

Tru-Q® – Making Accurate Analysis a Reality for All

Introduction

Tru-Q is a unique combination of new and existing technologies that make the promise of automatic, real-time element identification and composition determination a reality. These technologies include:

FLS – Robust algorithm for removing the X-ray background from the spectrum and fitting peak profiles of the identified elements to calculate peak areas that does not require any user set up.

QCAL – New and unique approach to determining the precise position, resolution and shape of all element peak profiles to bring a new level of accuracy to both the calculation of peak area and the intensity relative to that of a pure element (“k-ratio”).

XPP – The Matrix correction algorithm to convert k-ratios to element concentrations that has been proven to give more accurate results on all types of samples

PPC – Improved version of our special algorithm for predicting pile-up X-rays present at very high count rates and putting them back in their correct place in the spectrum

AutoID – Improved algorithm to analyse peak content of a spectrum and deduce the elements responsible, even when there are severe peak overlaps

By combining these technologies **AZtec®** offers unrivalled quality of results including automatic peak identification and automatic standardless analysis with no user intervention, even when data are collected at high count rates and short acquisition times. This note covers the main technology details and shows that with Tru-Q you can obtain quantitative results with an accuracy only previously achieved using well characterised and closely matched standard materials. Tru-Q is an important component in the hardware and software provided by Oxford Instruments that delivers reliable results in seconds using the speed of **Ultim®** Max and **X-Max®** silicon drift detectors (SDD).

Li 3 6.939 Lithium K α 0.0544 ρ 0.534	Be 4 9.012 Beryllium K α 0.1088 ρ 1.85	
Na 11 22.990 Sodium K α 1.0410 ρ 0.97	Mg 12 24.312 Magnesium K α 1.2536 ρ 1.74	
K 19 39.102 Potassium K α 3.3129 ρ 0.86	Ca 20 40.08 Calcium K α 3.6905 L α 0.3413 ρ 1.53	Sc 21 44.956 Scandium K α 4.0892 L α 0.3955 ρ 2.99
Rb 37 85.47 Rubidium K α 13.3757 L α 1.6942 ρ 1.53	Sr 38 87.62 Strontium K α 14.1429 L α 1.8066 ρ 2.60	Y 39 88.905 Yttrium K α 14.9334 L α 1.9226 ρ 4.47
Cs 55 132.905 Caesium L α 4.2865	Ba 56 137.34 Barium L α 4.4663	La 57 138.91 Lanthanum L α 4.6510 M α 0.8332

FLS – Filtered Least Squares Fitting

To measure the number of X-rays in a spectrum due to each constituent element it is necessary to remove the contribution of the X-ray background. There are two accepted ways of doing this; by fitting a theoretical background, and by removing it with a ‘top hat’ filter (Figure 1). Since the 1970s Oxford Instruments has used the FLS approach because it is a robust, operator-independent method that does not require any operator “tuning” in order to achieve good results. Therefore the results obtained are highly reproducible and can be provided in a completely automated way. With the background fitting approach immediate “out of the box”, standardless analysis is not possible as the operator is required to enter positions in the spectrum for background fitting and these positions depend on what elements are present. The FLS approach is therefore ideal for novice and occasional users. Furthermore, the ability to deliver immediate quantitative results is particularly useful in combination with SDD detectors because useful data can be obtained in extremely short acquisition times so that real-time analysis is possible.

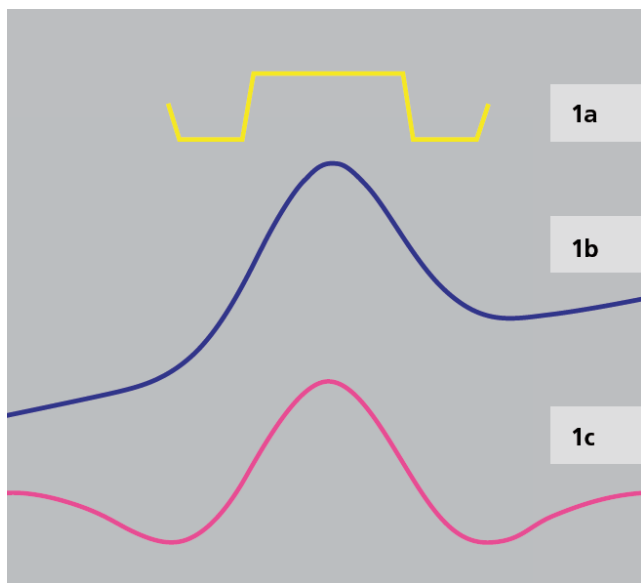


Fig. 1. FLS approach to background removal, (Statham, 1977, *Anal. Chem.* 49), 2149-2154. A ‘top hat filter’ (1a) is used to filter the spectrum (1b). The result of the filter is a bi-polar spectrum where background contribution is zero and positive and negative peak areas sum to zero (1c). By using the same filter on the element peak profiles; these can be fitted to the filtered spectrum and the peak areas for each element calculated.

QCAL – Complete hardware chain characterisation

The key requirement of automatic element ID (AutoID) and standardless quantitative analysis is to determine accurately the area under a peak for each element, even where peaks for different elements overlap. To achieve this it is vital to know precisely the peak profile for each element under all circumstances. This includes the width, position and shape of each peak profile (Fig. 2).

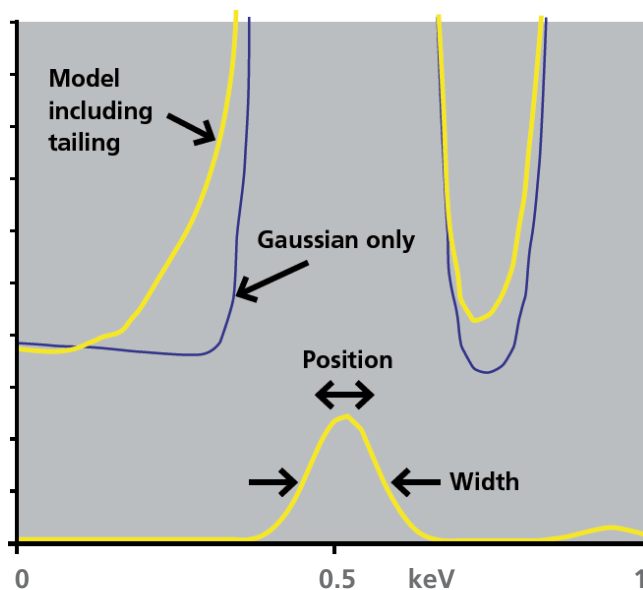


Fig. 2. Important factors that describe the characteristic profile of an element peak in an EDS spectrum. Spectrum from pure Ti at 20kV shown with two scales differing by a factor of 100. (Statham 2002, *J. Res. Natl. Inst. Stand. Technol.* 107, 531–546).

The relative sizes of X-ray peaks in a spectrum are rarely in proportion to the element concentrations. X-ray production varies dramatically with the energy of the X-ray peak and the number of X-rays detected depends on parameters that affect the efficiency of the detector such as transmission through the detector window and contact materials. All the components of the hardware chain, including detector, pre-amplifier and pulse processor, will affect how the emitted X-rays are translated into the spectrum that the software receives, for example each X-ray line of single energy becomes a broad X-ray peak. Therefore as part of **AZtec** development Oxford Instruments has characterised the complete hardware chain to understand, measure and parameterise all factors that influence quantitative accuracy.

This approach is embodied in QCAL, a quantitative calibration approach that delivers a unique set of parameters and an efficiency curve for each hardware type:

- **Ultim** Max 170 and 100
- **X-Max** 150, 80, 50 and 20
- **x-act**

This level of characterisation has only been possible because of the control of design and manufacturing process that Oxford Instruments has over all its hardware components including detectors and pulse processors. The following table gives some of the important parameters characterised by QCAL for each hardware type compared with alternative more generic approaches.

Parameter	QCAL Approach	Generic Approach	Benefit
Efficiency	Measure efficiency of hardware vs Energy (Efficiency Curve) for complete detector chain including window	Assume efficiency from manufacturers specifications e.g. window thickness	Precise understanding of how many X-rays to expect at each energy – therefore accurate determination of relative concentrations
Linearity	Characterise any non-linearity vs Energy	Assume hardware is linear	Improved accuracy of deconvolution when there are close overlaps
Dispersion	Characterise Dispersion (resolution) vs Energy	Use text book equations to determine Dispersion vs Energy	Improved accuracy of peak area measurement and improved deconvolution of close overlaps
Charge collection	Find optimum tailing parameters for all peaks	Assume peaks are always Gaussian	Better corrections for peak overlap in regions of the spectrum where tailing is significant
Rise time	Measure distribution of rise times to establish optimum pulse processor settings for ballistic deficit correction	Ignore ballistic deficit issues and get an additional uncharacterised tailing contribution on low energy side of peaks	Set up pulse processor for the optimum trade-off of speed vs peak shape to ensure accurate shape characterisation for all sensor sizes and count rates
Pulse pile-up	Characterise pile-up rejection capability and establish optimum settings for correction software	Assume constant and not dependent on timing and energy of pulses	The ability to predict which X-rays are pulse pile-up and correctly return them to the correct energies enables accuracy to be maintained at high count rate. Accurate characterisation avoids spectrum dependent artefacts and inaccuracies

This attention to detail in QCAL is necessary in order to deliver acceptable quantitative results without standards. The new level of accuracy of profile characterisation has facilitated further improvements to the accuracy of Oxford Instruments field-proven AutoID routine, particularly in reporting contributions of elements that are extremely closely

overlapped (e.g. Si K/ Ta M/ WM series). In addition, by using a single beam current calibration, QCAL allows **AZtec** to deliver true standardless analysis, with results similar to that which would normally only be achieved by using a full standards block to calibrate for every element.

Tests of un-normalised quantitative analysis using QCAL compared to the non-QCAL approach, using data from elements B-Bi obtained at 20kV, show that relative errors of 5% or less can be achieved for concentrations above 1 wt%. This represents a substantial improvement over what is achieved without QCAL (Fig. 3).

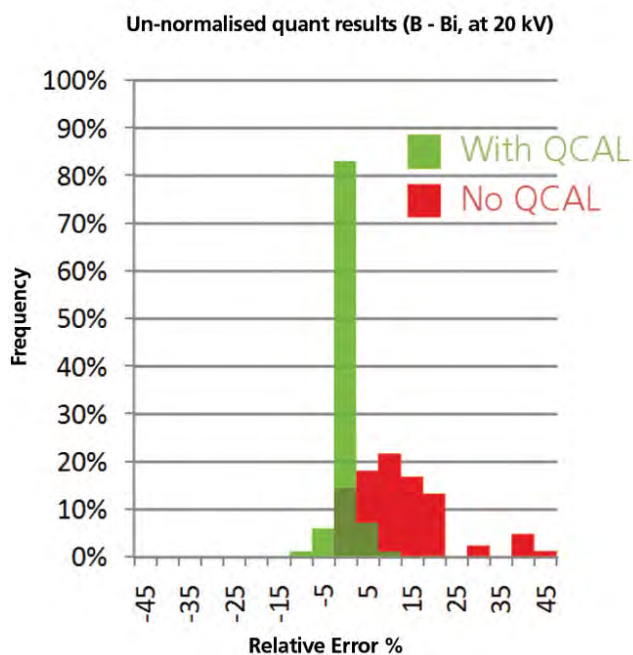


Fig. 3. Tests of un-normalised quant shows that, with QCAL, most errors are reduced to less than 5% relative, a level of accuracy only previously possible using standards-based analysis.

This result compares very favourably with a study by Newbury (1999) *Microsc. Microanal.* 4, 585-597, that found commercial systems typically gave relative errors of +/- 25% relative. What is particularly noteworthy is that the Newbury test, unlike the current tests, excluded the more difficult light elements (and calculated oxygen by stoichiometry) and also excluded elements of less than 5 wt%. Furthermore, results were normalised to a total of 100% (Figure 4a.) whereas without normalisation any absolute errors would have moved the centroid of the distribution away from 0% as seen for the non-QCAL results in Figure 3. In fact The QCAL results compare favourably with a study of standardised results presented in the same paper (Fig. 4b).

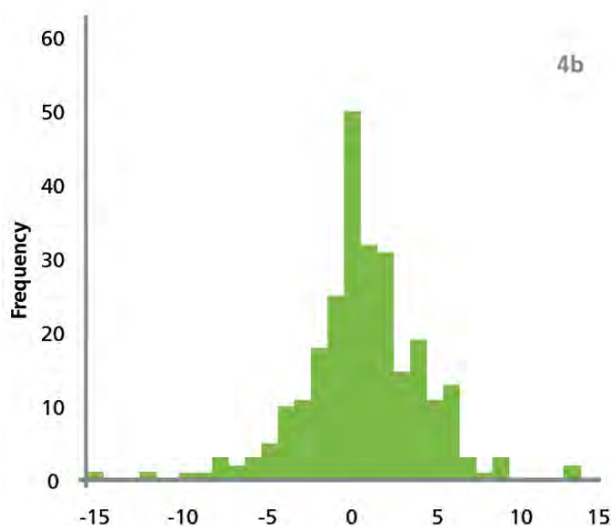
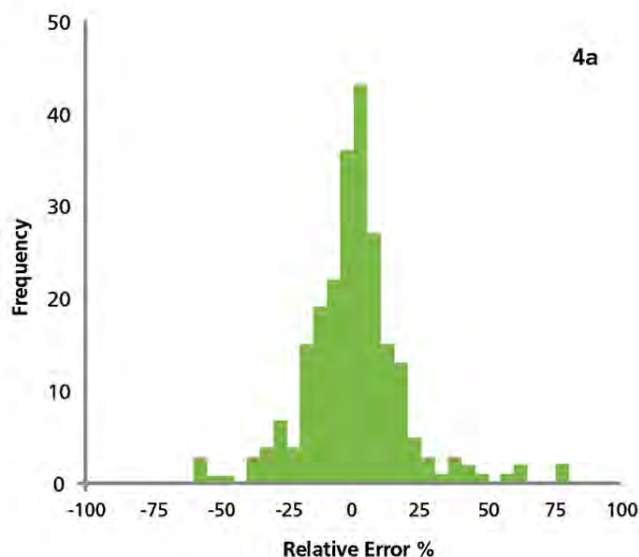


Fig. 4 a.) Tests of normalised standardless analysis using a 'commercial' system from Newbury (1999) *Microsc. Microanal.* 4, 585-597, which showed 95% of analyses within 25% relative error. b) Tests of un-normalised analysis with standards from the same paper, which showed 95% of results within 5% relative error.

XPP – Exponential model of Pouchou and Pichoir Matrix Correction

In 1998 Oxford Instruments launched the **INCA** microanalysis system. Up to this date we had offered a choice of correction procedures to correct for the effects that atomic number, absorption and fluorescence (ZAF) have on X-ray emission from a sample. However, **INCA** included just one correction procedure XPP (Pouchou and Pichoir (1988) in D.E. Newbury Ed. Microbeam Analysis) because we had confirmed by tests on over 2000 published results (Figure 5), that XPP gave more accurate results than published versions of the established ZAF and newer “Phi-Rho-Z” routines. XPP has also been tested on tilted samples and is particularly useful when using in conjunction with the high-tilt requirement for EBSD.

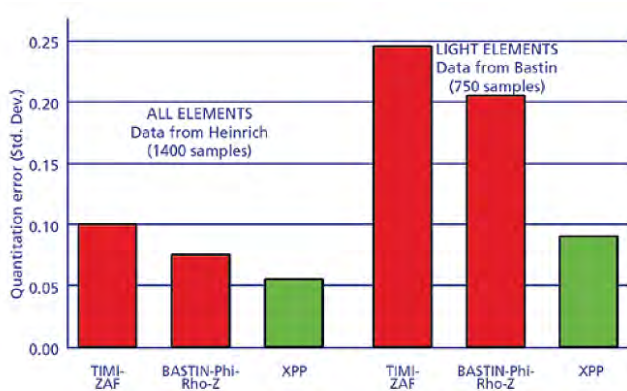


Fig. 5. Tests on published data show that XPP results are more accurate than older methods, particularly for light elements.

Therefore by using XPP the best quantitative results can be obtained on more types of sample, with greater reproducibility and less uncertainty. Results are also more consistent than when the user has to choose between several different matrix correction algorithms according to type of specimen.

PPC – Pulse pile-up correction

Oxford Instruments introduced a unique solution to the problems of pulse pile-up in 2006 (Statham 2006, Microchimica Acta, 155, 289-294). Pulse pile-up, little seen at count rates typical of traditional Si(Li) detectors, occurs at high count rates when two X-rays arrive at the detector so close in time that the hardware counts them as a single X-ray with an energy of the sum of the two X-rays. With the advent

of much faster EDS hardware in the form of SDD detectors, pile-up effects have become more commonplace. The most obvious evidence of pile-up are sum peaks caused by pile-up of characteristic X-rays, for example an oxygen peak in spectra from carbon-rich samples ($CK + CK = OK$) and an Ar peak in spectra from aluminium alloys ($AlK + AlK = ArK$). Sum peaks therefore cause element identification errors but other errors can occur, for example in quantification because peak heights are reduced by the loss of X-rays due to pile-up. The ratio of peak intensities for different elements may therefore change as a function of count rate causing a corresponding change in the calculated element concentrations.

The introduction of large area SDDs such as **Ultim** Max has made the acquisition of count rates in excess of 100,000cps commonplace, so pile-up correction is even more important to maintain the high levels of accuracy provided by the other components in **AZtec**. To predict the proportion of X rays that are likely to be unresolved by the electronics requires an accurate characterisation of timing and pulse waveforms in the pulse processor and this is provided by QCAL. If the spectrum has been acquired from a homogeneous area, the count rate for any energy band in the spectrum can be calculated so that PPC can determine where pile-up X-rays will appear in the spectrum, remove them and replace them at the correct energy. This takes place during and at the end of spectrum acquisition. Not only does the removal of sum peaks help avoid any spurious elements being detected but quantitative analysis is now more accurate when all peaks have been corrected for pulse pile-up losses.

The effects of pulse pile-up and its correction can be seen in spectra from the mineral standard orthoclase collected using **Ultim** Max 100 at about 400,000cps (Fig. 6). The spectrum shows clear evidence of pile-up including sum peaks such as:

- $AlK + OK = PK$
- $SiK + OK = HgM$
- $SiK + SiK = InL$
- $SiK + KK = PrL$

Perhaps less obvious are other sum peaks, which actually interfere with real X-ray lines e.g.

- $OK + OK = NaK$
- $AlK + SiK = KK$

The loss of counts from characteristic X-ray peaks of O, Al and Si becomes apparent when the original spectrum is compared with the PPC corrected spectrum (Figure 6). Furthermore, it is now clear that the perceived broadening of some peaks is also due to pile-up, for example at KK which is overlapped by SiK+SiK in the uncorrected spectrum.

The AutoID results of the uncorrected spectrum not surprisingly show a number of incorrect element identifications for the elements P, In, Pr and Hg.

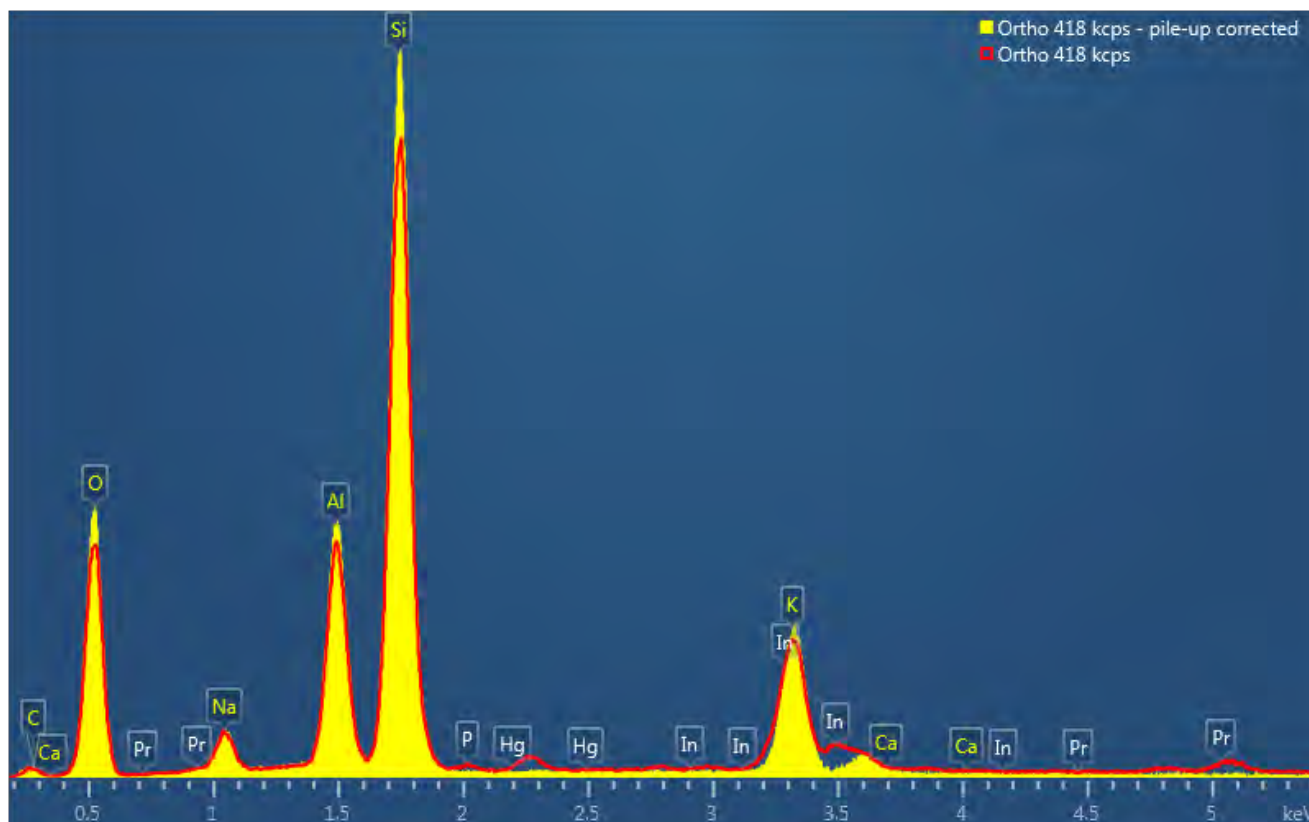


Fig. 6. Comparison of pile-up corrected (yellow) and non pile-up corrected (red) spectra collected at 400,000cps from the mineral orthoclase with **AZtec** and **Ultim Max 100**.

To further compound the problem, quantifying the uncorrected spectrum shows a reasonable result (Table 1/1) with a reasonable analytical total whereas in fact about 7wt% of the result is due to incorrectly identified elements and the total does not show that the results are misleading! An experienced user may be able to manually identify sum peaks and remove the misidentified elements from the analysis. However, this leads to poor un-normalised results because to the loss of X-rays due to pile-up (Table 1/2). It might seem that this effect could be removed simply by normalising and this has been done in Table 1/3 but the O and Na results are too high and the K is too low. When PPC is applied, sum

peaks are removed so that the correct elements are identified by AutoID. Furthermore, pile-up correction in Tru-Q uniquely replaces pile-up losses at their correct energy; therefore peak areas are corrected so that the analysis result (Table 1/4) shows an excellent un-normalised total for the constituent elements. Ca which is present at low concentrations and is heavily overlapped by the much stronger K signal is also now identified and correctly quantified. Comparing these results to those from a spectrum collected at a low count rate of 4,000cps (Table 1/5) shows there is no loss in accuracy when running at high count rate when using **Ultim Max** with Tru-Q spectrum processing.

	O	Na	Al	Si	P	K	Ca	In	Pr	Hg	Total
1) Ortho 418,000cps	43.28	2.54	8.98	27.55	0.4	6.58	0	3.81	1.40	1.47	96.02
2) Ortho 418,000cps - correct Element ID	40.91	2.39	8.60	27.12		7.52	0				86.54
3) Ortho 418,000cps - correct Element ID - normalised	47.28	2.76	9.93	31.34		8.69	0				100.0
4) Ortho 418,000cps - pile-up corrected	46.64	2.58	9.80	30.68		9.65	0.24				99.60
5) Ortho 4,000cps	46.51	2.53	9.89	30.51		9.68	0.24				99.35

Table 1. Quantification of spectra collected from an Orthoclase standard at 400,000cps.

The timing and thresholds in an electronics pile-up inspector can be adjusted to reject pulses that are closer together and thus reduce the magnitude of some sum peaks. However, there is a limit to what can be achieved and if this “tuning” is taken too far, noise fluctuations and variable rise times of pulses within the detector can result in X-ray events being rejected accidentally when there is actually no pile-up. Furthermore, if the timing is such that only partial pile-up occurs within the pulse measurement time, sum peaks no longer occur at exactly the sum of two photon energies and pile-up is then spread out over a range of energies. In this case pile-up losses and sum peaks can no longer be accurately predicted using a statistical approach. With QCAL, the pulse processor settings are optimised so that the pile-up effects are predictable and PPC can make an effective correction to the spectrum. The benefits of this approach are most obvious when reliable quantitative results are required as shown in the above example.

Conclusion

Tru-Q brings together a number of well established technologies like FLS, and new innovative technologies like QCAL. In combination, the results presented here show that Tru-Q delivers a new level of accuracy for automatic results that require no expert set up. In addition these results are reproducible even at high count rates thanks to pulse pile-up correction and the acquisition can be completed in seconds. As the AutoID and Quantitative analysis are automatic and require no user intervention, a result can even be provided while the data collects. The proven accuracy and robustness of the method means that results can be used and reported immediately. Nevertheless, there are more advanced interactive qualitative and quantitative analysis tools in **AZtec** that can still be used to investigate unexpected results and validate good analyses.

With Tru-Q in **AZtec** in combination with SDDs like **Ultim** Max, users can achieve standardless analysis in seconds to a quality equivalent to what would take hours for even an expert to achieve using manual interactive methods and full standards-based analysis.

www.oxford-instruments.com/AZtecLive

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