

Title: Laboratory Auditing by Jerry Bernos

LABORATORY AUDITING

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INTRODUCTION

In the early nineteen eighties with the advent of much tighter economic conditions in the oil and gas industry, many companies that relied on outside labs (either other company or independent third party) for BTU analyses began to check the quality of the analyses that they had been relying on from these outside labs. Most of the major companies began a program of conducting annual audits of the labs whose data affected their economic returns. Usually the results of these audits were used as the basis for decisions such as whether a third party lab would be allowed to continue analyzing the samples in question or whether one company would demand a major monetary settlement from another. If a settlement agreement could not be reached a lawsuit usually ensued. As auditing became more common place, an in an effort to head off unexpected problems and complications, many companies began to institute programs of internal auditing.

With so much at stake it is critical that companies and their involved personnel understand several key areas pertaining to laboratory auditing. What, if any, legally binding regulations pertain to laboratory operations? Secondly, the areas of laboratory operations most susceptible to error need to be identified and concentrated upon during an audit. Finally, it should be understood that the auditor himself has certain responsibilities and obligations that must be met if in fact the audit is to produce fair and unbiased results. Hopefully, if this understanding can be reached, laboratory auditing will be looked upon as a useful tool in assuring quality analytical results instead of as a trap to extract monetary gain from and/or to inflict unnecessary pain on the unsuspecting company.

REGULATORY CONCERNS

As concerns laboratory operations, there are no governmental rules or regulations that dictate that any one particular procedure or method of analysis is binding upon those companies performing laboratory analyses. One of the most common misconceptions concerning auditing is that laboratories must follow one of the procedures recommended by such industry accepted organizations as GPA, API, AGA, or ASTM. The Gas Processors Association publishes GPA-2261, "Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography", GPA-2177, "Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography", and GPA-2165, "Analysis of Natural Gas Liquid Mixtures by Gas Chromatography". These methods are generally considered the industry standards. API and AGA generally refer to the GPA publications. ASTM publishes several related methods, which are very similar in context to the GPA methods. These organizations are not regulatory bodies and can not and do not exercise legal control over laboratory operations. The procedures that are published and that are recommended by these organizations, however, have been well tested and shown to be effective in producing quality analytical results. Because of this, most companies when writing a contract for the purchase and sale of hydrocarbon products specify in the contract that one of the above

industry procedures be employed when performing analyses. Once placed into the contract, that procedure now does become legally binding upon the laboratories performing analyses for the parties executing the contract. Although possibly not legally binding, it is generally considered prudent to follow one of the above mentioned procedures. These procedures, when properly followed, have been shown to produce good analytical results and are generally looked for by auditors. Alternative methods can give equally good results but may be excluded by contract stipulations.

AREAS OF PRIMARY CONCERN

The major concern of any audit should be whether or not the laboratory being audited can produce accurate results on certified test samples. If the lab being audited can produce results that are accurate to within reasonable tolerances and are repeatable from analysis to analysis, then it is extremely difficult to justify faulting that lab. The results produced should be the bottom line.

Several areas that can cause problems do exist, however, and should be evaluated in any audit. A summary list of these areas follows.

1. Gas Chromatograph Application
2. Calibration Standard
3. Sample Handling
4. Sample Introduction
5. Peak Separation & Integration
6. Detector Linearity
7. Repeatability/Reproducibility
8. Calculations
9. Quality Control Procedures
10. Certified Test Samples

Each of these areas warrants some discussion as to where the major sources of error exist within that particular area.

Gas Chromatograph Application:

As stated earlier, unless the chromatographic method is specified by contract the laboratory is free to use any method, which is capable of producing accurate results. Four different applications are commonly encountered today.

1. "Early Backflush" where the heavy ends are backflushed off the column first as a single sharp peak followed by the other components eluting in the order N2, C1, CO2, C2, C3, IC4, NC4, IC5, and NC5.
2. "Multicolumn" where the heavy ends are eluted first followed by C3, IC4, NC4, IC5, NC5, CO2, C2, N2, and C1.
3. "Two Column Capillary" where the elution order is N2, C1, CO2, C2 eluting from the first column followed by C3, IC4, NC4, IC5, NC5 and the heavy end components eluting individually in order of molecular weight. This method is found almost exclusively with the newer portable chromatographs and with the on-stream analyzers that employ the portable chromatograph.
4. "Late Backflush" where the heavy end components are eluted as a lumped group after the other components elute as in the "Early Backflush" method.

With the "Early Backflush" method, the timing of the chromatograph switching valve is critical. Too soon and some of the pentanes are eluted with the heavy end peak and too late and some of the heavy ends can be lost at the end of the

analysis. The "Multicolumn" method is even more susceptible to errors in valve timing as several valve switches are required. If any switch is improperly timed some or all of any component can be lost. The "Two Column Capillary" method is susceptible to loss of heavy ends on samples containing relatively large amounts of heavy ends. The analysis run time must be long enough to ensure that all of the heavy end components elute before the analysis is ended. With the "Late Backflush", the heavy ends elute as a broad, flat multi-lobed peak that is difficult to integrate properly. This can lead to significant errors in the heavy end values that are determined by this method.

Calibration Standard:

The results of any laboratory's analysis can only be as good as its calibration standard. Any calibration standard should be checked to assure its validity before use. GPA standard 2177 lists a procedure for checking the Fidelity of reference standards. This method applies to both liquid and gas standards. Figure 1 shows an example of the plot resulting from the fidelity check on a good calibration standard. Once shown to be good, the standard must be properly maintained so as not to alter its original composition with use. The major problem encountered with standard handling is to allow the standard to cool below its hydrocarbon dew point while in use. This will definitely alter the composition of the standard. GPA standard 2198 outlines the proper procedures for selection, handling, and storage of calibration standards. Any audit should check both the fidelity of the reference standard(s) used to calibrate the chromatograph(s) of the lab being audited and the procedures employed to insure the standard remain valid during extended use.

Sample Handling:

All gas samples to be analyzed must be heated to a minimum of 20 deg. F above the flowing temperature of the line from which the sample was taken for a minimum of two hours prior to analysis. Failure to follow this protocol can result in the loss of heavy ends from the sample. Audit samples must also be heated in the same manner. Liquid samples must be back pressured to a minimum of 200 psig above line pressure and then thoroughly mixed prior to analysis. Liquids that are allowed to drop significantly below line pressure will flash into a two-phase sample usually resulting in the loss of the lighter components upon analysis. All laboratories should have in place a system to insure that all samples are properly identified and that any sample once received by the lab or the results of the analyses performed on that sample are not lost.

Sample Introduction:

A major source of error in any analytical procedure lies in the transfer of the sample being analyzed from the sample container to the chromatograph. The procedure must insure that all of the previous sample be removed from the chromatograph sampling valve before injection of the current sample. The procedure must also insure that the sample being introduced is not altered in the transfer process. Gas sample transfer lines should be heated so as not to drop out heavy ends in the transfer. The current sample should be purged through the sampling valve for a sufficient amount of time (a minimum of three minutes) to insure removal of all traces of the previous sample. Purge rate should be fast enough to insure a good purge but not so fast as to cause refrigeration of the sample during the process. In lieu of purging a vacuum can be pulled on the introduction system to remove previous sample. A minimum vacuum of 1-mm Hg is required. A combination of vacuum and purge might also be used. Liquid samples must be kept as a single-phase liquid sample during transfer. This is usually

accomplished by placing a block (purge) valve downstream of the chromatograph liquid sampling valve. Clear, high pressure, Nylon 11 type tubing is an excellent choice for the transfer lines as it allows the physical state of the sample to be observed during transfer. Line diameters should not exceed 1/8 inch. Again, purge rate and time should be sufficient to remove any previous sample from the system, but purge rate should not be fast enough to "flash" the sample. Filters placed in the system to protect chromatograph-sampling valves should not cause a pressure drop that results in the sample "flashing". If at any time during the transfer process and before injection the sample is noticed "flashing", the sample should not be introduced. The problem causing the "flashing" should be immediately corrected before proceeding with the analysis.

Peak Separation and Integration:

Any good gas chromatographic system will be equipped with a peak integration system that produces a chromatogram (chart) of the sample analysis. Observation of this chart will quickly show if the separation between the components of the sample is sufficient to allow for accurate results. Absolute baseline separation is not essential but separation should be sufficient to show clear separation between relatively sharp component peaks. This same chart should in some way indicate how the integration system measures the area of each peak. Peaks that are not completely baseline separated can be handled in two ways; by dropping an imaginary perpendicular line from the junction of the peaks to the baseline or by tangent skimming the second peak from a first unsymmetrical "tailing" peak. It is important to note, given the peak shapes and separation, that the integration system has properly handled each peak.

Detector Linearity:

Simply stated, detector linearity is the ability of the chromatograph detector to respond in a linear (straight line) fashion to increasing concentrations of the components being analyzed. Most modern gas chromatographs do have linear detectors and this problem is being encountered much less frequently than in the past. Linearity is difficult to prove or disprove in a short audit. One must run varying concentrations of the individual components of the sample and then graph the responses to see if the plot is in fact linear. This is very time consuming. The two components, nitrogen and carbon dioxide, tend to have the most non-linear responses. Using two or three certified standards with significantly varying amounts of each component of the analysis instead of one single test sample will greatly aid in picking up linearity problems. Linearity need only be tested with gas samples. If linearity exists for gases it will also exist for liquid samples.

Repeatability/Reproducibility:

The results of any chromatograph on any test sample should be repeatable within acceptable tolerances and the results of the same sample run on two different chromatographs should also be reproducible within acceptable tolerances. By analyzing the same sample three times on two different chromatographs (if available) and calculating the standard deviation of the analyses these parameters can be determined. GPA standards 2261 and 2177 list acceptable repeatability and reproducibility parameters for gas and liquid samples. The study that these numbers were derived from was performed quite some time ago. Modern technology has improved equipment and methods to the point that tolerances in the area of 1/2 of these listed values can be reasonably expected. Certainly no variation that is greater than the GPA published numbers should be considered acceptable.

Calculations:

The only factor determined by the actual chromatographic analysis is the molecular (mol) percent of each component. All other values expressed on an analysis are mathematically calculated using these molecular percentages and industry accepted constants. The proper calculation methods and formulas are listed in GPA 2261 and GPA 2177. The constants required for these calculations are published in GPA 2145. The values listed in the most current version of GPA 2145 should be used. An audit should include a check of the formulas and constants used in all calculations.

Quality Control Procedures:

All laboratories should have some form of quality control established and in use. As a minimum, the quality of the lab's calibration standard should be monitored regularly and the instrument calibration(s) checked and if necessary redone on a regular and frequent basis.

In addition, the occasional analysis of a helium blank (which can indicate prior sample carry-over) and the comparison of the agreement between calculated and measured sample gravity are suggested whenever possible. Historical data should be maintained on all samples run on a repetitive basis. The results of the current sample analysis should be checked against this historical data and any significant and unexplainable change in composition from history should be considered suspect. The current sample should be reanalyzed for verification of results. Use a different chromatograph for the verification analysis whenever possible.

Certified Test Sample(s):

Just as mentioned earlier for the lab calibration standard, a fidelity plot should be performed on the certified test sample(s). It would be extremely unfair to fault a laboratory's results when in fact the test sample's composition was not as reported. Poor manufacturing techniques or sample mishandling during previous use could easily lead to the test sample's composition being incorrectly assumed. This will certainly lead to erroneous audit results. After presenting their final results to the auditor(s), the laboratory being audited should have the right to ask that a fidelity plot be made using the data generated by their analysis of the test sample. If the test sample(s) can not pass this check the results of the audit should be considered invalid and not used. The audit should be redone.

OBLIGATIONS OF THE AUDITOR

Anyone who is called on to perform an audit should approach that task in an unbiased and open minded manner. Far too often auditors expect to find (or are expected to find) something in error rather than approaching the task with the attitude that they will honestly evaluate and report on their findings. An auditor should not assume the position that if the laboratory being audited does something in a different manner from the auditor that the data produced will not be as valid or correct. A good auditor can and often will learn better techniques and procedures from the observations of his audits.

An auditor should keep in mind that the audit should be an evaluation of the everyday operations of the laboratory as it deals with its normal samples. With this in mind, the composition of the test sample(s) should reflect the normal

compositional range of the samples encountered by the laboratory on a day to day basis. Use of test samples that have unusual components or rarely encountered compositions should be avoided. The purpose of the audit should never be to "trick" the laboratory into making mistakes.

Once the audit results have been determined, the results should be reported to all concerned parties and should be reported in a fair and accurate manner. The laboratory being audited has a right to be made aware of the audit results and the actual facts and figures that back up those results. In reporting errors found by the audit, one should be accurate as to the degree of error found. If the laboratory is found to be out of specification by 1% then comments such as "they missed by a mile" or "they weren't even close" are unfair and unprofessional.

Auditors must remember that the results of an audit are to be considered confidential information and are not to be shared with any parties not directly involved.

Finally, the conduct of the audit should not place any undue burdens on the laboratory being audited. Audits should be scheduled at times that are convenient for the laboratory. Expecting the laboratory to stop its regular operations at the first or last of the month is unreasonable. Certainly the lab should be requested to analyze enough samples to fairly evaluate its performance, but to ask the lab to run an unnecessary number of samples or to repeat analyses an unnecessary number of times is not good auditing technique.

CONCLUSIONS

Laboratory auditing can be a positive experience for both the lab being audited and for the auditor. Laboratories that strive to produce accurate results using industry accepted methods need not be unduly concerned when audited. An auditor who is reasonable and professional in his audits will usually be welcomed and assisted by the lab being audited. Both parties can gain from this association. Laboratory auditing is one of the most useful tools that this industry has to identify companies and or individuals that are not committed to upholding the quality standards that this industry requires. The proper conducting of laboratory auditing can and should lead to far more accurate and useful data being produced in our industry.