1- AND 2-DIMENSIONAL DETECTION SYSTEMS AND THE PROBLEM OF SAMPLE FLUORESCENCE IN X-RAY DIFFRACTOMETRY

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ABSTRACT

One of the possible sources of the background in a powder diffractogram is sample fluorescence: characteristic radiation from the sample, excited by the incident beam, which is accepted by the X-ray detection system. In this paper, the influence of the chosen X-ray optical geometry on the fluorescent background is determined experimentally from diffractograms recorded on a series of 10 samples with elements ranging from Ti to Ga. The samples were measured with incident or diffracted beam monochromators, beta filters in the incident or the diffracted beam, for Cu, Co and Mo radiation. A linear X-ray detection system was used. The recommendations how to tackle the problem resulting from these experiments, however, are generally applicable.

INTRODUCTION

For the correct interpretation of powder diffractograms, a good peak-to-background ratio is an important issue. The background in a powder diffractogram can originate from many sources, some of which are instrument-related, and some result from the sample itself [1]. The most important effects contributing to the background are:

- Diffraction from the continuous spectrum of the X-ray tube, the white radiation.
- Scattering of the X-ray beam at the air in the beam path. This effect will become more pronounced towards low 2θ angles.
- An amorphous component in the sample, which often results in shallow humps in the diffractogram. A well-known example is the hump caused by the glass walls of Lindemann capillaries in the Debye-Scherrer geometry.
- Fluorescent radiation of the sample excited by the incident X-ray beam. Almost all elements will emit fluorescent radiation but its effect will be most visible when the energy of the fluorescent radiation is close to that of the characteristic radiation used.

This paper solely deals with the last effect, as its magnitude can be hard to predict a priori: it depends strongly on the characteristic radiation, the element(s) in the sample and the X-ray optical system.

In the traditional diffractometer with the Bragg-Brentano focusing geometry, the problem of sample fluorescence was almost forgotten: the excellent energy-separating device in the diffracted beam (the curved monochromator of the Johann geometry, or an energy-dispersive detector), ensured that the detector accepts only information with the energy that corresponds to the characteristic radiation of the X-ray tube. The biggest disadvantage of the traditional X-ray diffraction geometry with the point detector, however, is of course the long data collection times required.
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In order to deal with this problem, 1- and 2-dimensional detection systems were made available commercially. These devices allow an increase in data collection speed up to two orders of magnitude. They do not, however, have a high energy resolution. For 1-dimensional detection systems, this problem can partly be solved with the application of a diffracted beam monochromator \[2\], for the 2-D detection system such a device is not commercially available.

There are basically four methods for removal of sample fluorescence:

1. Choice of the appropriate characteristic radiation
2. Use of an incident beam monochromator or beta filter
3. Use of a diffracted beam monochromator or beta filter
4. Use of Pulse Height Discrimination (PHD) in the detector

In this paper, the effectiveness of methods 1-3 is investigated for a photon-counting X-ray detection system that offers Pulse Height Discrimination: PANalytical’s X’Celerator detector \[3\]. The aim of this paper is to give the diffractionist an advice for the optimum choice of the X-ray optical configuration, depending on the elemental composition of the sample.

**EXPERIMENTAL**

A series of samples ranging from Ti to Ga was prepared covering the range of elements known as ‘problematic’ when working with the most widely used X-ray tube anode material: copper. When the pure elements were not available, the oxide was used instead. Solid samples were prepared out of powder materials by addition of 4 weight% Elvacite\textsuperscript{®} 2046\textsuperscript{1} and pressing with 20 tonnes pressure for 60 seconds. A trial experiment with Cu powder before and after the preparation demonstrated that neither the peak intensity nor the background was influenced. Unfortunately for some powders this preparation method did not work, for these samples, the backloading technique was used. Table 1 summarizes the samples and their preparation method, while the X-ray optical configurations are listed in Table 2.

Table 1. Samples used in this study, with their characteristic fluorescent lines.

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample</th>
<th>Preparation method</th>
<th>Kα (keV)</th>
<th>Kβ (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO\textsubscript{2}</td>
<td>Backloading in 27 mm holder</td>
<td>4.508</td>
<td>4.931</td>
</tr>
<tr>
<td>2</td>
<td>V\textsubscript{2}O\textsubscript{5}</td>
<td>Backloading in 27 mm holder</td>
<td>4.949</td>
<td>5.426</td>
</tr>
<tr>
<td>3</td>
<td>Cr</td>
<td>Mixed with 4% Elvacite\textsuperscript{®} and pressed</td>
<td>5.411</td>
<td>5.946</td>
</tr>
<tr>
<td>4</td>
<td>Mn</td>
<td>Mixed with 4% Elvacite\textsuperscript{®} and pressed</td>
<td>5.894</td>
<td>6.489</td>
</tr>
<tr>
<td>5</td>
<td>Fe</td>
<td>Mixed with 4% Elvacite\textsuperscript{®} and pressed</td>
<td>6.398</td>
<td>7.057</td>
</tr>
<tr>
<td>6</td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>Mixed with 4% Elvacite\textsuperscript{®}, backloading in 27 mm holder</td>
<td>6.924</td>
<td>7.648</td>
</tr>
<tr>
<td>7</td>
<td>Ni</td>
<td>Mixed with 4% Elvacite\textsuperscript{®} and pressed</td>
<td>7.471</td>
<td>8.263</td>
</tr>
<tr>
<td>8</td>
<td>Cu</td>
<td>Mixed with 4% Elvacite\textsuperscript{®} and pressed</td>
<td>8.040</td>
<td>8.904</td>
</tr>
<tr>
<td>9</td>
<td>ZnO</td>
<td>Backloading in 27 mm holder</td>
<td>8.630</td>
<td>9.570</td>
</tr>
<tr>
<td>10</td>
<td>Ga\textsubscript{2}O\textsubscript{3}</td>
<td>Backloading in 16 mm holder</td>
<td>9.241</td>
<td>10.263</td>
</tr>
</tbody>
</table>

Table 2. X-ray optical configurations used for this study. The X’Celerator detector was used, unless otherwise noted.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Time/ step</th>
<th>Scan time</th>
<th>Cu</th>
<th>Co</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHD + Monochromator in incident beam</td>
<td>84 s/step</td>
<td>60 min</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1} Elvacite\textsuperscript{®} is a trademark of Lucite International (http://www.luciteinternational.com). Elvacite\textsuperscript{®} is a thermoplastic acrylic resin used (in this case) to protect the powder sample for long-time use.
**Table 1: Scan Conditions**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Time/step</th>
<th>Scan time</th>
<th>Cu</th>
<th>Co</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHD + Monochromator in diffracted beam</td>
<td>100 s/step</td>
<td>72 min</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>PHD + Beta filter in incident beam</td>
<td>14 s/step</td>
<td>10 min</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PHD + Beta filter in diffracted beam</td>
<td>14 s/step</td>
<td>10 min</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Point detector and curved diffracted beam monochromator</td>
<td>4 s/step</td>
<td>5 hours</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All diffractograms were recorded with the same angular range: from $10^\circ$ to $100^\circ 2\theta$ on X’Pert PRO MPD diffractometers with a goniometer radius of 240 mm. The scan time was chosen in such a way that the diffractograms were recorded with about 10,000 counts in the main peak. The step size was close to 0.017$^\circ 2\theta$. Also a series was recorded with a point detector and a curved diffracted beam monochromator, representing the traditional Bragg-Brentano powder diffractometer. An automatic sample changer proved to be very useful for these experiments.

The following scan conditions were used:

- **Generator:** 45 kV, 40 mA for Cu, 40 kV, 40 mA for Co (45 kV for the measurements with beta filter), and 60 kV, 50 mA for Mo.
- **Incident beam optics:** $\frac{1}{4}^\circ$ divergence slit, $\frac{1}{2}^\circ$ anti-scatter slit, 0.04 rad Soller slits (absent with the incident beam monochromator), 10 mm mask.
- **Diffracted beam optics:** 5 mm diffracted beam anti-scatter slit, X’Celerator at full active length (2.1$^\circ 2\theta$), 0.04 rad Soller slits (absent with the X’Celerator monochromator measurements).

In the scans recorded with the proportional detector, the receiving slit was set to 0.3 mm in order to complete these scans in a reasonable time. The angular resolution of an X’Celerator-based diffractometer compares well with a receiving slit setting of 0.1 mm.

For the evaluation of the magnitude of the sample fluorescence, the background intensity was determined close to $90^\circ 2\theta$, in order to rule out any possible air scatter effect. Combined with a determination of the intensity of the strongest peak in the diffractogram, this allows a comparison of peak-to-background ratios for various configurations.

**DISCUSSION OF THE RESULTS**

As a starting point, the range of samples was measured with the traditional diffractometer geometry with a Cu tube, a curved diffracted beam monochromator and a point detector. Figure 1 shows the intensities of the background and of the strongest peak against the elemental composition of the sample.

It is clear from this figure that only when working with a Cu sample a significant fluorescence signal is detected: Cu K\(\alpha\) excited by the K\(\beta\) and the white radiation from the X-ray tube. The peak-to-background ratio of these diffractograms is very good, but the data collection time is by far the longest: 5 hours per scan.

For the linear detector, the influence of incident and diffracted beam monochromators on the background and peak intensities is shown in Figure 2 for Cu and Co radiation. The influence of beta filters is shown in Figure 3 for Cu, Co and Mo radiation.
Figure 1. Fluorescent intensity for a range of samples measured with Cu radiation, a point detector and a curved diffracted beam monochromator. The bars indicate the background intensity, while the diamonds represent the intensity of the strongest peak in each diffractogram.

From Figure 2 it can be concluded that in a configuration with a diffracted beam monochromator the range of elements giving rise to background increase is symmetrically spread around the characteristic radiation. In the case of an incident beam monochromator, the tube spectrum is reduced to $K\alpha$ radiation only. Now only fluorescent radiation from elements with an atomic number two positions below that of the anode material will give rise to fluorescence. The range is limited at the low-energy side by the PHD circuitry of the detector. It is clear from this figure that a proper choice of incident or diffracted beam monochromators and X-ray tube anode material restrict the range of elements that cause an increase of the background to a few only. A disadvantage of monochromators is that they cost intensity: for Cu radiation, the incident beam monochromator gives a reduction with a factor of 5 with respect to the Ni filter, for the diffracted beam monochromator this factor is 7.5.

Figure 3 shows the influence of the beta filter and its position in the beam path on the background intensity, as determined for three X-ray tube anode materials: Cu, Co and Mo. The beta filter position is quite important; its influence can be explained as follows:

- With the filter in the incident beam position, $K\beta$ is removed from the tube spectrum and only $K\alpha$ and white radiation now excite fluorescence. This explains the step in the fluorescent intensity between Co and Ni for Cu radiation, and between Mn and Fe for Co.

- With the filter in the diffracted beam position, all three components in the tube spectrum excite fluorescence. The step mentioned above is now less prominent. An additional step appears between Cu and Zn for Cu radiation, and between Co and Ni for Co radiation, caused by the fact that the beta filter in the diffracted beam now absorbs the fluorescent lines, a very effective process when these are above the absorption edge of the filter.

From these observations, a practical guideline can be derived: generally, the beta filter should be placed in the diffracted beam, with the exception of Ni samples when working with Cu radiation, and Fe samples when working with Co.
Figure 2. Background and peak intensities measured with the X’Celerator detector and a diffracted beam or an incident beam monochromator, with Cu or Co radiation.
Cobalt radiation is often advised instead of Copper for iron-containing samples. The results show that also when working with a Co tube and an iron filter, some fluorescence will occur. In practice the improvement upon switching from Cu to Co is much higher than can be concluded from the background intensities only. If one takes the peak intensities into account one can see that normally these will drop with an approximate factor of 2-3 when going from Cu to Co. When working with Co or Fe samples, however, the peak intensities will rise with a factor of 3! This interesting phenomenon is caused by the fact that Co and Fe have an absorption edge.
between Cu and Co Kα, which results in a much larger penetration depth for Co radiation, and thus a larger diffracting volume.

An alternative method to get rid of sample fluorescence when working with the first row of transition metals is to switch to Molybdenum radiation. All fluorescent radiation in the 6-10 keV range will now be rejected by the PHD circuitry. Figure 3 shows that this is indeed the case: upon switching to Mo radiation all fluorescent radiation from these samples is suppressed. Although the efficiency of the X'Celerator detector is low for Mo radiation, the net peak intensities are in the same range as those obtained with Cu radiation. This is due to the fact that the diffraction intensity is proportional to the energy of the characteristic radiation. A consequence of the use of Mo radiation is that the spectrum is condensed in the low-2θ regime, which restricts the use to samples with highly symmetrical unit cells. Nevertheless, Mo radiation can be a valuable alternative when working with mixtures of elements in the first row of transition metals.

Although this study helps answering a lot of questions regarding fluorescent samples, it also raises several additional questions, which could be subjects for a subsequent study, such as:

- Apparently, a considerable fraction of the fluorescence intensity is excited by the white radiation. The amount of white radiation is strongly dependent of the high voltage applied to the X-ray tube. One could possibly win some peak-to-background ratio by optimizing the kV and mA settings of the X-ray tube.
- In this study, the linear detector was used with its energy discrimination levels set to maximum intensity, the standard setting. As a result of this, the energy window accepted by the detector is rather wide. Initial experiments suggest that this window can be reduced considerably. Again, something that needs to be answered in an additional study.
- Only the first row of transition metals, giving rise to fluorescent K lines, was investigated. Also the Lanthanides and neighboring elements, with their L lines ranging from 5 to 10 keV, could give rise to an increase in the background. The solutions, however, will not differ from what has been described here. Generally, the effect will be less disturbing for these materials: the fluorescent intensity will be comparable, but the diffraction intensity will be much higher as this is proportional to the atomic number.

The results described in this paper can be used to predict the optimum instrumental configuration for a given analytical problem, as shown in the next section.

**SELECTING THE OPTIMUM CONFIGURATION FOR A GIVEN ANALYTICAL PROBLEM: A PRACTICAL EXAMPLE**

Figures 1, 2 and 3 can be used to estimate the optimum configuration for a specimen with one problematic element without going through extensive trials. In the case of mixtures of transition metals, however, selection of the optimum configuration can be more difficult. Let us consider the analytical problem of the phase identification of CoFe-nanocrystallites. It is expected that several iron and cobalt oxides are present in this material, some of them as minority phases. The amount of material to be investigated is small. What is the optimum X-ray diffraction geometry to choose?
According to Figure 1, for this particular problem the traditional powder diffraction geometry, Cu radiation and curved diffracted beam monochromator, is still very useful. The obvious disadvantage of this configuration is of course the speed. When switching to a linear detector in order to gain more speed and/or a higher sensitivity for minor phases, Figure 2 and Figure 3 show that when working with Cu radiation the presence of Co in the sample will give rise to sample fluorescence in all possible configurations. Also the intensity of the main peaks will be weak.

A possible alternative is Co radiation. When working with beta filters, Figure 3 shows that this improves the peak-to-background ratio already considerably. In order to prevent sample fluorescence completely, however, one needs to use an incident beam monochromator, as shown in Figure 2. The Johansson monochromator as used here will also take out the Kα₂ component.

One could also consider a switch to Molybdenum radiation. Sample fluorescence is now outside the detector’s energy window. A beta filter is sufficient so one can maximize the benefit of the fast detector. The only issue with Mo radiation is that the diffractogram is compressed to the low-2θ range and thus the angular resolution is reduced. For the phases expected in this analytical problem, all major reflections of the expected phases are above 20º 2θ for Cu radiation, so this forms no obstacle for switching to Mo radiation.

These assumptions were verified with the different configurations. It turned out that the information obtained with Cu radiation, the proportional detector and the curved diffracted beam monochromator, could be reproduced with Mo radiation, a Zr beta filter and a linear detector in a much shorter time frame: 5 hours against less than 10 minutes.

CONCLUSIONS

Sample fluorescence is an important contributor to the intensity of the background in X-ray powder diffractograms, especially when the fluorescent radiation is close to the characteristic radiation. This applies for instance to the first row of transition metals when the diffractometer is equipped with the commonly used Cu X-ray tube. Also the modern fast 1- and 2-dimensional X-ray detector with their limited energy-selective properties can be used with samples that contain high concentrations of these elements, provided that one makes the correct choice for the X-ray optical components. The guidelines for this decision process as given in this paper were used to predict the optimum configuration for CoFe-nanocrystallites and showed that also for this problematic sample one can benefit from the advantages of the these modern detectors: high-speed acquisition of powder diffraction data on a laboratory instrument.

REFERENCES

[1] Sources of background in the diffractogram and how these are influenced by the choice of optical components are a subject of most text books on X-ray powder diffractometry, such as: Klug, H.P.; Alexander, L.E. *X-ray diffraction procedures for polycrystalline and amorphous materials*, 2nd edition, John Wiley & Sons: New York, 1974.