Application Note

KEIT spectrometers

Real-time monitoring of **acrylate synthesis** with an in-line FTIR process analyser

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Abstract

The plastics & polymer industry is under pressure to accurately monitor components during production to improve efficiency and reduce waste. Current technologies struggle to accurately monitor these components in real time. Here we successfully demonstrate how the high-temperature Keit IRmadillo FTIR spectrometer (IRmadillo25H) can provide real-time, in-line analysis of components in the synthesis of acrylate including methyl methacrylate (MMA), formaldehyde, methyl propionate (MeP), & water thereby making it a powerful monitoring solution in the production of plastics & polymers.

IRmadillo™

Introduction

The plastics and polymers industry is facing unprecedented public scrutiny for environmental reasons. There is a desire to reduce the need for raw materials (especially petrochemical feedstocks) to ensure processes are efficient with minimal waste.

Additionally, there is an economic pressure on operations to improve efficiencies across manufacturing plants to reduce the costs of raw materials, processing, and waste disposal.

These two drivers to increase manufacturing efficiency are a key aspect of Industry 4.0 – the Fourth Industrial Revolution – where robotization, automation, and cyber-physical systems meet manufacturing. But in order for an automated plant to operate based on actual process conditions rather than timings or pre-determined routines (for such things as controlling valves, dosing pumps, etc.), the plant requires meaningful and accurate in-line analytical techniques.

Parametric measurements (such as temperature, pH or pressure probes) are useful for inferring aspects of the process, but in-line spectroscopy offers substantially more information and meaningful measurement opportunities.

Key Words

- Acrylate synthesis
- Methyl methacrylate (MMA)
- Plastics & polymers
- Petrochemical industry
- Mitsubishi/Lucite Alpha process
- Process control
- In-line process monitoring
- IRmadillo25H

Features & Benefits

- Mid-infrared/FTIR spectral analysis
- Vibration tolerant
- Long-term stability
- Low maintenance
- Compact design
- Real-time, multi-component analysis
- Easy to use

Different materials and chemical monomers are more or less suited to different techniques, and unsaturated carbonyls such as methacrylates are ideally monitored by Fourier transform infrared (FTIR) spectroscopy. Conventional FTIR instruments use an arrangement of moving mirrors and fragile fibre-optic probes – making them wholly unsuitable for manufacturing environments.

Here we present the use of a static-optics designed FTIR spectrometer – the IRmadillo25H – to measure the synthesis of methyl methacrylate (MMA). The specific chemicals of interest studied here are based on the Mitsubishi/Lucite Alpha process, but the instrument can be used to monitor any acrylate monomer or polymer synthesis process.

Experimental

A variety of different stock solutions were prepared in a laboratory with differing concentrations of MMA, formaldehyde, methyl propionate (MeP) and water. These were chosen to reflect the chemical conditions within the Alpha process. Samples were run at a variety of analyte temperatures from room temperature through to 100°C, again to reflect different processing conditions within an industrial environment.

Spectral acquisition was performed using the IRmadillo25H. The instrument was stabilised overnight and purged with dry nitrogen. A background scan was run for 30 min before acquiring spectra. All samples were analysed with 3 x 120 s scans.

Analysis was performed using Camo Analytics' Unscrambler 10.5. A variety of different pre-treatments and spectral transforms were used. Calibration models were built using partial least squares (PLS) methodology. The spectral range used was 800 – 1800 cm^{-1} with a resolution of 16 cm^{-1}.

Results and discussion

The reaction mechanism for MMA synthesis modelled here is:

$CH_3CH_2COCH_3 + CH_2O \rightarrow CH_{-2} = C(CH_3)COOCH_3 + H_2O$

The results for a calibration for MeP are shown in figure 1. There is excellent correlation between the reference and measured values with an R^2 of 0.97 between a concentration of 0 – 0.2 mole equivalents (to MMA). The limit of detection (LoD) for this calibration is 0.001 moles of MeP : moles MMA.

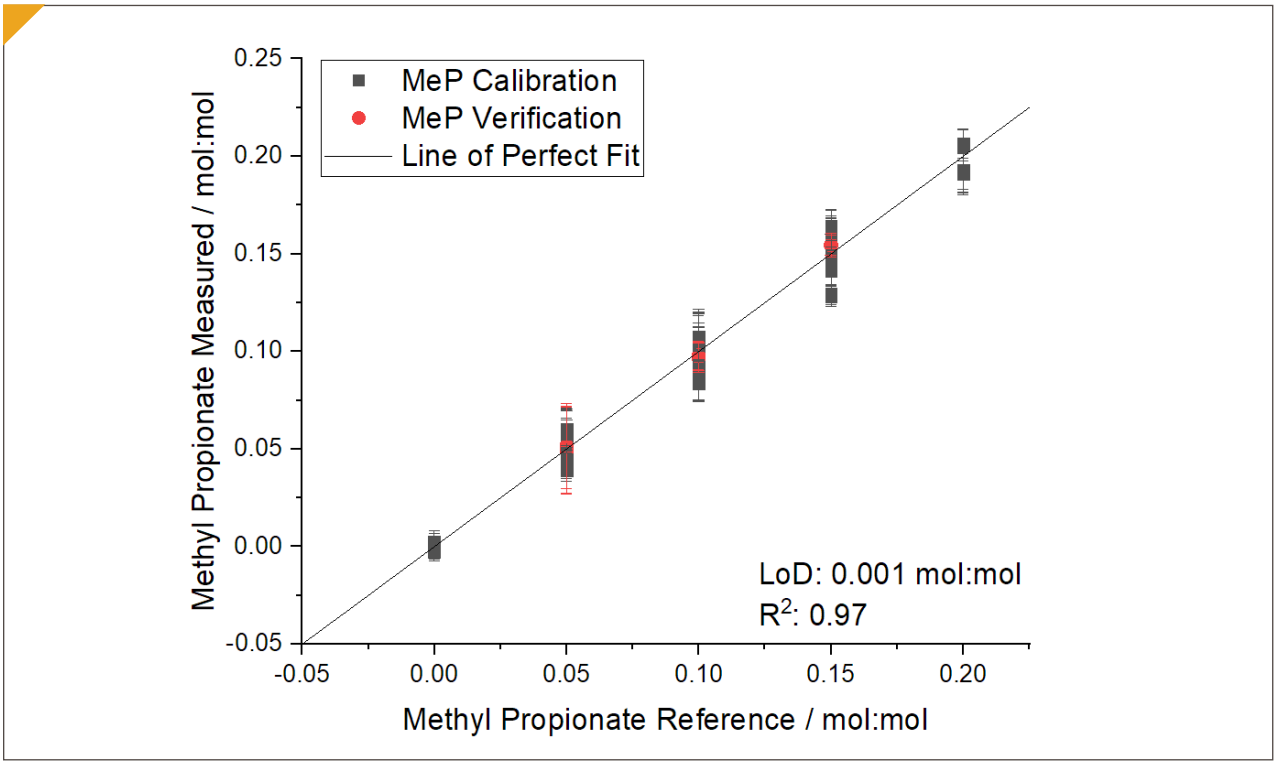

Figure 1: The calibration curve for methyl propionate (MeP) in the mixed chemical stream built at room temperature and 100°C

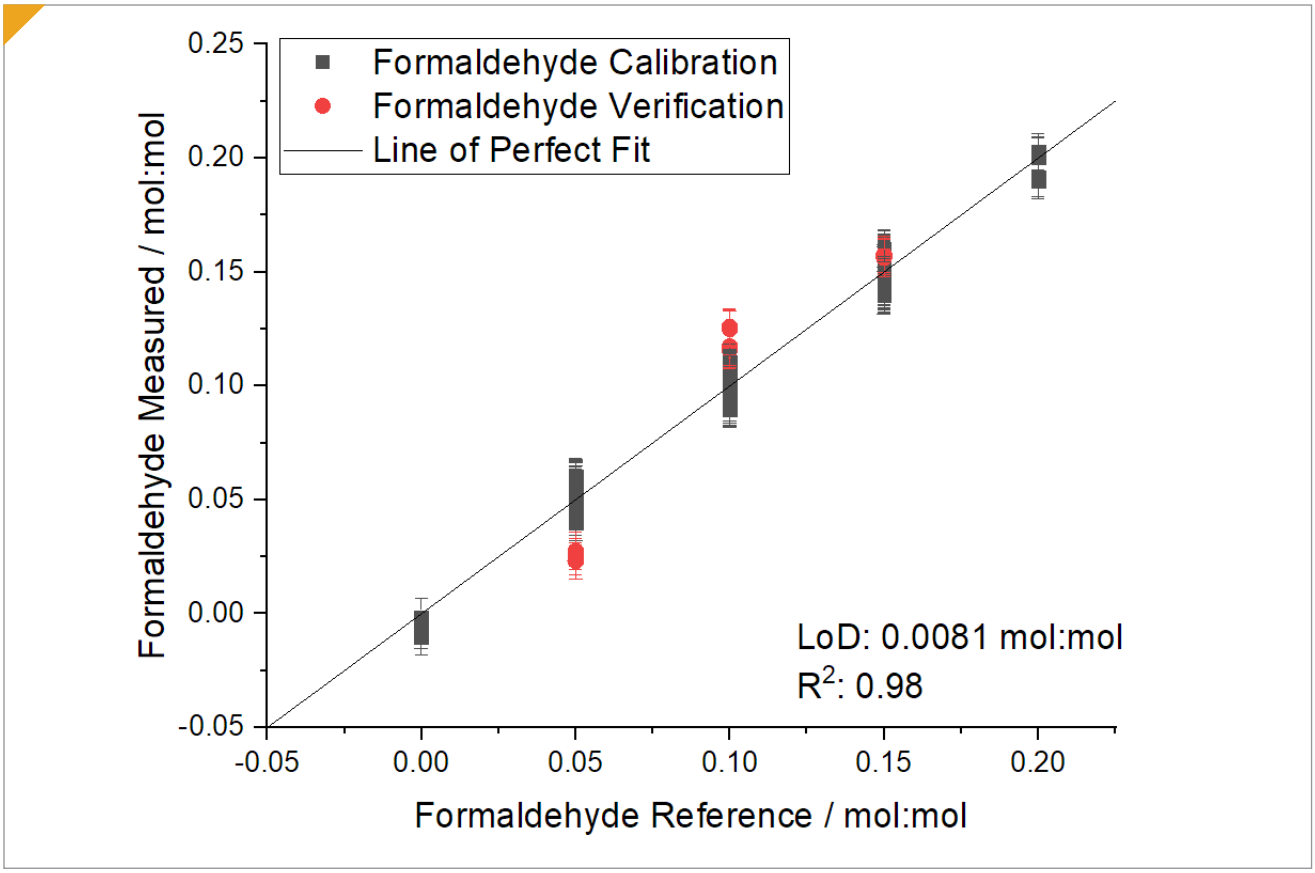

Figure 2: The calibration curve for formaldehyde in the mixed chemical stream built at room temperature and 100°C

The results for calibration of formaldehyde are shown in figure 2. The limit of detection for this calibration is 0.0081 mole equivalents (to MMA), and an R^2 if 0.98 shows excellent linearity.

Finally, the results for the calibration of water are shown in figure 3. In this case the limit of detection is 0.04 mole equivalents (to MMA) with an R^2 of 0.96.

These detection limits and results show that the IRmadillo25H is very capable of measuring chemicals of interest for acrylate synthesis. The measurement of formaldehyde and MeP in product streams allows fine tuning of the synthesis itself using feedback algorithms. Furthermore, the IRmadillo's ability to detect water in the streams enables control of drying columns for the recycling of unreacted reagents to minimise residual water in the MeP and formaldehyde streams, increasing both reaction efficiency and yield still further.

A note on analyte temperatures

The calibration work presented here was performed at two very different temperatures, room temperature (approximately 20°C) and 100°C. This was done specifically to demonstrate the temperature resistance of the new IRmadillo25H model.

The IRmadillo25H incorporates significant design improvements over its predecessor, the IRmadillo25, which have made the instrument capable of high-temperature and high-pressure measurements. These include a stabilisation of the infrared source to reduce the effect of analyte temperature on the infrared light present. As a result, a single instrument calibration over a temperature range of 80°C is possible.

In conventional process installations, the temperature has a much more limited variation, typically with a ΔT of 10 – 20°C under standard operating conditions. This means that the IRmadillo will have even greater performance once calibrated on a specific customer process.

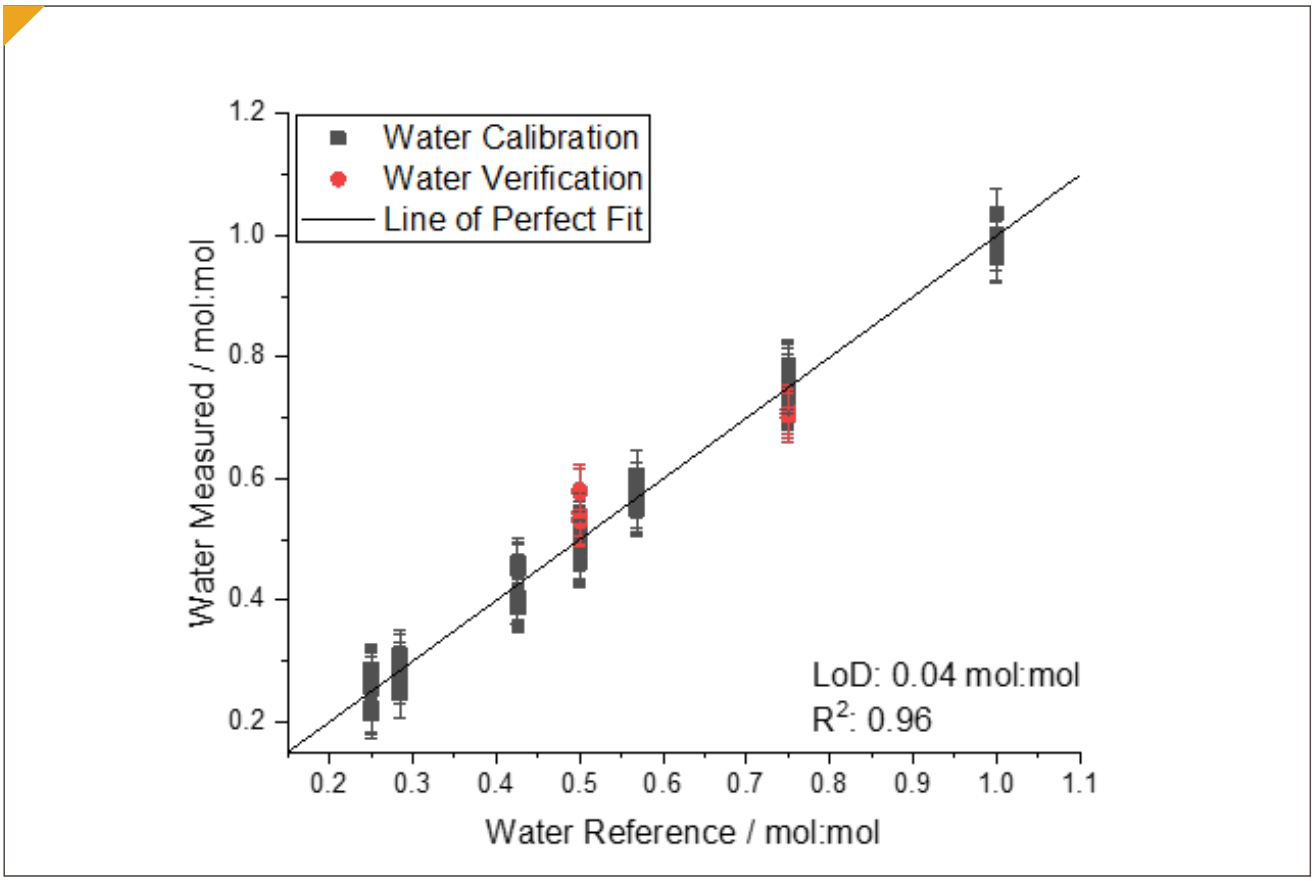

Figure 3: The calibration curve for water in the mixed chemical stream built at room temperature and 100°C

Conclusions

The IRmadillo25H static optics FTIR spectrometer has been shown to successfully measure the concentrations of methyl propionate, formaldehyde and water in a mixture containing those chemicals with methyl methacrylate too. The measurements have been demonstrated over an extended temperature range of 20 – 100°C with minimal impact of temperature on the measurement.

This shows that the IRmadillo25H is an excellent choice for process control and optimisation in the synthesis of acrylate monomers and polymers. The instrument is also ideal for the analysis of other chemicals that are used in polymer manufacturing such as carbonates and acetals, esters, and urethanes.

Keep in mind

This application note deals specifically with the chemicals present in the Alpha process for MMA synthesis. However, different feedstocks, such as esters and aldehydes, and by-products (not just water, but alcohols as well) can all be monitored and measured at the same time by the IRmadillo.

What does this mean for you?

The IRmadillo can easily be calibrated to measure different chemical concentrations simultaneously – it's a universal concentration meter for every chemical present in your process to enable real-time monitoring & control.

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