure/flow correct ? Same for flow line gas and cal gas ? Carrier flow correct (no leaks)?				
Chromatogram Quality Stable baseline ? Peak separation clear ? Peaks properly integrated? Retention Times correct ? Chromatogram clear ?				
Repeatability and Calibration 3 consecutive runs within 0.25% using cal gas as sample? Calibration factors within 10%				

Keep key data such as calibration runs, analysis reports and alarm logs, and any other relevant data. Save to memory in case subsequent troubleshooting or trouble analysis is required.

If all of the above functions are correct, chromatograms should have clearly defined peaks identified by correct retention times, and stable baselines. And good measurement data from the GC should then be available.

The foregoing focused on GC operation. Valid data must also be available from the flowmeter at the station, and operation of an Electronic Flowmeter and other data-handling devices in use must also be checked. Pressure and temperature transducers should be calibrated, particularly the temperature unit. The most common problem encountered in field trouble shooting and measurement system evaluation is faulty temperature information. Use the best calibration equipment and follow recommended procedures very carefully.

Summary

Careful attention to insure that custody measurements of flow and energy content are as accurate as possible pays handsome dividends. Sales/billing information will be accurate. Repeated measurements will be avoided along with time and costs required to settle disputes over values. And everyone involved in the measurement process can take pride in the professional results associated with their work.