Increased Hydrocarbon Processing Efficiency by Improving Analytical Performance

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This paper addresses some key analytical issues which affect the accuracy and precision of analytical measurements required by hydrocarbon processors. These issues include the use of appropriate calibration standards for customer specific applications as well as correct material selection for gas sampling and analysis systems.

Hydrocarbon processing plants, from refineries to petrochemical plants, are all vulnerable to inefficiencies which impact performance. Technologies are constantly being developed and deployed to provide a higher yield which can decrease both capital expenditures and operating costs. Selection and optimisation of the process will not only depend on the product specifications and product composition, but also on specific process conditions. The process gases used must be analysed owing to the variation in raw materials and process stream parameters. Due to the high capital costs of these plants, up time must be maximised along with high product quality while maintaining plant and environmental safety. To address these challenges, analytical instruments are used to monitor product quality, to detect catalyst poisons in the raw materials, as well as for emission compliance. The analytical results can be vital to the plant operational efficiencies and safety.

Flawed analytical results may be damaging to the product quality, expensive catalysts used in the processes, as well as environmental controls; all with potential significant cost impact. Therefore, it is important to have a reliable and consistent analytical system in place. Key issues to help ensure the reliability include the sampling system, analytical instrumentation and calibration.

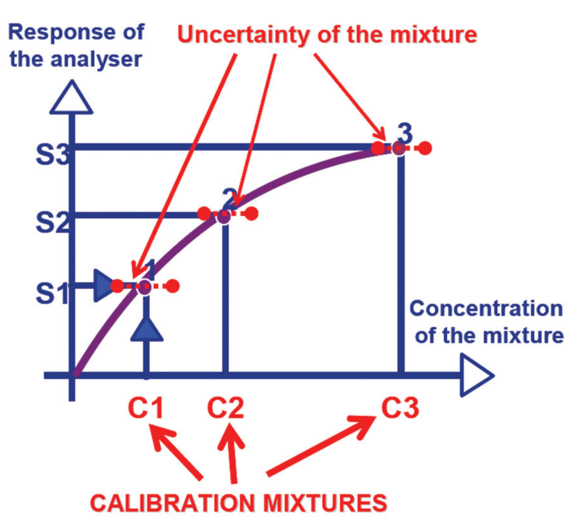

Figure 1: Uncertainty in analyser calibration

Calibration Standards

Accurate analytical measurements are necessary for both qualitative and quantitative information. If the analytical instrument is not calibrated properly, then the reliability of the measurement can not be guaranteed. The calibration standard establishes a known value to the measured response. Care must also be taken to use the appropriate type of calibration standard required for the application. This includes carefully considering the requirement for traceability and analytical precision as well as need of accreditation/certification. The traceability to National Standard Organisations is defined in ISO 17025. Certified mixtures are used to prove the trueness and traceability of the measurement.

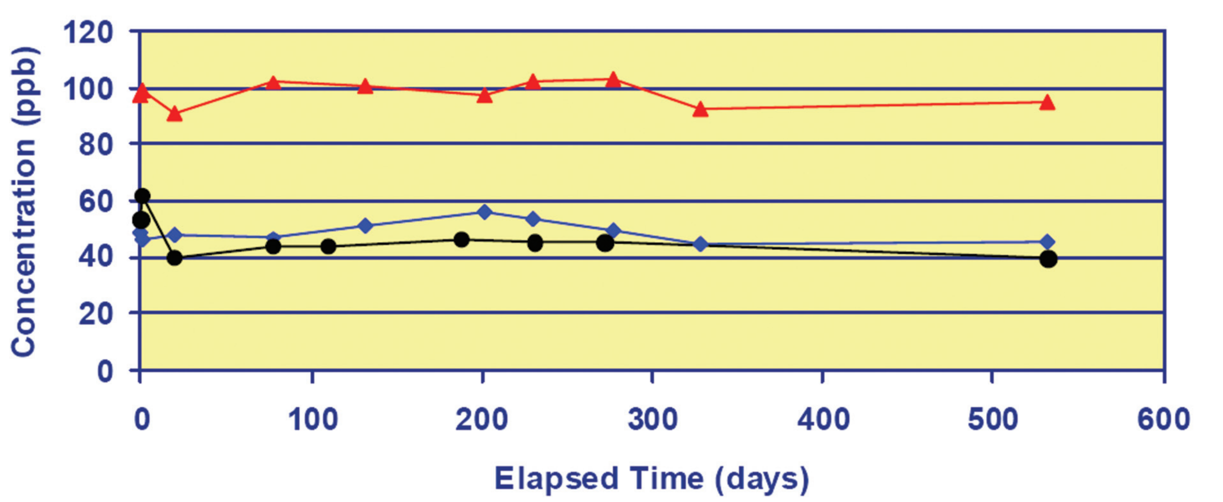

Figure 2: Stability evaluation of 3 low level H_2S mixtures in balance nitrogen: nominal 55 ppb (black and blue lines) and 100 ppb (red line)

They are most often used for regulatory compliance and to check critical parameters of the production process. As the costs associated with certification and documentation are inherently high for these types of mixtures, it is very important to understand the actual needs and requirements to avoid spending unnecessary time and resources.

The calibration of the analyser is the control and validation of the equipment's accuracy. The uncertainty of the resultant concentration depends on the trueness of the response curve. The tighter the uncertainty of the calibration mixture used for analyser calibration, the truer the response curve (Figure 1). The uncertainty is the maximum difference between the measured concentration and the true concentration. This is typically given at the 95% confidence interval, which is in compliance with ISO 6141.

In addition to the accuracy of the calibration standard, it is important to know the shelf life of the particular mixture (Figure 2). Stability of the mixture can not be guaranteed in excess of the specified shelf life. In some instances, regulatory agencies, such as the US EPA, set the shelf life of the mixture.

Shelf life studies are used to validate the appropriate cylinder material and surface treatments for storage of reactive mixtures[1]. Even minute flaws in the cylinder, cylinder valve or preparation technology can be detrimental to the stability of the low level reactive gases in spite of all preparation, manufacturing and analytical efforts undertaken. This is especially necessary for corrosive and reactive mixtures with concentrations less than 10ppm. The lower the concentration of the calibration mixture required, the higher the importance of cylinder preparation technology becomes. This is because the contact times associated with storage (which may be more than one year) will magnify any low level reactivity which may occur.

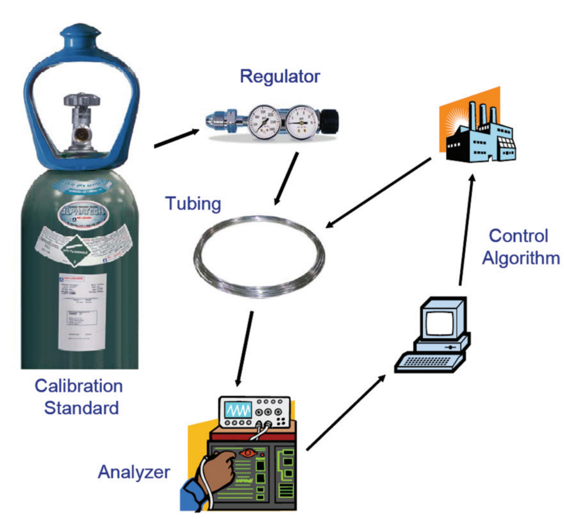

Figure 3: Monitoring system, including analyser calibration apparatus to ensure the accuracy of the analytical values used to control the process.

Sampling System:

A monitoring system typically includes a sampling method, sampling line to transfer the sample from the process to the analyser, an analyser and calibration system. The analyser typically provides real time feed back to the process. Each component can affect the entire monitoring system performance by interfering with the impurities present in the sample (Figure 3).

The sampling system must be designed to handle the gases contained within the process stream. The material is particularly important since it is in direct contact with the sample and could lead to reactions and adsorption on the tubing walls. Since the goal is to measure the impurities as accurately as possible, it is recommended to use a material that would minimise these reactions. The effect of material selection for transfer tubing is illustrated in Figure 4 for a hydrogen sulfide mixture. When using unpassivated tubing, it can take in excess of 250 minutes to reach a steady state signal[2]. Interestingly, it takes longer to achieve a steady state signal with stainless steel than with aluminum. This type of information must be understood in order to control the sampling systems impact on the reliability of analytical data.

The importance of material compatibility also extends to pressure regulation[3]. This is especially true for reactive or corrosive gases. A brass regulator which is common for use in industrial gases, such as nitrogen, would react with the H_2S mixture. Even stainless steel, which is used to handle corrosive and reactive gases, requires passivation prior to use. Figure 5 demonstrates the rapid decay of measurable H_2S response with the improper passivation of a stainless steel regulator.

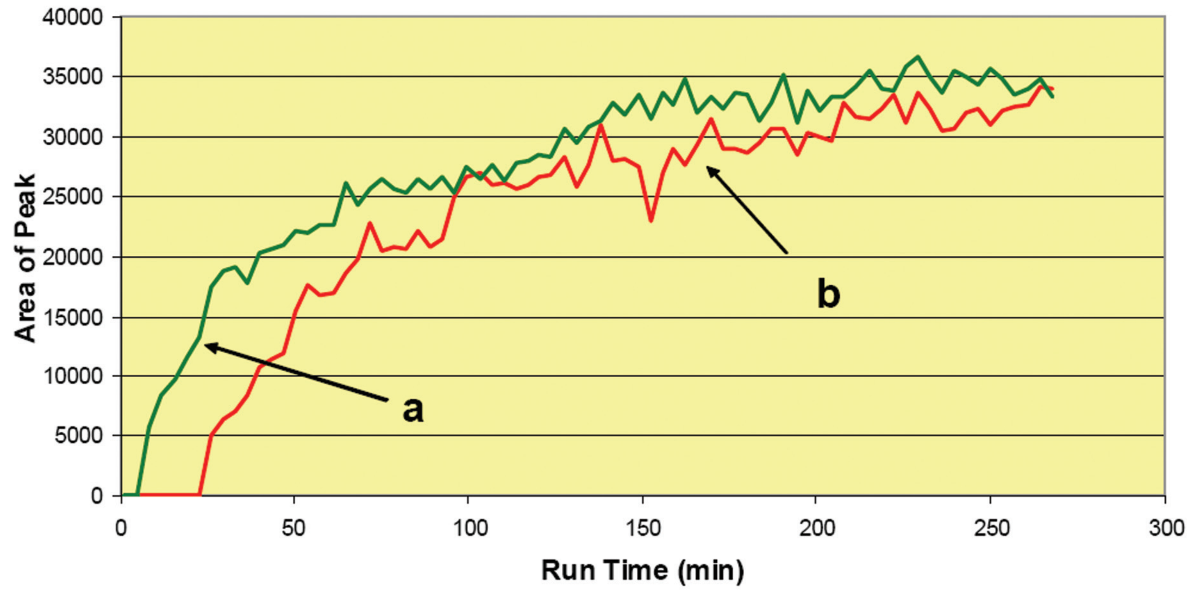

Figure 4: Effect of material selection on full scale response to 100 ppb H_2S in balance N_2 at a flow rate of 200 mL/min: (a) 10 foot segment of ¼" 3003 Aluminum Tubing (b) 10 foot segment of ¼" 316 SS Tubing

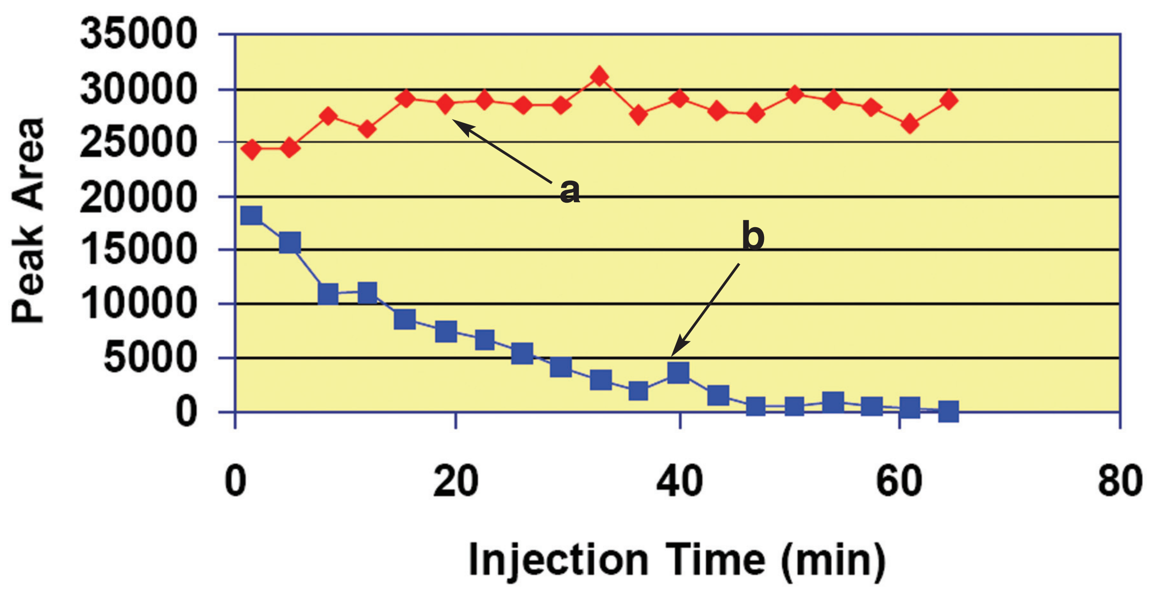

Figure 5: Impact of 100 ppb H_2S balance N_2 flowed at 100 mL/min through a standard 2 stage regulator (a) Passivated regulator (b) New regulator without previous service.

Conclusion

This article has demonstrated the importance of critical parameters, such as material compatibility, shelf life of calibration standards and the need for traceability in the overall analytical process. These considerations are some of the elements, which if adhered to, will help ensure reliable analytical process data.

References

1 Benesch, R., Haouchine, M., Jacksier, T. "The Stability of 100 ppb Hydrogen Sulfide Standards", Anal. Chem, 76(24)2004, 7396-7399

2 Haouchine, M., Benesch, R., Talbert, B., Jacksier, T., Biela, B,. Moore, R. "Monitor Sulfur Levels in your Olefin Feedstocks", Hydrocarbon Processing, (10)2007, 125 – 130

3 Talbert, B., Benesch, R., Haouchine, M., Jacksier, T. "A Study of Regulators for Delivering Gases Containing Low Concentrations of Hydrogen Sulfide", LCGC North America, 22(6) 2004, 562-568