UniQuant® 5

On methods of intensity measurement in XRF analysis
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Smart-Variable-Step (SVS) scanning versus Fine-Step (FS) scanning

Climbing the highest mountain

In conventional quantitative XRF analysis, intensities are measured at fixed spectral positions. Almost ten years ago, spectrometer manufacturers started to make software for analysing totally unknown samples for which no standards are available. They have all chosen the same method of intensity measurements, namely by Fine-Step (FS) scanning of the X-Ray spectrum. At the same time, the present author started to develop the UniQuant software which is based on far better concepts. It was like choosing the highest mountain to climb. Others may reach the top of a mountain only to find out that their mountain is much lower than Mount UniQuant. Like conventional methods, UniQuant is based on intensity measurements at fixed spectral positions. Although UniQuant was originally intended for standardless analysis of totally unknown samples, it has been so far developed that with the use of standards and regression analysis, it may give results that are as precise and accurate as with conventional XRF analysis.

The advocates of Fine-Step scanning

In sales situations and at symposia, sometimes it is emphasised that Fine-Step scanning is far better than measuring at fixed positions, in particular in view of trace analysis.

If this would be true, why then is conventional quantitative XRF analysis based on fixed spectral positions and not on Fine-Step scanning? The arguments used are clearly in defence against UniQuant. This leaflet reviews several of the false arguments in favour of Fine-Step scanning.

What is Smart-Variable-Step scanning?

In SemiQuantitative (**SQ**) programs, intensity measurements are generally done by Fine-Step (FS) scanning of the wavelength spectrum. In contrast, the quantitative UniQuant (**UQ**) program prescribes measurements to be made at about 100 spectral positions. The goniometer scans the entire spectrum in varying steps from one position to the next, where each position corresponds with an XRF wavelength of one of 79 elements. We refer to this method as Smart-Variable-Step (SVS) scanning. The predicate 'Smart' is used here because for a given total time per sample, all potentially present elements are measured with highest possible precision.

Relative Merits

To appreciate the relative merits of both FS and SVS scanning methods one should be aware that the SQ programs and UniQuant differ fundamentally in their concepts of finding net peak intensities, which are the gross peaks corrected for background continuum and spectrally interfering XRF lines.

SQ: The concept of SQ programs makes the use of FS scanning mandatory. This is because, for the purpose of line overlap corrections, very many (over a thousand) spectrally interfering lines must be measured in addition to the about 100 analyte lines.

UQ: Due to its concept, UniQuant can abstain from measuring any of the potentially 3000 interfering lines and devote all its time to the 100 analyte lines.

SQ: When an interference is strong, an SQ program may itself search an alternative free analyte line. If things get difficult, the help of the analyst is required and this is where the use of spectrograms comes in.
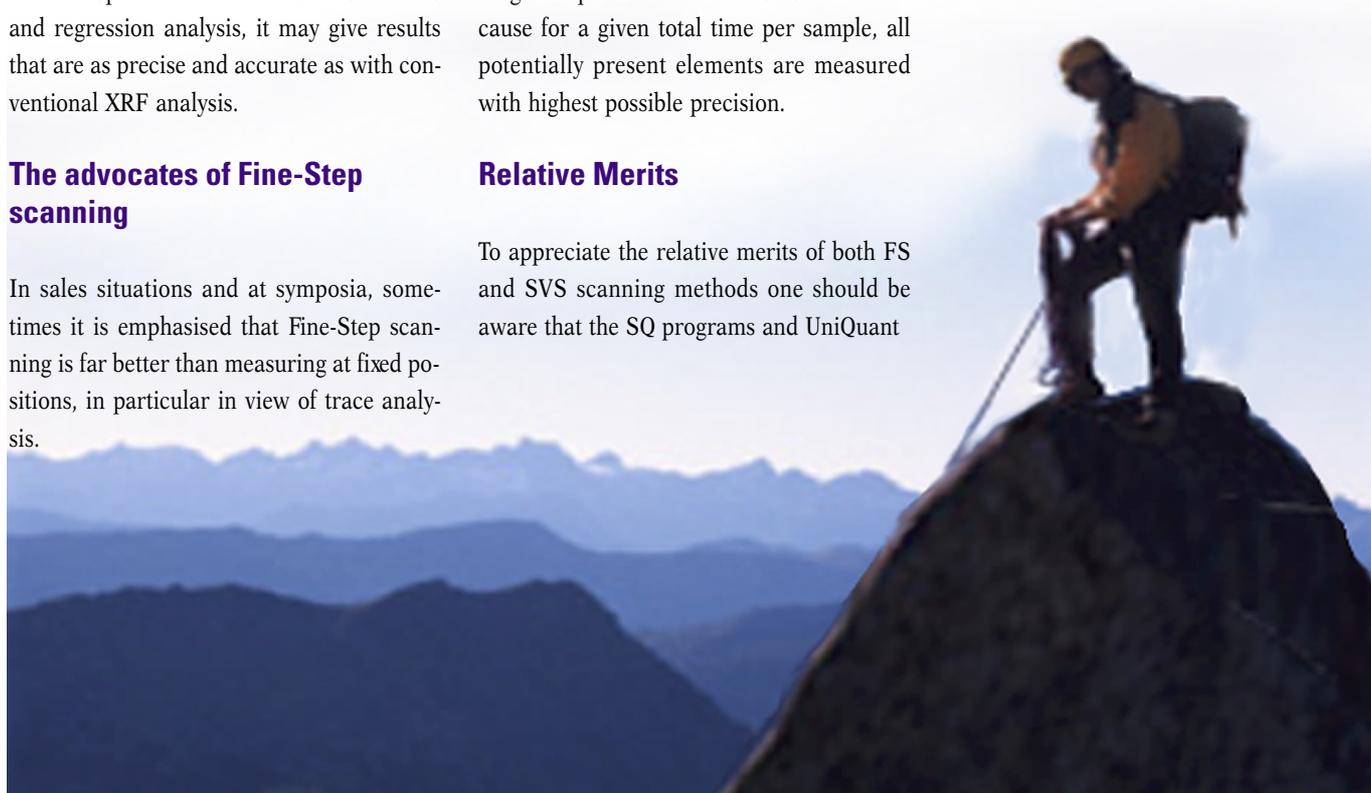
UQ: In the results obtained from each analyte line, UniQuant gives a full quantitative account of corrections made for the various line overlaps. Thus it tells exactly which elements caused an interfering line and to what extent in equivalent mg/kg. What is the magic here? The answer is that UniQuant fully exploits the combination of two favourable facts:

- Modern spectrometers can be programmed for spectral positions (wavelengths) with a very high precision.
- Both analyte XRF lines and interfering XRF lines are always at their same spectral position (apart from chemical shift of soft XRF lines).

Thus, there is no need for scanning and/or searching.

Trace Analysis

SQ: With SQ programs, scanning speed must be relatively fast in order to keep the total measuring time within 15 minutes. This fast scanning leads to relatively large counting errors. To partially compensate for this, instrumental parameters are chosen for highest possible intensity. However, this is at the expense of spectral resolution making the line overlap corrections even more difficult. The time of scanning across XRF lines of trace elements is so short that their intensity may not be distinguishable from the stochastic fluctuations of the background. On the other hand, the same fluctuations are easily mistaken as peaks from a trace elements. A partial solution of this problem is possible for samples of which it is known which trace elements can be expected and which not. The analyst may then enter certain directives to the program for the scanning speed to slow down where it may be useful or to skip specified ranges of the spectrum assuming that these do not contain lines from unexpected elements. It should be clear that such specific approach may not work for less well known samples.

UQ: UniQuant measures trace elements much the same way as in conventional analysis, that is with fixed time, 10 seconds for example. This is a factor 100 longer than with FS scanning, where the dwelling time in the vicinity of the peak is as low as 0.1 seconds. As a consequence, with UniQuant, Detection Limits are better by a factor 10 with respect to SQ programs if the latter are not tailored to samle specific conditions.

What about background calculations?

The most simple case is that of an XRF peak without any spectral interference in its vicinity. The background under the peak can easily be calculated from additional measurements at both sides of the peak. Any program can do that. However, the situation is far less simple when a lot of interfering lines are cluttering in the vicinity of the analyte line.

SQ: It may be impossible to find a spectral position in the vicinity of the analyte line that is suitable to measure a background intensity.

UQ: In such cases, the background may be determined by considering a wide spectral range, like one would do visually. This is exactly what UniQuant does. Fine-step scanning would not have an advantage. On the contrary, fine-step scanning tempts to look at too small spectral ranges with the danger of overestimating backgrounds.

What about confirmation by other lines of the same element?

Suppose that Zr is analysed by its ZrLa line. If this line gives a net intensity whilst Zr is not expected to be present, one may suspect that the ZrLa peak intensity is due to a spectral interference by a line from another element or by a spectral impurity of the radiation that is incident to the sample. In order to verify if indeed Zr is present, one may check

the intensities of other XRF lines of Zr, like ZrKa and ZrLb.

SQ: If a fine-step scan was made across the entire spectrum, data for ZrKa and ZrLb are available. This is sometimes presented as an advantage for FS scanning based SQ programs. The truth is that such verification may be very much needed by SQ programs.

UQ: By contrast, for UniQuant such checks are not required. This is because, as part of its results, UniQuant gives a full account of which parts a peak intensity is composed of, namely:

- Background continuum in equivalent mg/kg.
- Spectral impurity in equivalent mg/kg.
- Spectral line overlaps in equivalent mg/kg and from which elements.
- Counting error in equivalent mg/kg and this is possible for UniQuant because it measures with fixed times at the spectral positions of interest.