New advances in on-line monitoring of chemical products

Introduction

In industrial processes, performance depends on the ability to detect and counteract problems in the process rapidly.

A wide range of on-line analysis techniques exist that can be used for a reliable monitoring of manufacturing conditions. Among them, spectroscopic methods are continuing to develop in order to provide non-invasive and non-destructive real-time analysis. Raman spectroscopy is one of them. It can give direct access to the concentrations of the monitored product which allows efficient tuning of the process.

In this note, an industrial application, which concerns the real-time monitoring of chemical products, is described. To adapt to the industrial environment, the Raman equipment requires specific features that will be reviewed.

Goal of the analysis

The identity of the chemical product can not be revealed for confidentiality reasons. However the purpose of coupling Raman spectroscopy to the manufacturing unit is the following. This product "x" is one of the constituents of a complex chemical product, and has to be neutralised at a further step of the process. The product "y" used for neutralising it is highly toxic and therefore, only the right amount should be added to the original mixture. Deriving the concentration of "x" consequently allows a proper dosage and avoids further re-treatments, which would otherwise be necessary.

If a Raman probe is not used, a different method of analysis has to be used to estimate the concentration. However, it requires sampling of the product and manual intervention for chemical dosage which make it rather inconvenient and expensive. For this reason, such analyses are done twice a day.

On the other hand, implementation of a ***continuous,*** on-line Raman method provides updated information within seconds or minutes of any changes in the product. The operator therefore has access to a detailed history of production that helps him to optimise the process conditions.

Experimental set-up

Plant installation

A remote Raman probe is directly installed at the production plant (fig.1).

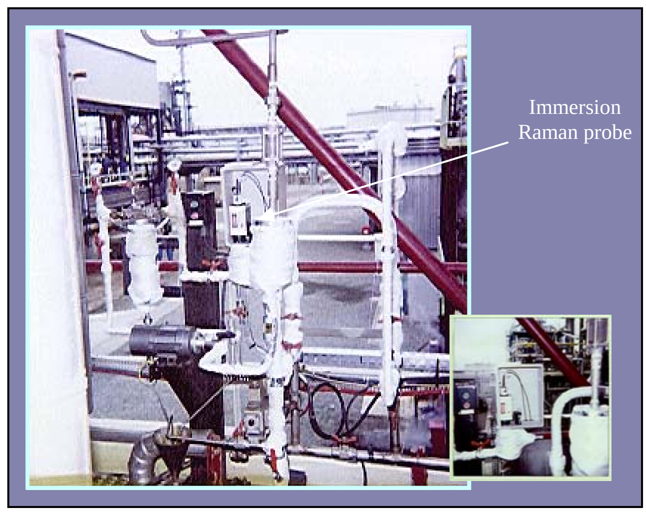


Figure 1 : Experimental set up at the plant

This probe is coupled via optical fibres to a spectral analyser (fig.2) installed in a pilot room located about 200 m from the sampling point.

The bypass device (fig.1) involves a pump for feeding purposes and a filtering stage to get rid of impurities that would otherwise generate fluorescence.

After filtering, the mixture enters a container in which the flow slows down to avoid emulsions. Indeed, too much turbulence can cause signal loss.

The immersion package with which the probe is equipped (fig.2) is made in such a way that the sampling optic can be selected in order to achieve optimum coupling to the analysed solution.

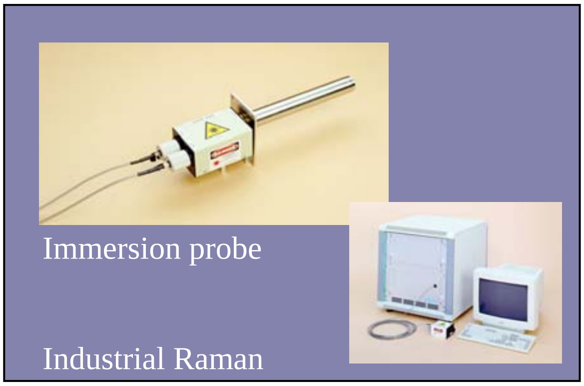


Figure 2 : Raman equipment

The industrial product in this example, generates fluorescence in the visible range, resulting in a very intense background that masks Raman data and prevents reliable measurements. The use of a near infrared laser source (namely 785 nm) is necessary to avoid the excitation of this fluorescence. In order to optimise the system for this range of the spectrum, specially selected detectors and optics are used. High sensitivity NIR detectors provide efficient detection in the near infrared range, even when the Raman signal is rather weak. In addition, NIR optimised optical fibres now exist that can transport signal over large distances (a few hundred meters).

Data are acquired using a very high throughput spectrograph, that is especially engineered to fit an industrial environment. Its compact and robust design, with no moving parts, makes it very stable and resistant. Its unique optical configuration allows the acquisition of the ***full*** Raman range in one shot. No scanning device is therefore required. Moreover, the various parts are mounted on separate units to be easily accessible in case of service intervention, such as laser source exchange.

Spectra-derived information is automatically updated every 3 minutes using dedicated software.
An additional multiplexing capability of the instrument allows the ***simultaneous*** recording of information from several sampling points. In this particular case, two productions units are monitored using the same Raman analyser.

As, for the chemical species of interest in this study, the Raman signal is unusually weak, so a repartition of the laser power between the two measurements points is not favourable. Consequently, to keep the integration time reasonable, the system works under a ***sequential*** operation mode, which means that the full laser power is distributed in turn to each probe.

Spectral data analysis

Spectra of solutions with different concentrations of the target product are shown in figure 3. Only the interesting spectral range is considered. The “A” band is associated with the species to be monitored, “B” and “C” bands correspond to other constituents for which the concentration is constant.

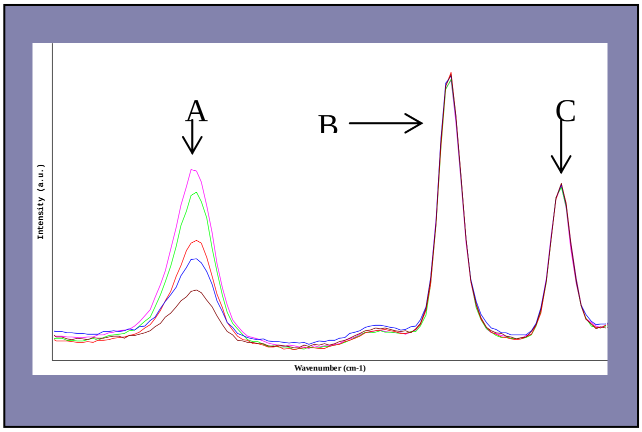


Figure 3 : Spectra showing intensity variations according to concentration changes

To get rid of external fluctuations that could effect the quantitative analysis (laser intensity, sample transparency, flow variations, temperature…), the ratio between bands A and B or C is calculated (B or C being used as normalisation bands).

A calibration is directly realised at line to determine the correlation between spectral band intensity and concentration. From this relationship, the software can then make on-line predictions on samples of unknown concentration.

Concentration profiles and values are displayed on a computer screen (fig.4). An example is given for a system where four hands are connected. The four associated windows appear on the screen, in which the four spectra are simultaneously displayed. In each spectrum, one can select by means of cursors the Raman bands associated with the components which one wishes to be quantified. The resulting intensity or concentration profiles can be plotted below accounting for the evolution of the process.

The user can pre-define output values that are displayed on the right side of the screen and that are calculated from the intensity values of the pre-selected Raman bands.

Figure 4 : Example of IndSpec software display when four measurements points are considered. Concentration profiles and values are automatically calculated and displayed on the screen, as shown on the left upper corner for one of the spectrum.

The spectra and derived concentration data are stored in a spreadsheet format from which evolution diagrams can be plotted.

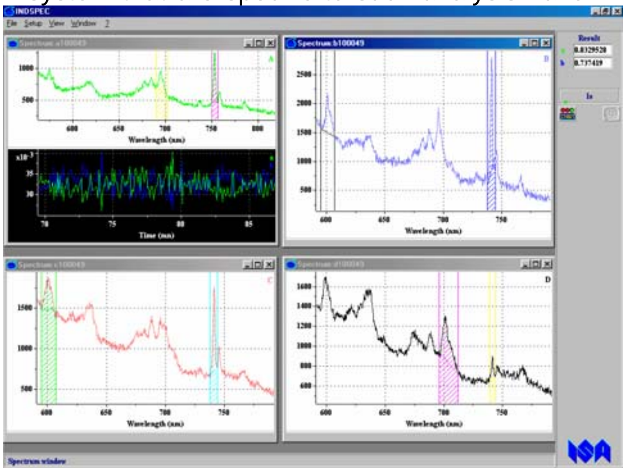
Simultaneously, data is transferred to the unit pilot board, for example via a digital/analogue converter that releases 4-20 mA electronic signals. These quantitative data must lie within a well defined interval to attest of the good quality of the product. When out of the range values occur, this results in the activation of alarms that reveal problems in the process. This enables faster detection and operator intervention when problems do occur.

If the monitored products at the different sampling points are not similar, different calibration functions can be entered into the software so that each specific component is analysed and quantified separately.

Because of the engineering concept, implementation, and automation of such recent Raman systems, the operator no longer needs to be familiar with spectroscopic techniques. He has direct access to the information of interest, which are in this example concentration values.

Summary

The application of Raman spectroscopy to on-line monitoring of chemical products has been described. The important functions of the system that are specific to such analysis have



been highlighted.

Recent developments in the field of detectors, laser sources and software have made such analysers more compact and reliable, as well as easy-to-use. For an important number of industrial processes, Raman spectroscopy has become the analytical tool of choice for on-line applications.

HORIBA JOBIN YVON

France : HORIBA Jobin Yvon S.A.S., 231 rue de Lille, 59650 Villeneuve d'Ascq. Tel : +33 (0)3 20 59 18 00, Fax : +33 (0)3 20 59 18 08. Email : raman@jobinyvon.fr www.jobinyvon.fr
USA : HORIBA Jobin Yvon Inc., 3880 Park Avenue, Edison, NJ 08820-3012. Tel : +1-732-494-8660, Fax : +1-732-549-2571. Email : raman@jobinyvon.com www.jobinyvon.com
Japan : HORIBA Ltd., JY Optical Sales Dept., 1-7-8 Higashi-kanda, Chiyoda-ku, Tokyo 101-0031. Tel: +81 (0)3 3861 8231, Fax: +81 (0)3 3861 8259. Email: raman@horiba.com
Germany: +49 (0) 6251 84 75-0 **Italy:** +39 02 57603050 **UK:** +44 (0)20 8204 8142
China: +86 (0) 10 6849 2216