A new life for the wavelength-dispersive X-ray spectrometer (WDS): incorporation of a silicon drift detector into the WDS for improved quantification and X-ray mapping

R Wuhrer¹ and K Moran²

¹ Western Sydney University, Advanced Materials Characterisation Facility (AMCF), P.O. Bag 1797, 2751 Penrith, NSW, Australia
² Moran Scientific Pty Ltd, 4850 Oallen Ford Road, 2580 Bungonia, NSW, Australia

E-mail: richard.wuhrer@westernsydney.edu.au

Abstract. The wavelength-dispersive X-ray spectrometer (WDS) has been around for a long time and the design has not changed much since its original development. The electron microprobe operator using WDS has to be meticulous in monitoring items such as gas flow, gas purity, gas pressure, noise levels of baseline and window, gas flow proportional counter (GFPC) voltage levels, count rate suppression, anode wire contamination and other detector parameters. Recent development and improvements of silicon drift detectors (SDD’s) has allowed the incorporation of a SDD as the X-ray detector in place of the proportional counter (PC) and/or gas flow proportional counter (GFPC). This allows minimal mechanical alteration and no loss of movement range. The superiority of a WDS with a SDD, referred to as SD-WDS, is easily seen once in operation. The SD-WDS removes many artefacts including the worse of all high order diffraction, thus allowing more accurate analysis. The incorporation of the SDD has been found to improve the light and mid element range and consequently improving the detection limit for these elements. It is also possible to obtain much more reliable results at high count rates with almost no change in resolution, gain and zero-peak characteristics of the energy spectrum.

1. Introduction

The electron probe microanalyzer (EPMA) instrument has been around for a long time, which utilises the X-ray microanalysis techniques of wavelength-dispersive and energy-dispersive X-ray spectrometry (WDS and EDS). The WDS design has not changed much since its original development. WDS exhibits far better spectral resolution than the conventional EDS. The combination of EDS and WDS produces a very powerful analytical technique allowing for excellent quantitative X-ray mapping (QXRM). However, the electron microprobe operator using WDS has to be meticulous in monitoring items such as gas flow, gas purity, gas pressure, noise levels of baseline and window, gas flow proportional counter (GFPC) voltage levels, count rate suppression, anode wire contamination and other detector parameters.

Over the last couple of years we have been developing and testing alternative configuration WD spectrometers, using Amptek PIN (p-intrinsic-n type diode) and silicon drift detectors (SDD’s) in place of the sealed proportional counter (SPC) and gas flow proportional counters (GFPC’s) respectively.
The new system configurations allow the SDD detector to be incorporated within the WD spectrometer with minimal mechanical alteration and no loss of movement range by directly replacing the gas counter with the SDD sensor and connecting to the electronics outside the spectrometer housing using a 9-pin feedthrough.

Our current research demonstrates the dramatic superiority of SDD over proportional counters (PC), whether gas flow or sealed. The very low energy resolution of the PC means that it is not really known what X-rays are being counted by the detector, for example from secondary fluorescence and other X-rays (especially high order lines). Even the application of pulse height discrimination can usually only partially remove higher order lines, and at the expense of greatly increased sensitivity of the gas counter to temperature or pressure changes. Secondary fluorescence X-rays are often similar on the peak as on the background and so may be removed by background subtraction, but the peak/background (P/B) ratio can be significantly reduced. The superior energy resolution of a SDD, typically an order of magnitude better than PC, immediately brings to light such problems, and allows for them to be more effectively removed from the measured signal.

The superiority of a WDS with a SDD, referred to as SD-WDS, is easily seen once in operation by removing many artefacts, allowing for more accurate analysis. The incorporation of a SDD, in the light and mid element range, allows improvement of the detection limit for these elements. It is also possible to obtain much more reliable results at high count rates with almost no change in resolution, gain and zero-peak characteristics of the energy spectrum.

2. Microanalysis (EDS and WDS)

Electron probe microanalysis (EPMA) utilises the X-ray microanalysis techniques of wavelength-dispersive X-ray and energy-dispersive X-ray spectrometry (WDS and EDS) to measure the characteristic X-rays generated from a sample bombarded with electrons and thereby identify the elements existing in the sample. The combination of EDS and WDS produces a very powerful analytical technique also allowing for excellent quantitative X-ray mapping (QXRM) [1-5]. Traditionally, the EDS is used for fast elemental analysis to determine what elements are present and the WDS then utilised to acquire precise major and trace elemental quantitative analysis. The WD spectrometers exhibit far better spectral resolution than the conventional EDS, as can be seen in figure 1 [1, 6].

For major element analysis, the EDS and WDS have the same electron volume for X-ray production, but the X-rays arrive at each detector through different azimuthal paths.

3. Conventional WDS design

WDS is made up of two components; a crystal which discriminates X-rays according to their wavelength, and a detector which measures the intensity of X-rays being passed by the crystal. Each part has its own characteristics, so we will look at each in turn before considering the overall performance of the spectrometer (figure 2) [7-9].

The WD spectrometer, also sometimes referred to as Bragg’s spectrometer, consists of a crystal with the diffracting planes parallel to the surface. The crystal is mounted on a shaft, with an X-ray detector on an arm geared to the shaft in the ratio 2:1 to maintain equal angles of incidence and reflection (figure 2) [6, 9].

At a given angle (ignoring high order reflections), Bragg reflection is satisfied for specific wavelengths only. The detector records the intensity of the incoming X-ray signal at that point of the spectrum. The spectrometer therefore, acts as a monochromator. Different wavelengths are selected by changing theta (θ) of the diffraction crystal [6, 9, 10].
Figure 1. a) Comparison of EDS and WDS energy resolution. WD spectrometer with a proportional counter using different crystals [6], and b) EDS spectrum (red) that has a Cu-Kα line resolution of ~140 eV with a WDS spectrum overlayed (aqua) with a resolution of ~40 eV.

Figure 2. Images of a conventional JEOL WD spectrometer showing the internal mechanism consisting of the gas flow proportional counter (GFPC) and crystal(s).

4. Diffraction crystals

X-rays incident on a crystal are coherently scattered by the atomic electrons. At a certain angle of incidence (θ), X-rays of a given wavelength scattered by atoms in parallel planes, are in phase, causing strong “reflection” (figure 3). Thus for diffraction (electromagnetic alignment) Bragg gave us the formula shown in eq. 1, which gives us the condition at which this strong reflection occurs. It turns out that the Bragg condition is very sensitive and only a small deviation in the angle theta (θ) is enough to lose the constructive interference. This gives high spectral resolution. A number of different crystals are necessary to cover the full range of X-ray wavelengths for all elements in the range B-U [6, 9].

\[ n \lambda = 2d \sin(\theta) \]  

(1)

where \( n \) is the order of reflection (or integer multiple of wavelengths), \( \lambda \) is the X-ray's wavelength, \( d \) is
the crystal interplanar spacing, and $\sin(\theta)$ is the X-ray's angle of incidence. In this case, the angle of incidence and diffraction must be equal i.e., $\theta_i = \theta_r$. Where $i$ is the incident and $r$ is the reflected beam angle.

![Diagram of Bragg's Law](image)

**Figure 3.** Diffraction according to Bragg's law. Coherent scattering of X-rays of wavelength $n\lambda$ only occurs when $2$ times $X = \text{the path difference} = n\lambda = 2dsin(\theta)$. Where incident = reflective angle theta ($\theta$). Modified from [8, 9, 11].

Ideally the Bragg condition would only be satisfied for one wavelength, i.e., where the difference in path length between the diffracted waves is equal to one wavelength. Unfortunately, the Bragg condition is also satisfied if the path length difference is two, three, or in fact any integer value of the wavelength. This is what the ‘$n$’ term in the Bragg equation reflects. Although these higher multiple wavelength ‘orders’ rapidly decrease in intensity, it is not uncommon to detect 2nd, 3rd or even 4th order diffraction lines for major elements.

The spectrometer for the EMPA is arranged as a linear focusing type of spectrometer where the source to crystal distance ($D$) is equal to $2r\sin(\theta)$ and $r$ is the radius of the Rowland circle. Then by substitution and assuming that $n = 1$, $D = r\lambda/d$. Since $r$ and $d$ are fixed for the spectrometer and diffracting crystal being used, this shows that $\lambda$ varies proportionally with $D$.

Table 1 shows the four most commonly used crystals that give coverage for nearly all elements as stearate (ultra-light elements B - F), TAP, PET, and LIF. This table shows their full names, chemical formulae, energy range, elemental coverage and their nominal d-spacing’s. For example, for X-ray energies higher than about 6.5 keV we can only use the LIF crystal. In other areas there is some overlap between the crystal ranges. The overlap between PET and LIF is particularly large. In these regions we can have the choice between two crystals, as can be seen in Table 1.

Another important parameter with respect to the diffraction crystal is whether it can be ground or not, as this determines the type of geometry of the spectrometer. In this selection of crystals, LIF is the only one easily ground. There are two types of analytical geometries currently in use. The first type, the Johann geometry, is constructed by bending the analytical crystal to a radius of $2R$, where $R$ is the radius of the focusing circle, the Rowland circle (figure 4) [8-11]. The second type, the Johansson geometry, is bent to a radius $2R$ and then ground to radius $R$, so that all of the points of reflection lie on the Rowland circle, which maximizes the collection efficiency of the spectrometer. Further to this, the sample, crystal and detector must lie on the Rowland circle and remain on it for all wavelengths of interest in order to focus X-rays efficiently [8-11].
Table 1. Some of the diffraction crystals used for WDS [6-17].

| Crystal  | Name                  | Formula       | 2d (Å) | Wavelength range (Å) | Elemental range | Energy range keV | SDD window |
|----------|-----------------------|---------------|--------|----------------------|-----------------|------------------|------------|
|          | **LIF** Lithium Fluoride | **LiF**       | 4.0267 | 0.863 – 3.595        | Ca - Sr          | 3.44 - 14.37     | Be 0.5 mm  |
|          | **PET** Pentaerythritol | **C(CH2OH)4** | 8.742  | 1.873 – 7.805        | Si - Fe          | 1.59 - 6.62      | Be 0.3 mm  |
|          | **TAP** Thallium Acid Phthalate | **CO2HC6H4CO2Tl** | 25.78  | 5.525 – 23.02        | F - P            | 0.54 - 2.24      | C1 (90 nm Si3N4) |
|          | **STE** Pb Stearate    |               | 100.7  | 21.57 – 89.91        | B - O            | 0.138 - 0.575    | C2 (40 nm Si3N4) |

Figure 4. a) Schematic diagram illustrating the configuration of the X-ray source, analytical crystal and detector on the Rowland circle of the wavelength spectrometer [8], b) Johannson focussing geometry and effective crystal area from the source and through the slit, and c) Johann focussing geometry and effective crystal area [6, 9, 10].

A detector slit may be used at the focus of the X-rays in order to reduce stray radiation, and to block radiation of a different wavelength that may be diffracted either because of the focussing geometry or because of imperfect crystal fabrication. The resolving power of the spectrometer will increase with decreasing slit width, while the peak intensity will decrease with decreasing slit width. An adjustable
slit has the advantage that the best slit width may be chosen for a given application. For maximum precision in detecting large signals, a large slit width would be utilised. For best detection limits the slit would be adjusted for maximum $P^2/B$. For studies of peak shifts due to chemical bonding very small slit widths would be chosen to obtain the best resolution [9].

5. X-ray detectors

A variety of X-ray detectors may in principle be used: these are the scintillation counter, Geiger-Mueller counter, gas filled proportional counter and solid state detector. Detectors used in WD spectrometers are most commonly gas proportional counter types in which incoming X-rays enter the detector through a collimator (slit) and thin window, are absorbed by atoms of the counter gas and a photoelectron is then ejected by each atom absorbing an X-ray (figure 5). The gas-filled proportional counter is preferred for use because of its efficiency, small dead time and good proportionality for the photons of interest [6, 10, 11].

In most gas filled proportional counter designs, the cylinder body is earthed and a fine wire is biased at a positive potential of ~1,000 – 2,000 volts. An X-ray photon passing into the counter may be absorbed by an atom or molecule of the gas producing a photoelectron and an excited ion. The photoelectron or Auger electron, produced by decay of the excited ion, produce additional electron - ion pairs [9, 10-13]. The photoelectrons are accelerated to the central wire producing an electrical pulse which has amplitude proportional to the energy of the original X-ray photon.

The two general types of proportional counters are either sealed or gas-flow. The sealed proportional counters are typically used for high-energy X-ray lines and have a relatively thick Be window that prevents leakage of Xe gas in the detector. The gas-flow proportional counters are used for low-energy lines, have ultrathin windows (mylar or polypropylene), and use a counter gas (generally P-10; which is argon gas with 10 % methane) that flows through the detector at a constant rate [6, 10-13]. There are often problems with contaminants depositing on the wire, consequently affecting the output results and accuracy.

As shown in figure 6a, there are mainly three distinct gas gain behaviours. With no applied potential, there is no impetus for the ion pairs to move to the electrodes and the ion pairs simply recombine so no pulse is measured. Applying a small potential causes the ions to begin to drift toward the electrodes; some will reach before recombining. The proportion that reaches the electrodes increases with the potential until it is sufficient for all of them to be collected [6, 8, 9, 11]. This gives a gas amplification factor of 1.
At first, increasing the potential further will not increase the gas gain because the ions will not have sufficient potential energy to cause any ionisation. When the potential has been increased enough, the electron/ion pairs will gain enough kinetic energy from the applied potential to start producing secondary ionisations and the gas amplification will start to increase. Over the range of gas amplification factors of about $10^{-2}$ to $10^{-5}$ the gas gain increases proportionally with the applied potential. More importantly, the energy pulse in this region is proportional to the energy of the absorbed X-ray. This is the proportional counter (PC) region and is the region that the detector needs to be maintained at (and this is why it is called a gas proportional counter) [6, 8].

When the energy of the ion pairs becomes large enough the quench gas can no longer prevent an avalanche occurring and the proportionality breaks down. This final region, is called the Geiger counter region, the ion pairs from a single incoming X-ray gain enough kinetic energy to cause a complete cascade ionisation of all the gas. It is difficult to determine anything about the energy of the X-ray absorbed, it simply registers a high-energy pulse.

When many pulses arrive together there is a temporary reduction of the gas amplification factor, because of the screening of the wire by the positive ion sheath formed in the chamber. This screening effect is the worst aspect of the proportional counter and can severely limit count rate performance. In figures 6b and 6c, the very bad aspects of the PC are on show. For the Ti spectrum at 10 kcps, the dotted lines show a substantial escape peak above the baseline, while the peak for 30 kcps has shifted down to nearly 50% of the energy of the original peak. Its escape peak has gone below the detecting window and a substantial sum peak is now visible. The energy shifts on the aluminium peak are even worse, with a shift down to a 50% energy peak from 1 kcps to 20 kcps. Some instruments have auto gain shifting to compensate for this effect, which does alleviate it to some degree.

X-ray pulses arriving close together may not be detected as separate pulses. Instead they are recorded as one pulse with the energy of both pulses added together. Where they are formed from a major peak they are called sum peaks and form a peak at twice the energy of the original peak. There is also a small possibility of getting 3 and 4 times the original peak height but this is rarely seen [9].

The job of the counter window is to isolate the counter gas from the vacuum in the spectrometer. Absorption of X-rays by the window is an undesirable effect, so the window needs to be as thin and transparent to X-rays as possible [8]. For these the window is now commonly supported by a grid. Whilst the grid is effectively opaque and therefore reduces the effective area of the window this is
more than compensated by the low absorption of the very thin window. Due to the thinness of the windows, they are not fully gas impermeable and so the gas in the counter needs to be continuously replenished with a slow bleed of gas (hence why they are called gas flow counters) [8, 9].

6. Problems with a conventional WDS

As can be seen from the above discussion points of X-ray detectors, there are many variables that can affect the output and performance of the X-ray detector and the quality of the data produced from the WD spectrometer. Some of these issues include: count rate suppression, gas flow, gas purity, gas pressure, noise levels of baseline and window, GFPC voltage levels, anode wire contamination, electronic stability, high escape peak contribution when present, wavelength position error (easily solved by integrating the peak).

A WDS is an imperfect monochromator, with resolution characteristics depending on crystal, slit combination and diffraction angle. The major complications for the WDS are:
1. The gaseous detector resolution and stability, as seen in the section above;
2. High order diffraction;
3. Signal intensity as a function of beam displacement from the x, y or z alignment condition;
4. Changes in solid angle versus diffraction angle; and
5. Spectral holes from diffracting crystal absorption.

The worst of these are detector resolution and stability. This can be substantially solved by replacing the gas detector with a silicon drift detector SDD [4, 5]. The poor resolution directly affects the discrimination of the second worst problem, i.e., removal of high order diffraction.

Pulse height suppression is exacerbated by the age and cleanliness of the detector and central wire. The central wire contaminates easily and thus causes electric field shielding, which greatly enhances pulse height suppression (PHS). The absolute voltage of the wire also affects PHS. The greater the voltage, the greater the PHS. There are also affects due to localised temperature and pressure changes. These shifts can be substantial at moderate to high count rates and thus will affect the ratios of intensities from unknown to standard.

The effect of PHS can be mitigated by having the unknown and standard with similar intensities and more accurately plotting count rate versus beam current (BC) to determine a ‘combined’ dead-time, which includes losses due to actual dead-time, escape peaks, sum peaks and PHS. This combined dead-time is usually not linear. Xe gas counters suffer less from these effects when new, but as the Xe slowly escapes from the detector, it gets progressively worse (this may take many years to occur).

These changes are always ongoing with time. The poor resolution combined with these poor characteristics produce a detecting system that is substandard and has to be constantly monitored, to such an extent, that only very experienced operators are able to understand these effects. We are forced to introduce other means of correction, e.g., modified dead-times and substantial overlap tables. There are also escape peaks interfering with elements of energy greater than 3 keV for Ar and 4.1 keV for Xe. With the SDD replacement, the escape peak for energies above 1.74 keV (due to the Si from which the SDD is made) is substantially smaller and easily removed.

7. Incorporation of a silicon drift detector into a conventional WDS

For quantitative analysis on a WDS we must keep track of all the interferences that are possible that affect our result. For best sensitivity it is imperative that backgrounds are as low as possible. For both these conditions this is best done by careful control of excitation conditions and by proper control of pulse height discrimination (energy discrimination). Since the pulse distribution is proportional to the energy distribution of the X-rays being detected at any position on the spectrometer, then the position of the energy peak within the discriminators must be continuously adjusted for each position on the spectrometer. For a PC this is easiest to maintain with fixed baseline window settings and varying the detector voltage to keep the peak in the correct position within the discriminators. Setting a very wide window, or even to operate in integral mode, is not ideal because background and interference rejection
are ignored. However, setting a very tight window (relative to the broad peaks measured in the PC) greatly increases the sensitivity of the detector to any changes in the gas (for example changes in pressure or temperature). For operation with the SDD we know exactly where the peak needs to be measured and the optimisation is so stable that it is now possible to change the integration width at each position on the spectrometer. Interference effects, such as high electron noise entering the light element SD detectors, can be easily subtracted from the X-ray count.

Over the last couple of years we have been testing the WD spectrometers using Amptek SDD’s [4, 5] in place of the sealed proportional counter (PC) and GFPCs (figures 7a and 7b) [4]. Initial work used an Amptek SDD and more recently the Amptek Fast 123 system. These system configurations include the detector, preamplifier, digital processor and power supplies all in one unit. The original, proof-of-concept, work [4, 5] was not optimised and was performed under difficult circumstances, by having to place the complete Amptek 123 system inside the spectrometer (figure 7b). This severely limited the movement range of the spectrometer, but did show that the concept was worth developing.

![Figure 7. Photographs of a JEOL WD spectrometer, with b) a gas flow proportional counter fitting (GFPC), and c) an Amptek 123 EDS mounted (25 mm²) in a JEOL spectrometer through an old proportional counter fitting, which has been bored out to allow alignment of the EDS [4, 5].](image)

### 7.1. Silicon drift detectors (SDD)

The silicon drift detector (SDD) is a reverse biased photodiode with an electrode structure that leads to much lower electronic noise and enables much higher count rates than traditional planar diodes. Any free charge created within the diode leads to a temporary increase in its conductivity. Near perfect semiconductor crystals show some residual conductivity due to random thermal excitation of electrons across the energy gap. To minimise this leakage current, detectors are operated at around minus 10 °C to -50 °C. The Si detector has no internal gain and 1 - 10 keV X-rays produce output pulses containing only 260 - 2,600 electrons, or about $10^{16}$ coulombs. Figure 8a is a schematic sketch of a SDD, showing the electrode structure as a series of drift rings, which produce a radial field, guiding the electrons to a very small, low capacitance anode. The small value of the anode capacitance, which is practically independent of the total area of the device, translates into the signal having much lower electronic noise at short peaking times. This is the key to the excellent energy resolution and high count rates of the SDD.
In Amptek’s FAST SDD®, a low noise CMOS preamplifier is mounted inside the package alongside the photodiode, further reducing noise. The signal is further amplified by a main amplifier before being converted to digital format. The whole signal is extracted digitally from which the pulse is extracted and digitally filtered. The spectrum is then analysed using a multichannel pulse height analyser which sorts the detector pulses according to their height, and hence X-ray energy, and records the number received in each channel (a channel being a small energy range, usually 10 eV).

Resolution values of 125 eV for Mn are easily achievable. The only disadvantage with this device is that it loses efficiency rapidly over 10 keV due to its detector thinness. However, they are excellent for high speed quantitative analysis, as count rates can approach 100 kcps with almost no loss in resolution, and very small gain and zero shift of the spectrum.

More recently, Amptek have produced a different option that allows the detector/preamplifier to be incorporated within the WD spectrometer, separated from the electronics unit and connected using a 9-pin vacuum feedthrough (figures 8 and 9). This allows the detector to be operated remotely from its electronics box. Thus, a very lightweight detector is able to be mounted in the detecting position behind the secondary slit. The SDD can be operated at varying time constants and optimised for resolution or count rate. The SDD detector area is 25 mm² (5.6 mm diameter).

This gives a high-resolution spectrum of all the energies being diffracted, enabling observation of all the high order diffraction and other artefacts of the system. All of this is very important adding to the information about the EM probe, enabling better results.
Figure 9. a) New Amptek configuration SDD (SD-WDS), b) internal electronic wiring, c) feedthrough design, d) external configuration where the detector has been separated from the electronics unit, and e) Amptek SDD viewed through slit design of WDS.

8. Amptek silicon drift detectors and results from incorporation
As discussed above, gas detectors are entirely unsatisfactory for the collection of X-rays under conditions where there are large variations in count rates. The new SD detectors on the contrary are extremely stable. With the incorporation of SD detectors (SD-WDS), the ability to accurately and finely discriminate the energy spectrum means that high order diffraction becomes a problem of the past. The longer pulse conversion time for the SD detectors means more accurate dead-time correction. Because of their stability this correction is easy to determine.

SD detectors were incorporated in four spectrometers on a JEOL 733. The spectrometers have dual crystals on each spectrometer. For best performance, the best crystals of each type were chosen so that there would be only one crystal per spectrometer, maximising the efficiency of that spectrometer and allowing the best possible detector to be allocated for each spectrometer (table 1). For X-ray detectors to have satisfactory efficiency for long wavelengths, the detectors are fitted with ultra-thin windows:
1. For the LIF crystal. A SDD with a slightly thicker Be window means that it can be used at much higher beam voltages with few stray high energy electrons affecting its performance. All X-rays on this spectrometer can easily penetrate the 0.5 mm Be window.

2. For the PET crystal. A SDD with a thinner Be window is a compromise to prevent as many high-energy electrons as possible without attenuating the incoming X-rays.

3. For the TAP crystal. A SDD with a C1 window is purely to prevent attenuating the incoming X-rays. This window has better light exclusion performance than the thinner C2 window.

4. For the STE crystal. A SDD with a C2 window is to maximise the collection of the soft X-rays.

Previous preliminary work at 20 keV, 45 nA, 50 s, using the TAP crystal and SDD with Be window as shown figure 7b revealed the following:

- GFPC Si count rate was 125 kcps with P/B equalling 211 (giving a detection limit (DL) of 90 ppm).
- SDD Si count rate was 36 kcps with a P/B equalling 2,000 (giving a detection limit (DL) of 56 ppm).

In this case the SDD detection limit was lower due to the exceptional P/B ratio. If the SDD had the same area as the GFPC, then the DL would have been even lower.

After the new configuration SDD were fitted to the WDSs, the Si count rate was 45 kcps and the P/B was 1,750. Having a Be-window was better for removing electrons than having the current ultra-thin window (C1-Si3N4 90 nm window). The new system could be improved by installing a better electron trap.

To compare the old (PC) with the new (SDD), two elements on each spectrometer, which are reasonably well separated, were used to test the performance of the WD spectrometers. From the EDS and WDS resolution data, shown in figure 10, the resolution data has been plotted as a function of energy and is shown in figure 11. This data matches results shown in figure 1a. Figure 12 shows a direct comparison of specific elements on each spectrometer, comparing manufacturer’s best specifications, with the last known data using the instrument’s proportional counters and with data from the new Amptek SDDs.

Investigation of the effect of count rate has revealed almost no change in resolution or gain with increasing count rate from 12 kcps to 120 kcps (figure 13). Figure 14a shows the count rate versus beam current and figure 14b the zero shift (eV) versus beam current (nA). From Figure 14a, the graph of actual counts shows a residual dead-time. This dead-time time constant (TC) was calculated as 1.2 µs and includes losses from sum peaks.

The new SDD detector technology is now good enough to handle the high-count rates experienced by WDS and they are extremely stable and provide a simple way of checking their own integrity by being able to calibrate against a known spectrum. As an example of poor count rate stability in the PC, figure 6c shows a pulse height analysis plot of Al-Kα at 20 kcps. A second order Ag-La (2.98 keV) would appear at the same place as the first order Al at 1,000 cps. A very good gas counter can resolve the peaks but there will always be a major contribution of the second order Ag-La if the count rate changes. When this is compared to a SDD, there is no problem in separating the Al from the Ag (figure 15). With the SDD there is < 5 eV drift and < 2 eV change in resolution up to 100,000 cps (at 1.2 µs pulse processing TC). For the SDD, the dead-time can be measured carefully and is much easier to keep control of as it is no longer subject to pulse height suppression. Most dead-time is automatically corrected within the SDD processor. From the graph of “Actual” counts in figure 14a, it can be seen that a residual dead-time correction is required for this detector. This residual dead-time was measured at 1.2 µs (not to be confused with the pulse processing TC).
Figure 10. Figure caption at top of next page.
Figure 10. Represents the results from two elements from each spectrometer, where the elements are reasonably well separated in their respective spectrometer. Results are from SD incorporated in a WDS (SD-WDS). For each element, there is an energy distribution representing the full spectrum collected on the wavelength peak corresponding to the element and there is a wavelength scan around the wavelength peak. The energy resolution of each is indicated. For each crystal:

1) STE. Carbon K, EDS energy resolution for the C-K peak is 45 eV. The wavelength scan equivalent energy resolution is 11 eV. Boron K, EDS energy resolution for the B-K peak is 45 eV. The wavelength scan equivalent energy resolution is 6 eV.

2) TAP. Copper L, EDS energy resolution for the Cu-L peak is 60 eV. The wavelength scan equivalent energy resolution is 5 eV. Flourine K, EDS energy resolution for the F-K peak is 60 eV. The wavelength scan equivalent energy resolution is 2 eV.

3) PET. Silver L, EDS energy resolution for the Ag-L peak is 105 eV. The wavelength scan equivalent energy resolution is 6 eV. Phosphorus K, EDS energy resolution for the P-K peak is 90 eV. The wavelength scan equivalent energy resolution is 4 eV.

4) LIF. Copper K, EDS energy resolution for the Cu-K peak is 160 eV. The wavelength scan, equivalent energy resolution is 40 eV. Manganese K, EDS energy resolution for the Mn-K peak is 130 eV. The wavelength scan equivalent energy resolution is 20 eV.

Figure 11. Experimental data obtained from EDS versus WDS full width half maximum (FWHM) resolution testing as a function of energy.
Figure 12. Spectrometer performance data for crystals LIF, PET, TAP and STE. Figures a) to d) above compare the manufacturer’s best performance, with the previous proportional detector performance, and the new SDD performance (SD-WDS). In all cases the counts for the SDD are lower because the detector active collection area is 6 mm$^2$ compared to 20 mm$^2$ for the PC. For the SDD the peak to background (P/B) ratios are much better for all the crystals.

Figure 13. a) Vanadium spectra of count rate change from 12 kcps to 120 kcps (four superimposed vanadium spectra 12 to 120 kcps. 10 nA - 12,300 cps, 20 nA - 24,600 cps, 50 nA - 61,500 cps and 100 nA - 123,000 cps vanadium), and b) Expanded range of vanadium spectra showing almost no resolution and gain shift, just a small zero shift of < 7 eV.
8.1. Light element results
Figures 16a and 16b show the SDD energy spectra from the WDS peak (blue) and background (red) positions measured using the STE crystal for 8.5 % and 0.7 % carbon respectively. In both cases the red spectra represent first and second order diffracted bremsstrahlung and high energy electrons entering the detector. Figure 16c shows the comparison between 8.5 % (red) and 0.7 % (blue) carbon after the background spectra have been subtracted from both peak spectra. For analysis, only the integral on the energy spectra at the carbon peak are used in quantitation. All other artefacts are removed, especially the high order lines as shown.
Figure 16. Results from SD-WDS. a) Carbon peak (blue) and background (red) in 8.5 % carbon, b) carbon peak (blue) and background (red) in 0.7 % carbon, and c) after background removal of both spectra 8.5 % carbon is shown as red and 0.7 % carbon shown in blue. Carbon as measured using a STE crystal at 15 keV and 50 nA. DL = 0.03 % carbon in 50 sec. Carbon can now be easily calculated at the sub 0.1 % level with a lot more confidence. All spectra include high order diffraction and secondary fluorescence [4, 5].

8.2. High order interferences

Typical X-ray interference problems, including high order interferences on all crystals, can now be easily removed through use of a SDD system. These were not easily removed with the use of a proportional counter. Figures 17a and 17b show high order interferences. Figure 17a shows the fourth order magnesium peak, which dominates the spectrum and the actual bremsstrahlung is very small. Figure 17b shows high order interference on a LIF crystal by a second order copper peak, measured in an area at the point where scandium (Sc) should be. In this case the spectrum is dominated by the copper second order peak and the bremsstrahlung at this energy is about a third of the second order copper peak. Figure 17b also shows fluorescence from elements like Al, Cr, Fe, Ni, Zn and Pb. These fluorescence peaks are due to the mechanical components in the spectrometers.

Figures 18-21 have been included to show the spectra from a high-density material (PbS) to maximise the bremsstrahlung and the number of high order lines, mainly those of Pb. Now that we can easily remove high order interferences on every crystal, we finally have an “X-ray display of first order lines only”. No more higher order lines, unless you actually want to display them.
Figure 17. SDD pulse height distributions (energy distributions) of bremsstrahlung measured at a) 0.312 keV on a STE crystal, and b) 4.02 keV on a LIF crystal. On spectrum a), sample MgO, the magnesium peak is a fourth order diffraction. On spectrum b), sample copper, the copper K is a second order diffraction. These energies appear at their actual energy position and thus are easily removed through proper processing of the full-spectrum at each wavelength position.

Because of the high resolution of the SDD, it is now easy to discriminate between the actual energy of the wavelength peak and multiples of that energy, which are high order diffraction peaks. Integrating only the first order energy, at the wavelength required, removes all other energies. Figures 18 to 21 show a simultaneous spectrometer scan on a PbS standard using four spectrometers with the crystals LIF, PET, TAP and STE utilising the SDD in the WD spectrometers. From the use of the SDDs, the subsequent removal of all the high order lines (which would normally be seen from a PC detector), means that there are now no high order lines displayed from the TAP crystal. This is illustrated in figures 18a and 18b. These are the same spectra but with black lines indicating where the Pb (Figure 18a) and S (Figure 18b) high order lines would have been.

Both the Pb and S first order lines should be seen from the PET crystal and if you remove the high order lines, there will be no other lines displayed from the PET crystal. Figure 19 shows this, with the black lines indicating where all the Pb high order lines would have been. Figure 20a sulphur labels show where the first order S-lines are and figure 20b lead labels, show where all the first order Pb-lines are.

Only the Pb-lines should be seen on the LIF crystal, and if you remove the high order lines, then there will be no other lines displayed on this crystal. Figure 21a shows this and the black lines indicate where all the Pb high order lines would have been.

If you remove the high order lines there will be no lines to be displayed on the STE crystal. This is illustrated in Figure 21b. The black lines indicate where the Pb and S high order lines would be. The indicators have only been displayed to the 9th order. The spectrum does display carbon from the carbon-coated sample.
Figure 18. a) Full spectrum wavelength scan on PbS using the TAP crystal, showing where all the high order lines for lead (Pb) would normally appear, and b) the same as figure 18a, except showing high order lines for sulphur (S).

Figure 19. Full spectrum wavelength scan on PbS using the PET crystal, showing where all the lead (Pb) first order lines are shown and where the high order lines have been successfully suppressed by the SD-WDS.
Figure 20. a) Full spectrum wavelength scan on PbS using the PET crystal, labelling the first order lines for sulphur on a normalised vertical scale, and b) the same spectrum wavelength scan expanded on the vertical scale labelling all the first order lines for lead.

In the past it has been difficult to interpret the wavelength spectra when converted to an energy spectrum, due to the complication of having to explain all the high order peaks. High order peaks confuse the tools normally used for finding elements displayed in the energy spectrum. Now it is very easy to interpret the results. There are no sum peaks and no escape peaks or high order overlaps in the ED space spectrum. In the spectra overlayed in figure 22, the vertical scales of each spectrometer are normalised to the maximum height of the most significant peak in the respective spectrum. Hence the Ca-Kβ on the LIF crystal looks as high as the Ca-Kα on the PET spectrum. Note the background rising as the energy increases, which is the opposite of what happens in a “real” EDS spectrum. Figure 22b shows the log scale spectrum in figure 22a. The reason for the increase in bremsstrahlung with increasing energy is due to the rapidly increasing collection efficiency of the WDS at very low angles.
Figure 21. a) Full spectrum wavelength scan on PbS using the LIF crystal, showing where all the first order lines and high order lines for lead would normally appear, and b) full spectrum wavelength scan on PbS using the STE crystal, showing where all the high order lines (up to ninth order) for lead would normally appear. Carbon is the peak shown from the carbon coating on the sample.

Every spectrometer crystal has a different energy range (table 1). When converting each wavelength scan, this range needs to be taken into account. This is done when converting to an EDS spectra of fixed eV per channel. This is why the different colour portions of the graph cover varying energy ranges, even though they cover the same spectrometer distance, as shown in figure 22b.

The biggest advantage of a SDD is stability, followed by much improved resolution (160 eV down to 70 eV for Al). There is also now the ability to actually analyse all the interferences that the detector sees, giving the opportunity to resolve these interferences or, at the very least, a method of digitally removing them (i.e., it is easy to see X-rays arising from unshielded brass crystal holders, etc.).
Figure 22. Wollastonite sample results. a) A simultaneous wavelength scan from three spectrometers converted to an energy scan TAP = red, PET = pink, LIF = green, and b) Log scale version of figure 22a.

8.3. Trace element results
Trace elemental analysis measuring low concentrations of Si and Sr in apatite at 15 keV is shown in Figure 23. This sample has a silicon (Kα at 1.739 keV) concentration of 0.06 wt% and strontium (Lα1 1.806 keV and Lβ1 1.871 keV) concentration of 0.39 wt%. The wavelength scan for this material in the region of Si and Sr is shown in figure 23a. While the energy distribution at the peak and the background, between the two peak positions, is shown in figure 23b. It can be seen that the peak to background ratio is substantial enough to detect much smaller concentrations than those shown. From the Si spectra shown, the peak minus background is 1,800 counts for 30 seconds, giving a 2 sigma confidence level of 0.003 %. This result, showing the complete spectra at the peak and background, ensures the result is only obtained from the energy at the specific wavelength positions, giving an higher degree of confidence in the result.

8.4. Advantages and disadvantages of SDD incorporation
The major advantages and disadvantages, determined at this stage, of incorporating the SDD as a replacement for the proportional counter, can be seen in table 2.

8.5. Processing the full-spectrum data at each wavelength position
The Moran Scientific EDS software used in our investigations automatically accommodates 6 ED spectrometers, with the first spectrometer having the highest priority for EDS analysis work. When incorporating the SDD’s into WDS, these detectors are mapped into the system as minor EDS systems and are available for all other software (WDS and mapping software). Currently for this early research work, we are using simple integral processing of the full energy width of the true energy position minus a background region to remove high energy electrons. Where the full energy width
Figure 23. a) Wavelength scan for silicon and strontium showing peaks from left to right, silicon Kα 1.739 keV (0.06 wt%), strontium Lα1 1.806 keV and Lβ1 1.871 keV (0.39 wt%), and b) Energy spectra for silicon and strontium. Red is silicon, grey is strontium, and green is the common background between the two peaks (30 second analysis on peak).

Table 2. Advantages and disadvantages of the SDD over the PC and/or GFPC detectors.

| Advantages                        | Disadvantages                   |
|-----------------------------------|---------------------------------|
| Stable                            | Heat dissipation*               |
| High resolution                   | 9 pin feed through*             |
| Full spectrum                     | Effected by light (UTW only)**  |
| Better dead time calculation      | Magnets required (UTW only)*    |
| Cost                              | Cost                            |
| Ease of mounting                  |                                 |
| Easier to control                 |                                 |
| No P10 gas required               |                                 |
| Possible theoretical BG may be obtained |                               |
| No count rate drift error         |                                 |
| No baseline window error          |                                 |

* Requires an engineering solution, and ** Phosphorescence of the sample does not seem to affect the SDD.
(ΔE is approximately 2x FWHM), varies with the resolution of the peak energy, as shown in the EDS peak resolutions of figure 11, the integration of the energy window (ΔE) varies proportionally with the energy. To accurately position the integrals it is imperative to have minimal resolution, gain and zero changes in the acquired spectra.

Most maps today are not fully quantitative and they require the accurate measurement of the live-time at each pixel. Standardless analysis can only be considered as an approximation. Trace WDS mapping requires background stripping. For example, the P/B ratio for Si on EDS is ~ 100, WDS ~ 1,000 and for SD-WDS ~ 2,000. With background removal for both EDS and WDS this ratio can be improved. With SD-WDS, the option to estimate the background at the peak position, while at the peak position, enables an effective improvement to the mapping detection limit.

9. Conclusion
Analysis of major elements using the WDS was never much of a problem; the same applied using the EDS, with the proviso that only a restricted set of conditions is used for the analysis. Even minor elements can be accomplished with both EDS and WDS accurate overlap files. It is always important to analyse as many pure elements as possible for all the other elements in the analysis file, to obtain an idea of which overlaps occur. This process is always more difficult for trace and light elements. It is especially difficult when there were many rare earth and transition metal L-line elements present.

Our current research demonstrates the dramatic superiority of SDD over PC (whether gas flow or sealed). With a proportional counter it can be difficult to know what is being counted by the detector. As shown in previous figures, an SDD immediately brings to light problems such as secondary fluorescence, electron scattering and high order diffraction artefacts. Often with a PC the extra noise is similar on the peak as on the background, enabling it to be removed by background subtraction, but the P/B ratio can be significantly reduced. Most PCs have an order of magnitude poorer energy resolution than the SDD; this means that if interferences are present you can get a corresponding improvement in background by removing them, either by energy discrimination, or physically removing their source. It is important to know whether they are there, so that you can remove them to improve your performance. The simplicity of a WDS without a proportional counter is easily seen, once in operation, and removes many artefacts allowing for higher confidence and accurate analyses.

Only a system that had SD Detectors incorporated in the WDS (SD-WDS) would be considered for purchase today. The stability and removal of high order interferences, using SDDs, makes the operation of the WDS much more accurate and easier for the operator to use and understand.

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