

New applications of the good old wavelength-dispersive X-ray fluorescence

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Abstract. Wavelength-dispersive X-ray fluorescence can be characterized by its advantages and drawbacks. Unbeaten spectral resolution in a range below 5 keV, good operational stability, excellent ability of making averaged analysis, and good presentation of peak shape which gives the basis for the chemical speciation are the advantages. Among the drawbacks, the following are important: system with sequential analysis of particular elements, low output of energy supplied to the device, and great cost of instrument which can be amortized only in routine operations. In routine geological and environmental analyses, the WD-XRF performs better than other simpler instrumental or wet techniques. WD-XRF is continuously improved, by applying new multilayer interference mirrors (MIM) for detection and quantification of very light elements. Bad spectral resolution of MIM noted earlier is now improved by tailoring their shape to the shape of gratings. The progress in the long wavelength spectral region joined with efficient and precise wavelength resolution systems enables the application of WD-XRF for speciation analysis. In another effort, XRF spectrometry is treated as a tool for obtaining quantitative basis for the judgement on Linnaean systematic classification of plants and opens the field to a new discipline – quantitative biology.

Keywords. Wavelength-dispersive X-ray fluorescence; X-ray multilayers; chemical speciation; botanical classification.

PACS Nos 07.85.Nc; 07.85.-m; 07.85.Fv; 82.80.Ej

1. Introduction

Although well founded and intensively exploited but not in a stadium of such stormy progress as, for example, Raman spectrometry, classical wavelength-dispersive X-ray fluorescence (WD-XRF) method still is useful and amazes us with new ideas which can be coupled with the method. This paper aims to present some new features added to the method since the last reviews of the method [1,2]. Another aim is to prove that this method can be one of the most promising options in many analytical laboratories. The method is one of the best suited among instrumental methods for routine actions. At the same time, new strictly scientific applications are evolved and they were potentially of great application output.

Part of the improvements concerns the method as such and connected instrumentation. Wavelength-dispersive version of XRF, although very old compared to modern instrumental technique, is not a dead field.

Relatively small progress was made in theory of the process. The WD-XRF is supported by several well-known principles; its qualitative foundations are drawn from Moseley law; the quantitative base is determined by Sherman [3,4] and independently by Shiraiwa and Fujino [5,6]. The attenuation of photons obeys very simple Lambert–Beer law. A very interesting paper by Rousseau [7] explains why the Sherman equation cannot be changed, from the intensity as a function of concentrations (as it is constructed) to the concentration(s) as a function of intensities as is really interesting for analytical chemists. In that situation, the models using Monte Carlo simulations gained greater popularity. The very elegant way of using Laplace transform for solving the quantitative problems in XRF was given up. This approach was once proposed by Philibert [8]. It is fortunate because the application of Lambert–Beer law for both incident and escaping X-ray photons implies the immediate use of Laplace transform as a way for solving the relevant equations. However, the problem presented in such a way is both elegant and at the same time ill-posed from the mathematical point of view.

Perhaps, greater progress was made in the efforts to derive a realistic equation describing the bremsstrahlung. The accurate description of this phenomenon will help in the determination of the spectral background and will improve some of the correction methods. Several contributions were made in this direction, with Kawai and Ishii [9] suggesting that continuous radiation can be well approximated by the Planck’s distribution for black-body emission. This approach is very interesting as one can intuitively feel that the emission of X-rays from the anode can be treated as a kind of black-body radiation. Later on, Tanigaki and Kawai [10] tried to explain the position of this time synchrotron emission compared with black-body radiation and concluded that it is rather gray-body radiation. Trincavelli and Castellano presented more traditional version of bremsstrahlung modelling, supported mainly by different theories applied in the quantification of electron microprobe [11]. The theoretical rationale in this model is deeply involved somewhere, but so many times modified that it is difficult to treat it in a different way from the *ad hoc* corrected numerical model.

2. Newer discoveries

2.1 Smart use of principles

The idea of observing the spectral $K\alpha/K\beta$ ratio is revitalized in different cases. The ratio has been used by Scofield [12,13] to prove that the initial and final electronic states are not ‘frozen’, but ‘relaxed’. The rationale of using this ratio in the analysis is simple – then at least a part of the chemical matrix and geometrical effects is cancelled. It was applied to determine the coating thickness. In a limited range of coating thickness, this method works very precisely and is close to linear regime, both for the spectral lines of the covering element and for the element beneath [14]. As the measurements of coating thickness is still important in the applications of XRF technique, the method described above is not the only technique leading to linear relationships. Kataoka *et al* [15] proposed

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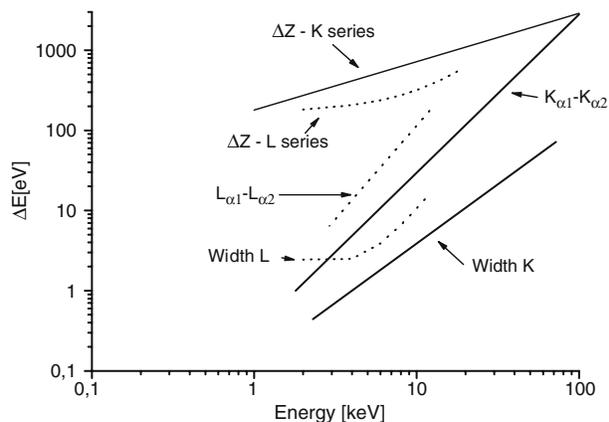
the use of a combination of several take-off angles for different combinations of K lines of the elements from the coating and underlayer. The method enables even quantification of complex coatings composed of several layers with two elements of variable composition. Both methods give much better results than simple immediate measurements of the line intensities of elements in upper or underneath layers.

2.2 Improvement in optical components

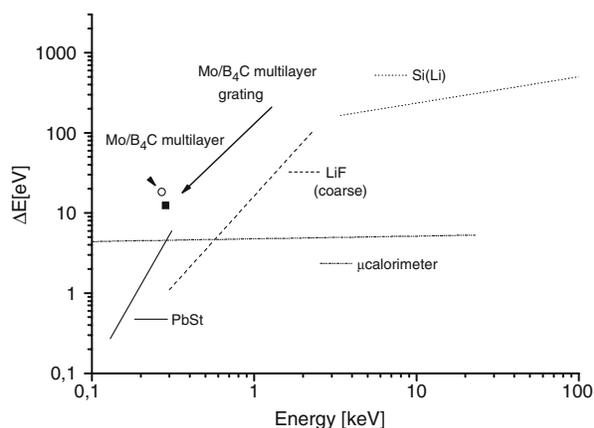
The fundamentals of WD-XRF lie in the use of crystals as spectral dispersive elements in splitting the fluorescence spectrum according to wavelengths. The dispersive structures can be put in order according to increasing interplanar distances. Natural crystals were used for the analysis in spectral range down to Ca; next, the crystals of organic soap-like substances as TIAP were used for analyses in a range down to O; finally, multilayered composites with ordered interplanar distances d were used for the analyses in the range down to B. The multilayers gave enormous prospect for the analysis of light elements up to boron and heavier elements in higher spectral orders. Unfortunately, the spectral resolution of the multilayers was insufficient for the analysis of mixtures, except for those cases where the spectral distances between lines were very large. Great progress has been observed in this field during the last years, together with the introduction of new ideas. One is to superpose the gratings on multilayered structures [16–20] and this structure is known as lamellar multilayer amplitude grating (LMAG). It is a really fascinating new field of optics. At first, the X-ray emission induced by electrons in multilayer environment can be analysed with high-resolution WDS Johann spectrometer to reveal the structure of the emission bands, in particular components of the multilayer. Such analyses show that the amorphous components of the multilayers are always partially crystallized which is disadvantageous and results from the interdiffusion. The original low resolving power [1,21] of raw multilayers can be greatly improved by etching them with grooves as the gratings [22,23]. The operation is simply aimed at lowering the density of mirror material without significant deterioration of high reflectivity. Depending on the period and size of the grooves, the spectral resolution can be increased even by a factor of three. The width of both multilayer column and groove are in submicron range. The position of LMAG among the more popular dispersive structures is shown in figure 1. The obtained effects allow the analysis of the very light elements from Be to O. Moreover, it widens the analytical field with possibilities of making quantitative analyses of beryllium alloys, boron [17] and borate and boride compounds, especially with heavy metals. The analyses of heavy metals in higher spectral X-ray series (L [23], M [24], even N) also can be performed easily. In that case, the spectral resolution probably assures chemical speciation studies. The results obtained by Jonnard *et al* [19] on the differentiation between carbon from cellulose and from B₄C are worthy to be compared with the electron microprobe speciation on C compounds by Bastin.

2.3 New instrumental configurations

The invention of new X-ray optics elements such as polycapillary pseudolens or pseudo-semilens enabled the changes in traditional configurations of WD-XRF spectrometers.



(a)



(b)

Figure 1. (a) Presentation of basic characteristics of X-ray spectra – the spectral distances between analogous spectral lines in K- and L-series, split between $\alpha 1$ and $\alpha 2$ lines, spectral widths of K and L lines; (b) spectral resolution of the selected available detectors.

Some older inventions such as doubly curved crystals were also involved. The exhaustive set of configurations leading to the formation of WD microprobes is cited here based on the materials of X-ray Optical Systems, Inc. [25], but without any preference from the author (figure 2). Some other publications describing interesting configurations of WD-XRF instrument are also cited.

The first option consists of using the polycapillary pseudolens for transmission and concentration of the beam from the tube towards the restricted space on the sample. Another option is to direct the beam from the tube on doubly curved crystal and diffract it on that structure in a focussed way leading the beam towards the sample. It concerns the

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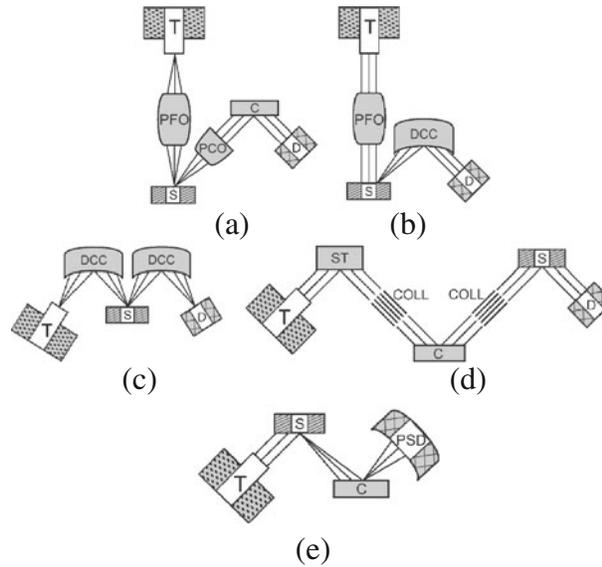


Figure 2. Different recent configurations of WD-XRF devices applying new types of optical elements, as polycapillaries or doubly curved crystals: (a) microprobe with take-in X-rays converged using polycapillary lens and take-off X-rays collected by polycapillary deconcentrator; (b) microprobe with take-in X-rays converged using polycapillary lens and take-off X-rays thrown on doubly curved diffractor; (c) microprobe with take-in X-rays converged and take-off X-rays collected with doubly curved crystals (adopted from [25]); (d) probe with primary radiation excited from secondary target and monochromatized with Bragg crystal thrown on the sample [26]; (e) probe with the sample radiation collected with position-sensitive detector [27]. Symbols: T – tube, PFO – polycapillary focussing optic, PCO – polycapillary collimating optic, S – sample, C – crystal, DCC – doubly curved crystal, D – detector, PSD – position-sensitive detector.

impinging X-rays. Now we have two possibilities concerning the emitted X-rays. First is to collect the divergent rays by the pseudosemilens and form a parallel beam which is further thrown on a flat monochromator and counter. The second option is achieved by putting the doubly-curved crystal and directing the beam into the counter.

The systems mentioned allow to restrict the irradiation area and pass to the microprobe type of instruments. In addition, we obtain lower spectral background and associated lower detection limits.

In a more conventional way, Sitko *et al* [26] proposed monochromatization of the primary beam by directing it on the secondary target, and additional purification of the beam on the diffracting crystal and collection of secondary radiation from the sample by the thermoelectrically cooled Si-PIN detector. This system is somewhat like a reversed conventional WD-XRF system, using Bragg diffraction to the primary and not to the secondary beam. The monochromatization of primary beam and obtaining very simple quantitative relationships between intensity of the signal and concentration of the components is an advantage of this invention.

Another system invokes the idea of using the position-sensitive detector for collecting diffracted secondary radiation. The system built by Mokuno *et al* [27] for the PIXE analyses can well be used for X-ray excitation, with the limitation of the diffractometer movements to minimum.

3. New and unique applications

Of course, WD-XRF is still unbeaten in standard geological analyses. Excellent performance of the device with respect to stability, repeatability and reliability gives the method great preponderance over other possible techniques. The linear calibration in low concentrations is another virtue. The range of low concentrations can be much prolonged if one applies the precise dilution of samples in relevant fluxing agents. Lastly, the matrix effects in XRF [28], although sometimes large quantitatively, are restricted in the sense of amount of influencing substances and moreover, can be strictly calculated and are predictable.

XRF is one of the few analytical techniques where it is possible to use very reliable fundamental parameter methods or apply strictly experimental techniques as calibration curve or standard addition method. Finally, the mixing methods are also possible and sometimes advised.

During the last few years, some unique applications of WD-XRF have been introduced. In our opinion, those concerned with the quantitative determination of biological species seem to be the most exciting. The efforts of biologists to segregate all the organisms got a stable base since the time of invention of the Linnaean classification of plants and animals. The idea of species evolution was the next step in classification. It evolved in the system of phylogenetic classification. In both efforts, the classification of the existing or extinct species and understanding of their mutual relationships and changes are tedious and, scientists met with great difficulties in setting the rigorous delimitations and continuous work is performed. During the last few years, some ideas have evolved about the application of chemical methods for the quantitative estimation of chemical differences between species. The work is going in two directions – either to differentiate the whole patterns, or to find the differences between selected species. The role of XRF in both versions, both WD and ED [29], can be significant. Although the essential idea of using chemistry for establishing species segregation is intuitively based on the differences either in DNA, optionally RNA or on differences in proteins and here the XRF is much useless, the smart use of the method can be very profiting. For example, the exploration of Compton and Rayleigh components of the spectra and extracting the principal components allows differentiating between seeds of several related flower plants. The well-known chemometric methods of principal component analysis (PCA) or hierarchical cluster analysis (HCA) [30] give real tools for the segregation of quantitative species. Especially, hierarchical cluster analysis seems to be most promising because of its similarity to the hierarchical Linnean way of classification (figure 3). It is to be noted that botanical objects are treated here as complex organic compounds which can be finger-printed by their unique chemical compositions. The chemical hierarchical classification was compared in figure 3 with the botanical classification of those plants in Reveal system [31]. As one can see, both systems when superimposed, show some discrepancies, which is very interesting and can be a subject of

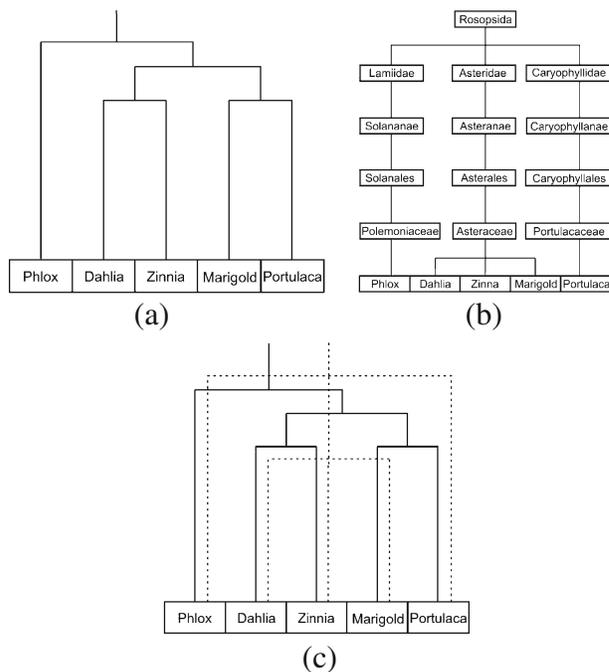


Figure 3. (a) Hierarchical cluster analysis of chemical differentiation of seeds of 5 plants; (b) hierarchical scheme resulting from botanical taxonomy [31]; (c) both schemes superimposed on each other (chemical results – solid lines; biological results – dotted lines).

further studies. The procedure can be repeated for differentiation of complex chemical mixtures such as paints [32], vegetable oils [33] and similar systems. The other problem, differentiation of different tissues [34], lies just half-way between the differentiation of organic compounds and differentiation of the whole organisms belonging to different taxonomic species. The possibilities do not end here – the unique patterns of inorganic trace components can serve as a tool for differentiation of bacteria [35] or cancerous tissues [36].

Perhaps, those applications will evolve in a new kind of quantitative biology with WD-XRF instrument as the useful tool.

4. Conclusions

Two new schemes were introduced in WD-XRF during the last years. The first one was concerned with better spectral resolution in the high wavelength region, enabling efficient registration and determination of light elements up to boron. Here, the introduction of multilayers was a breakthrough, now significantly deepened by tailoring the multilayers to the gratings shape. There is no special rival in this field for LMAG except some

soap-like pseudocrystals (e.g., lead stearate) but a good combination of spectral resolution and the optical brightness gives a preponderance to LMAG. The second one was concerned with the application of optical squeezing techniques for focussing primary beam and to collect the secondary beam from small spot and transforming it into the parallel bundle of X-rays going to the detector. Here, the polycapillaries and/or doubly curved crystals play the main role. Such new configurations of the spectrometer lead to quite efficient wavelength-dispersive milli- and even micro-microprobes. This type of instrumentation is now in demand.

Among new applications, those leading to the so-called quantitative biology seem to be the most interesting ones and probably have a great future.

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