



ENSURING AN ACCURATE RESULT IN AN ANALYTICAL INSTRUMENTATION SYSTEM – PART 2: CALIBRATING THE ANALYZER

By Dean Slejko and Tony Waters

In many analytical instrumentation systems, the analyzer does not provide an absolute measurement. Rather, it provides a relative response based on settings established during calibration, which is a critical process subject to significant error. To calibrate an analyzer, a calibration fluid of known contents and quantities is passed through the analyzer, producing measurements of component concentration. If these measurements are not consistent with the known quantities in the calibration fluid, the analyzer is adjusted accordingly.

Later, when process samples are analyzed, the accuracy of the analyzer's reading will depend on the accuracy of the calibration process. It is therefore imperative that we understand how error or contamination can be introduced through calibration; when calibration can – and cannot – address a perceived performance issue with the analyzer; how atmospheric pressure or temperature fluctuations can undo the work of calibration; and when and when not to calibrate.

System Design

One common problem in calibration is incorrect system configuration. In many cases, the calibration fluid is mistakenly introduced downstream of the stream selection valve system and without the benefits of a double block and bleed (DBB) configuration (Figure 1). A better place to introduce the calibration fluid would be through the sample stream selection system, as in Figure 2. The purpose of a sample stream selection system is to enable rapid replacement of sample streams without the risk of cross contamination. In figures 1 and 2, each stream in the sample stream selection system is outfitted with two block valves and a bleed valve (to vent) to ensure that one stream – and only one stream – is making its way to the analyzer at one time. Over the years, stream selection systems have evolved from double block and bleed configurations comprised of conventional components to modular, miniaturized systems (New Sampling/Sensor Initiative, ANSI/ISA 76.00.02). The most efficient systems provide fast purge times, low valve actuation pressures, and enhanced safety characteristics, together with high flow capacity and consistent pressure drop from stream to stream for a predictable delivery time to the analyzer.

A stream selection system provides the greatest insurance against the possibility of the calibration fluid leaking into a sample stream. Nevertheless, some technicians will bypass this assembly and locate the calibration fluid as close as possible to the analyzer with the intent of conserving this expensive fluid. If only a single ball valve is employed, as in Figure 1, the attempt to conserve calibration gas may result in biased analyzer readings. The analyzer may be properly calibrated, but there is always the risk that a small amount of calibration gas could leak into the sample stream and throw off the measurements.

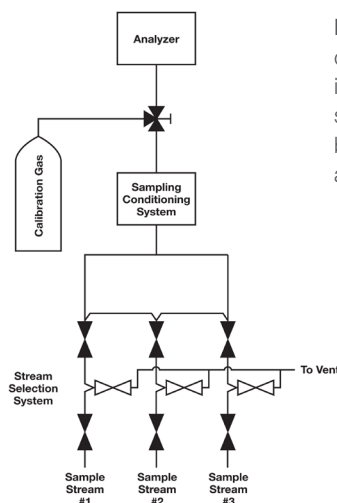


Figure 1. In this configuration, calibration gas is incorrectly introduced downstream of the stream selection system without the benefits of a double block and bleed assembly.

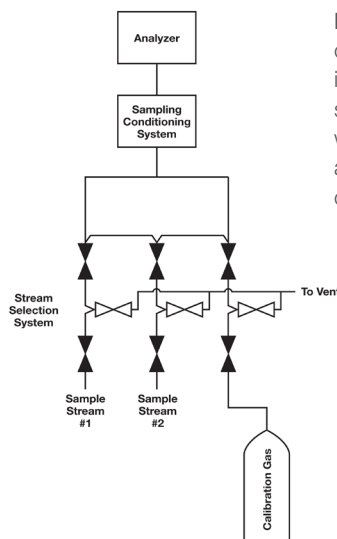


Figure 2. As shown in this configuration, the calibration gas is best introduced through the sample stream selection system, where a double block and bleed assembly guards against the risk of contamination.



In some applications, the U.S. EPA requires that the calibration fluid be introduced at an early point in the sampling system, usually near the probe. The reasoning is that the calibration fluid should be subjected to all the same variables as the sample stream. This makes good sense, and such a setup will provide, in addition, a fair estimate of the amount of time it takes for a sample to travel from the probe to the analyzer. As noted in the first article in this series, that period of time is often underestimated or unknown.

However, a relatively large quantity of calibration fluid is required if it is to run through the entire sampling system. It is not surprising, therefore, that many facilities cannot entertain this option. A good compromise is to run the calibration fluid through the stream selection system, dedicating one stream to the fluid. Here it stands the best chance of reaching the analyzer without being contaminated by the sampling streams, and, when not in use, two block valves will prevent it from contaminating the sample streams. With miniature modular platforms, the amount of calibration fluid required will be minimal.

Limitations of Calibration

To effectively calibrate an analyzer, the operator, technician, or engineer should understand, theoretically, what calibration is, what it can correct, and what it cannot. Let's start with the difference between precision and accuracy. A shooter's target is a good metaphor for explanatory purposes. In Figure 3, the shooter has produced a series of hits (in red) on the target. Since the hits are very close together in one cluster, it can rightly be said that the shooter is precise. Time and again, he is hitting the target in the same place. Precision yields repeatable outcomes. However, the shooter is not hitting the center of the target and, therefore, he is not accurate. If he or she makes an adjustment and lands all of his hits in the center of the target, then he will be both precise and accurate.

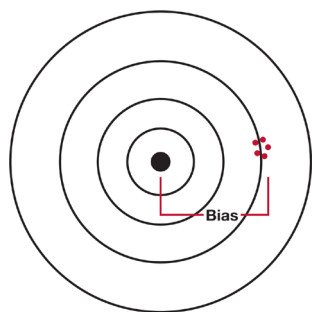


Figure 3. The shooter is precise but not accurate. If the bias is corrected, the shooter will be both precise and accurate.

The same terms can be applied to analyzers. An analyzer must first be precise. It must yield repeatable results when presented with a known quantity in the form of a calibration fluid. If it does not, then the analyzer is malfunctioning or the system is not maintaining the sample at constant conditions. Calibration cannot correct for imprecision.

If the analyzer produces consistent results but the results are not the same as the known composition of the calibration fluid, then the analyzer is said to be inaccurate. This situation can and should be addressed through calibration. This is called correcting the bias.

Even if the analyzer is found to be precise and accurate when tested with calibration fluids, it is still possible that it will yield inaccurate results when analyzing the sample stream. If the analyzer is asked to count red molecules and it encounters pink ones, what does it do? The pink molecules look red to the analyzer so it counts them as red, resulting in an inflated red count. This is called positive interference: A molecule that should not be counted is counted because, to the analyzer, it looks similar to the molecule that should be counted. For example, in a system designed to count propane molecules, propylene molecules may show up. It's possible that the analyzer will count them as propane because it was not configured to make a distinction between the two.

No analyzer is perfect, but they all strive for "selectivity," which means they respond to just the molecules you want them to and not to anything else. Some analyzers are more complex and are programmed to chemically inhibit certain types of interference. For example, a total organic compound (TOC) analyzer is designed to measure carbon content in wastewater so it can be determined if hydrocarbons are being disposed of inappropriately. To do so accurately, the analyzer removes a source of positive interference – inorganic carbons, like limestone, which are present in hard water. Then, it measures the organic carbons only. Without this initial step, the analyzer would measure both organic and inorganic carbon, confusing hydrocarbons with hard water.

Another type of interference is negative interference: A molecule that should be counted isn't counted because another molecule is hiding it. For example, in fluorinated drinking water, an electrode is used to analyze the amount of fluoride in the water. However, hydrogen ions, which are common in drinking water, hide the fluoride so the count is inaccurately low. The analyzer may read 1 ppm, which is a standard dose but, in fact, the water may contain 10 ppm. The solution is to remove the source of interference. By introducing a buffer solution, the hydrogen ions are removed and the electrode can accurately measure the fluoride.



With an understanding of positive and negative interference, as well as precision and accuracy, we begin to grasp the formidable challenges we face in enabling analyzers to yield desired results. In the field, you will often hear something like this: “The analyzer

is not working. It needs calibrating.” There is an easy assumption that if the analyzer is not producing the desired result, calibration is the answer. But as we have just seen, calibration has its limitations. It is not the answer to all problems.

Controlling for Atmospheric Changes in Gas Analyzers

Gas analyzers are essentially molecule counters. When they are calibrated, a known concentration of gas is introduced, and the analyzer’s output is checked to ensure that it is counting correctly. But what happens when the atmospheric pressure changes by 5 to 10 percent as it is known to do in some climates? The number of molecules in a given volume will vary with the change in atmospheric pressure and as a result the analyzer’s count will change. There is a common misperception that atmospheric pressure is a constant 14.7 psia (1 bar.a), but, based on the weather, it may fluctuate as much as 1 psi (0.07 bar) up or down. In order for the calibration process to be effective, absolute pressure in the sampling system during calibration and during analysis of samples must be the same. Absolute pressure may be defined as the total pressure above a perfect vacuum. In a sampling system, it would be the system pressure as measured by a gauge, plus atmospheric pressure.

To understand the degree of fluctuation in measurement that may be brought about by changes in absolute pressure, let’s refer to the perfect gas law:

$$PV = nRT$$

where **P** = pressure, psia; **V** = volume, cubic in.; **n** = number of moles (molecules); **R** = gas constant; and **T** = absolute temperature, °F.

Rearranging this equation to read:

$$n = PV/RT$$

shows that as temperature and pressure change, the number of molecules present in the standard volume also changes. Pressure changes are more critical than temperature fluctuations. One atmosphere of pressure is defined as 14.3 psi. Therefore, a 1 psi variation in pressure can change the number of molecules in the analyzer volume by about 7 percent. Temperature, on the other hand, is measured on the absolute scale, keeping in mind that absolute zero is -460°F (-273°C), so a 1°F (0.5° C) temperature variation changes the number of molecules by only about 0.3%. In sum, it is probable that one might get a large

change in pressure in percentage terms. It is not probable that one would get a large temperature change in percentage terms.

If pressure is so critical, how does one control for it? Some analyzers, especially infrared and ultraviolet, allow atmospheric pressure to affect the reading but then later correct for it electronically. However, many analyzers, including nearly all gas chromatographs, do not correct for atmospheric pressure fluctuations; most systems do not correct for it; and many system engineers or operators are satisfied to ignore it. Some believe that atmospheric fluctuations are not significant. Others maintain that any atmospheric fluctuations are compensated for by other related or unrelated variables affecting the analyzer, and it all comes out in the wash. Nevertheless, atmospheric fluctuations can be extremely significant. Let’s suppose that when you calibrate your analyzer, the atmospheric pressure is X, but, later, when you inject the process gas, the atmospheric pressure is X + 1 psi (0.07 bar). The answer may be as much as 7 percent off the measured value.

With environmental regulations, most analyzer systems now vent to flare stacks or other return points. Since pressure fluctuations from such destinations will affect pressure upstream in the analyzer, there are vent systems, equipped with educators and regulators, designed to control for these fluctuations. Unfortunately, these systems employ regulators that are referenced to atmosphere. As a result, while these systems control for fluctuations from the vent, they do not control for fluctuations in atmospheric pressure, which, by far, could be the greater of the two sets of fluctuations. For such a system to control for atmospheric as well as vent pressure fluctuations, an absolute pressure regulator is required. Unlike a normal regulator, an absolute pressure regulator is not comparing pressure inside the system to pressure outside the system, which is itself fluctuating according to the weather. Rather, it is comparing pressure inside the system to a constant set pressure that does not fluctuate at all (or very little). Often, this set pressure is actually 0 psia (0 bar.a).



Validation versus Calibration

The best method for calibration is one that employs an automated system of regular validation, with statistical process control. Validation is the process of checking the analyzer at regular time intervals to determine whether it is on or off the target. In validation, a reading is taken and that reading is recorded. It is the same process as calibration, except that no correction is made.

An automated system will run a validation check at regular intervals, usually once a day, and analyze the outcome for any problem that would require an adjustment or recalibration. The system will allow for inevitable ups and downs, but if it observes a consistent trend – one that is not correcting itself – then it alerts

the operator that the system could be going catastrophically wrong.

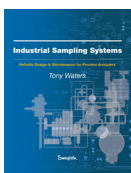
A human being can manually validate a system at regular intervals, just like an automated system, but, more often than not, the human being will also make an adjustment to the analyzer, even if the system is just 1 percent off. The result is a series of occasional and minor adjustments that introduce additional variance and make it difficult to analyze trends and determine when the system is truly running off course. It is better to allow an automated system to run unattended until a statistical analysis of the results suggests that attention is required.

Conclusion

Calibration is an important process and an absolute requirement in analytical systems, but care must be taken to perform this process properly. The operator, technician, or engineer should understand how best to introduce the calibration gas into the system (i.e., through a DBB configuration so the possibility of cross-stream contamination is minimized) and how to control for atmospheric fluctuations in gas analyzers (i.e., through an absolute pressure regulator). Further, the technician or operator

should understand the limitations of calibration – what problems it can address and what problems it cannot – and how frequent adjustments to the analyzer based on incomplete data can introduce error. If the analyzer is regularly validated with an automated system and is properly calibrated when a statistical analysis justifies it, then calibration will function as it should, and provide an important service in enabling the analyzer to provide accurate measurements.

Resource



For more information, see the Swagelok book *Industrial Sampling Systems* (2013), the definitive sampling systems reference guide by expert Tony Waters.

Author Biographies

Dean Slejko is product manager for analytical instrumentation for Swagelok Company, focusing on advancing the company's solutions and services in sample handling system applications. Prior to joining Swagelok, Dean held market and product management positions involving solutions for process control, power management, and utility metering applications. Dean earned a bachelor of science in environmental engineering and a master's degree in business administration from Case Western Reserve University and is a licensed professional engineer in the state of Ohio.

Tony Waters has 45 years' experience with process analyzers and their sampling systems. He has worked in engineering and marketing roles for an analyzer manufacturer, an end-user, and a systems integrator. He founded three companies to provide specialized analyzer services to the process industries and is an expert in the application of process analyzers in refineries and chemical plants. Waters is particularly well known for process analyzer training courses that he has presented in many of the countries of Asia, Europe, and the Middle East, as well as North and South America. His presentations are always popular and have equal appeal to engineers and maintenance technicians.