

## Lab Report XRF 439

# Comparison of different energy dispersive detectors for element analysis with the M1 MISTRAL

Different energy dispersive detectors are available for spectroscopic measurements of X-ray spectra, such as proportional counters (PC), PIN-diodes and silicon drift detectors (SDD). The physical principles of these detectors are very different. A PC uses a mixture of a noble gas with a quench gas that is ionized by an incident radiation. The electrons are accelerated in the electric field and can ionize other gas atoms resulting in an internal amplification. In this case the energy for generation of the primary signal is relatively high.

In solid state detectors (PIN, SDD), the incident radiation generates charge carriers which are collected by an electrical field. The energy to generate the primary signal is significantly lower than for a PC, i.e. a higher number of primary charge carriers can be generated. This reduces the statistical error and improves the energy resolution.

This report studies the analysis performance of the M1 MISTRAL when equipped with a PC or an SDD and compares it with theoretical values of a PIN-diode.

### Instrumentation

All measurements were performed using the M1 MISTRAL spectrometer equipped either with a large area proportional counter or with a high resolution silicon drift detector (Bruker's XFlash® 5030). The M1 MISTRAL features following technical parameters:

Excitation	W-tube (max. 40 kV, 40 W) glass side window
Dimensions	size (WxDxH): 450x550x420 mm, 46 kg
Prop-counter	1100 mm <sup>2</sup> sensitive area 900 eV energy resolution (Mn K $\alpha$ )
SDD	XFlash® 5030 silicon drift detector 30 mm <sup>2</sup> sensitive area < 150 eV energy resolution up to 200,000 cps input count rate

## Results

### Energy resolution

The energy resolution of a PC for Mn-K $\alpha$  radiation is in the order of 900 eV, for PIN-diodes about 190 eV and for an SDD less than 150 eV.

The better energy resolution of solid state detectors offers following advantages:

- better peak-to-background ratio and therefore higher sensitivity for analysis of traces or of thin layers
- higher flexibility for analysis of unknown samples, in particular for a more detailed qualitative analysis, since peak overlaps are reduced.

Figure 1 shows the acquired spectra of a jewelry alloy sample comprised primarily of Au and with contributions of Ag, Cd, Cu and Zn, measured with a PC and an SDD. The difference in energy resolution is demonstrated by the fact that the PC's spectrum does not show the contribution of Zn and that a separation of Ag and Cd is not possible.

The limits of detection are also different in both cases. For a spectrometer with a PC, they are in the order of 0.5 %, whereas for a SDD the limit improves to around 0.01 %, i.e. by a factor of 50.

### Sensitive area

The energy resolution of a spectrometer is determined by the detector and the electronics. The electronic noise depends mainly on the detector capacity. Therefore, detectors with better energy resolution need to be smaller, which results in a smaller sensitive area and poorer radiation collection. On the other hand, due to the smaller dimensions, the solid state detectors can be positioned closer to the sample. This compensates partly for the smaller sensitive area.

To get comparable count rates, the collimator size can be adjusted. In a PC, the spot size goes down to 0.3 mm or even smaller, but for PIN or SDD it should not be smaller than 0.5 mm.

### Count rate capability

The PIN-diode and the SDD feature very different count rate capabilities. At similar input count rates, the SDD delivers a significantly higher amount of net counts (see table 1). The detectors' dead times for an input count rate of approx. 8 kcps are also shown in table 1. The dead time is relatively high in the case of PIN-diodes, whereas it is typically very small for SDD.

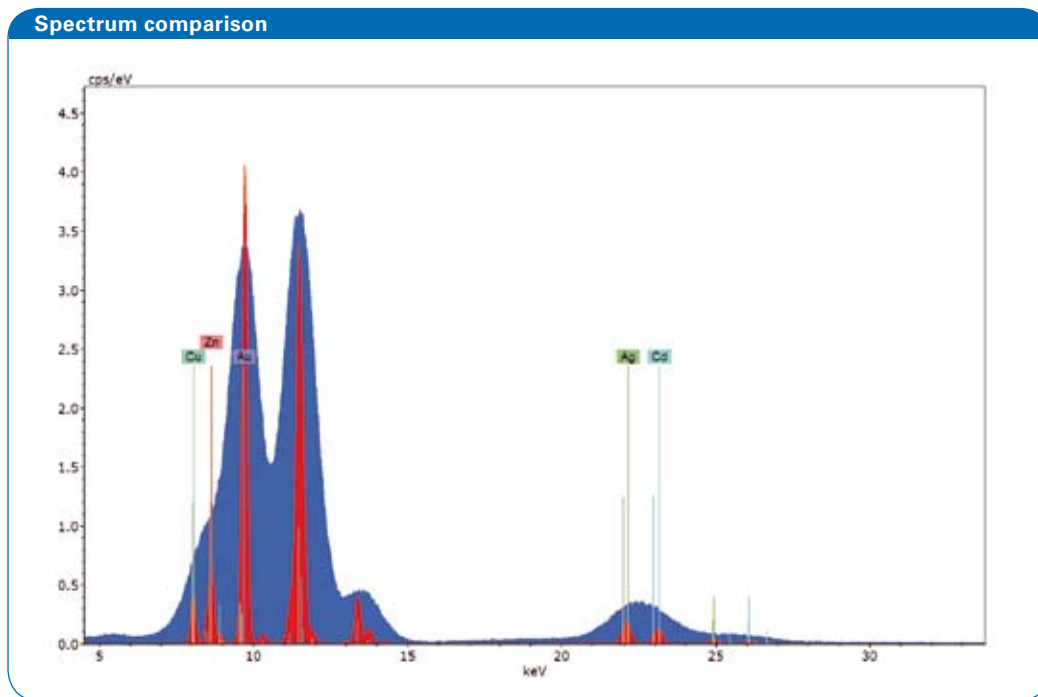


Fig. 1 Spectra measured with PC (blue) and SDD (red) of a jewelry alloy (concentrations approx. Au: 80%, Ag: 5 %, Cd: 5 %, Zn: 6%)

Tab. 1 Comparison of detector properties

Detector	PC	PIN	SDD
Sensitive area / mm <sup>2</sup>	<b>1100</b>	25	30
Captured angle / sr	0.427	0.0229	0.033
Dead time for 8 kcps	11 %	46 %	<b>1 %</b>
Net counts for approx. 8 kcps input count rate	7100	4200	7900
Max. count rate / kcps	10 50*	10	200

\*with Bruker electronics

Regarding prop-counters, peak shifts can occur due to high charge concentration close to the counting wire in cases of detection of high count rates or high energetic X-rays. The low charge carrier mobility influences the collection time and increases the dead time.

The M1 spectrometer has a special stabilization system for the PC that allows count rates up to 50 kcps.

### Stability

The stability of the detectors used in the M1 MISTRAL is similar due to Bruker's specially adapted electronics. Both short and long term stability are mainly determined by the counting statistics, which results in better stability at higher count rates.

This is shown in Figure 2, which illustrates a measurement with an SDD repeated over a long time. The sample was measured several times over a period of approx. 120 hours for 60 seconds per measurement. It can be seen that the measured intensity is statistically distributed.

The behaviour of a PC is very similar, although the statistical error is even smaller due to the larger sensitive area. The calculated standard deviations for both measurements are shown in table 2. These results lead to the following statements:

- The larger sensitive area of the PC allows higher count rates and lower statistical error.
- The comparison between measured standard deviation and statistical error is negligible, which shows that the stability is mainly determined by the counting statistics.

Tab. 2 Results of repeated measurements

Detector	PC	SDD
Mean intensity	522039.3	100810.2
Rel. Std-dev	0.143 %	0.295 %
Stat. error	0.138 %	0.314 %

### Accuracy

The accuracy of analysis depends mainly on the intensity error. This error is determined by the collected intensity i.e. by the statistical error, by the error for the peak fitting procedure and by the spectrometer stability.

The PC's statistical error is smaller. The error resulting from peak fitting is smaller in case of less overlap. In this case, the system is also more robust in case of small peak shifts.

Tab. 3 Accuracy determination results

Detector	PC	SDD
R-square from fitting	0.999893	0.999827
Average deviation	0.137 %	0.122 %

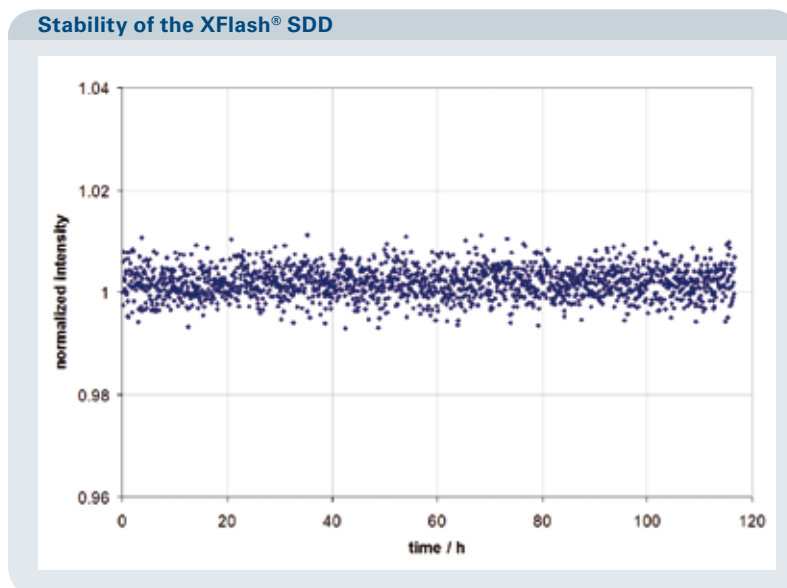


Fig. 2 Diagram showing the normalized intensity over the time.

### Deviation for PC and SDD

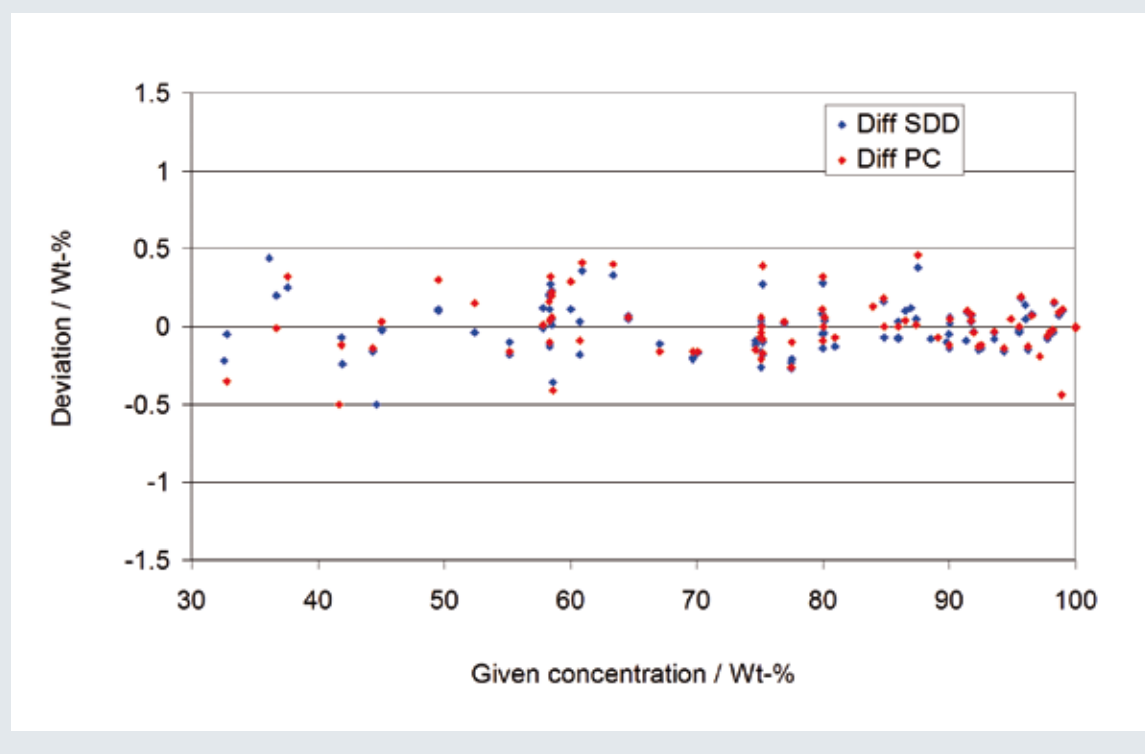


Fig. 3 Diagram showing the accuracy of a prop-counter and an SDD for a measurement time of 60 seconds.

In order to test the accuracy, around 80 jewelry reference samples were measured with both type of detectors. The concentration of Au varied from approx. 35 % to 100 %. Figure 3 shows the deviation from the given value for these measurements. The results are summarized in table 3. This shows that the disadvantageous counting statistics of the SDD is compensated by a smaller error in peak deconvolution.

#### Investment

The investment costs are different for every type of detector. PIN-diodes are more expensive than PCs by a factor of 3 - 5. The SDD is the high end solution.

#### Conclusions

The detector selection should be based on the type of analytical task the user is usually confronted with. For the analysis of unknown samples with flexible qualitative composition and for the detection of small concentrations, solid state detectors are the best choice. However, prop-counters are well suited for quality control with known qualitative composition.

Both detector types are very similar in terms of accuracy. The smaller statistical error of the PC is compensated by the SDD's reduced problem with overlaps. The detectors' performance regarding stability is similar.

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