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WDS

QUANTAX WDS with XSense: A powerful tool for high spectral resolution applications

Application Note # WDS-01

Introduction

High spectral resolution (synonymous with high energy resolution) is one of the primary arguments for the deployment of wavelength dispersive spectroscopy (WDS) in X-ray microanalysis. Well defined, isolated elemental peaks in WDS spectra can easily be identified and quantified, whereas the limited spectral resolution of energy dispersive spectroscopy (EDS) frequently leads to extensive peak overlaps causing serious analytical challenges.

Such peak overlaps concern all fields of scientific and industrial X-ray microanalysis applications including samples from biological, geological and material sciences.

This application note highlights the differences in EDS and WDS energy resolution and demonstrates the advantages of high resolution WDS during qualitative and quantitative analysis. To this end we present typical examples for EDS peak overlaps found in natural and synthetic samples such as mineral raw materials, solid lubricants, gemstones, and semiconductors.

Samples

The samples investigated for the present study are

- Cubic zirconia: ZrO_2 with Y_2O_3 (Y $L\alpha_1$/ Zr $L\alpha_1$), gemstone
- Galena: PbS (S $K\alpha_1$/ Pb $M\alpha_1$), mineral raw material
- Molybdenite: MoS_2 (Mo $L\alpha_1$/ S $K\alpha_1$), solid lubricant
- Tungsten- and tantalum silicide: WiS_2 (Si $K\alpha_1$/ W $M\alpha_1$) and $TaSi_2$ (Ta $M\alpha_1$/ Si $K\alpha_1$), semiconductors.

Figure 1
Ring with cubic zirconia, a popular sythetic genstone for jewelry.

Measurement conditions

Using Bruker's QUANTAX WDS and QUAN-TAX EDS systems, the analyses were simultaneously carried out on a FEG-SEM under high vacuum using a 20 kV accelerating voltage. The electron microscope was equipped with the wavelength dispersive spectrometer XSense and the energy dispersive detector XFlash® 6 | 30 with 123 eV resolution for Mn Kα.

WDS energy range scans were done using a PET analyzer crystal at 20 s dwell time and 0.5 eV step size. Simultaneous EDS acquisitions were performed with the optimum pulse processor for best resolution collecting ~ 1 x 10^9 total pulses.

WDS and EDS spectral resolution

The energy or spectral resolution of an X-ray spectrometer is usually defined via the full width at half the maximum height (FWHM) of an elemental line peak. This (measured) width depends on the natural width of the elemental line, which is typically in the range of 0.5–10 eV (Zschornack, 2007) and the degree of peak broadening added by the spectrometer per its response function.

Peak broadening in EDS and WDS has completely different origins and differs substantially in magnitude. In SDD-based EDS, peak broadening due to statistical noise caused by the discrete number of generated charge carriers, electronic noise and incomplete charge collection is - depending on the energy - of the order of several tens up to >100 eV. In contrast, peak broadening in WDS, where optical aberrations and imperfections of the analyzing crystals are the main contributors, is substantially smaller - typically in the single digit eV range.

From the data in Table 1, the difference in spectral resolution becomes very obvious. While EDS shows FWHM resolutions in the 71–91 eV range, WDS delivers outstanding 4–12 eV resolution.
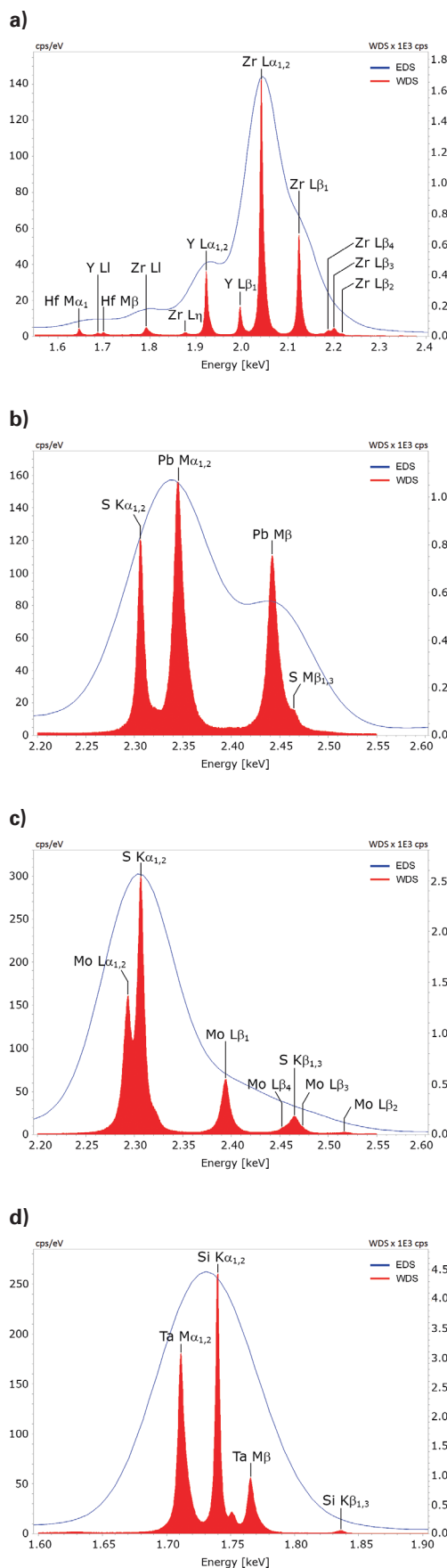
Element	Atomic No.	X-ray line	Energy [keV]	FWHM EDS[1] [eV]	FWHM WDS[2] [eV]	Resolution improvement
Si	14	Kα	1.740	75	3.5	21x
S	16	Kα	2.307	85	6.0	14x
Y	39	Lα	1.922	82*	6.5	13x
Zr	40	Lα	2.042	83*	7.3	11x
Mo	42	Lα	2.293	87*	7.8	11x
Ta	73	Mα	1.712	71*	5.6	13x
W	74	Mα	1.775	74*	6.5	11x
Pb	82	Mα	2.345	97*	11.9	8x

Results

Cubic zirconia (basically ZrO_2) is a popular synthetic gemstone used as an economic substitute for diamonds in jewelry (Figure 1). Calcium oxide (5–8 wt.%) or yttrium oxide (15–18 wt.%) are often added to stabilize the ZrO_2 crystals. Moreover, other elements such as Hafnium may also be present in minor amounts. The EDS spectrum of a cubic zirconia (Figure 2a) shows a sum peak of overlapping Zr L line family peaks, thus the contribution of the other elemental lines cannot be identified easily. The WDS spectrum, in contrast, clearly resolves the various Zr L energy lines from the Y L energy lines and even detects Hf using M series energy lines.

Galena is a sulfidic mineral of the composition PbS and crystallizes in the cubic crystal system. Due to its high lead content of 86.6 wt.%, PbS is the most important lead ore, which was used in ancient times by the Egyptians, Babylonians and Romans. Like many sulfides, galena has elemental peaks (Pb M series) that directly overlap with the S Kα peak in EDS spectra. The result is a broadened peak with an additional lower peak on the high energy side (Figure 2b). In contrast, WDS clearly separates the individual peaks of sulfur and lead in the corresponding spectrum.

Molybdenite is a sulfidic mineral of the composition MoS_2 that crystallizes in the hexagonal crystal system and forms aggregates of platy crystals. Besides graphite, molybdenite is the most important mineral for the production of mineral lubricants. For MoS_2 the overlap between the L series peaks of Mo and

the S Kα peak is even more pronounced than the elemental peak overlap for galena: only a broadened peak with a tail towards the high energy end can be seen with EDS, whereas the WDS spectrum clearly separates the individual peaks of both elements (Figure 2c).

Tungsten and tantalum silicide (WSi_2 and $TaSi_2$) are inorganic silicide compounds. They are used as contact materials in microelectronics. Furthermore, they also find use in microelectromechanical systems and for oxidation- or temperature-resistant coatings. WSi_2 and $TaSi_2$ also occur as refractory phases in semi-conductor materials such as Si wafers. To achieve a high spatial resolution during quality control, the analyses have to be carried out at low accelerating voltages, complicating the identification of these phases. Only the W and Ta M series energy lines are generated at low accelerating voltages, which overlap with the substrate Si Kα line. The resulting EDS sum peak masks the presence of the refractory phases (Figure 2d). By comparison, elements such as W and Ta are identified with confidence using WDS.

Resolution vs. deconvolution

Due to the limited resolution of EDS, peak overlaps occur more frequently in EDS than in WDS (cf. Goldstein et al., 2007). With the deconvolution method a versatile tool exists, that can help mitigate analytical problems arising from EDS peak overlaps (cf. Friel et al., 2016).

A typical example is shown in Figure 3a, where the measured EDS peak (gray) of tungsten silicide (WSi_2) with overlapping

Table 1

Comparison of QUANTAX WDS and EDS resolution for selected X-ray lines.
[1] determined using an XFlash® 6 | 30 with a resolution of 123 eV for Mn Kα,
[2] determined using XSense WDS with a PET diffraction crystal,
*α and β lines were resolved by peak fitting.

Si Kα, W Mα and W Mβ lines is shown with the deconvolution result for Si (orange peak) and W (magenta peak). Although deconvolution often helps extract relevant information from an EDS overlap, its validity can be severely limited in cases with tight overlaps, poor statistics, or if peaks of substantially different amplitudes interfere.

The challenges with deconvolution are further exacerbated when overlapping elements lack additional lines outside the region of the overlap, reducing the number of sampling points for the deconvolution algorithm. In this regard, analyses carried out at low accelerating voltages are particularly error-prone, since high energy X-ray lines may not be available.

In such cases, WDS is the best choice: Significantly better peak resolution allows true separation of individual peaks (as shown for WSi$_2$ in Figure 3b), leading to reliable and unambiguous results.

This advantage of WDS over EDS is shown by the quantification results in Table 2 obtained for WSi$_2$ at 5 kV. While the quantification based on the deconvolution of the EDS spectrum yields a noticeable, deconvolution-induced error, WDS delivers excellent quantification accuracy.

Figure 3

Spectra of WSi$_2$:
a) EDS spectrum with deconvolved Si and W peaks,
b) WDS spectrum.

Table 2

Atomic proportions for WSi$_2$ determined at 5 kV in at.%.
[1] standardless,
[2] standard-based

Element	Stoichio-metry	EDS[1]	EDS[2]	WDS
W	33.3	30.2	32.6	33.4
Si	66.7	69.8	67.4	66.6

Conclusion

QUANTAX WDS is a powerful tool for scientific and industrial applications where spectral resolution is critical for the discovery, correct identification and quantification of all elements in an X-ray spectrum.

The resolution of X-ray lines provided by a QUANTAX WDS system clearly outperforms the capabilities of EDS and numerical deconvolution methods, making it an ideal complement even to high-resolution EDS detector systems.
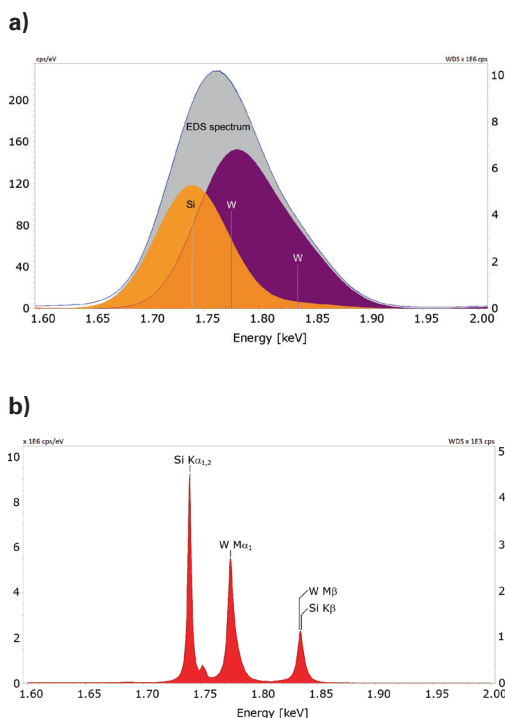
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