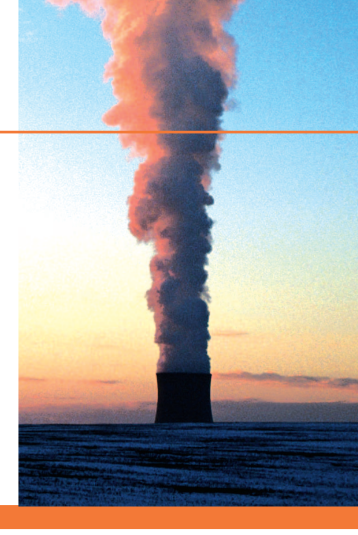

FTIR
COMES OF AGE

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Over the last few years, FTIR technology has moved from the laboratory to the emissions monitoring field, becoming a powerful method of measuring gas mixture components continuously with a single instrument. Today industry is beginning to recognise FTIR as the future of emissions monitoring. This article explains the technology and some of the problems and outlines a typical application.

WHAT IS FTIR?

An 'FTIR' (Fourier Transform Infra Red) is an infrared spectrometer able to collect full IR spectra, typically in the mid-IR range used for measuring gases. The unit will detect anything with an IR absorbance – in practice this includes most inorganic and organic compounds except for certain gases such as hydrogen, oxygen, nitrogen and inert gases such as argon.

In use, the vent gas is pumped into the sample cell for measurement and the FTIR produces an IR absorbance spectrum of it. If the cell contains no IR absorbers e.g. nitrogen only, then there will be no absorbance and the sample spectrum is a flat baseline. Generally, compounds in the cell will absorb IR and the result is a series of peaks, shown below. The pattern of peaks is unique to each compound (its spectrum) and can be used for identification (fig 1). The height of the peaks is proportional to the concentration in the cell.

Results are extracted from the sample spectrum by identifying peaks specific to components, and measuring the peak heights or areas. Concentrations are then calculated by comparing the sample peaks with corresponding peaks in calibration spectra of the pure material of known concentration. In practice the analysis may be more difficult, as many peaks will overlap and interfere and it may not be possible to locate unique ones. Today analysis is carried out automatically using software and more complex mathematical routines.

WHAT CAN FTIR DO?

Since the FTIR will record a combined spectrum of any compounds present it is a truly generic analyser. By suitable configuration it is possible to measure virtually all emission components with one machine. For example, Protea started using FTIR eight years ago and over that time has completed over 600 emissions profiling projects involving over 250 different components at widely varying concentrations in many different situations using the same high-resolution analysers. The same machine can also measure a wide range of concentrations (0.5 ppm to several percent) by changing cell size or by suitable sample dilution.

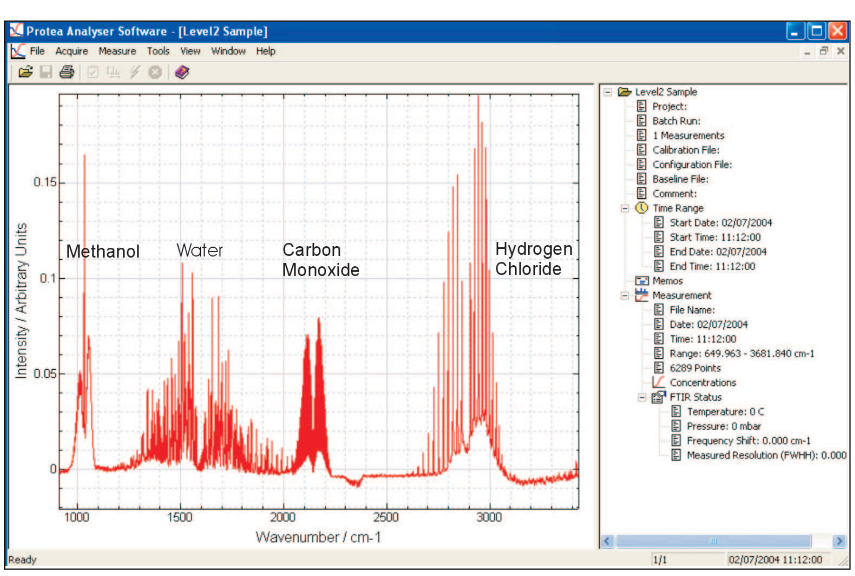

Figure 1

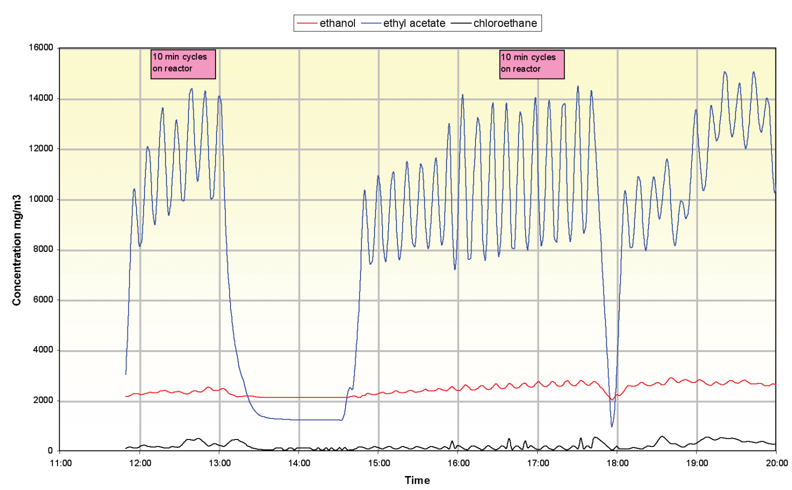

Figure 2: Concentration Profile

This ability to measure anything makes the analyser ideal for monitoring unknown mixtures, with components being identified from the spectra. It also affects the sampling approach. With FTIR the sample is heated or diluted to maintain it in the gas phase and everything is measured -any corrections for water are done on data analysis rather than physical conditioning. Samples that are wet or liable to condense do not need to be conditioned.

Emissions Monitoring

The most common FTIR application is continuous monitoring of emissions. The quality of data generated is very high, with concentration profiles being produced for each component present (fig 2).

By measuring flow at the same time, the mass release profiles (kg/hr versus time) can be generated. Mass profiles are required for emission reduction studies.

FTIR Versatility

The wide range of compounds and concentrations makes FTIR suitable for several other gas application areas:

- Trace components in air or pure gases, generally at sub-ppm levels
- COSHH monitoring at ppm levels
- Process Streams at ppm to % levels.

THE VALIDATION CHALLENGE

The ability to detect such a wide range of compounds makes validation complex. Different approaches are used for fixed continuous emission monitors (CEMS) and mobile units for investigative or confirmatory monitoring.

CEMS

The analyser itself must be validated for the compounds and concentrations specific to the application by checking with calibration gas and any approval only applies to that particular use.

Investigative Monitoring

Such monitoring may involve a wide range of mixtures, so validation must be able to accommodate these unpredictable applications. This is achieved by using one of the generic standard methods, EPA320 or ASTM6348. Both have a similar approach:

1. Configure the analyser to produce on-line results, based on what is expected in the vent.
2. On site, validate this model and the sampling system by injecting calibration gas into the line and checking against on-line results. Depending on the level of validation required this could be a single reference calibration through to calibration of target compounds over a range of concentrations.
3. Complete the monitoring and estimate uncertainty
4. Afterwards, check the results to see if any compounds not included in the model are present. If they are, correct results accordingly.

Although this approach appears complex, we find it can be applied quickly with practice. Protea's new 104M analyser has simplified this work as it incorporates features for in-line calibration, sample and calibration dilution and model building and checking.

SCRUBBER MONITORING EXAMPLE

In the process studied organic products were batch-chlorinated and further processed in several vessels all venting through a scrubber before release to atmosphere. This project was to monitor the inlet and outlet of the scrubber, to provide profiles of gases before and after treatment. These were used alongside scrubber operating data to assess performance and measure final emissions.

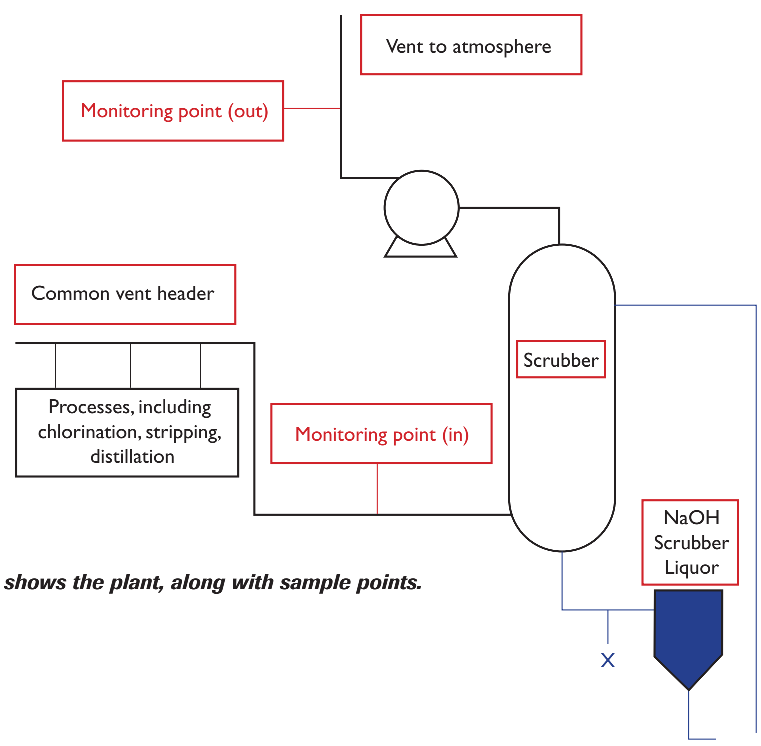

Fig 3 shows the plant, along with sample points.

Figure 4: 104M FTIR in use

Monitoring Set up

A separate FTIR was used at each point to maintain the required 2 minute sample frequency. Using a single FTIR with a sample change over is possible, but this increases time between samples to 20+ minutes due to sample purge times between high and low concentrations.

As the process was known, there was a reasonable understanding of potential gas composition including raw material, product, solvents, by-products and HCl.

Concentrations were high and both inlet and outlet sampling lines had to be diluted between 7 and 20:1 to reduce concentrations to the measurable range for the instruments. This is easily done on Protea's new 104M FTIR, which has an integral sample system with programmable dilution and in-stack dilution probe.

Flow was measured using Protea PF100 intrinsically safe logging meters, so that mass emissions could be calculated.

The FTIRs were configured to measure hydrogen chloride, chlorobenzene and dichlorobenzenes on line. Validation was by injection of 1000 ppm propane in nitrogen calibration gas into the sample probe, using the 104M injection feature.

The monitoring was carried out over a 24-hour period to capture 2-3 batches of production, which is the minimum recommended to capture variability between batches. During this time process data was recorded.

Results

After the run, checking original spectra identified other components including sulphur dioxide and carbonyl sulphide. The model was changed to incorporate these new analytes and the spectra reanalysed to give accurate results. This illustrates one of the key FTIR strengths: the original spectra contain all the data needed for full analysis and are recorded. Any unexpected compound or interference can be corrected after the event without having to repeat measurements. In fact, in the case of investigations where most of the components are unknown, it is common to only record spectra and do all the spectral analysis after the site work.

Conclusions

The figures below show some key profiles for this scrubber and emissions assessment:

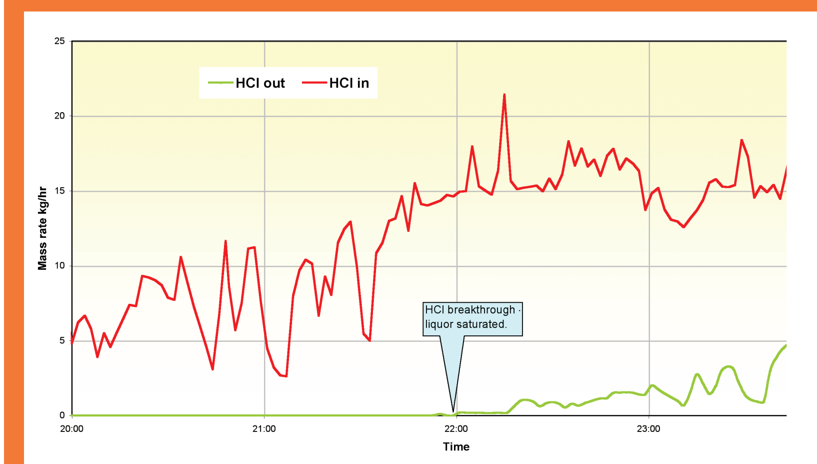

Figure 5: Hydrogen chloride Profiles

Fig 5 shows the point of saturation of scrubber liquor, allowing HCl to breakthrough. This is due to charging liquor on a batch basis and not replacing frequently enough. The problem was curable by switch to continuous basis and the profiles and process data were used to quantify the exact changes needed.

Using profiles of other analytes (fig 6) it was also possible to match up feed activity with release of carbonyl sulphide ultimately providing information on process pathways and emissions control.

Without FTIR and quite a lot of experience, such a study would have been both expensive and difficult to carry out. More importantly, the greater understanding of the process and the benefits coming from it would not have occurred.

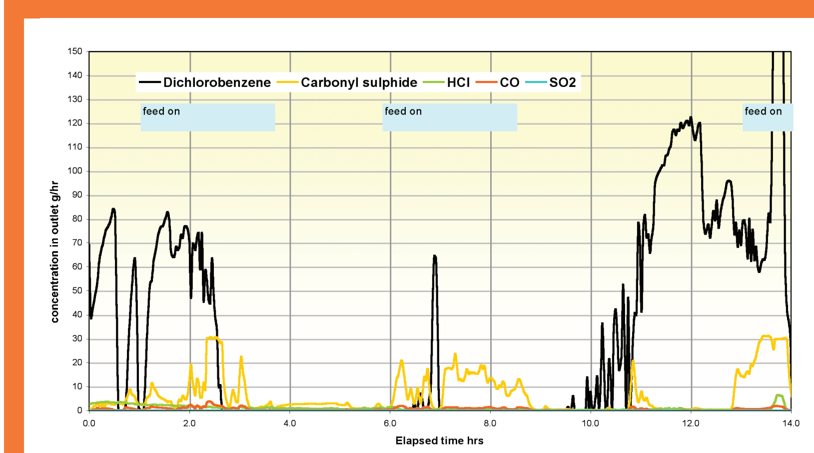

Figure 6: Other Profiles

BRINGING FTIR IN-HOUSE

FTIR is a powerful technology offering significant opportunities to companies in terms of data quality and the ability to monitor such a wide range of gases in one analyser. The introduction of new generation analysers such as Protea's new 104M model with its integral sampling and calibration features alongside powerful software has simplified operation significantly and made the technology suitable for many more users.

AUTHORS

Richard J Camm is Managing Director of Protea Limited, a company specialising in the development, application and commercialisation of new monitoring technologies such as FTIR.

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