White Paper

Title: MAP Headspace Gas Testing – good measurement practices
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Overview of MAP Headspace Gas Measurement:

In order to measure the concentration of the constituents of headspace gas (O2, CO2, CO, etc), the integrity of the headspace gas must be maintained as a gas sample is withdrawn from the product package and transported into the analyzer for measurement. The difficulty of doing this is often a function of the package characteristics itself – and may lead to considerable measurement errors if a gas sample of insufficient volume or integrity is drawn from the package headspace.

This White Paper discusses this problem in depth, along with sampling and testing methods that may significantly improve the accuracy of gas measurement for difficult packages.

Sample Volume Considerations:

The gas volume used for gas measurement can vary significantly by the design of analyzer and the accuracy required. Typically 25 to 50 ml of headspace gas ensures adequate (better than 95% final reading) measurements in standard Bridge Headspace Gas Analyzers intended for use on collapsible plastic film bags or barrier film sealed trays of product. Very precise (better than 99% of final reading) measurements on soft packages can take up to 100 ml of gas to obtain, due to the flushing requirements for entrapped volumes in the gas analyzer itself to obtain very low O2 levels after exposure to ambient air. The sample time of the Bridge headspace gas analyzers is customer variable from the factory default value to higher or lower values to account for the package headspace volume, package rigidity, and the final accuracy required.

Test Accuracy as a function of Headspace Volume for Soft Packages:

The sampling pump in Bridge headspace gas analyzers transports the headspace gas from the product package into the gas analyzer for measurement. A 10 second sample time (the factory default for the O2/CO2 gas analyzers) will result in about 40 mL of headspace gas being withdrawn from the product package, and the internal volume of the soft package reduces commensurately. If it reduces enough that the package material begins to press on the product contained in the package, a vacuum will begin to be pulled on the package. As a vacuum is created, the sample pump will draw less and less gas per second out of the package – until it reaches a zero gas flow condition when the package is fully collapsed.

To ensure accurate measurements, a delivery of 25 ml of measureable gas is required. This means you must have at least 25 mL of headspace gas volume in a soft package for accurate gas measurement on each headspace gas test without resorting to special test methods. The 10 second sample time will draw all of the headspace gas out of the package, stall and hold it in, and make the measurement. There is no issue with stalling the pump for the last 4 seconds of the measurement – and accuracy is maximized by pulling virtually all of the headspace gas into this analyzer.

Gas Sampling Considerations for Rigid Containers:

The sampling pump in Bridge headspace gas analyzers immediately produces a vacuum in the headspace of rigid containers as it draws sample gas into the analyzer for measurement. Due to this, as the sample gas is extracted from hard containers, the vacuum the pump is working against gradually increases ands the gas sample rate reduces until it reaches zero. This means that the starting headspace gas volume in hard containers must be greater than it is in soft packages in order to assure gas measurement accuracy. As an example, to ensure delivery of 25 ml of headspace gas as above, a rigid container must contain about 100 ml of headspace gas at atmospheric pressure. Again, once about 25 mL of gas is extracted for measurement, the pump flow rate will be reduced to zero, and the gas sample will be contained and measured.

MAP Headspace CO2 vs O2 testing – Response Time Issues:

From the discussion above, it can be seen that headspace gas testing is easiest when the package has a high volume of gas protected by a flexible film. As the sample of gas is drawn from the container (bag, pouch, tray, etc) the barrier film collapses – and the pressure inside the package stays close to ambient pressure. This places the sample pump under the least stress, and assures a full sample of gas is transported into the analyzer for accurate headspace testing. While the CO2 measurement is very fast (only a few milliseconds), the O2 sensor takes seconds to respond – and is the limiting case, so that is what we will deal with here.

The analyzer response time is strictly a function of two factors – the time it takes to bring a new sample of gas into the analyzer (gas transport time) and the time it takes the analyzer to make the measurement (sensor response time). We have tested the analyzers for both aspects, which are shown on the attached graph – showing the typical response time for an oxygen measurement starting at an ambient O2 level of 20.60%.

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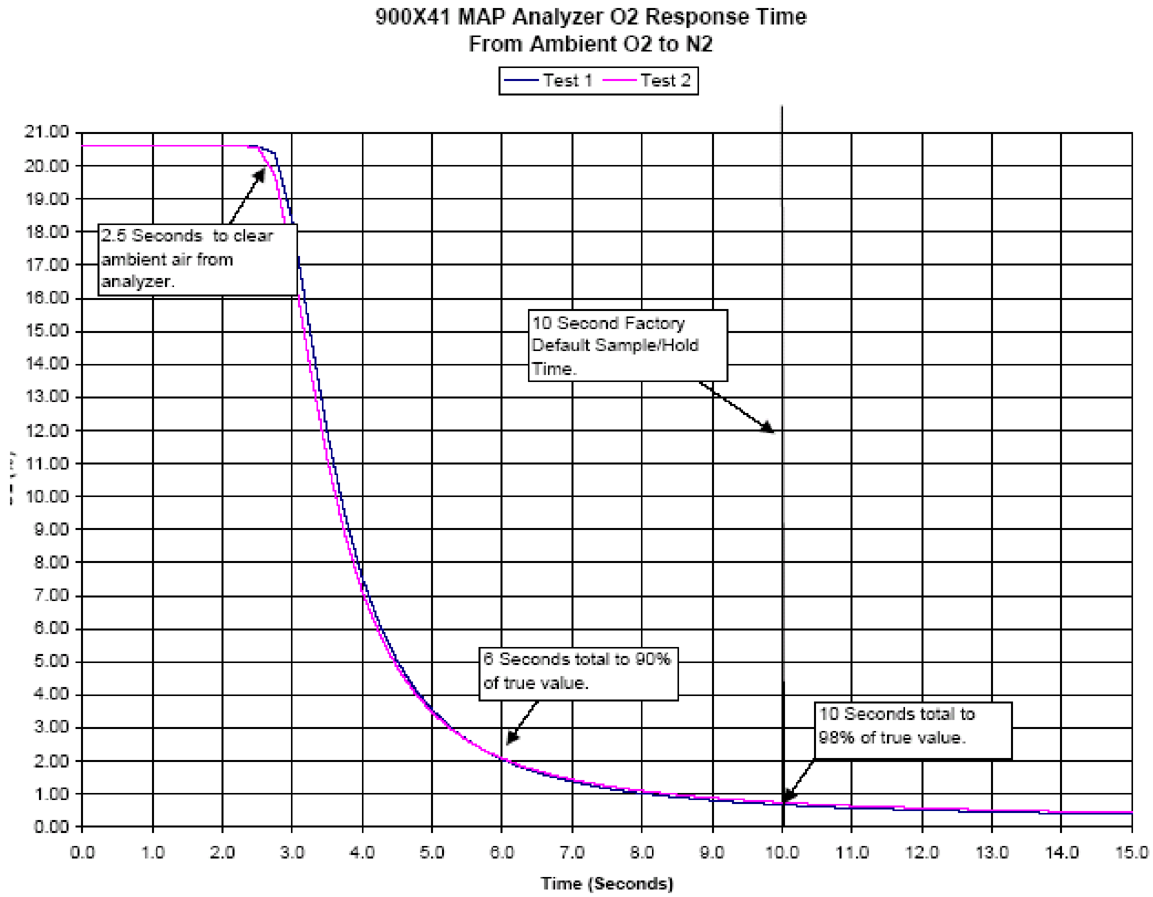

As you can see on the attached graph, it takes a few seconds to bring the gas in and a few seconds to make the measurement.

The overall time it takes to make gas measurement to 98% of the final value is about 10 Seconds – the factory default sample time. This characteristic means, however, that there will be a 0.400% residual O2 measurement on the first package filled with N2 gas measured after the analyzer O2 sensor has been exposed to room air. For measurements of low level residual O2 – which may typically be in the 0.500% to 0.050% range – the 'Test Twice after a Zero' technique outlined below can greatly improve the O2 measurement accuracy.

<u>Test Twice on the first package– the benefit of using the first package test to 'pre-condition' the analyzer:</u>

You should Zero Calibrate the analyzer on ambient air (Push the ZERO button) before a critical measurement is made to assure analyzer accuracy. Doing this exposes the

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analyzer internals to ambient air – which contains 20.60% O2 in it. While this makes sure the O2 sensor is calibrated correctly for future measurements, it also floods the analyzer gas lines and the sensor itself with high amounts of oxygen. When going from room air to the MAP headspace test, you may see high residuals on the first test, and then really good readings on the second and later package tested. This is because of the gas volume and time it takes to replace all of the gas in the analyzer with headspace gas, especially the gas hidden in small crevices, and to condition the sensor itself to small O2 gas levels. (The NDIR optics used for CO and CO2 measurement do not have this problem, as they respond in only a few milliseconds.)

As an example, say that you are using an analyzer that measures CO2 and O2 – and you are using it for the first package measurement after Zeroing the analyzer. The starting readings should be 0.05% CO2 (ambient air has 0.05% CO2 in it) and 20.6% O2. If the product headspace gas has 20% CO2 and 0.00% O2 in it, you will see the CO2 go from 0.05% up to almost 20.00%, and O2 go from 20.60% to 0.500% - about 98% of the final reading

A second test of the same headspace gas would yield 20.0% CO2 again, but about 0.100% O2 this time – due to residual O2 gas diffusion and the response time of the O2 sensor. The point is that the first test brings you close to the true O2 value, and consecutive tests keep you there and continue to improve the accuracy. Using this technique, the first test can be considered an 'O2 Preconditioning' test, greatly improving the accuracy of the second and later tests.

Further tests will simply improve the accuracy of close to zero readings.

The graph on the next page shows this:

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