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LIGHT ELEMENT ANALYSIS

Hans Dijkstra*

*Thermo Fisher Scientific BV, Scientific Instruments Division
Takkebijsters 1, NL-48107 BL Breda, The Netherlands*

** hans.dijkstra@thermofisher.com*



SUMMARY

In this presentation an introduction is given into X-ray microanalysis of the light elements, specifically boron, carbon, nitrogen and oxygen. Both EDS and WDS microanalysis will be discussed. This presentation will be at a basic introductory level.

INTRODUCTION

In some sense the analysis of the light elements in the periodic system is comparable to the analysis of medium or heavy elements. The sample has to be prepared and properly cleaned, should be placed in the electron microscope at a well-known geometry, and the proper settings on the microscope should be selected such that the most reliable, reproducible and accurate results are achieved. But with light elements deviations from the optimum procedure are often negatively affecting the results very quickly. This means the operator has to be much more aware of how the sample preparation and the analysis conditions affect the X-ray generation and detection process, so that the validity of an analysis can be properly judged.

For this paper a lot of text, drawings and graphs have been shamelessly borrowed from existing textbooks and from contributions of other authors at previous EMAS Regional Workshops. My thanks and my apologies go to all these authors.

THE LIGHT ELEMENTS

When we talk about light elements in this paper we are referring to elements with atomic number lower than 10. However, hydrogen and helium do not have any electrons in the L-shell, and as such cannot generate characteristic X-rays, just as lithium which does have one electron in the L-shell but the Pauli principle does not allow that electron to relax to the K-shell. So beryllium is the lightest element that we can analyze, followed by boron, carbon, nitrogen, oxygen and fluorine. The characteristic X-rays of these elements have a relatively low energy, as displayed in Table. 1. The X-ray energies are displayed as one value, in spite of the fact that there are two X-ray lines: the $K\alpha_1$ and the $K\alpha_2$. These two lines are so closely

together for the light elements that even with a high-resolution WDS spectrometer they cannot be separated.

Table 1. Wavelengths, X-ray energies and critical excitation energy for the light elements.

Element	Z	Wavelength [nm]	Energy [eV]	Critical excitation energy [eV]
Be	4	11.40	109	112
B	5	6.76	183	192
C	6	4.47	277	284
N	7	3.16	392	400
O	8	2.36	525	532
F	9	1.83	677	687

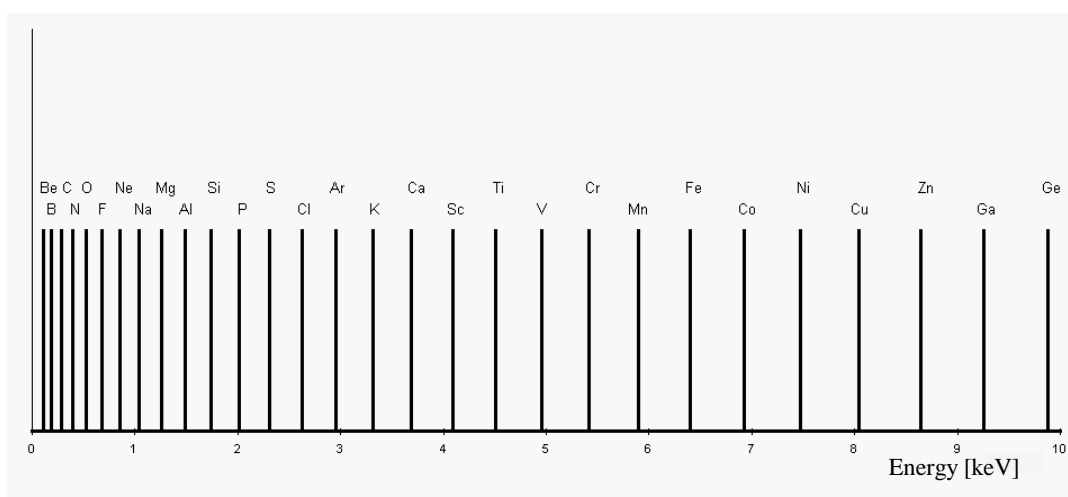


Fig. 1. $K\alpha$ X-ray energies of elements with atomic number 4 to 32.

As can be seen these X-ray energies are relatively close together, making peak overlaps a real possibility if the energy resolution of the X-ray detector is not good enough. And even with the best EDS and WDS detectors some overlaps between the $K\alpha$ X-ray lines of the light elements and the L- and M- lines of other heavier elements cannot be resolved.

X-ray emission of the light elements is relatively low. This is mainly caused by the fact that the so-called fluorescence yield is very low, making the generation of a characteristic X-ray an event with a low probability. Furthermore, these low-energy X-rays have a high probability of being absorbed by the sample before they can escape through the surface and reach the X-ray detector. However, this is partially compensated by the fact that an electron

loses only a small amount of energy to generate such an X-ray, so many X-rays can be produced by a single impinging electron.

In the first decades of EPMA and SEM neither WDS nor EDS could be performed on these low-energy X-ray lines. In WDS there were no natural crystals with sufficient large $2d$ -values. Furthermore, the windows of the proportional counters absorbed the soft radiation for the most part. Both drawbacks could be solved in the seventies and eighties of the last century.

In EDS analysis there was a limitation by the detector window. Standard windows are made up of a ten to fifteen microns thick Be-foil. These windows absorb almost all radiation below 1 keV. The development of thin (0.3 micron) polymer foils on a supporting grid allows measurements of low-energy X-rays.

In WDS there were no natural crystals with sufficient large $2d$ -values. Only the development of synthetic multi-layer crystals in the nineteen seventies allowed proper detection of these so-called soft X-rays.

SPECIMEN PREPARATION

The low-energy X-rays of the light elements are easily absorbed in most materials. As a result, those X-rays that make it to the detector must have come from the area closest to the surface of the sample. This places a lot of emphasis on the surface preparation. To do quantitative analysis it is a requirement to have a sufficiently flat, often polished, sample. The sample is best to be mounted exactly perpendicular to the electron beam, as small uncertainties in the detector take-off angle can generate a large uncertainty in the quantitative results. Tilted specimens can be analyzed, but only when the exact tilt angle is known and the quantification procedures are optimized for tilted sample analysis.

Many materials that contain light elements are electrically non-conductive, such as most minerals and ceramics. This requires the sample to be analyzed under low vacuum conditions, or to coat the sample with a conductive coating. The coating material has to be selected carefully: a carbon coating will strongly absorb boron and carbon X-rays, but other coatings may have even worse effects on X-ray analysis.

Another important factor to take into account is the contamination of the sample surface. Hydrocarbons, either from the vacuum system or from a sample that is not properly cleaned, can be cracked under the electron beam and form a thin carbon coating, affecting the quantitative results not only for carbon but also for other light elements as their X-rays may be absorbed by the carbon coating.

WAVELENGTH-DISPERSIVE SPECTROMETRY

Among the natural crystals, normally used in wavelength-dispersive spectrometers, only the phthalates such as potassium (KAP), rubidium (RAP), and thallium (TAP) have a sufficiently large interplanar spacing to be used for light-elements analysis. Their 2d-values are about 2.6 nm and allow the analysis of fluorine and in some spectrometers oxygen too. However, the X-ray yields are rather low.

Synthetic crystals, either of the stearate-type or sputtered multi-layers, may have much larger 2d-values, up to more than 20 nm. Sputtered multi-layers have a considerable higher yield than the common Pb-stearates, but an inferior spectral resolution. In Fig. 2 the Bragg angles of the light elements are plotted versus the 2d-lattice spacing. The regions are marked, which may be used at conventional spectrometers for mechanical reasons. The Bragg angle should be between 15° and 65°. Pb-stearate has a 2d-value of 10 nm and may be used for boron to oxygen, whereas for some spectrometers the Bragg angle for oxygen is already too small. Beryllium needs a larger 2d-value which can only be achieved with multi-layers. Other multi-layers with 2d-values of about 6 nm are used for the analysis of oxygen and fluorine.

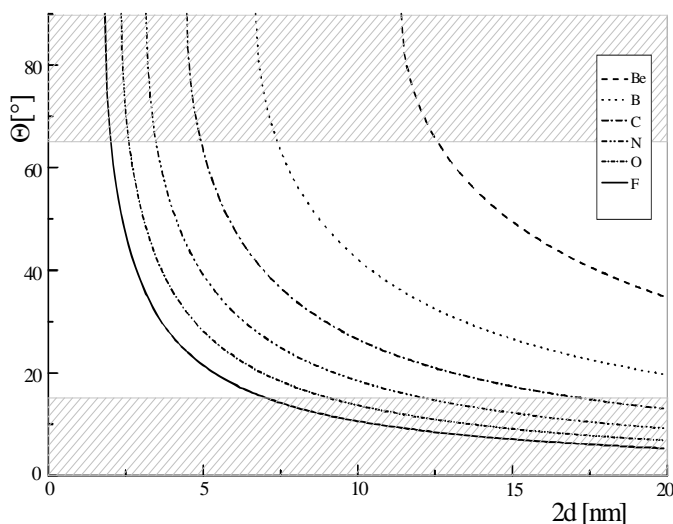


Fig. 2. Diffraction angles versus 2d-spacing for the $K\alpha$ -lines of the light elements.

The count rates for light elements, measured with multi-layers, are not significantly less than for heavier elements, but it must be considered that the maximum yield is only achieved over a very small region of wavelengths. Therefore, it is desirable to have several multi-layers with different 2d-values and composed of different pairs of elements.

The yield of stearates is about 5 to 10 times less than that for multi-layers, but varies not so strongly with wavelength. Usually multi-layers have the same dimension and mounting form as conventional spectrometer crystals and can be interchanged immediately. If it is

compatible with the design of the spectrometer, use of larger crystals can enhance the yield further.

Compared to the conventional crystals used for “normal” wavelengths, the spectral resolution of synthetic multi-layers is rather bad. But it is good enough to distinguish between K-lines of different light elements. Overlaps with lines of heavier elements sometimes demand special deconvolution techniques to determine the real peak intensity. Overlaps are often caused by higher-order reflections. In those cases the effect can be reduced by suitable adjustments of the pulse-height discriminator. It is a favourable factor that multi-layers show only to a very small extent reflection of higher order than 2. The width of the energy distribution is a dominant factor in pulse-height analysis. The counter voltage should not be taken unnecessary high, because the distribution broadens with increasing voltage. Furthermore, use of a counting gas with an elevated methane fraction results in a narrower distribution. Alternatively, this effect is achieved by reducing the counting-gas density by lowering the pressure. This has the additional advantage to reduce the absorption of high-energy X-rays and thus to discriminate reflections of higher orders.

An additional aspect of WDS analysis of the light elements is peak shifts, caused by variations in the orbital energy levels of the L shell electrons due to variations in bonding with other elements in the sample. For example, the peak maximum for C K α may be at values between 4.434 nm and 4.453 nm for different carbides, see Fig. 3. The use of the same position of the spectrometer therefore results in errors in the intensity measurements. These errors can be avoided if before each measurement the position of the peak maximum is detected precisely, which may be impractical for very small peaks. Generally the peak shift effect decreases with increasing X-ray energy and, therefore, it is less significant for e.g. oxygen radiation.

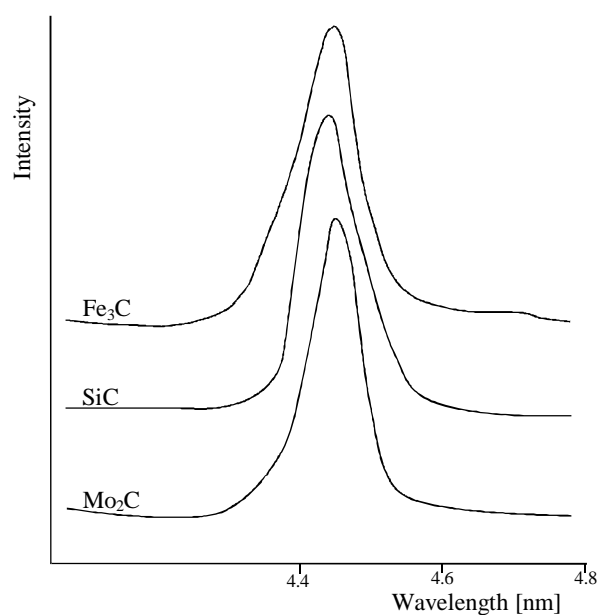


Fig. 3. Profiles of C K α peak for different materials, showing chemical bonding effect.

The area of the peak is needed for quantitative analysis, for this value represents the total emission. Normally, the height of the peak is proportional to the area. Because of variations in peak width and peak shape this does not apply to light elements. The peak area may be determined by moving the spectrometer step by step across the whole peak and integrating the counts.

This method is very time-consuming and thus impractical for routine measurements. A more practical approach is to measure just once both the peak height and the peak area for all compounds to be considered. Then peak-to-area ratios may be calculated for each compound, so that at future measurements of samples which contain this compound the determination of the peak maximum is sufficient.

For carbides of metals the peak-to-area ratios have been found to have a broad range: in the literature values of 0.715 to 1.048 (relatively to Fe_3C) have been reported. The variations of the peak-to-area ratios are smaller for O in oxides. Relating to Fe_2O_3 values have been found between 0.974 and 1.015. For boron in borides similar small values have been reported.

ENERGY-DISPERSIVE ANALYSIS

Soft X-rays emerging from light elements are totally absorbed by the Be-window used in conventional standard-detectors, see Fig. 4.

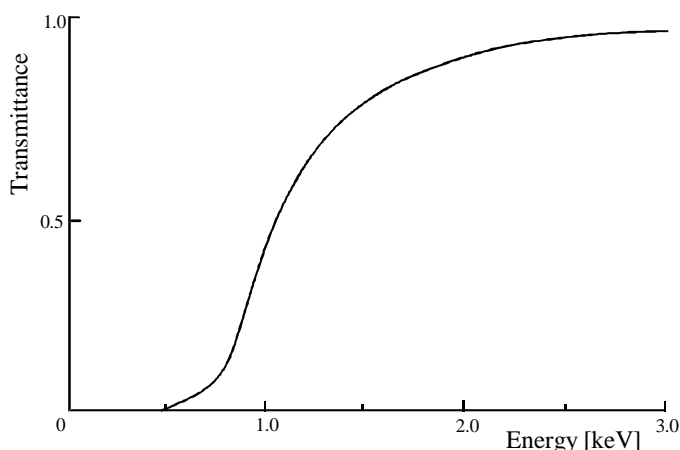


Fig. 4. Transmittance of a Be window of 8 μm thickness for low-energy X-rays.

A detector with a thin window or a removable window is required. Nowadays, in nearly all detectors ultra-thin windows are used which consist of a polymer membrane on a supporting grid. The transmittance of such a window is shown in Fig. 5. In addition to the absorption in the window there is considerable absorption of light element X-rays in the metallic layer and the “dead layer” in the front region of the detector. From this it follows that the detection

sensibility for soft X-rays must be less than for those X-rays with higher energies. The essential value to describe this is the minimum detection limit (MDL). It is determined by the peak-to-background ratio, which is a function of the peak- and background-intensities and of the width of the peaks, i.e. the energy resolution. The latter is, therefore, an important value for the ability of a detector for light element analysis. The energy resolution at low energies is mainly determined by the electronic noise of the detector and the preamplifier and to a lower extent by statistical fluctuations in the ionisation processes, which are more important at higher energies.

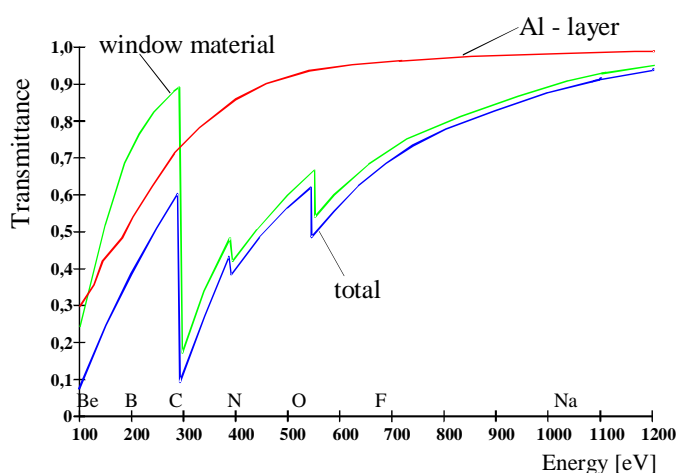


Fig. 5. Transmittance of a thin window detector with 0.4 μm thickness of the polymer foil and a 4 nm thick Al foil.

In the last decades Si(Li) EDS detectors have improved steadily, and they allow to distinguish the K-lines of light elements among themselves and to identify overlaying L- and M-lines. Progress has also been made in reducing the zero-peak and hence in detecting the boron $K\alpha$ -peak at 183 eV. Most modern detectors now have a very narrow zero-peak allowing the detection of even the beryllium $K\alpha$ -peak at 109 eV. Further improvements have taken place in the reduction of incomplete charge collection. This effect causes an asymmetry of the peak, often referred to as low-energy tailing.

The resolution of EDS detectors in the low-energy range is in the order of 50 to 80 eV. This is so high that peak shifts, as observed in WDS analysis, can not be seen with EDS.

QUANTITATIVE ANALYSIS

The classical ZAF correction procedure as developed in the 1960's and 1970's proved insufficient for light element quantification, as they were unable to cope with the strong absorption of the low-energy X-rays. So in the 1980's a lot of effort was placed by various

scientists into developing new quantification procedures, the so-called $\Phi(\rho z)$ or phi-rho-z procedures (Fig. 6).

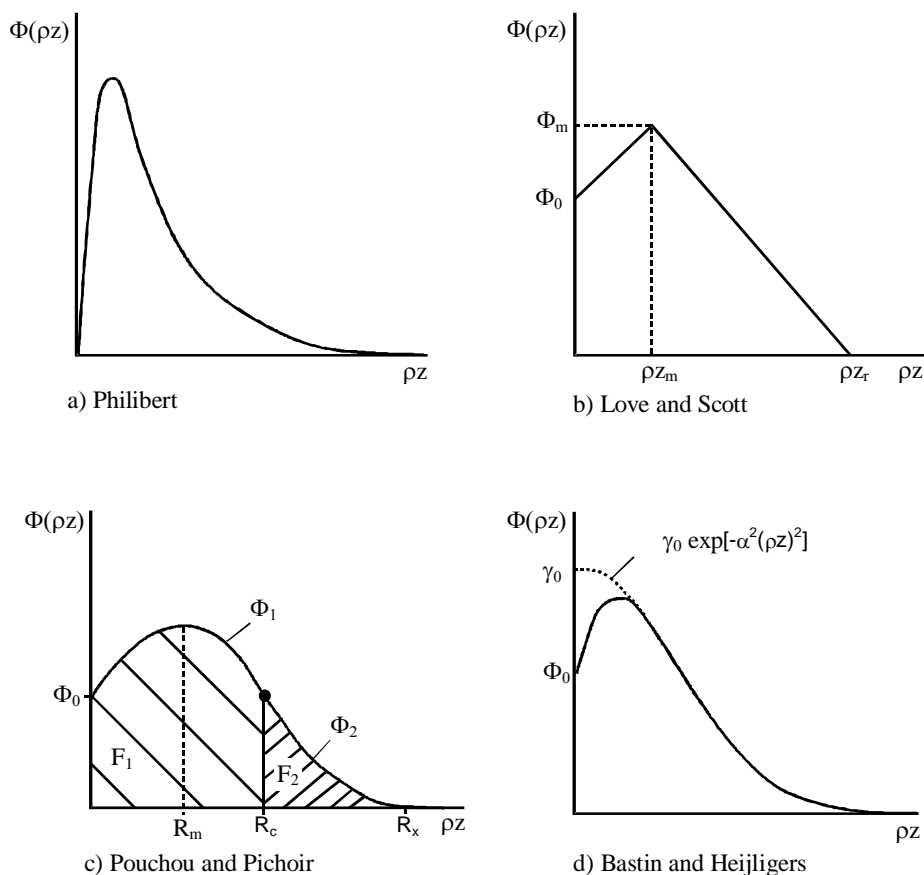


Fig. 6. Different $\Phi(\rho z)$ models.

It has been proven by all the experts in the field that these $\Phi(\rho z)$ models all function a lot better than the classic ZAF parameterisation. Although each author prefers his own model, they all agree the differences in results between these $\Phi(\rho z)$ models are small, and only very accurate measurements can show the differences.

Besides the $\Phi(\rho z)$ model also knowledge of the mass attenuation coefficients (MAC) of the elements in the sample for the lines in question is of eminent importance. Due to the heavy absorption they affect the results significantly. Most $\Phi(\rho z)$ models come with MAC sets that are optimized to give the best results.

From all this the reader may falsely assume that with proper sample handling and a modern quantification procedure it has become easy to do accurate quantitative analysis. That is not correct: many things can go wrong and with light element analysis any small mistake can have large consequences.

With WDS the operator needs to take more care than usual to select the proper diffracting crystal, check peak positions and peak-to-area ratios, and return to standards more often. And obtaining good reliable standards that are stable and homogeneous is often problematic. With EDS analysis, especially if it is standardless, it is important to calibrate the detector for light element sensitivity, as variations in window thickness can have a large impact.

CONCLUSIONS

Light element analysis can be done properly with both WDS and EDS. Compared to the analysis of heavier elements the operator has to be much more careful in every step of the analysis process. WDS has the potential of generating more accurate results than EDS, and allows much better analysis of trace elements. However, inexperienced operators will find that EDS results are often more consistent and reliable, and much faster to achieve. The debate continues.

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