CHALLENGES AND OPPORTUNITIES IN IMPLEMENTING STATIC-OPTICS FTIR IN BIOFUELS PRODUCTION

Manufacturers face a difficult juggling act to balance cost, accuracy and real-time measurement of their analytical instrumentation to optimise efficiency and therefore profitability of their processes. The myriad choices of analytical instrumentation can be overwhelming based on the complexity of the technique chosen and its ability to be implemented on or in-line to a process. This paper introduces static-optics FTIR, and briefly explains what makes it different to traditional approaches and some benefits for its use in biofuels production.

Why use static optics for monitoring biofuels production?

Traditional process sensors (parametric instruments) such as temperature probes, pH probes, flow meters etc. are relatively inexpensive, make continuous measurements and can be implemented across an entire manufacturing or production facility. They give real-time measurement of key process parameters and are a critical part of the regulatory control layer. While these sensors are more than adequate to control simple process conditions such as heat and mass balance, they do not allow measurement – or therefore control – of process quality. To truly optimise a process, its composition needs to be monitored in real time.

A solution to this in many petrochemical and oil and gas applications has been the implementation of near-infrared spectroscopy (NIR). Spectroscopy as a concept is significantly more informative than parametric measurements as it directly measures the interaction of light and molecules, meaning it is possible to calibrate for chemical concentrations. However, traditional spectrometers based on Michelson interferometers are fragile and contain sensitive moving parts, so must be kept far away from mechanical movement or vibration – which is unavoidable in production facilities. NIR light is suitable for fibre optics, which means the process probes can be positioned far away from the spectrometer itself, protecting the delicate optics. Unfortunately, NIR spectroscopy is very limited in the information provided, as it does not directly measure "fundamental transitions" in molecules but instead measures "combinations" and "overtones" – a bit like trying to count the steps in a staircase by running up them two or three at a time rather than singly. You can understand whether it's a tall or short staircase, but you will not be able to determine the exact number of steps. To get accurate and complete measurements, a higher resolution technique would be a better choice.

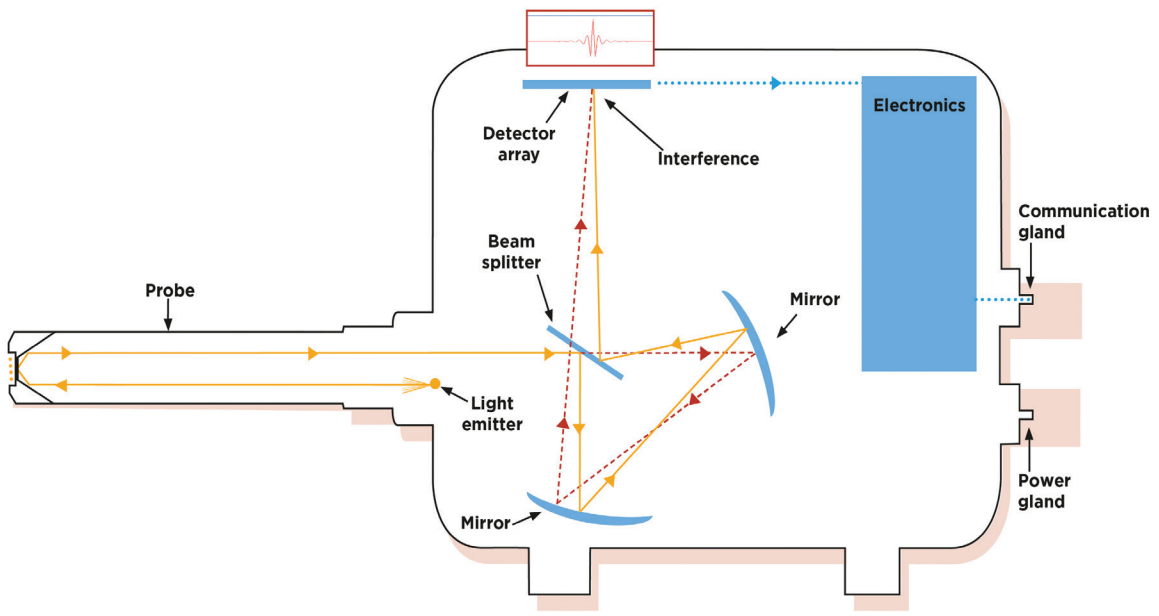

Image 1: Schematic of the internals of a static-optics FTIR spectrometer. The design creates an interferogram on the surface of the detector with no moving parts, making the design resistant to vibration and movement.

In the laboratory, these sorts of precise measurements are made with Fourier transform mid-infrared (FTIR) spectrometers. Traditional FTIR spectrometers are incompatible with production installations because the fibre probes required are very poorly performing, relatively expensive and extremely fragile. This renders classical FTIR instruments unsuitable for on-line measurements, and is the principal reason why NIR is so ubiquitous in the refining world today. Recent advances in static-optics FTIR such as the IRmadillo replace the delicate array of moving mirrors with a fixed optical path (hence the term "static optics"), meaning the spectrometer can be installed directly into or onto the process of interest with no fibres – taking FTIR out of the laboratory and into the process. Image 1 shows the light path through the instrument, where an interference pattern is created on the detector, which is transformed into a spectrum using a Fourier transform.

The basics of instrument calibration – and its challenges

The difficulty with using spectrometers for process control has always been calibration – the spectral data needs to be turned into meaningful calibration data. This is easy to do because of

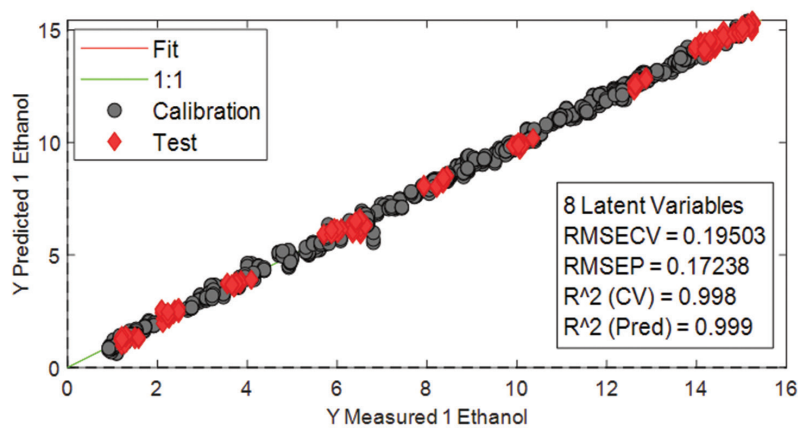

Image 2: Prediction vs measurement plot showing performance of calibration (y axis) against reference data (x axis).

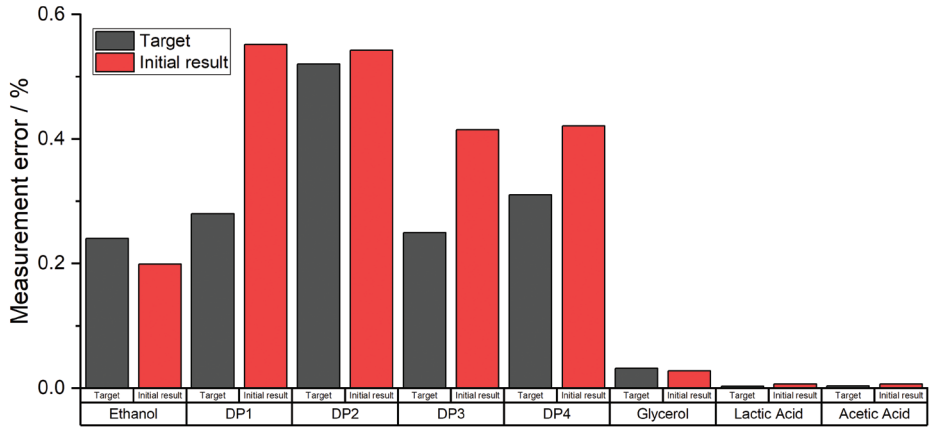

Image 3: Instrument measurement errors and targets for hybrid calibration approach.

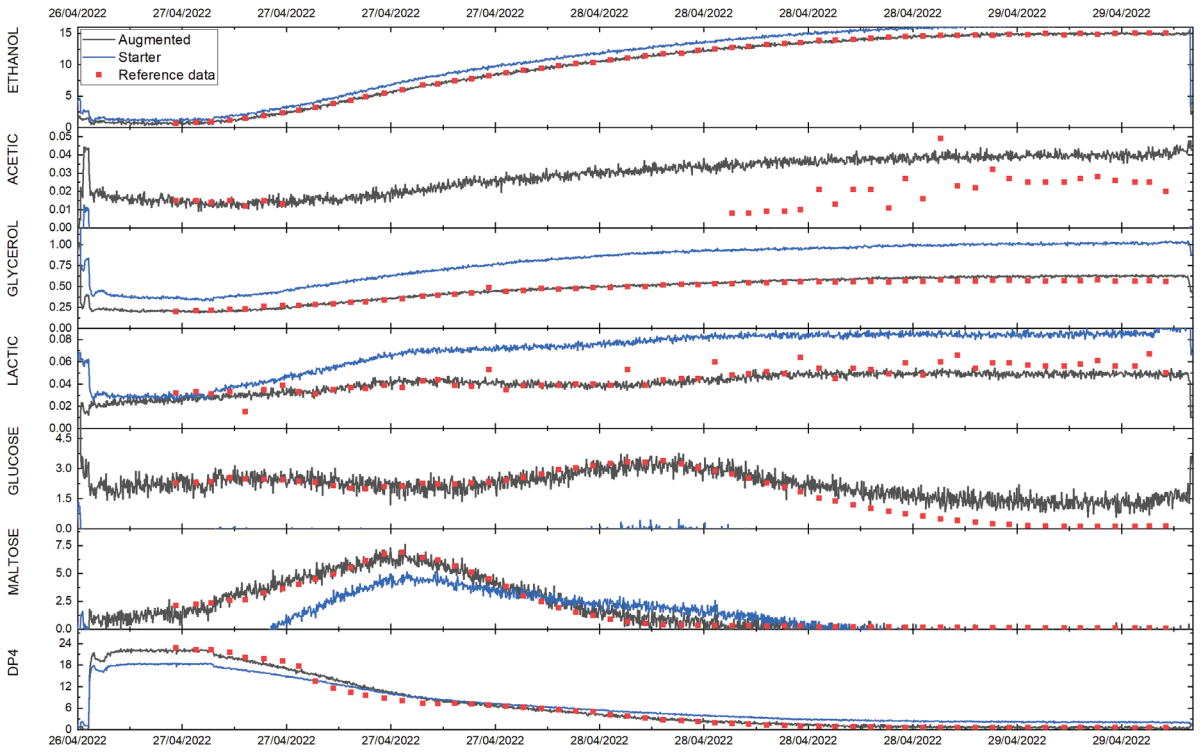

Image 4: Calibration performance over an ethanol fermentation batch for both starter and augmented calibrations. Reference data from HPLC shown for comparison

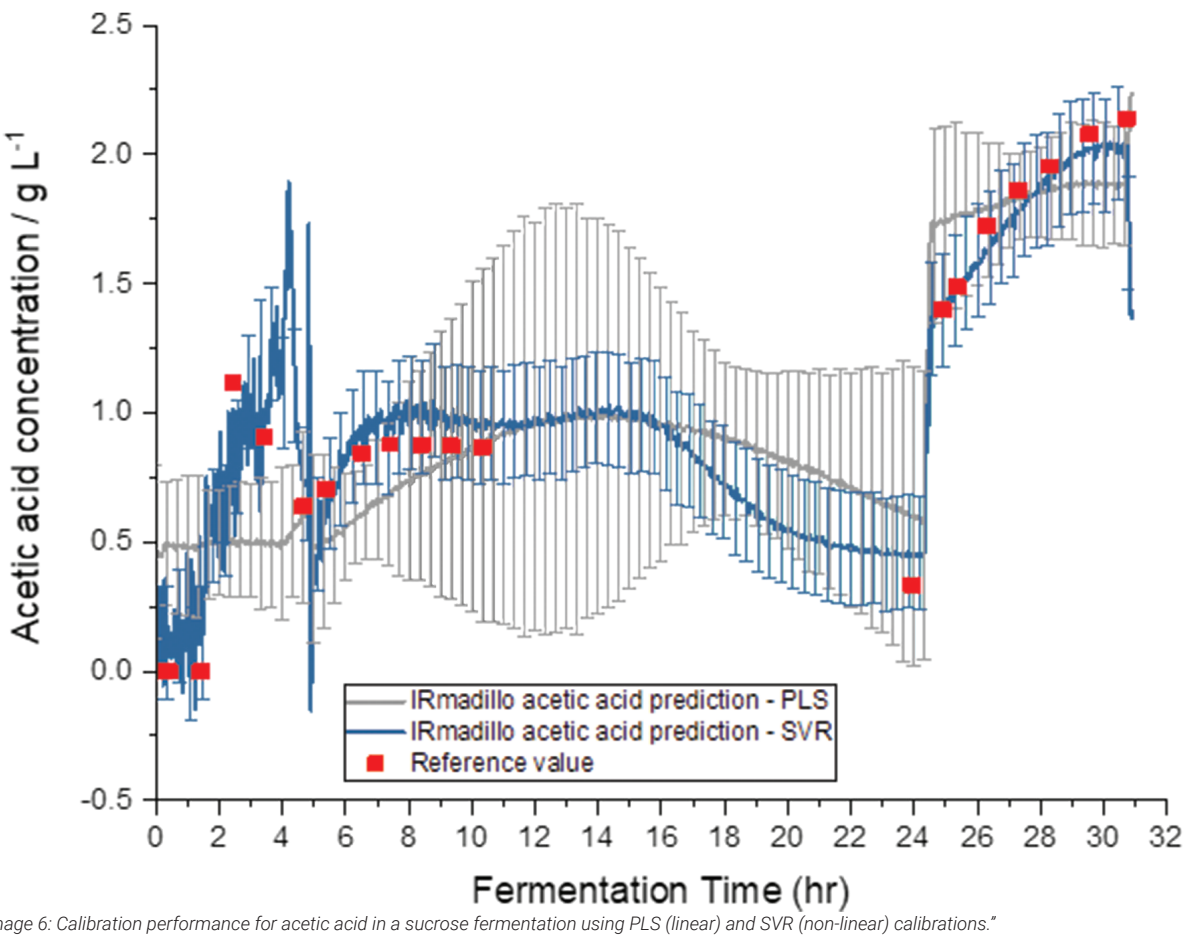

Image 6: Calibration performance for acetic acid in a sucrose fermentation using PLS (linear) and SVR (non-linear) calibrations."

Beer's Law:

$A = \varepsilon cl$

where A is the absorbance recorded in the instrument, **ε** is the "extinction coefficient" (which should be constant for a given feature in the spectrum), c is the concentration and l is the path length (broadly – but not always – a constant for a given installation).

The most common approach is to use chemometrics – also known as multivariate analysis – where the entire spectrum is analysed and compared to known reference values to build multi-dimensional regression lines. This approach is extremely powerful, and works for the vast majority of use cases (an example where it doesn't work is given below).

Individual calibrations can be built for each chemical of interest, and are all independent from each other. Image 2 shows an example calibration performance for ethanol in a fuel ethanol fermentation process built using partial least squares (PLS) methodology. The black circles are points and data used to build the calibration whilst the red diamonds are points and data used to test it – having not been a part of the calibration dataset. This is a crucial aspect of calibration building: perform blind validation by predicting samples that were not used to build the model – that is the only true way to ensure the calibration is not just "fitting noise".

The problem, however, is that every instrument typically needs a unique calibration built for it, and "calibration transfer" approaches normally need a dataset of 10s of samples – almost as many as building a fresh calibration from scratch. This can make multiple instrument installations prohibitively expensive to implement, reducing the uptake of advanced measurement and control schemes. This is especially true with NIR installations, where in excess of 100 datapoints are typically needed to build calibrations – NIR spectra simply do not contain enough data to use fewer datapoints.

A new approach to calibration – how augmentation replaced transferring

A secondary benefit to static-optics instrumentation design is that instrument to instrument variation is greatly reduced. This means that the residual variation is small enough to be included as one of the "factors" within a calibration, and can effectively be calibrated away. This is extremely valuable in applications where multiple parallel processes are performed – for example, industrial fermentation where multiple vessels are performing the same process and should run the same calibration. Keit recently developed a new approach to calibration that takes advantage of just this benefit: an instrument was installed in a particular

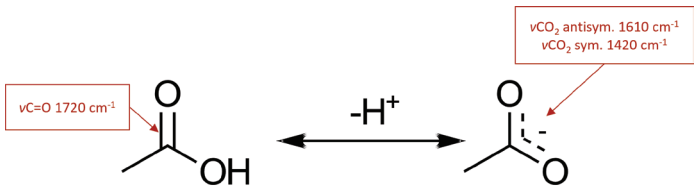

Image 5: Chemical structures of acetic acid (left) and deprotonated salt (right).

process using a calibration built on a different instrument, and additional data from the process was used to 'augment', or refine, the calibration. This is known as a hybrid calibration. Typically this instrument-specific data needs only to make up 1 – 10 % of the total dataset, dramatically reducing the amount of sampling required to ensure an instrument is calibrated efficiently.

An example of fuel ethanol production by fermentation is shown in image 3. The initial calibration was built over 6 months using process data from an installation in Europe. This calibration was then augmented with an additional 2 batches of data (16 data points) from an installation in the USA. The results are extremely promising with very close fits to the target calibration errors.

Keit also views this approach as the beginning of "pre-calibration" for the static optics FTIR, as the starter calibrations – whilst not 100% accurate – do in general show the correct trends for chemistry of interest. This is shown in image 4 with starter and augmented calibration results for a given ethanol fermentation displayed with reference data. The calibrations for the majority of chemicals are offsets which means they can be used for indicative performance (i.e. increases or decreases of concentration) until augmentation is possible. It is envisaged that by building hybrid calibrations of multiple installations even augmentation will not be required in the foreseeable future.

Where advanced calibration approaches are required – non-linearity and equilibria

It is obvious in the example above that acetic acid modelling is not accurate – even after augmentation. This is because of the way that off-line sampling, such as HPLC, does not always match the reality of on-line process conditions. Both acetic and lactic acids exist in equilibria with their salts, and the exact concentration differences depend on the pH of the process and concentrations of other acids. The spectrometer will observe both of these different chemicals with different spectral features – the C=O stretch in the acid occurs at 1720 cm^{-1} whereas in the salt it splits into 1420 and 1610 cm^{-1} features. However, when the sample is removed from process and analysed by HPLC the total amount of acid after quenching is reported. This means the assumption that a single chemical has a directly linear correlation with spectral features made above starts to break down, and calibrations using non-linear methodology such as locally weighted regression (LWR) and support vector regression (SVR) are required to accurately model these processes. An example of this is shown in image 6 – an acetic acid calibration using PLS and SVR principles. The PLS model struggles to accurately measure the acid whilst the SVR calibration does a very good job. The augmentation approach may also be suitable for non-linear calibrations, and subsequent work will establish its performance.

Additional applications in renewable fuels production

The use of static optics FTIR for monitoring, controlling and improving renewable fuels production is not limited to just ethanol fermentation. Example use cases and applications are:

Ethanol production:

- Early identification of fusil alcohols to prevent batch failure
- Optimisation of liquefaction processes
- Optimisation and control of fermentation
- Distillation control and efficiency improvements

Bio diesel production:

- Process measurement and control – such as catalyst measurement, free fatty acid (FFA) measurement and glycerol detection in finished product streams

Renewable diesel pre-treatment control

- Measure metals, P, FFA and TAN to control bleaching/pre-treatment and prevent catalyst degradation and damage (see example in image 7)

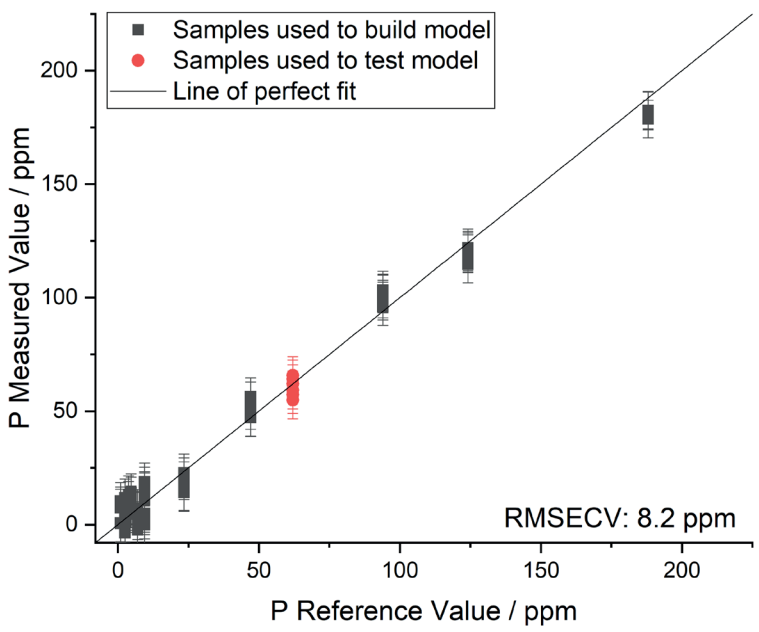

Image 7: Prediction vs measurement plot for P in triglyceride oils.

Conclusion

This work shows that by implementing a static-optics design instead of traditional Michelson-based interferometers (which rely on moving mirrors), it is now possible to use FTIR for in-line process monitoring and control reliably and robustly. The highest effort aspect of using spectroscopy for process control – calibration – has been made significantly easier through hybrid calibration, taking different datasets from multiple installations and instruments and creating an overarching calibration encompassing all of that variation. Because the level of information in FTIR (compared to NIR) is very high, and the variation between static-optics instruments is comparatively low, these hybrid calibrations are effective and efficient.

About the author:

Jonathon Speed, PhD, CChem, is Director of Product and Applications at Keit Spectrometers. As a frequent speaker at industry events and author in the field of vibrational spectroscopy, he holds a PhD in Raman spectroscopy and is experienced in the use of spectroscopic techniques & chemometrics to study a wide range of industrial & biochemical processes.

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Green solution for lab water conservation

California water officials recently had no alternative but to impose new drought rules throughout the state to discourage wasteful water practices. Whilst unaffected by the new regulations, scientists in the Department of Chemistry at the College of the Sequoias decided to evaluate an alternative waterless condenser from **Asynt** - the CondenSyn. The CondenSyn proved to be the perfect alternative to traditional water condensers previously used for reflux reactions.

This proactive investment in 22 CondenSyn waterless condensers has already drastically reduced water usage by the Department of Chemistry, and eliminated the risk of lab flooding accidents that are a potentially costly drawback of using water condensers and something that can be difficult to avoid.

Andrea Smith, a chemistry lab technician at the College of the Sequoias, commented: "Our area (the central valley of California) has been in drought-like conditions for quite a few years. Households and businesses are under severe water restrictions, having had to reduce water consumption yearly. While the college was not under the same restrictions, it only made sense that we should also strive to reduce our water usage/waste. It was laboratory supply company - Quark Glass - who suggested that the Asynt CondenSyn waterless condensers offered us an elegant eco-friendly but effective alternative to water-cooled condensers.

"We are currently using the CondenSyn waterless condensers for our teaching labs that require students to perform reflux reactions in water, methanol, or ethanol. This semester, we will use them in the preparation of methyl salicylate/oil of wintergreen (an esterification using salicylic acid and sulphuric acid refluxed in methanol), and the preparation of the analgesic benzocaine, another esterification using p-aminobenzoic acid and sulphuric acid in ethanol. Not only are the CondenSyn waterless condensers making the labs eco-friendlier, but they are also saving money as the department's rate of water consumption has been reduced dramatically. For example, with every single overnight reflux run, a lab can save almost 3,000 litres of water - times that by twenty students and it is around a staggering 60,000 litres. Our students have found the CondenSyn units to be easy to use as there are no water connections to make, we can use them open to atmosphere, and the 19/22 ground glass joints are perfect for our commonly used round bottom flasks."

More information online: ilmt.co/PL/VOzE

For More Info, email: **57673pr@reply-direct.com**

New interface software for improved flowmeter functionality

Titan Enterprises launches their advanced interface software for the Atrato® ultrasonic flowmeters.

The Atrato line of patented ultrasonic inline flowmeters consists of four models operating over a flow range of 2ml per minute up to 20 litres per minute. The USB connection gives the Atrato computer interface capability, enabling the user to directly monitor the flowrate being measured and alter the operating parameters using a PC.

Titan's development of the Atrato's new interface software features four key functionality improvements: the ability to connect, configure and operate multiple Atrato flowmeters on a computer simultaneously whilst minimising CPU usage; additional capability to run simple local and remote-control batching operations using an inbuilt relay; remote start/restart capability for long shut-down periods; the ability to increase signal gain via the software for liquids with poor acoustic properties.

The Atrato interface software enables the user to log the flow data directly via the USB. This data-logging capability gives a continuous picture of the flow characteristics of the system being monitored, such as flow, alarms, relay and pulse. The upgrade integrates developments in both the Atrato's internal software and the PC interface software, providing a combination of increased versatility and advanced operational features.

Atrato flowmeters are industry proven with good chemical compatibility, ideal for laboratory applications, cooling equipment, pharmaceutical, chemical and petrochemical processes, water and OEM high precision applications. With no moving parts, mechanical wear is virtually eliminated, critical for long-life and repeatability and reducing the requirement for recalibration.

Taking advantage of proprietary embedded signal processing software developed by Titan Enterprises, both viscous and non-viscous liquids can be routinely measured precisely. The low flows that the Atrato flowmeter is capable of measuring vary from laminar to turbulent and are highly immune from viscosity. With unparalleled turndown, repeatability, and linearity, the Atrato can monitor flow over a range of 250:1.

The Atrato interface software is supplied with the flow meters and can also be downloaded from Titan's website. Although the upgraded software is 'backward compatible' and will work with older Atrato models, not all the new features will be accessible.

More information online: ilmt.co/PL/2p4J

For More Info, email: **57447pr@reply-direct.com**

Throw away your circulating bath, free up your lab and achieve faster and more precise viscosity measurement results

If you regularly carry out high and low temperature rotational viscometry in your laboratory and need to work within international standards such as ASTM, DIN, or AASHTO, **Anton Paar's** air-cooled, peltier-controlled PTD 175 with ViscoQC 300 rotational viscometer, offering an unsurpassed temperature range from -45 °C to +175 °C, complies with all of these standards.

The PTD 175 controls temperature with no need for a liquid circulating bath, saving a considerable amount of lab space. Time is saved with each test thanks to the highly rapid and efficient heating (typical: 9.4 K/min) and cooling (typical: 2.3 K/min) rates. This instrument also provides a unique T-Ready™ function signal when the sample has reached set temperature

The PTD 175, a hand-held viscometer and temperature instrument ready to use straight out of the packaging, offers one solution from low temperature engine oil to high temperature asphalt binder. There is virtually no maintenance required and no bath liquid needed. This instrument provides the most accurate viscosity measurement with temperature accuracy of ±0.1 °C, with built-in digital levelling for repeatable results. The instrument's touchscreen makes it simple to operate and eliminates the need for a PC and the device controls sample temperature of DIN/SSA/UL/L1D22/4B2 measuring systems

More information online: ilmt.co/PL/mKKk

For More Info, email: **57773pr@reply-direct.com**