



Determination of Water in LPG

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Corrosion: A cost factor

Every year, corrosion costs oil refineries around the world as much as 15 billion US dollars (according to NACE International), and it is associated with significant risks to safety. To prevent corrosion, pipes and equipment are made from corrosion-resistant materials, and substances that promote corrosion are kept to a minimum. One of the most corrosion-promoting substances is water, which is present in liquefied petroleum gas (LPG) and gas flows to varying degrees and comes into contact with pipes and reactors as a result. Water also impairs the function of some catalysts that are used in refineries. Determining water in LPG and gas flows is thus a crucial element of plant monitoring, particularly during turnaround periods; that is, when the refinery is shut down for maintenance and repair.

Water Content Determination at the BP Castellón Refinery

Online analyzers monitor the water content of LPG and gas flows at critical points in the BP Castellón plant that is located on the Spanish Mediterranean coast. To support the online analyses and to measure additional samples, further measurements are carried out in the plant's laboratory. In the past, a water-selective sensor was used for this purpose. However, the painstaking process of calibrating and stabilizing the sensor made water content determination an onerous task. In addition, the final results had to be calculated manually, and the method yielded insufficient measuring precision as a result of the sensor becoming saturated by humidity. Therefore, finding a more robust method for water determination was a must.

Karl Fischer for Gases?

The ambient conditions in the refinery's laboratory and the low detection limits that the application requires made the search for the right method challenging. Several new instruments, mostly online analyzers, were tested but it proved difficult to achieve stable, reproducible results under the given conditions. Eventually, the Karl Fischer Gas Analyzer from Metrohm was tested. The 875 KF Gas Analyzer met all requirements of the application and was therefore the right choice for the laboratory. For the Castellón refinery, it presented a new approach: while the staff was already familiar with Karl Fischer water determination in a range of sample types, the method had never been applied to gaseous samples or liquefied gases at the laboratory.

The KF Gas Analyzer

The KF Gas Analyzer is a rugged analysis system for routine water content determination in liquefied and permanent gases. The instrument is controlled using *tiamo*TM – the software widely known from other Metrohm titration applications. As the analyzer determines water content by a coulometric method, it achieves detection limits in the ppm range. The mass flow controller which enables highly precise gas measurement also contributes to the system's excellent measuring accuracy. One of the main advantages of the Gas Analyzer is its sample injection system which, in contrast to other analyzers, does not encounter water condensation issues. What's more, the sample flow and pressure requirements are within the optimal range for the analysis at the refinery.

Determination

When a new gas is analyzed, a correction factor has to be produced as a one-off determination before measuring. This can then be used for all subsequent water content determinations in the same gas. The factor ensures that the mass flow controller measures accurately, regardless of the varying pressures and temperatures of the gases. To carry out the water determination, the appropriate method has to be selected in the *tiamo*TM software – simplicity itself, as the method comes pre-installed. The analysis then runs fully automatically.

Example Determinations

The water content of a propane gas sample was analyzed with the KF Gas Analyzer. The six-fold determination showed that it contained 6.5 ppm (by mass) water with a relative standard deviation of 9.2%. For samples with higher water content, the standard deviation will be significantly lower. One of the main benefits of the Karl Fisher method is that it is not influenced by any residuals from the scavenging process, like methanol or ethylene glycol. The addition of methanol thus does not mask the water content of the product.

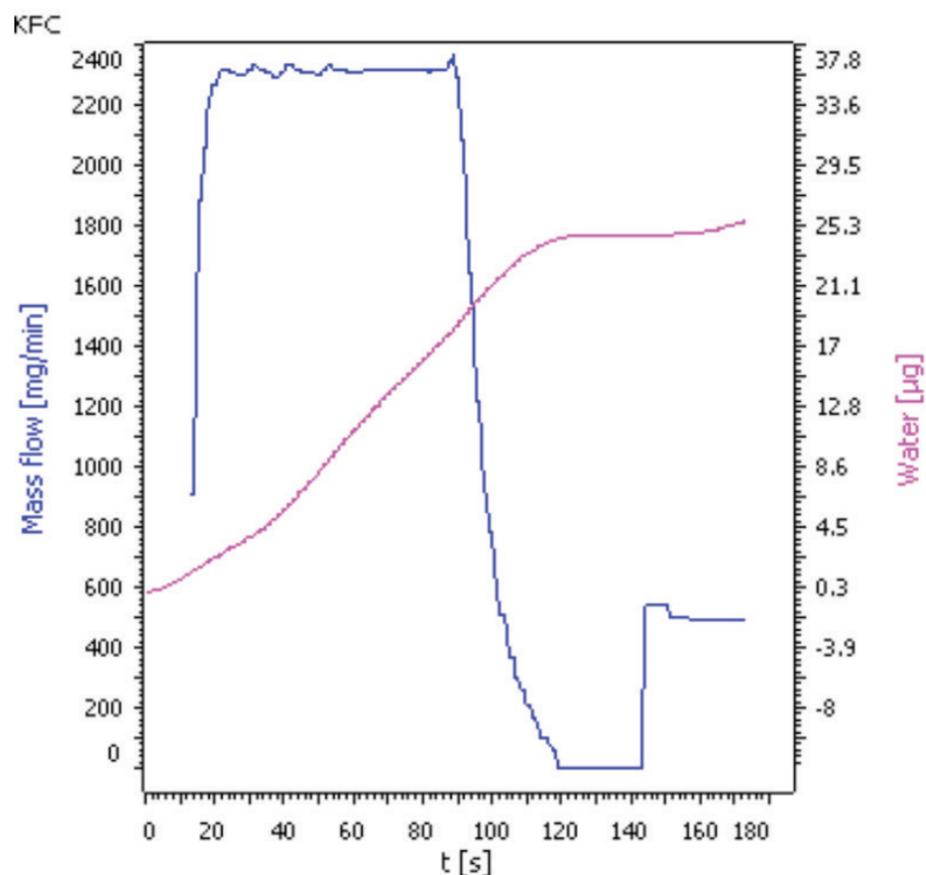


Figure 1: This typical curve of a Karl Fischer water determination in propane depicts the mass flow in blue and the amount of water that has been titrated in pink.

Conclusion

The KF Gas Analyzer determines the water content of gaseous samples and liquefied gases reproducibly with detection limits in the ppm range. Just as important, however, is the reassurance offered by Metrohm's excellent technical support and rapid troubleshooting – known at the BP Castellón plant from the many years of experience that it has had with Metrohm instruments and Gomensoro (Metrohm's distributor for Spain, with the exception of Catalonia and the Balearic Islands).

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