

Industrial and Environmental Applications of X-ray Fluorescence Spectrometry

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Role of X-ray Fluorescence Spectrometry in the Plastics and Petrochemical Industry

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Software Developments for X-ray Fluorescence Spectrometry

Many of the improvements to X-ray fluorescence (XRF) instrumentation in recent years have come as a result of developments of software rather than hardware capability. One aspect of XRF spectrometry that has often been neglected is the area of qualitative analysis. This is probably because a complete spectral scan can occupy considerable instrument time, and the interpretation requires human time and expertise. The results reported are often operator dependent. Software packages are now becoming available that eliminate much of the manual effort, are less person dependent, and by faster scanning speeds and/or overnight operation, interfere much less with the daily work pattern.

ICI have developed their own software package for automating qualitative XRF analysis. Initially, a data file is produced by scanning the sample over the complete X-ray spectrum (0.34–20 Å) using a minimum of three crystals. The first stage of the computer program is to convert the count data to spectral data via a nine-point smoothing routine (Savitzky - Golay). The peaks are picked from the second differential and a wavelength is assigned to each peak. Possible identities for each peak are determined from a database of X-ray spectral lines. The net peak count rate is computed from adjacent background values.

Elements are tentatively identified by the presence or absence of a major transition ($K\alpha$ or $L\alpha$). The more detailed interpretation considers lesser transitions and higher order lines. Where multiple identities have been assigned (possible line overlap) the intensity ratios of the transitions (e.g., $K\alpha:K\beta$) are considered. The computer print-out serves two purposes: (1) to give the analyst a clear indication of how the X-ray spectrum has been interpreted; and (2) to give the customer a summary indicating the elemental composition of the original sample. For qualitative work the elements are categorised as major, minor or trace. If the sample is available in the form of a finely ground powder it is possible to provide semi-quantitative information. This is achieved by presenting the powder smeared across a support window to simulate a thin film. Matrix effects are minimised in this way and 1% standards produce an effective calibration.

Another example of software which is likely to make a stronger impact in the future is a program used for quantification based on fundamental parameters. This approach, to calculate elemental concentration from X-ray intensities, is

founded almost entirely on theoretical considerations. The main disadvantage of empirical methods of matrix correction is the reliance on a suite of known standards. Fundamental parameter methods do not need this. In the past their application has been limited by the lack of user-friendly software, and often restricted to the types of analyses where all sample elements can be measured (thus allowing normalisation), e.g., metal alloys. Better software is now available that, for instance, can be used to determine components in complex engineering plastics where matrix effects can be severe. Zinc (as zinc borate), chlorine (as dechlorane flame retardant), antimony (as oxide) and fibre-glass have been determined in nylon using just one standard. The better programs allow the analyst to describe a compound, such as glass or the polymer, by either a chemical formula or by the percentage of each element in the compound. In this particular instance, better results were achieved by using Ca $K\alpha$ as the marker element for glass, rather than Si $K\alpha$.

Surface Measurements

One area where XRF can be effective is in differentiating the composition of the surface of, for example, a plastic moulding from the bulk composition. One way is to remove the top layer by rubbing with an abrasive paper—a technique originally developed for sorting metal alloys with the minimum sample requirement. This takes a total sample mass considerably less than 1 mg but thinly spread over the surface of the abrasive paper disc. Hence it is possible to obtain a distinct spectrum from an energy dispersive (ED) XRF analyser and produce at least semi-quantitative information. We now prefer to use fine (30 μm) diamond on a polyester backing rather than the original wet and dry abrasive paper.

Alternatively, by careful selection of a characteristic line with a relatively small critical depth, measurements can be made which only relate to the very surface of a sample. By progressively removing thin layers from the surface, a profile can be built up monitoring the element intensities each time the plastic is skimmed on the lathe. The values given in Table 1 are indicative of the changes in concentration that take place.

XRF for Plant Analysis

X-ray fluorescence analysis is being used increasingly in a works environment.¹ Apart from technical performance, an important consideration is that once the instrument has been calibrated, routine operation of the equipment should be

Table 1. Surface effects on flame retardant nylon moulding

	Analyte line					
	Si Kα	Cl Kα	Zn Lα	Zn Kα	Sb Lα	Sb Kα
Wavelength/Å	7.13	4.73	12.25	1.44	3.44	0.47
Critical depth/μm	30	70	8	580	60	13 000
Depth removed/μm	X-ray intensity/10 ³ counts s ⁻¹					
0	37.5	79.6	3.58	134.3	43.9	110.8
10	42.0	77.6	3.80	134.1	43.4	110.8
20	61.6	74.2	3.80	133.4	41.9	110.4
50	81.2	70.3	3.71	132.6	40.6	109.4
90	82.1	70.1	3.67	132.6	40.7	108.6
150	77.7	71.5	3.62	132.4	41.5	107.3
170	77.3	71.0	3.71	132.3	41.3	106.5
240	80.1	70.9	3.60	131.7	41.4	104.9
270	77.3	71.4	3.65	131.6	41.5	103.7
380	77.9	72.5	3.62	131.6	42.3	99.9

straightforward to non-specialist personnel. In addition, training for new laboratory staff should be relatively simple. Two types of instrument which come into this category, and are similarly priced, have been considered for quality control type applications in ICI. These machines have been evaluated for determining trace and minor components in polypropylene and polyester plastics.

The first is a compact simultaneous wavelength dispersive (WD) XRF instrument [e.g., Oxford QX spectrometer (Oxford Analytical Instruments)]. The QX spectrometer has the advantage of increased sensitivity for the low elements, e.g., a few p.p.m. of phosphorus in the low atomic number matrix. There is a limit of ten channels (elements) that can be fitted to the machine. However, two of these fixed channels can be replaced by a scanning channel. This is equipped with an LiF crystal and sealed proportional counter and hence can measure from K to Mo (K lines) and Sn to U (L lines). The other disadvantage with simultaneous instruments is the lack of count information on the background regions. This could be a disadvantage with the measurement of granules or powders which can suffer from variable packing density and hence variable scattered background. We simulated a background position by setting up a channel on the $I_{L\alpha}$ line (this element was absent in our samples). In practice our results on polymer granules showed very little variation due to surface effects.

The alternative is an ED-XRF instrument (e.g., Tracor TX-5000). This analyser has the advantage of increased flexibility, i.e., the ability to identify and measure elements across the Periodic Table (above Na). However, if the plant laboratory has a fixed number of routine tests and no requirement to measure unknowns, then this may not be much of an advantage. Sensitivity in the mid-range elements is comparable to the QX instrument for our element/matrix systems. Choice of instrument type depends on the actual application envisaged.

On-line XRF Analysis

The application of modern XRF analysis techniques can be most beneficial when an instrument is installed on-line to monitor the concentration of various components (elements) that are essential for the efficient running of the plant. ICI has installed a Tracor TX-7000 ED-XRF analyser on a terephthalic acid plant. The instrument monitors catalyst concentrations in the organic liquor. Control of catalyst concentration is important for the efficiency of the oxidation of *p*-xylene and to prevent loss of the acetic acid medium. The active part of the analyser head is a flow cell through which the liquor is pumped. The corrosive nature of the medium demands careful selection of materials: 316 stainless steel is used for the cell body and 50 μm Kapton (polyimide) film for the cell window. The sample is excited by an Rh target X-ray tube (18 kV). The spectral information is captured by an Si(Li) detector with a Peltier cooling system as an alternative to the normal cryogenic system. This eliminates the need for regular topping up of the liquid nitrogen dewar.

Energy resolution is marginally poorer with this device (ca. 180 eV) but sufficient to resolve the peaks of the elements of interest (Mn, Co and Br). Under compromise conditions (18 kV, 0.3 mA, Al beam filter) a spectrum can be accumulated in 200 s live time. A special calibration cell has been used to set up the system over the range 0–300 p.p.m. of cobalt, 0–300 p.p.m. of manganese and 0–800 p.p.m. of bromine. Cross-checks have also been made with analyses carried out in the plant laboratory.

Reference

1. Warren, P. L., Farges, O., Horton, M., and Humber, J., *J. Anal. At. Spectrom.*, 1987, 2, 245.