Real world continuous caustic scrubber monitoring using online NIR spectroscopy

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When talking about "process monitoring" or even "Process Analytical Technologies" the inference is nearly always that the medium to be monitored is the reaction mixture/sample stream. This can prove quite a technical challenge as many plants are "multifunctional" and therefore the time and opportunity to construct effective models and monitoring protocols for short-lived product campaigns can be severely limited. However, there are often "auxiliary" services, common to many processes, that can benefit from continuous monitoring and, although less glamorous than the reaction itself, can yield a significant return on investment. One example is caustic scrubbers. Caustic scrubbers play a vital part in the clean up of effluent gases from chemical plants. A recent collaboration (SONAR[1]) between a number of medium-sized chemical companies, academics, technical consultants and instrument solution providers was established by SOCSA[2] and CPACT[3] to demonstrate the feasibility and financial returns available to those undertaking continuous process monitoring of caustic scrubber solutions. The project was funded by the UK Department of Trade and Industry (DTI) as a demonstration of monitoring a "generic" process, applicable across the industry.

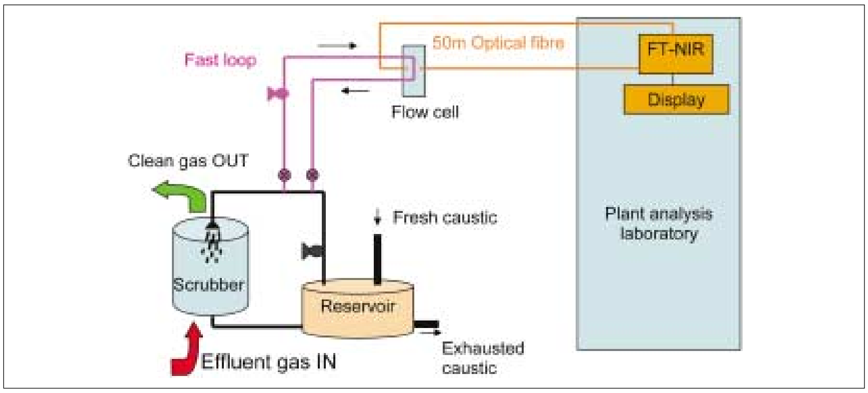

Figure 1. Diagram of caustic scrubber stream monitored by a remote FT-NIR analyser. In this example the system is an open loop (i.e. the analyser advises the operators of the caustic strength, but does not actuate valves itself), but would easily lend itself to full closed-loop control of the caustic strength.

Limits of emissions from chemical plants are constantly being tightened. Often the last line of defence in the effluent gas clean up chain is a caustic scrubber. Periodically these scrubbers need to be recharged to keep the caustic strength at effective levels. However, rates of caustic consumption can vary considerably depending upon the content of the effluent gas and the chemistry taking place in the plant. Therefore reliance is placed upon grab sampling and wet chemical analysis. This is both time consuming and potentially leads to operator exposure to corrosive and possibly toxic scrubber streams. Continuous caustic stream monitoring using near infrared (NIR) spectroscopy removes the risk of operator exposure or of rapid, unpredicted scrubber exhaustion. Continuous monitoring also allows the maintenance of the optimum caustic strength and prevents unnecessary disposal of active scrubber solution.

In essence, a caustic scrubber consists of a spray of caustic solution, which is used as a counter flow to wash an exhaust gas stream (Figure 1). The general design lends itself to the installation of a flow cell as the caustic stream is already flowing around a "fast loop". An NIR flow cell can be placed either directly in the caustic loop, or on a sample loop. The SONAR demonstration project decided upon the latter option for an installation at A.H. Marks near Bradford, UK, a medium-sized plant manufacturing fine chemicals (Figure 2). NIR spectra were collected once a minute using an

Figure 2. NIR flow cell installed in scrubber line at A.H. Marks. Caustic scrubber solution is pushed by a pump (bottom left) into the bottom of the cell and exits at the top. Fibre optic connections enter via the stainless steel conduits on each side of the cell.

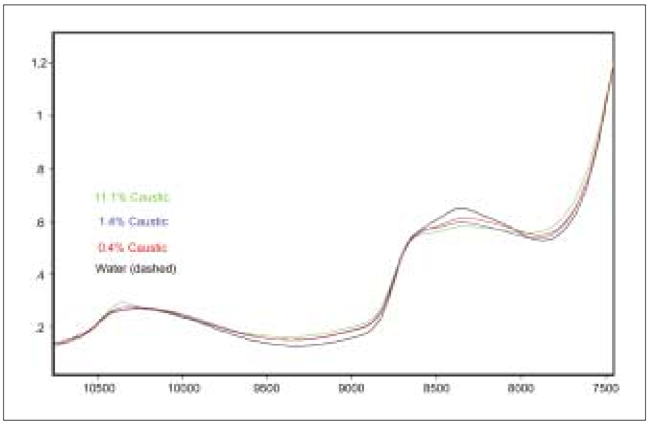

Figure 3. Relationship between NIR spectra and caustic concentration for pure caustic solutions.

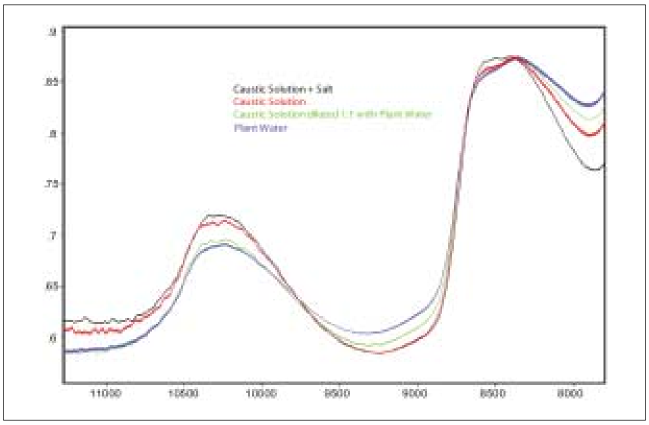

Figure 4. The blue, red and green NIR spectra are of plant water, caustic solution and diluted caustic solution, respectively. The addition of salt (NaCl), which has no NIR spectrum of its own, to the caustic solution (black spectrum) alters the OH signals of the caustic/water spectrum significantly. This effect can interfere with calibrations for caustic strength, particularly at low caustic concentrations.

ABB Bomem FT-NIR spectrometer placed remotely, in the plant laboratory.

Monitoring high to moderate caustic concentrations is not particularly difficult as the hydroxyl ion is active in the NIR spectra (Figure 3). However, the devil is in the detail. As the scrubber solution does not make contact with the product, it does not need to be a reagent grade chemical, and therefore typically contains many impurities. These impurities are often ionic and cause interferences in the NIR spectra (Figure 4). This effect is compounded as the caustic solution ages and accumulates additional ionic impurities scavenged from the effluent gas stream. The usefulness of the monitoring occurs when the method is accurate enough reliably to determine the caustic concentration at the minimum effective level of 1%. This allows the caustic scrubber to be run right down to that level, rather than the previous practice of periodic manual titrations which required that the caustic reservoir be recharged when a level of 4% had been reached. However, the lower the level of caustic, the more significant are the effects caused by the ionic impurities. These interferences can also cause inaccuracies in other analytical methods such as pH monitoring. Therefore it is necessary to devise a model that can differentiate between variation in the NIR spectra arising from changes in caustic concentration and variation due to different ionic interferences. To do this, it is necessary to use data from multiple batches, and where possible, multiple plants and to use a multivariate algorithm that is able to use all of the information available in the spectrum. It is also important that the model is robust and does not require constant maintenance.

A multivariate (PLS, partial least squares) model was constructed using data from multiple batches and multiple products (Figure 5) over a period of several months.

The system remained in-line monitoring caustic strength for over six months, including a spectrometer source change. The calibration required no adjustment after the new source was fitted and predictions were as accurate as with the previous source. Caustic concentration was reported every 100 s, resulting in continuous monitoring of the scrubber performance and the ability to reduce the caustic action level from 4% to 1%. The system is ideal to be integrated into a closed loop control system to automatically replenish the caustic reservoir as and when necessary.

The project was a clear demonstration of the usefulness on-line monitoring. However, the real importance of this work is not so much in the science as in the economics of the analysis. Caustic scrubbers are common to many plants and

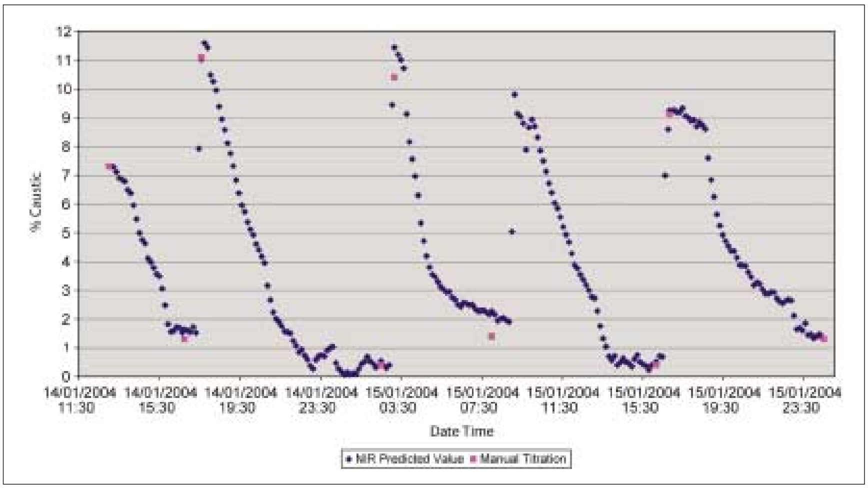

Figure 5. NIR monitoring of caustic scrubber strength (blue data). Note that only one NIR data point in five has been shown to aid clarity. NIR predictions were actually made every 100 s. The results of manual titrations are shown as purple data points. The diagram shows five cycles during which the scrubber is slowly exhausted and then recharged.

processes and so this is a highly "portable" application, both in terms of the physical equipment and the model. The entire analysis system was transferred from one plant to another, totally different, plant 30 km away. Although these two plants made totally different products, they both used caustic scrubbers. Much manpower and resource normally has to be expended to develop models in the early stages. By focussing on a "common application" a great deal of "common learning" can be transferred to new locations. This greatly reduces the cost of entry into the process analytical community.

Arguments can be made for including such monitoring purely on environmental grounds (reduction of waste and lowering of gaseous emissions), as well as on health and safety grounds (by the reduction of operator exposure to the scrubber stream when taking samples for titration). However, the economic argument is also a very powerful one. Caustic is a relatively cheap chemical. Even if one factors in the reduction in costs of disposal of "partially exhausted" caustic (arising from reducing the amount of "exhausted" caustic being generated), it is unlikely that the capital cost of a full spectrum analyser such as the one described above, could be recouped in a reasonable period for a single scrubber.

However, chemical sites usually have multiple plants, and therefore multiple scrubber units. Fibre optically coupled NIR easily lends itself to multiplexing and thereby dramatically reduces the cost of analysis per analysis point. One of the chemical sites involved in this project calculated that the annual saving per analysis point could be as much as £15,000 to £18,000. Based on these figures the return on investment (ROI), or payback period, is under 12 months if three or more scrubbers are monitored. The plant in question actually had more than seven scrubber streams easily accessible to a single NIR analyser.

Conclusions

Many companies are cautious of the investment of resource that may be needed to develop a new in-line analytical method, in the light of short campaign times and complex reaction analyses. By focussing on some of the more common applications, using the transferable knowledge from other similar applications, the plant manager can reduce the risk and cost of entry to the implementation of process analytical technology.

Acknowledgements

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Notes and eReading

1. SONAR (www.socsa.org.uk/sonar.htm).
2. CPACT, Centre for Process Analytics and Control Technology (www.cpact.com).
3. SOCSA, Specialised Organic Chemicals Sector Association (www.socsa.org.uk).
4. Mahesh Shivhare, "Progress Review on Cost Benefit Analysis", CPACT 2004 (www.socsa.org.uk/Costben.pdf).
5. Paul Dallin and John Andrews, "Choosing Your Approach", *Spectrosc. Europe* **15(3)**, 27 (2003) (www.spectroscopyeurope.com/Process_15_3.pdf).