BRAGG AND BARKLA POLARIZATION IN EDXRF

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ABSTRACT

The use of a combination target consisting of an HOPG Bragg crystal and an Al₂O₃ Barkla scatterer for the excitation of the elements Na to U represents further progress in the development of using polarized excitation in EDXRF. The high, integrated reflectivity of the HOPG crystal improves detection limits and sensitivities for Na, Mg, Al, Si, P and S-traces in light and heavy matrices in comparison with direct and secondary target excitation. The Al₂O₃ target has proven itself to be a useful Barkla scatterer for the excitation of elements with Z > 26 in which the achieved detection limits are in the range >0.1 µg/g. The combination of the Al₂O₃ target and the HOPG crystal in a multilayer, results in a polarization filter for the whole primary spectrum of an x-ray tube, thus enabling overview analyses with measuring times ≤ 100 s. Detection limits between 1 - 50 µg/g are achieved for the elements Na - U.

INTRODUCTION

One of the most important advantages of EDXRF is the simultaneous analysis of elements from Na up to U. The primary radiation scattered at the sample is recorded simultaneously with the fluorescence signal. In practice, the sample is excited several times. The excitation conditions are optimized for a small range of elements [1].

The sensitivities and detection limits obtained with direct excitation could be improved up to an order of magnitude by using polarized radiation for the excitation of traces in light matrices [2-5]. The polarization effect of x-ray radiation can be observed in the processes of Rayleigh and Compton scattering, Bragg reflection, Raman scattering and Bormann transmission. The phenomenon of polarization, first examined by Barkla [6], has been used and continuously improved since the beginning of the 70’s [4-13].
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In contrast to radiation from secondary targets, the polarized x-rays produced by Barkla scattering are polychromatic. Thus, enabling excitation of fluorescence lines for an energy range higher than 8 keV [14, 15]. The lower limit is determined by the ratio cross-section for scattering to mass absorption coefficient.

The use of single crystals for polarization of x-rays is limited for a certain energy range. This depends on the anode material used and the lack of single crystals for energies higher than 15 keV [16]. The scattering efficiency of single crystals can be up to four orders of magnitude higher than for Barkla scatterers [11]. Like for secondary targets, the Bragg reflected radiation is monochromatic.

The constant simultaneous excitation of the elements Na to U is neither possible with only Barkla nor with only Bragg targets. It would be desirable to use a combination of both for an optimal excitation of all elements.

The aim of this study is to present a suitable excitation device which is realized by a combination target consisting of an HOPG (highly oriented pyrolytic graphite) crystal and a Al₂O₃ Barkla scatterer. The performance of the excitation device is demonstrated for different applications.

RESULTS AND DISCUSSION

The use of a cartesian geometry for the arrangement of tube, target, sample and detector allows a great flexibility for the excitation conditions. Barkla scatterers, Bragg reflectors or secondary targets can be used as targets. Each serves as polarizer for the incident radiation from the tube. The optimum excitation conditions are achieved with intense monochromatic radiation. The energy for which is slightly higher than the absorption edge of the element of interest. This can easily be realized with secondary targets, but only for a small group of elements per target. The Bragg reflected x-rays are also monochromatic but more intense. This is valid for energies < 5 keV. Due to their polarization and assuming that the Bragg crystal contains no elements which produce fluorescence radiation, it is possible to achieve detection limits lower than for secondary targets.
The conditions for Bragg reflection are given in Bragg's law:

\[ n\lambda = 2d \sin(\vartheta) \]

where \( n \) represents the order of reflection, \( \lambda \) the wavelength of the incident radiation, \( d \) the distance of lattice planes and \( \vartheta \) the incidence angle. The wavelength of the incident radiation is defined through the angle \( \vartheta \) as 45° given by the cartesian geometry and the lattice distance of the single crystal. The crystal used for reflection should have a highly integrated reflectivity, lattice planes with low Miller indices, no impurities, no characteristic radiation in the range 1 - 10 keV, thermal stability and should be commercially available. Different investigations show that an HOPG crystal possesses one of the highest integrated reflectivities in comparison with other crystals [17]. Also it fulfils the other requirements mentioned above.

A further condition for using Bragg crystals for low energies is a highly intense primary radiation. This can be realized with an end-window tube equipped with a thin Be window. Because of the shorter distance between anode and target, high intensities can be achieved between 2 and 6 keV.

The combination of HOPG ((002) plane, \( 2d = 6.71\,\text{Å} \)) with Rh L\( \alpha \)-radiation results in \( \vartheta = 43.2^\circ \). The Rh end-window tube used is equipped with a 75 \( \mu \text{m} \) Be window. The integrated reflectivity for the 002 plane is 0.0032 rad with a degree of polarization \( P=0.99 \) [18]. This corresponds to results found by Chabot [19].

Figure 1 shows the excitation spectra of an HOPG (highly oriented pyrolytic graphite) crystal in comparison with normal graphite. It can easily be seen that second and third order reflection can also serve for excitation. Excellent excitation is achieved for the elements Na to Ti for various applications.
Figure 1. Excitation spectra of an HOPG crystal compared with a graphite sample at a
BRAGG angle of 43.2°, measured in air (96.4% absorption of Rh Lα-radiation)
using a Rh end-window X-ray tube at 30kV and the detector in sample position.

A Barkla scatterer is the optimal solution for simultaneous excitation of elements with \( Z > 22 \).
Polarized \( \times \)-rays can be obtained by scattering at an angle of 90°. The material should be
amorphous or polycrystalline, without any impurities and it should have a low mean \( Z \) and a
high density. These conditions are normally fulfilled by materials such as Be, BeO, B\(_4\)C and
Al\(_2\)O\(_3\).

A multilayer target would be the best solution for obtaining optimal excitation conditions for
each element from Na - U. Table 1 lists the different combination possibilities for a Bragg
crystal and a Barkla scatterer. Since HOPG also serves as a Barkla scatterer, it can be used up
to an energy of 25 keV. Above this the Al\(_2\)O\(_3\) target would be the best solution.

Table 1. Conditions of multilayer polarization targets for different energy ranges.

<table>
<thead>
<tr>
<th>energy range (keV)</th>
<th>1 - 6</th>
<th>6 - 15</th>
<th>15 - 25</th>
<th>25 - 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>polarization type</td>
<td>BRAGG</td>
<td>BARKLA</td>
<td>BARKLA</td>
<td>BARKLA</td>
</tr>
<tr>
<td>effective materials</td>
<td>HOPG</td>
<td>HOPG</td>
<td>HOPG</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>optimal ( \rho d ) (g/cm(^2))</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

For investigations, a multilayer consisting of a 1mm thick HOPG crystal on a 5 mm thick Al\(_2\)O\(_3\)
substrate was produced [20]. Figures 2 and 3 show the spectra of the standard sample GSD-12
(sediment) [21] excited by Al\(_2\)O\(_3\), HOPG and the combination of the Al\(_2\)O\(_3\) and HOPG.
Figure 2. Comparison of spectra of the standard sample GSD-12 (sediment) excited with an Al$_2$O$_3$ Barkla scatterer, an HOPG crystal and the combination of these targets (logarithmic view).

Figure 3. Two parts of the spectra shown in figure 2: Difference in the excitation of the elements Si, Fe, Sn, Sb and Ba depending on the target used (linear view).

The comparison of the detection limits of four elements representing the energy range of interest, listed in table 2, shows the dependence of the excitation conditions on the target. For Si, the best result is achieved with the HOPG crystal due to excitation with Bragg reflected Rh L-radiation. Since Al$_2$O$_3$ is a better Barkla scatterer than carbon, the best result for Sn is achieved with the Al$_2$O$_3$ target. The detection limits obtained with the combination target show only a slight deterioration for light elements like Si compared with the HOPG and for heavy elements like Sn compared with Al$_2$O$_3$. In general, it can be said that the combination target combines the performance of Bragg reflection and Barkla scattering.
Table 2. Lower limits of detection for the elements Si, Cu, Sb and Sn determined for GSD-12 with different excitation targets: \( \text{Al}_2\text{O}_3 \) barkla scatterer, HOPG crystal and the combination of these targets. Measuring time 500 s. No filter used.

<table>
<thead>
<tr>
<th>target</th>
<th>LDD Si [µg/g]</th>
<th>LDD Cu [µg/g]</th>
<th>LDD Rb [µg/g]</th>
<th>LDD Sn [µg/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>3112.6</td>
<td>2.9</td>
<td>0.7</td>
<td>1.9</td>
</tr>
<tr>
<td>HOPG</td>
<td>106.0</td>
<td>2.2</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )/HOPG</td>
<td>128.6</td>
<td>2.7</td>
<td>1.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

APPLICATIONS

For the preparation of solid samples, 4 g of well homogenized sample material was mixed with 0.9 g of wax (Hoechst, Germany). A pellet was then produced by pressing a 32 mm pellet at a pressure of 15 tons. For the preparation of fusion tablets, 0.75 g sample and 6 g lithium tetraborate were mixed and smelted to a glass bead with a diameter of 39 mm. The measurements were conducted using a Spectra X-LAB 2000 EDXRS instrument equipped with a 1.2kW Rh end-window tube and a Si(Li) semiconductor detector.

The following two sections list typical applications which emphasize the performance of the HOPG crystal for the determination of ‘light’ elements and the performance of the combination target \( \text{Al}_2\text{O}_3 \)/HOPG for overview analyses.

i) HOPG crystal

The HOPG crystal shows excellent excitation capabilities for ‘light’ elements. Because second and third order reflection can also be used for excitation, the investigation was extended to include the elements F - Fe. In comparison with a Cd secondary target for organic samples, the efficiency could be improved by a factor of 8 for the elements Na, Mg, Al, Si, P and S. The samples were measured for 400 s. Table 3 lists the lower limits of detection obtained with a Cd secondary target and with an HOPG crystal. The comparison shows an improvement factor between 5 and 10. This drastic improvement opens new fields of application, such as main component determination in rocks, slags, ceramics and refractories. Table 4 lists the concentration range, root mean square deviation (RMS) and correlation coefficient \( r \) determined for fusion tabletts of ceramics, minerals and refractories. The samples were measured twice using the HOPG crystal (300 s) and an Al secondary target (240 s). The
resulting correlation coefficient $r$ indicates the high quality of the calibration for all listed elements.

Table 3. Comparison of efficiency and lower limits of detection between a BRAGG polarizer (HOPG) and a Cd-secondary target for a typical organic sample BCR-101 spruce needles [22] (400s measuring time).

<table>
<thead>
<tr>
<th>$\text{BCR-101}$</th>
<th>$\text{LLD [\mu g/g]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Element}$</td>
<td>$\text{Cd-sec. target}$</td>
</tr>
<tr>
<td>Na *</td>
<td>1030</td>
</tr>
<tr>
<td>Mg</td>
<td>200.0</td>
</tr>
<tr>
<td>Al</td>
<td>60.0</td>
</tr>
<tr>
<td>Si</td>
<td>26.0</td>
</tr>
<tr>
<td>P</td>
<td>12.0</td>
</tr>
<tr>
<td>S</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*sample BCR-186 (pig kidney) [23]

Table 4. Concentration range, root mean square deviation (RMS) and correlation coefficient $r$ determined for fusion tabletts.

<table>
<thead>
<tr>
<th>oxide</th>
<th>conc. range $[\text{mg/g}]$</th>
<th>$\text{RMS*} [\text{mg/g}]$</th>
<th>$\text{correlation coefficient } r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>0.0 - 70.0</td>
<td>0.34</td>
<td>0.99989</td>
</tr>
<tr>
<td>MgO</td>
<td>0.0 - 970.0</td>
<td>1.1</td>
<td>0.99999</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.0 - 890.0</td>
<td>1.0</td>
<td>0.99999</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.0 - 990.0</td>
<td>1.1</td>
<td>0.99999</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.0 - 10.0</td>
<td>0.23</td>
<td>0.9952</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.0 - 36.0</td>
<td>0.28</td>
<td>0.9997</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.0 - 75.0</td>
<td>0.41</td>
<td>0.99985</td>
</tr>
<tr>
<td>CaO</td>
<td>0.0 - 650.0</td>
<td>0.71</td>
<td>0.99999</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.0 - 37.0</td>
<td>0.25</td>
<td>0.99971</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.0 - 1.0</td>
<td>0.06</td>
<td>0.9735</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.0 - 500.0</td>
<td>0.38</td>
<td>0.99999</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0 - 2.0</td>
<td>0.09</td>
<td>0.9884</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.0 - 135.0</td>
<td>0.86</td>
<td>0.99669</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.0 - 630.0</td>
<td>0.65</td>
<td>0.99999</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>0.0 - 12.0</td>
<td>0.3</td>
<td>0.9943</td>
</tr>
</tbody>
</table>

\[ RMS_j = \sqrt{\frac{\sum (c_j - c_{j^{\text{cal}}})^2}{n - p}} \]

$j$: calibrated element

$i$: standard

c$_j$: calculated concentration

c$_{j^{\text{cal}}}$: certified concentration

$n$: number of standards

$p$: number of calibration parameters

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ii) combination target Al₂O₃/HOPG

Rapid semiquantitative analysis of the elements Na - U in different matrices is possible using the combination target. An additional measurement is necessary to analyze the scattering behavior of the sample. The influence of non-detectable elements is determined using the scattering intensity. Calibration is based on fundamental parameters for fluorescence as well as scattering. For practical use, a method called ‘TURBOQUANT’ was created. Up to 60 elements, from Na - U, can be determined with a total measuring time of 100 s which includes two separate measurements (50 s with Mo secondary target, 37.0 kV, 5.10 mA and 50 s with combination target, 50.0 kV, 0.98 mA). Figure 4 shows the spectrum of BCR-176 [24] obtained with the combination target within 50 s. A comparison between certified and determined concentrations is shown in table 5. The good agreement with the certified values proves the performance of the method.

Figure 4. Overview analysis of standard sample BCR-176 (city waste incineration ash) within 50 s. Excitation with combination target Al₂O₃/HOPG and Rh end-window tube.
REFERENCES

(9) P. Wobrauschek, J. Trace and Microprobe Techniques 3, 6, 195 (1988).
(21) River sediment (Yangchun), State Bureau of Metrology, China.
(22) Spruce needles, Community Bureau of Reference, Brussels.
(23) Pig kidney, Community Bureau of Reference, Brussels.
(24) City waste incineration ash, Community Bureau of Reference, Brussels.