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Analysis of Boron with Energy Dispersive X-ray Spectrometry

Advances in Light Element Analysis with SDD Technology



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Advances in Light Element Analysis with SDD Technology

The analysis of light elements (from Be to F, refer to periodic table in fig. 1) presents a special challenge for energy dispersive X-ray spectrometry (EDS). Some of the problems are due to inherent physical effects, while others are technical in nature, relating to the design of the instrument used for analysis and the measurement procedure. Along with the demand for fast and efficient tools for analysis at the micro- and nanometer scale, the need for light element analysis with EDS has grown. With the recent advances in EDS hardware and software, dramatic progress in the detection and quantification of light elements has been made. Specific examples for the analysis of boron are discussed in detail.

Samples investigated by scanning and/or transmission electron microscopy combined with energy dispersive X-ray spectrometry (EDS) show a wide variety. Determining the element composition and their local distribution at the micro- and nanometer scale is, for example, essential for the control of manufacturing processes (e.g., semiconductors, steel and other metals, ceramics, polymers), for understanding specific chemical reactions (e.g., in rocks and inorganic materials), for monitoring health threats (e.g., toxic particles) and even for solving crimes (forensic samples). Many of these samples contain light elements. Of special interest are, most notably, oxygen (e.g., in ceramics, rocks, inorganic compounds), carbon and nitrogen (e.g., inclusions in steel). Recently boron has also become a “popular” element for EDS analysis. The applications for boron are manifold – for instance in ceramics, in fiberglass for insulation, in laundry detergents, in nuclear reactors for shielding, as a doping agent in the semiconductor industry and, in combination with transition metals (e.g., Ni or Co), it is used in galvanic coatings to improve mechanical and physicochemical properties (e.g., microhardness, corrosion resistance) of surfaces in modern machines and instruments. Using boron as an example, this article discusses advances in detector technology

1	2																	18	19	20
H	He																	Ne	Na	Mg
1.007	4.002																	20.18	22.99	24.30
Hydrogen	Helium																	Neon	Sodium	Magnesium
3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20			
Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca			
6.94	9.01	10.81	12.01	14.01	16.00	18.99	20.18	22.99	24.30	26.98	28.09	30.97	32.06	35.45	39.95	39.09	40.08			
Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon	Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon	Potassium	Calcium			
0.0007	0.0002	0.183	0.277	0.392	0.525	0.673	0.849	0.938	1.254	1.488	1.740	2.010	2.309	2.622	2.958	3.14	3.24			
0.0007	0.0002	0.183	0.277	0.392	0.525	0.673	0.849	0.938	1.254	1.488	1.740	2.010	2.309	2.622	2.958	3.14	3.24			
Hydrogen	Helium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon	Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon	Potassium	Calcium			

Fig. 1: Upper part of the periodic table: The light elements beryllium, boron, carbon, nitrogen, oxygen and fluorine present a challenge for X-ray spectrometry.

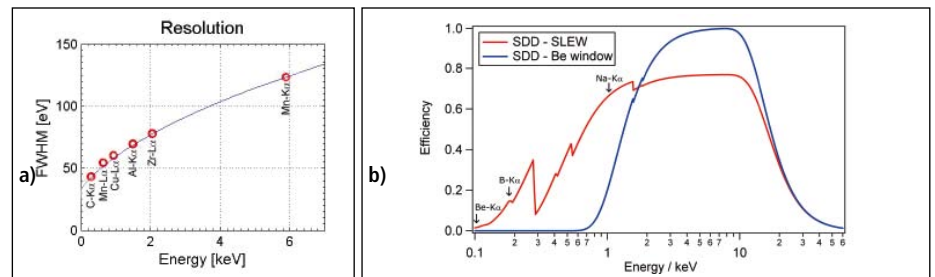


Fig. 2: a) Peak resolution (FWHM = full width at half of the maximum) of various elements (e.g., C-K α \leq 46 eV, Mn-K α \leq 123 eV) measured with a Bruker XFlash 10 mm² SDD on a standard sample (EDS-TM001), specifically designed by the German Federal Institute for Materials Research and Testing (BAM) for testing the resolution of EDS detectors [5]. b) Efficiency curves for an SDD with a super light element window (SLEW) compared to an SDD with a conventional Be window.

that have led to an improved detection and quantification of light elements with EDS, as well as remaining challenges for the analyst.

Technological Advances

An important development was the introduction of the first commercial Peltier cooled silicon drift detectors (SDD) for EDS in 1997 by Röntec GmbH (now Bruker Nano GmbH). Within the past decade, SDDs have become state-of-the-art, outperforming liquid nitrogen cooled Si(Li) detectors in almost every aspect [1]. The high count rate capability of SDDs further stimulated a rapid evolution in pulse processing, which in turn has led to a dramatic improvement of the peak resolution – also for light elements (see Fig. 2a for carbon). Rapid advances and falling costs of computing power and data storage have also led to improved software for EDS, including extended atomic databases [2] and better quantification routines.

The introduction of new materials for detector entrance windows was another

big step towards light element analysis using EDS. Until 1982, beryllium was the only window material used in EDS detectors [3], not allowing X-ray transmission below the Na-K α line (fig. 2b). After many years of development work, ultrathin layered polymer-Al windows with a support structure (e.g., Si-grid) are the accepted standard today. With these windows, even the detection of beryllium is possible (fig. 2b). If no entrance window is used (which is possible, but contamination from the SEM environment is significant), the maximum efficiency of a Si(Li) detector for Be-K α is about 2% [4]. Windowless SDDs can reach efficiencies well above 10% for Be-K α .

Remaining Challenges for the Analysis of Light Elements with EDS

Inherent physical problems for the analysis of light elements with EDS are the low fluorescence yield, absorption and peak overlaps with L, M and N lines of heavier elements. Even though the excitation volume of light elements is generally larger than for heavier elements at a given ac-

celerating voltage, less X-rays are produced because the formation of Auger electrons is favoured (“low fluorescence yield”). Due to their low energies, many of the few X-rays produced are not able to leave the sample because they are absorbed before they can reach the sample surface. Moreover, some of the photons that manage to travel towards the detector face absorption by the detector entrance window and other components of the detector. The latter explains the trend seen in the curve for detector efficiency, which generally decreases with decreasing photon energy (fig. 2b).

How Realistic is it to Analyze Minor Amounts of Boron with EDS?

Even though the inherent physical problems appear to be overwhelming, with proper analytical conditions and an appropriate EDS detector, one can get quite far these days. An important parameter for light element analysis is the accelerating voltage. Because of the low photon energies, optimum overvoltages for the light elements are achieved at very low accelerating voltages (≤ 5 kV). However, K lines of many other elements, which may also be present in the sample, are not excited at these conditions. Thus, L and/or M lines need to be used for quantification of these elements. To demonstrate this – also with respect to the accuracy of quantification results – spectra of a nickel-boride (Ni_3B) reference sample were obtained and evaluated at 2, 5, 10 and 15 kV accelerating voltage (fig. 3). Quantification was carried out standard-based (with pure element standards for B and Ni) using the XPP optimized PhiRhoZ model. The spectra (fig. 3) and quantification results (table 1) underline the importance of using low accelerating voltages in order to ensure a sufficient peak to background ratio for the quantification of boron.

Figure 4 shows an element map of boron for an area within a weld seam with a Cr-Ni stainless steel as base metal. A microstructural and chemical analysis of the crystals forming at such interfaces helps identify the reasons for failure or prove the stability of a weld seam. The high resolution (4096x3072 pixels) element map shown in figure 4 was obtained with a large area Bruker XFlash detector at an input count rate of 150 kcps. The high count rate capability of the silicon drift detector allowed the acquisition of this map within just a few minutes. The sample contains phases with three different boron contents as indicated by the color scale in red (highest B content: Cr-

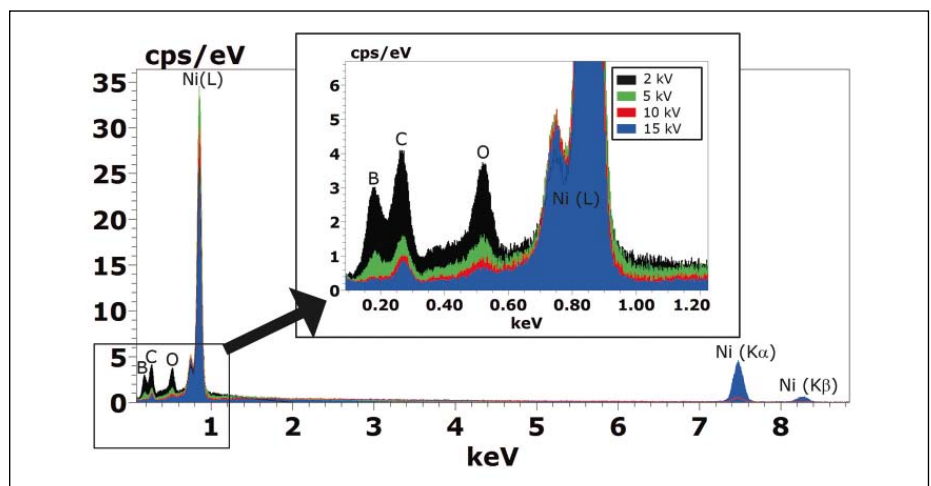


Fig. 3: Spectra of Ni_3B acquired at 2, 5, 10 and 15 kV (input count rate: 4-5 kcps, acquisition time: 60 s). The spectra were obtained with a Bruker XFlash SDD ($\text{Mn-K}\alpha \leq 123$ eV, $\text{C-K}\alpha \leq 46$ eV). Carbon (coating) and oxygen (minor oxidation) were not quantified, but taken into account for peak deconvolution. Sample: courtesy of U. Burkhardt, MPI Dresden, Germany.

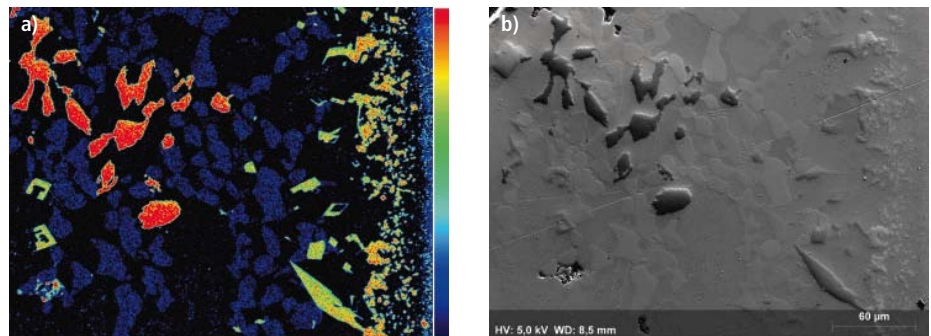


Fig. 4: Element map of boron for an area within a weld seam a) and corresponding SE image b). The sample contains phases with three different boron contents as indicated by the color scale in red (highest, Cr-boride), green (intermediate, Cr-Ni-boride) and blue (lowest boron content, Ni_3B).

	Mass%		Atom%	
	B	Ni	B	Ni
Ni_3B (2 kV)	5.9	94.1	25.4	74.6
Ni_3B (5 kV)	5.7	94.2	24.8	75.2
Ni_3B (10 kV)	6.8	93.2	28.5	71.5
Ni_3B (15 kV)	10.9	89.1	39.9	60.1*
given value	5.8	94.2	25.0	75.0

*quantified using Ni-K α .

Tab. 1: Quantification results for Ni_3B (average of five measurements for each condition).

boride), green (intermediate B content: Cr,Ni-boride) and blue (lowest B content: Ni_3B). Just 10 years ago, it would have been impossible to produce such a detailed light element map with an EDS detector.

Conclusions

The introduction of new materials for detector entrance windows and the development of silicon drift detectors, combined with advances in pulse processing and software capabilities, have triggered dramatic progress in the analysis and quantification of light elements. Never-

theless, the analyst still needs to take special care in the measurement procedure, assuring an optimum overvoltage for light elements, considering absorption and peak overlaps.

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