Application Note

KEIT spectrometers

Monitoring **alcohol and ether** content **in gasoline** on line and in real time: comparison with ASTM D5845

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Abstract

There is a need in the Petrochemical industry to accurately monitor alcohol and ether additives content in the production of gasoline. The current industry standard (ASTM D5845) relies on a remote sampling technique. Here we successfully demonstrate how the Keit IRmadillo™ FTIR spectrometer can provide real-time monitoring of alcohol and ether concentrations in gasolines as per ASTM D5845. Furthermore, it was simultaneously demonstrated that the IRmadillo can be calibrated to classify different types of gasoline present in a mixture, making it a powerful monitoring solution for the efficient production of gasoline.

IRmadillo™ FTIR Spectrometer

Introduction

Measuring the content of a single class of fuel oxygenate additive (such as an alcohol or an ether) can be performed using vapour pressure calculations, but to monitor mixtures a more advanced form of measurement is required.

ASTM D5845[1] is a standard method of testing type and concentration of alcohol and ether oxygenates in gasoline and to quantify the amount of desired oxygenate additive using FTIR spectroscopy; however, it is aimed at off-line measurements performed on sample extracts.

Here we show how the IRmadillo can be calibrated as a process analyser for on-line and real-time measurements of alcohols and ethers in gasoline. This allows for process control and optimisation and ensures a process engineer can validate that an entire product batch is within specification, rather than just an extracted sample.

The IRmadillo is a robust and rugged analyser that can combine an FTIR spectrometer with pre-calibration to analyse processes. It does not use fibre optic probes or have any moving parts, meaning it can withstand challenging and dangerous manufacturing environments. It is designed from the ground up for “fit and forget”.

Key Words

- ASTM D5845
- Alcohol
- Gasoline
- Fuel additives and oxygenates
- Petrochemicals
- On-line process monitoring

Features & Benefits

- Mid-infrared/FTIR spectral analysis
- Vibration tolerant
- Long-term stability
- Low maintenance
- Compact design
- Real-time, multi-component analysis
- Certified safe for use in hazardous and potentially explosive environments

Experimental

ASTM D5845 calibration samples were purchased from ASI Standards and no additional preparation was performed. The IRmadillo was purged before and throughout the measurement with a supply of dry N_2 and allowed to thermally stabilise prior to use. A background scan of 30 minutes was performed. Three subsequent spectra were obtained using 120 s scans, so that the calibration was performed on triplicate scans. The entire process was repeated on a second instrument to show reproducibility.

The spectra were analysed using Support Vector Machine Regression (SVR) models (built on Camo Analytic's Unscrambler 10.5) due to strongly non-linear behaviour of the chemicals. No transformation of spectra was required.

Results and Discussion

Concentrations of alcohols and ethers in gasoline

It was found to be important to use multivariate analysis (also called chemometrics) and a non-linear approach to build the calibration. In this case, a radial transform and SVR modelling were used (contact Keit for more information if required). This is because of interactions between the alcohols and ethers within the mixture, resulting in FTIR band shifts and non-linear behaviour in the spectra.

The IRmadillo performs comparably to the off-line approach as laid out in the ASTM method. The relative errors in measurement for each chemical of interest are shown below in Figure 1. The results are very similar in most cases – all within 1 wt%. For TAME and ETBE the IRmadillo actually exceeds the performance capability suggested in the ASTM method.

A plot indicating the overall performance across the entire concentration range is shown in Figure 2. This shows the measured and reference values for each sample, laid out by chemical, for each of the two IRmadillo instruments used.

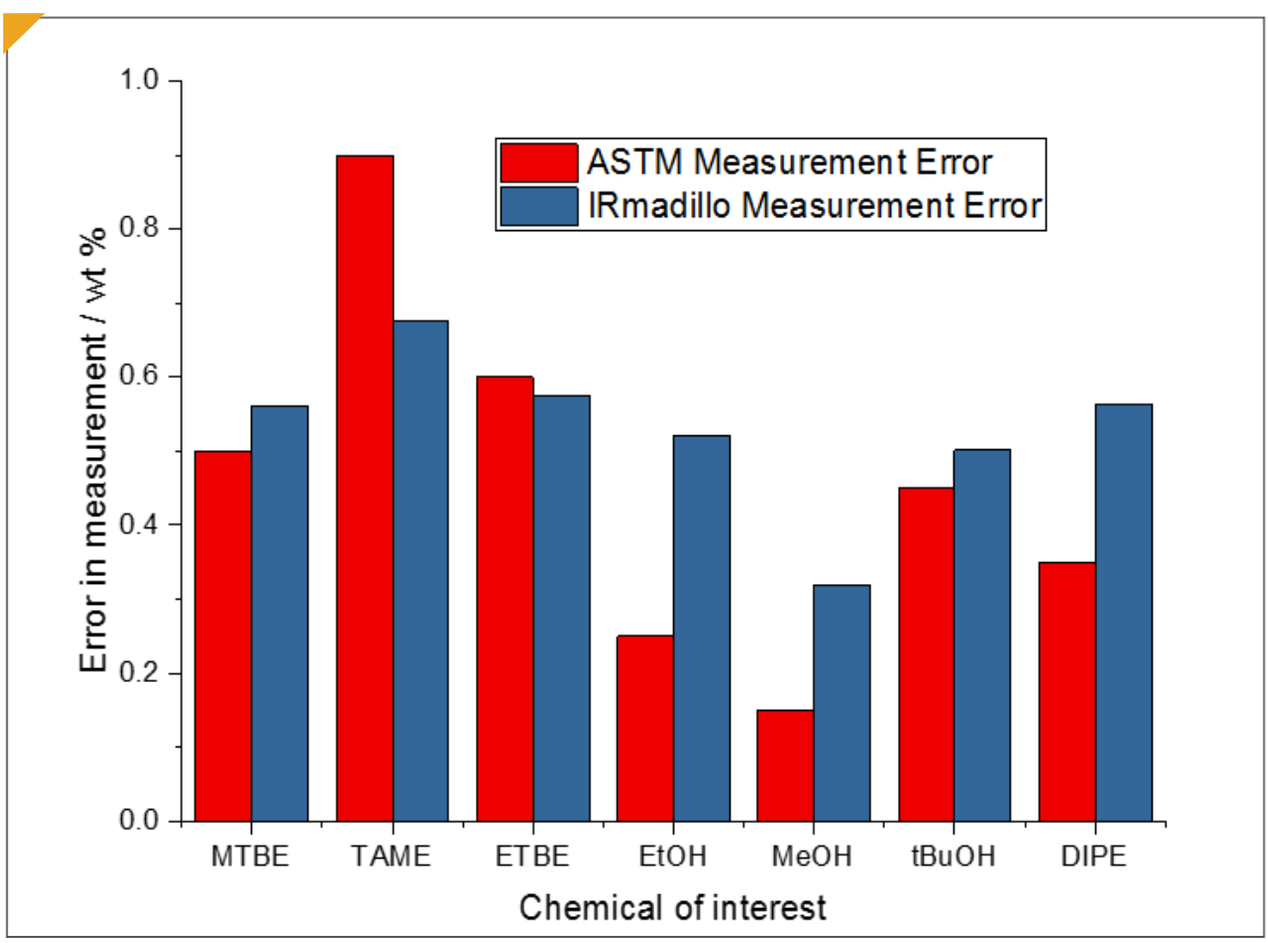

Figure 1: Graph of error in measurement for the published ASTM D5845 method and the IRmadillo on-line monitoring calibration.

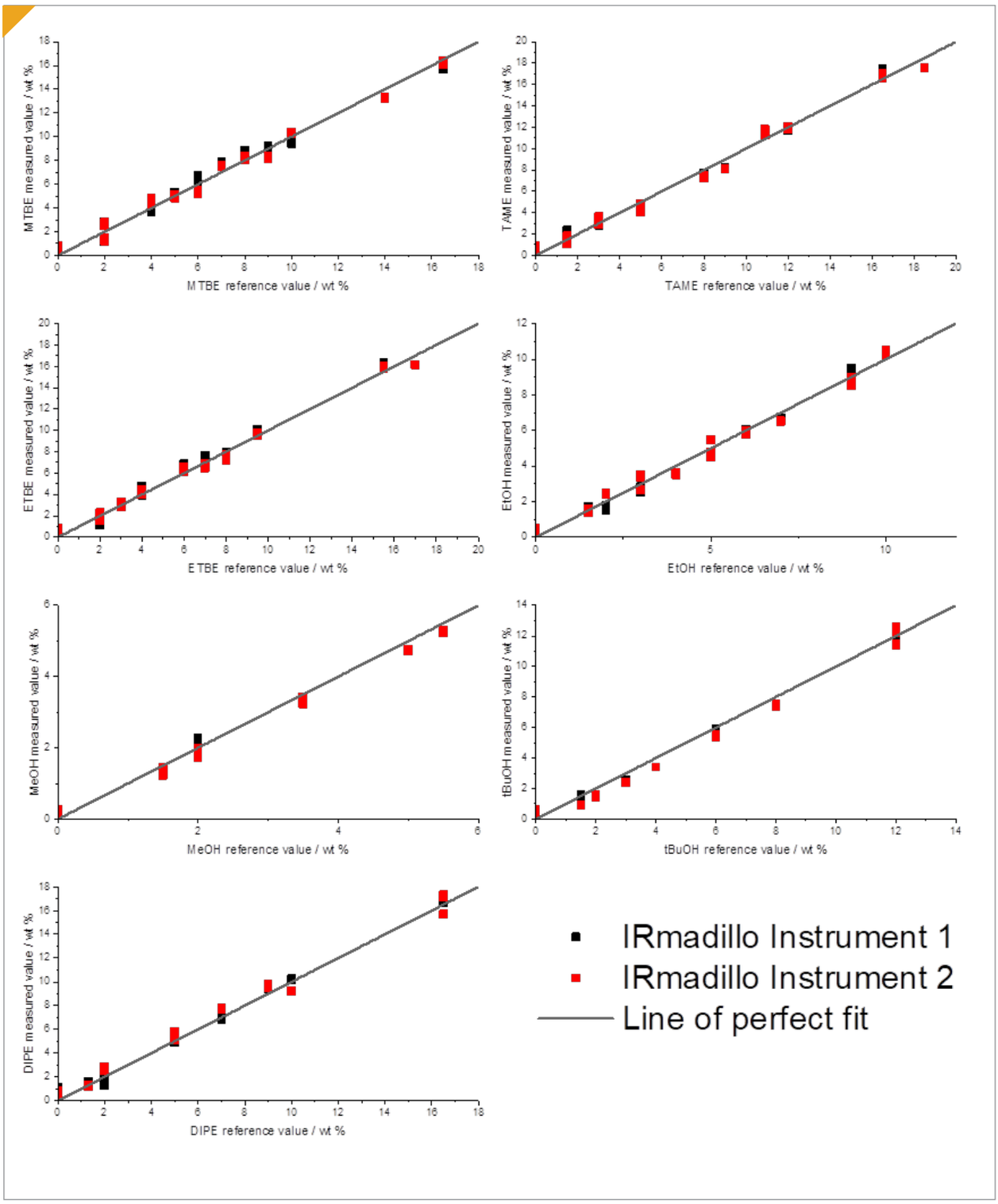

Figure 2: Plot of measured vs reference values for the alcohols and ethers of interest in gasoline as measured by two IRmadillo instruments.

It is clear that the relationship between the measured and reference points is extremely linear, with excellent measurement characteristics in all cases. The divergence from the reference value to the measured value is low, and the difference between the two instruments is likewise very small. This shows the inherent reproducibility of the instrument, removing the need for off-line checks and ensuring robust measurement.

This means that multiple instruments can either be installed at multiple locations within one site or even across multiple sites running the same calibration, and ensuring the same performance.

Classification of types of gasoline

The IRmadillo instruments were also used to test the classification of gasolines between base A and B (as stated in the ASTM standard). The same type of model that was used in the concentration calibration can be used to classify which variation of gasoline is present.

In this performance analysis, there were a total of 36 samples each in triplicate (108 individual spectra). All 108 were correctly classified with 100% accuracy. This means that the IRmadillo can be used to simultaneously monitor the concentration of additives and classify which product is being processed at any time.

The ability to classify gasolines means that the IRmadillo can verify when product changeover has been completed if multiple products are processed in the same installation. This type of measurement could be performed within 10's of seconds, improving efficiency and reducing costs for plant operations.

Conclusions

The IRmadillo process analyser has been calibrated for monitoring alcohol and ether concentration in gasolines as per the ASTM D5845, and has been shown to be consistent with the performance expected in the standard.

This means the IRmadillo is an effective analyser for on-line, real-time measurements of gasoline processes. Furthermore, the IRmadillo can classify which type of gasoline is present (base types A and B were used in this study), enabling real-time process control.

References

ASTM D5845-01(2016), Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol and tert-Butanol in Gasoline by Infrared Spectroscopy, ASTM International, West Conshohocken, PA, USA, 2016, www.astm.org

IRmadillo™
FTIR Spectrometer

Keep in mind

The IRmadillo is a process analyser based on FTIR spectroscopy technology. This means that it looks at **every molecule** present in a mixture - not just one - **every time** it runs. It can also measure concentrations from the 10's of ppm up to 100% concurrently.

What does this mean for you?

It means the IRmadillo can be calibrated to run multiple measurements simultaneously. For example, you may choose to:

- Monitor the concentration of alcohols and ethers in gasoline, as well as
- Classify the type of gasoline, and
- Monitor residual water content

...all with one IRmadillo instrument at the same time!

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