Introduction of Non-destructive Elemental Analysis for In/Online Through Real Case Studies

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Automation and labor saving in the manufacturing process of industrial products have been adopted for the purpose of lower cost and higher quality. Inline analysis and online analysis are required actually to reduce labor costs and to perform full inspections, which used to be limited to sampling inspections. X-ray fluorescence analysis is a non-destructive and a non-contact method of elemental analysis, which was used mainly in laboratories. Now, it becomes to be applied to inline film thickness measurement in roll-to-roll processes, and online measurement of elements contained in oil, plating solution, wastewater, etc. In this report, examples of actual in-line and on-line measurements are presented.

Introduction

X-ray fluorescence analysis is a common analytical technique used mainly in laboratories. The energy and intensity of the X-ray fluorescence emitted when a sample is irradiated with X-rays reveal the elements contained in the material and their composition ratios. There are two types of methods: the wavelength-dispersive method, in which the wavelength of the X-rays is separated by a spectrometer for measurement, and the energy-dispersive method, in which the energy of the X-rays is analyzed for measurement. HORIBA has been manufacturing and selling energy dispersive instruments since 1971 and has a lineup of : XGT series which converges X-rays and irradiates them to a small area to perform elemental analysis and measurement of elemental distribution in a small area; MESA series which irradiates X-rays over a wide area from the underside of a sample on a sample tray, enabling elemental analysis; and SLFA series which measures sulfur contained mainly in petroleum products. On the other hand, the analysis needs of the market are also changing with technological advances. In the analysis of industrial products, automation to save labor and 100% inspection to ensure high quality are desired due to increased cost and quality awareness, and such requests from customers are increasing. Since X-ray fluorescence analysis is non-destructive and non-contact, elemental analysis can be performed at a wide variety of sites as long as a small analysis module is available. In this paper, we will introduce a case study of the application of the MESA-50,[1] a compact X-ray fluorescence analyzer with a footprint of A4 size and an extremely compact X-ray optical system. In-line and on-line automated analysis is applied to this optical system. The definition of in-line and on-line analysis in this paper is as follows. A conceptual diagram is shown in Figure 1.

In-line analysis:	Direct analysis of a moving measurement object.
On-line analysis:	The measurement object is diverged from the main flow and introduced into the analyzer.

In-line analysis

In in-line analysis, a sample in the form of a sheet such as a film, a substance coated on a film, or a sample moving on a conveyor belt is continuously measured. The installation method must be individually designed to suit the production line. Of particular importance for this inline analysis is the time resolution of the measurement and the accuracy of the analysis.

Industrial products in sheet form are usually manufactured in a Roll-to-Roll process (Figure 2) and operates at very high speeds. The measurement time of a typical XRF measurement is tens to hundreds of seconds, so even if a measurement takes only a few tens of seconds, the sheet may move several tens of meters or more at the fastest, and the object to be controlled may be “hidden” from the analyzer. The measurement variation in X-ray analysis depends on the statistical variability of the X-ray generation (the total number of counts of X-rays obtained), assuming that the electronics of the instrument are stable.

Since the variation is inversely proportional to the square root of time, a trade-off with the measurement variation must be considered in order to shorten the measurement time. Although counts can be obtained by irradiating high intensity X-rays for a short time, the problem is that a large amount of X-rays saturates the detector, making it impossible to measure. To improve the saturation of the detector, the processing of the detector signal is speeded up. Normally, in energy-dispersive X-ray fluorescence analysis, the trapezoidal processing of signals (Figure 3) is performed with sufficient signal processing time per signal to ensure the energy resolution of the detector. This process causes a dead time during the measurement. By shortening the trapezoid processing time, the dead time is reduced and more signals can be received. This is an effective measure for in-line measurement where the energy resolution is poor because the target element is fixed, but the effect of interference with other elements is small. In addition to this, only the intensity of the required element is extracted to speed up the measurement.

Figure 4 plots the measured values of a stopped Ni foil of 2 µm thickness analyzed at 200 ms. The mean, standard deviation, and RSD of this measurement are shown in Table 1. Good results were shown for an XRF measurement with a very short time resolution.

Figure 5 shows the measurement results when samples with different thicknesses were operated. It can be seen that the thickness trend is obtained according to the difference in thickness. The shape of the measurement points per measurement can be calculated by the formula in Figure 6.

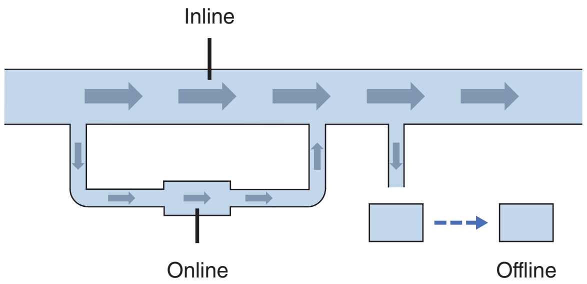

Figure 1 Conceptual diagram.

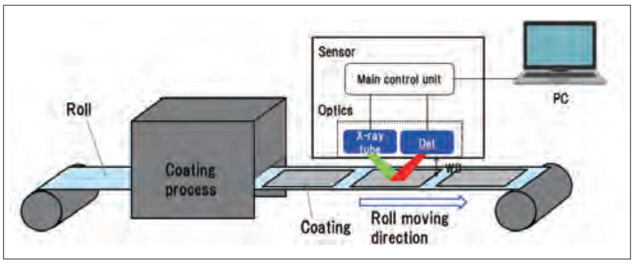

Figure 2 Roll to Roll process.

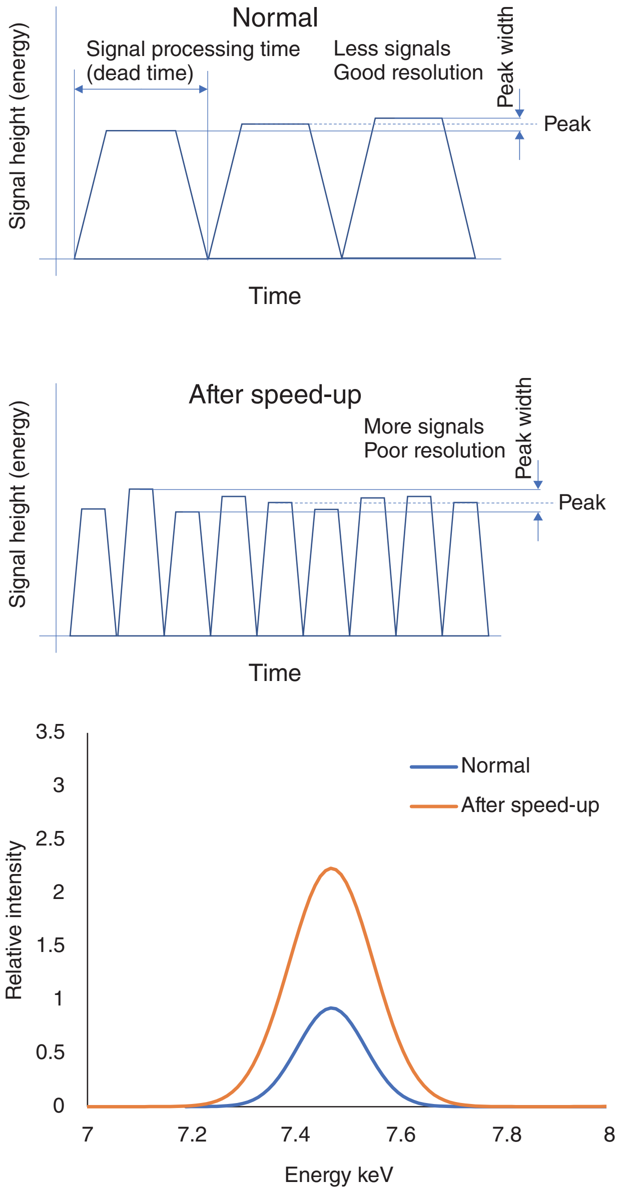

Figure 3 Signal processing.

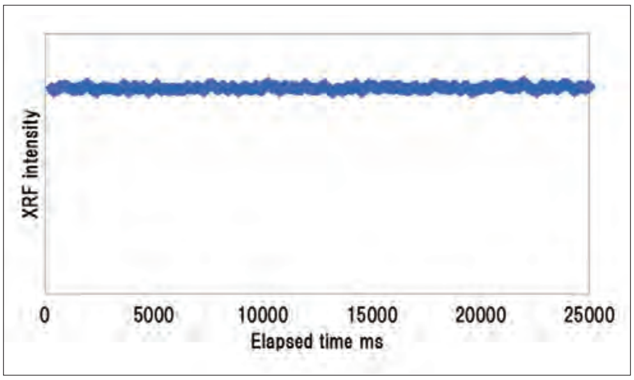

Figure 4 Result of 200 ms continuous measurement.

Table 1 Measurement results when the Roll is stopped.

Measured value µm	2.01
Standard deviation µm	0.02
RSD %	0.995

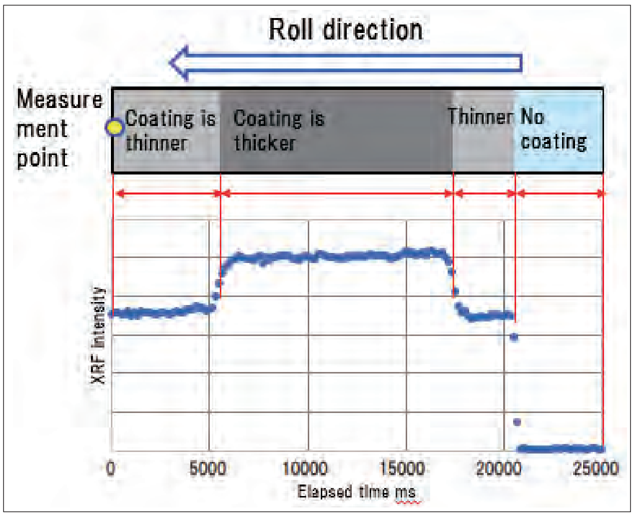

Figure 5 Measurement results during Roll operation.

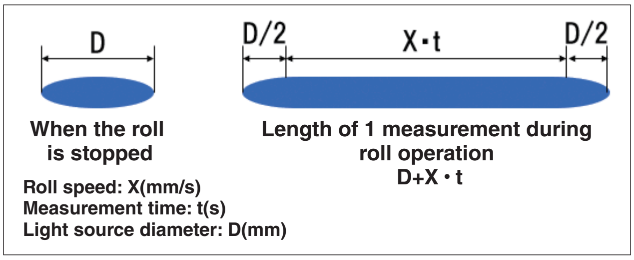

Figure 6 Shape of measurement point.

On-line Analysis

In on-line analysis, continuous measurement (Figure 7) of a liquid sample supplied through piping to a flow cell set in an analyzer is performed. The structure of the flow cell (Figure 8) determines the performance of the analyzer, and although a thin resin film that easily transmits X-rays is often used for the X-ray irradiation section, a sturdy film with a certain thickness should be used in consideration of leakage of the liquid sample and deformation of the film during measurement. If the pumping pressure is high before branching, it is necessary to reduce the pressure before introducing the film into the cell in order to prevent damage to the film. When using a pressure reducing valve, cleaning should be taken to avoid clogging with solids.

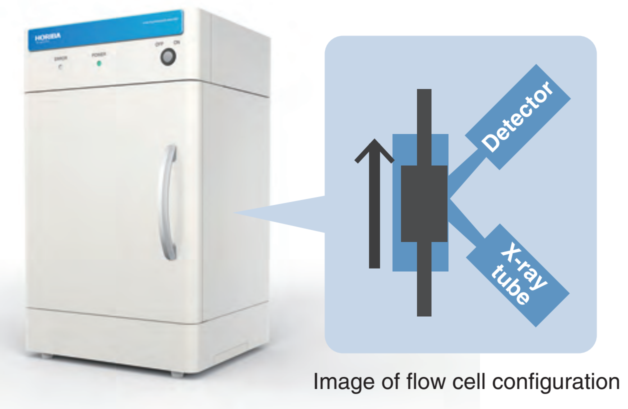

Figure 7 Flow example of MESA-50U.

When a highly viscous liquid sample is introduced, it may be heated to reduce the viscosity of the sample, and a sturdier film should be selected. A thicker film is more difficult for X-rays to pass through so there is a trade-off with analytical accuracy.

When measuring a liquid sample passing through a flow cell, if the sample adheres to the piping or the inner surface of the flow cell, the sample is measured by irradiating X-rays to a mixture of the residual liquid and the liquid that is currently passing through, and correct analysis values cannot be obtained. Therefore, it is desirable for the liquid sample to be replaced instantly. To achieve high replacement performance, it is necessary to eliminate protrusions in the piping and flow cell, and to use a material with good sliding properties for the inner walls. Figure 9 shows a graph of replacement performance when analyzing a heavy oil sample. It can be seen that the analysis values of the 0.2% sulfur and 1.0% sulfur samples switch within a few minutes.

If the replacement performance is not sufficient, a cleaning solution from another line is introduced to flush out the deposits on the piping and the inner wall of the flow cell. If the deposits are still not removed, or if a more accurate analysis is required, the piping and flow cell should be replaced with new ones.

If stable measurement is not possible due to deformation of the film caused by the flowing liquid sample, a valve can be installed after the branching to stop the flow to the flow cell (Figure 10). However, consideration must be taken to ensure that the replacement performance is not impaired by the retention of liquid sample by the valve.

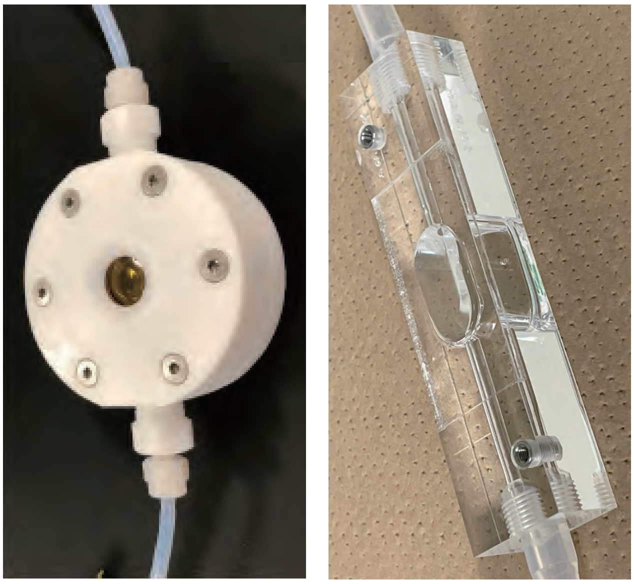

Figure 8 Example of flow cell.

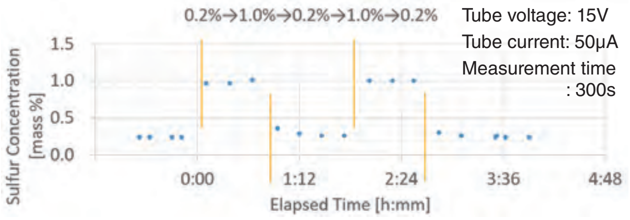

Figure 9 Replacement performance Data example (Heavy oil C).

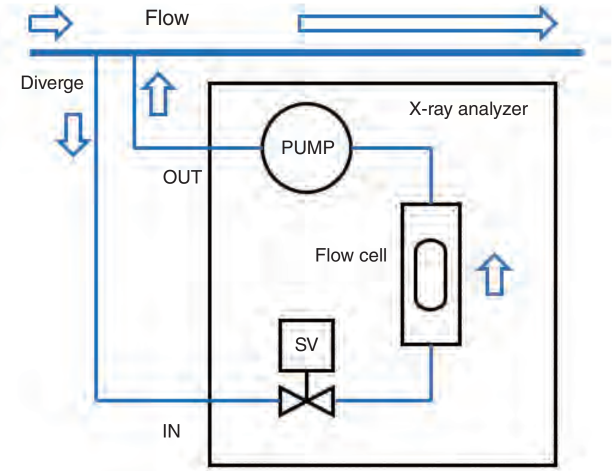

Figure 10 Flow example.

Conclusion

As described above, in-line and on-line analysis enables the acquisition of a large amount of continuous data that would not be possible with human intervention. The large amount of data obtained enables early detection of abnormalities occurring in the process and trend management, which may lead to the discovery of events that could not be detected by laboratory analysis, in addition to automation and labor savings. We hope that the in-line on-line analyzers introduced in this paper will be widely used in various industrial product manufacturing sites.

* Editorial note: This content in based on HORIBA's investigation at the year of issue unless otherwise stated.

References

[1] T. Aoyama, X-Ray Fluorescence Analyzer MESA-50, Readout, 2013, 40, p.30-33,

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