Gas Chromatograph's Response Factors and Why They Are Important

Emerson hosted the webinar "Gas Chromatograph's Response Factors". These are the questions asked by the audience members along with the answers provided by our subject matter experts.

■ How much does a variation of the carrier pressure affect GC's Response Factor (RF)?

The variation in carrier pressure does not directly impact Response Factors. It can indirectly impact Response Factors. If the pressure is increased, flow will increase and the components will elute out faster. The Retention Time (RT) will shift in - all else being constant. The shifting of when components elute may cause components to be affected by valve setting (valve timing) and/or inhibits time events. The peak area of certain components thus can be impacted. If the peak area of a component is impacted, then the Response Factor of that component will be impacted as Response Factor = peak area/calibration concentration.

■ What can cause Retention Time (RT) to shift in a day and night cycle?

Retention Time (RT) is impacted by order of elution, pressure, and flow of the carrier gas and time events. It can also be impacted by restrictions/contamination as they impact flow and pressure. When one thinks of changes happening from day to night, one thinks of things affected by temperature variation. An increase in temperature would increase the flow, thus RT would move in slightly. A decrease in temperature would cause a decrease in flow, thus the RT would move out slightly. These changes in RT should be very small. If there is enough change in temperature to create noticeable changes in flow and RT, one would be concerned about hydrocarbon dropout. As the temperature drops, it is possible to drop below the hydrocarbon dew point (HCDP) of the sample if the sample line is not heated. The heavier hydrocarbons would drop out first. As the hydrocarbons drop out, the composition of the sample being analyzed would change. This should be noticeable in the analysis report.

■ What effect does Response Factor (RF) deviation have on Response Time (RT)? For example, one of the webinar slides showed a RF deviation of 0.26 and a RT deviation of 0?

As shown on the webinar slide, there may not be any affect. Response Factor (RF) and its deviation is impacted by concentration variation of the component. The calibration gas/known standard certificate lists a tolerance. It is possible for the GC to be operating properly but have a slight variation of the concentration. Retention Time (RT) is impacted by order of elution, pressure and flow of the carrier gas, and time events. It can also be impacted by restrictions/contamination as they impact flow and pressure.

■ Sometimes when there are rains or storms, the Response Factors can change due to changes in atmospheric pressure. Is there any recommendation to avoid this effect?

No. The sample loop is vented to atmospheric pressure to ensure a consistent sample size. If the GC did not vent to atmosphere, then the sample pressure would determine the amount of sample in the sample loop. Sample pressure is more likely to vary within a given time period than the atmosphere's pressure. There would also be variation in pressure between the sample pressure and the calibration gas pressure if the sample loop was not vented to atmosphere.

■ Will a bad or almost empty calibration bottle negatively impact Response Factors and Response Factor Order?

Yes. If what is in the calibration cylinder does not match what is on the certification, then the Response Factors will be inaccurate and likely in the wrong order.

■ In case of liquid calibration, would the vaporizer condition affect Response Factor or not?

If the vaporizer is working correctly, then it should not affect the Response Factors of the components. Potential errors would be if the liquid fractionated before it hit the vaporizer or if the amount of the liquid entering the vaporizer was too large and not all of it is vaporized.

■ Can you miss a Response Factor shift slowly over time if calibrating daily, causing miss measurement, let's say 1% a day?

Yes. The GC makes slight adjustments to the Retention Times and Response Factors during calibration. As long as the shifts are less than the limits, the Response Factors and Retention Times will be updated. This is why Emerson recommends doing a validation every 30, 60, 90 days. Please check our webinar recording on Validation that goes over this in detail. You are looking at the Response Factors and Retention Times of each component for shifts by comparing the current calibration report with the validation from 30 days ago, 60 days ago, and 90 days ago, or by comparing the last 3 calibration reports.

■ How are the Ideal Response Factors calculated for a calibration gas?

There is Response Factors (RF), Relative Response Factors (RRF) and Ideal Relative Response Factors. Relative Response Factors are calculated by taking the Response Factor of component A and dividing it by the Response Factor of component B. One may divide the other components in the stream by component B as well as use another component. The components of the Response Factors must follow the same path, use the same sample loop and the same detector. The Response Factors must be calculated from a known standard or calibration gas. Relative Response Factors should not change. A change in a Relative Response Factor means there is an error in the system. An Ideal Relative Response Factor is based on many years of experience with specific applications such as C6+ and C9+.

■ How is Relative Response Factor (RRF) and Ideal Relative Response Factor calculated?

The RRF (relative response factor) is calculated by taking the Response Factor of Component A divided by the Response Factor B. Component A and Component B must flow through the same sample loop, flow path and detector. Relative Response Factors should not change. The Ideal Response Factor is developed over years.

■ Where do you find the Relative Response Factor (RRF) and the Ideal Response Factor?

The Ideal Relative Response Factor check is only available on the Rosemount 370XA model. The ideal ratio is based on many years of testing of C6+ gas chromatographs. A user would not be able to see the Ideal Ratio nor the allowable variation.

■ Do we have the option of graphing the Response Factor like it was indicated on the webinar slide using MON software?

For the 370XA and 700XA models, there is the option for natural gas applications. It is found by logging onto MON2020, and clicking on Logs/Reports on the Menu bar. It is called Molecular Wt. vs. Response Factor. The factory will plot the Response Factors using this feature before we ship a 370XA and 700XA gas chromatographs.

■ What is the linearity of the calibration curve?

Specification 2198-16 goes into great details on linearity check and fidelity plots. The fidelity plot is based on the Response Factors from the calibration gas using peak area measurement. The Response Factors are plotted against the molecular weight of the components. For hydrocarbons, if all is in order, the resultant plot will form a straight line. The slope of the plot should remain constant. For Rosemount XA Series gas chromatographs, the fidelity plot is available in MON2020 software for standard natural gas applications. It can be found under Logs/Reports, Molecular Wt vs. Response Factor.

■ If your Response Factor is high for N_2, where would you start investigating the leak at? Is there a common place where a leak might come from?

Air most often happens to get into the GC system when the calibration cylinder is changed. Emerson recommends purging the line several times to remove the air before calibrating the GC. If the calibration cylinder was not changed nor repair made to the valves or regulators, the external fittings on the sample handling plate and at the regulators are next places to check.

■ I have a C6+ application where Neo Pentane Response Factor is always a little higher than I pentane. This happens on all our calibration cylinders. Any thoughts as to why?

Neo-C5 and i-C5 have very close boiling points. What you are seeing is dependent on amounts of n-C4, neo-C5, and i-C5 in the calibration gas. It is caused by separation from n-C4 to neo-C5 which is somewhat less than complete.

■ Why couldn't you use Helium as the carrier gas for this specific application? Assuming this is for the analysis of Ar, N_2 and H_2 and H_2 is shown as the calibration gas for Ar and N_2.

Helium could be used. By default, Emerson selected H_2 as the carrier for such as applications because it tends to be less expensive and more readily available than Helium.

■ Should the sample pressure and the calibration pressure be the same?

Not necessarily. More critical is the pressures for the calibration and the unknown sample are in the range of 15–30 psig. The fix sample loop is equalized to atmospheric pressure in the first 5–10 seconds of the analysis cycle. If pressure is too little, there may not be enough pressure to clear the sample loop. If the pressure is too high, then venting the sample loop to atmosphere pressure may not be fully completed and the pressure of the sample loop is not set to atmospheric pressure.

■ What is the maximum sample gas pressure?

For most of the Emerson gas chromatographs, the sample pressure is between 15–30 psig. Consult the product's manual for specific requirements.

■ On the Final Calibration Report, you have a ratio split after the C6+. What does that stand for?

The ratio split stands for the amount of C6s, C7s and C8s you believe are in your unknown sample. There are 4 standards within the Rosemount XA GC series. You can also custom configure the splits to match your requirements.

■ If I have several different heavier hydrocarbons, am I correct that the C6+ category will not necessarily be enough info for me to accurately estimate the Hydrocarbon Dew Point (HCDP)?

Emerson will only supply a hydrocarbon dew point when C6s, C7s, C8s and C9+ are measured. When assigning ratios for C6+ components and assuming nothing heavier than C8s, the error rate on the hydrocarbon dew point calculation can be as high as 40%.

■ Do you plan to go over Force Calibrations and when it is necessary to perform them?

The presentation on Response Factors does not cover Force Calibration. Our upcoming webinar on June 12th will review calibration of a GC. There is also a webinar recording on the Validation of your GC that discusses Force Calibration. In general, you should never do Force Calibration unless you know why you are doing it.

■ How to know when is the time to calibrate an installed GC? Will the GC tell me when to calibrate?

For most applications, one can set an auto-calibration. The GC and the GC manufacturer don't dictate the time frame for a GC calibration. One's calibration requirements are set by one's customer, tariffs and specifications one needs to comply to regulatory requirements, company's operating procedures, etc. Once one has determined the calibration frequency, the GC can be set to calibrate itself at that frequency.

■ What are the benefits of auto-calibration?

The biggest value of auto-calibration is that the GC does it on its own without intervention from the technician. One can set the frequency, number of runs, number of runs to average, and the alarms one wants to receive if calibration fails per defined limits.

■ Can a Gas Chromatograph tell me the water content? (usually very small for pipeline/natural gas quality)

Water content can be measured with the Rosemount 700XA, 1500XA and Model 500 GCs. Rosemount reports the water value using the Relative Response Factor for Methanol. Most of our water measurements are at 50–1500 ppm with a TCD.

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