

## Refinery Sector Rule: Top 10 Calibration Gas Lessons Learned

For businesses trying to adhere to the [Refinery Sector Rule](#) (RSR) that went into effect earlier last year, compliance is no easy feat. Among the overwhelming number of new challenges refineries are now facing, one particular objective has proven to be exceptionally difficult to achieve: 98+% destruction of Hazardous Air Pollutants (HAPs).

To measure HAP destruction, refineries monitor the gases emitted through their flare tips and measure the [Net Heating Value](#) (NHV). To indicate at least 98% destruction, those emissions must meet a minimum 270 British Thermal Unit (BTU) NHV. Most U.S. refineries have taken the necessary steps to install instrumentation and implement calibration/validation regimens to meet these requirements. Others are still working toward compliance with deadline date extensions.

The process of gaining needed capabilities has generated some experiential education related to calibration/validation (Cal) gases. At the top is the reminder that all is subject to change via EPA or other regulatory authority requirements or approval of Alternative Monitoring Plans (AMPs). Variables can be general, regional, localized, site specific or company-by-company among others.

An active vendor observation of the most common RSR lessons learned includes:

### 1) RSR compliance gas blends are component-based

Some of the early consent decree requirements utilized BTU NHV targets as their basis for formulating calibration standard blends. If the BTU target concept is taken to an extreme, a blend designed to meet a 448 BTU NHV target could be as simple as 50% methane and 50% nitrogen. The Rule outlines the inclusion of specific components in the development of calibration gas compositions.

### 2) Use Option(i) standards to help identify the source of flare gases?

There's no substitute for the advice of environmental regulatory consultants, engineers & legal personnel to assure Rule interpretations & tactics employed are consistent with approved Flare Management Plans (FMPs).

The Option (i) guidelines provide a list of eleven required and four optional components. If, based on pre-survey or experiential knowledge, it's expected that one of these components can be present in the flare gas stream, then it should be included in Option (i) calibration gas blend formulation.

### **3) You can also use Option (ii) standards**

Often overlooked is the section of the Rule just below Option (i) which outlines Option (ii) blend requirements. Option (ii) standards utilize hydrogen plus C1 through C5 normal components. And the default component NHV calculations are at the "n" (normal) value level.

Some refineries have found that reducing the number of components that must be validated daily can speed up the analyzer test cycle. This might also reduce the potential for a "miss" by reducing the number of targets that must be hit accurately on a daily or quarterly basis.

### **4) When setting up blends, ratios matter (LMH; MDL)**

Daily calibration/validation MID (M) gas standard concentrations are a primary target. The actual gas received should have all components coming in at 90-110% of their targeted concentration. Quarterly concentrations use LOW (L) and HIGH (H) standards which are to be at 40-60% and 140-160% of MID respectively (i.e. LMH = Low, Mid, High).

All component concentrations must be at levels above the minimum detection limit (MDL) for the analyzer. If an expected concentration is below the analyzer MDL, RSR states that "a calibration gas with a concentration at four to five times the limit of detection for the instrument may be substituted." Additional approval steps might be needed if the analyzer manufacturer is not

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comfortable that the device is repeatable for measurement at four times MDL.

## **5) RSR standards don't equal GPA standards**

Prior to the development of RSR flare standards, a large portion of hydrocarbon based calibration standards were utilized for quality control and custody transfer validation of natural gas in pipelines. Pipeline related calibration gases were largely defined by Gas Producer Association (GPA) guidelines which provide standard reference conditions and prescribed Net Heating Value calculations. RSR conditions and NHV calculations differ in some areas from GPA guidelines. It is important that gases used for RSR compliance and their corresponding COAs reflect standard reference conditions, NHVs and other requirements detailed in the Rule.

## **6) Calibrate, then verify**

A client recently noted that they were seeing some “out of spec” measurements on C-4 or C-5 components and thought it might be advisable to increase the component concentrations to improve repeatability. The analyzer manufacturer was contacted and provided a high integrity response noting that the minimum Cal gas was already at 15 times the analyzer's MDL. They noted that the first step was to be sure the analyzer was actually properly calibrated.

Interestingly enough, after calibrating the analyzer to known component concentrations, all issues with repeatability were resolved.

## **7) HRVOC requirements can impact choices**

Some sites have HVROC, which are Title V HAPs limits or other requirements that must be met in addition to their RSR requirements. Several sites have determined that using Option (i) standards provides them the ability to meet both their RSR requirements and also their additional compliance requirements. For these sites, use of Option (i) standards can have the effect of achieving a two-for-one which reduces the need for separate validation runs and associated calibration gases.

## **8) Minor component additions are conditionally allowed with Option (ii) standards**

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In addition to HRVOC rule requirements, some sites are also under other permit limits for Benzene or other constituents. The EPA has noted that addition of a minor component to Option (ii) can be allowed if it provides the site the ability to more easily meet compliance requirements. The note is added that the added minor component to Option (ii) standards can only be used in Net Heating Value calculations if the EPA provides prior approval to do so.

### **9) ALT 124 Oks Mass Spec**

The originally issued version of the rule outlines guidelines for use of Gas Chromatographs (GC's) or Calorimeters. ALT 124 adds Mass Spec analyzers as a widely acceptable alternative method for measurement compliance and outlines requirements for system performance validation.

### **10) ALT 131 Oks BTU Based Validation\***

There are a number of provisos related to validation by BTU NHV in ALT 131, including “1) Certified gas standards must be prepared consistent with the requirements in §63.671(e)(2)” and “2) You must use certified calibration gases that meet the requirement in Section 7.1 of PS 9 for daily calibration check” among others. There is also a note that “You must include a copy of this approval letter in the report of each testing program or periodic reporting period where these alternative testing procedures are applied.” ALT 131 warrants some additional reading and clarifications to assure it is employed properly.

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As with most new regulatory requirements, the RSR is chock full of specifics that need to be managed. This necessitates employing the support of environmental compliance professionals, engineers, and/or regulatory agency personnel.

It will (at the least) be most interesting to see how the pending EPA updates to the Ethylene MACT and/or possible Chemical Sector Rule (CSR) will address the different flare components in petrochemical production operations.

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