X-Ray Fluorescence Elemental Analysis for Polymer and Film Coating Characterization Applications

16th International MOCON Conference – Permeation Measurement Today

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Where to Find SPECTRO
Elemental Analysis Using XRF

- Basics
- Highlights / Limitations
- Applications
XRF Basics – Principle

Excitation

X-ray

Nucleus

K Shell

L Shell

Atom

Electron

Characteristic Radiation
XRF Basics – Principle
**ED-XRF Instruments**

- ED-XRF instruments are available as handheld, portable and laboratory units.
- Depending on the configuration they can be used for bulk or small spot applications.
Applications XRF

- Process control applications (bulk analysis)
  - *Substances which influence the performance or the color of polymers. Concentrations can be up to several %*
    - Stabilizers, i.e. Ca- and Zn- compounds, CuI, KI, KBr …
    - Fillers, i.e. talcum, chalk and lime stone (CaCO₃), kaolin, feldspar …
    - Pigments, i.e. rutile or anatase (TiO₂), ZnO, ZnS, Fe₂O₃…
    - Flame retardants, i.e. brominated compounds, organo-phosphor and inorganic flame retardants …

- Process control applications (coating thickness)
  - *Substances which influence the surface capabilities of polymer films*

- Compliance Screenings

- Test for non-intentionally added substances (NIAS)
Applications XRF

Examples for process control applications

- Trace element content of Ti
- Medium content of TiO$_2$ in ABS
- Medium content of CuI in polyamide
- Aluminum based coatings for food packaging
- Silicone based release coatings
- Platinum based coatings
XRF Applications
Example: Analysis of Low Levels of Ti in Polymer

- The content of low levels of Ti can be a challenge for any XRF instrument
- With optimized excitation and detection lower levels of detection can be reached

<table>
<thead>
<tr>
<th>Intensity</th>
<th>Conc. In mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.83</td>
<td>0.71</td>
</tr>
<tr>
<td>38.05</td>
<td>0.75</td>
</tr>
<tr>
<td>39.2</td>
<td>0.77</td>
</tr>
<tr>
<td>39.13</td>
<td>0.77</td>
</tr>
<tr>
<td>38.07</td>
<td>0.75</td>
</tr>
<tr>
<td>39.44</td>
<td>0.78</td>
</tr>
<tr>
<td>39.11</td>
<td>0.77</td>
</tr>
<tr>
<td>39.94</td>
<td>0.79</td>
</tr>
<tr>
<td>39.14</td>
<td>0.77</td>
</tr>
<tr>
<td>38.37</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Average: 0.76
Std dev.: 0.022
One of the typical analysis application examples is the analysis of TiO$_2$ as pigment.
- Cul is used as stabilizer in polyamide
- Using XRF the content of Cu and the content of I can be determined
- In addition, typically present elements like K and Br can be analyzed as well
Even at high concentrations of Cu, a good correlation can be achieved.

Also the precision of the analysis is very good.
Aluminum coating
- Measurement of coated side
- Measurement of print side
Silicone based release coatings
- Coat weight typically 1..2 mg/m²
Pt thin film coating
RoHS

Max. concentrations
- Cd: 0.01 %
- Cr (VI), PBB, PBDE, Hg, Pb: 0.1 %

Packaging directive

Halogen-free regulations

In the US e.g. consumer product safety improvement act (CPSIA)
- Pb in children’s products
- Pb in paint in consumer products

In California e.g. California’s Safe Drinking Water and Toxic Enforcement Act (Prop 65):
- Some examples:
  - Books with vinyl or PVC covers ≤ 90 ppm Pb
  - Brass cooler drains and other brass products designed for evaporative cooler pads, pumps, motors, accessories ≤ 100 ppm Pb, otherwise warning

… and many more
RoHS Screening and halogen-free testing
- Substances previously used may still find their way into new products via recycling
- XRF accepted as screening procedure
  • i.e. in IEC 62321-3-1
Dossier – Non-intentionally added substances (NIAS)

June 2018, 2nd edition

Birgit Geueke

1 What are NIAS?

Food contact materials (FCMs) and food contact articles (PCAs) may contain non-intentionally added substances (NIAS) which can potentially migrate into food. NIAS comprise all substances that have not been added for a technical reason during manufacturing of FCMs and PCAs. They have various sources and can be grouped into side products, breakdown products, and contaminants (Figure 1A). NIAS can enter the supply chain of FCMs/PCAs at any level, e.g., during chemical syntheses of raw materials as well as manufacturing processes, a comprehensive prediction of all potential side products remaining in the final FCM is currently impossible [9].

Oligomers are typical side products formed during the synthesis of polymers [7]. In terms of quantity, oligomers can strongly contribute to the overall migration of a plastic FCM [8, 9]. Although their presence is usually known to the manufacturer, the risk assessment of oligomeric mixtures is challenging, because of their complex composition.
Investigation of Inclusions in a Polymer Surface

- To identify and analyze inclusions in a polymer surface XRF instruments with a small spot size are suitable.

- This example shows the identification and analysis of wear particles on a polymer surface.

- After a visual inspection particles are identified on the polymer surface.

- The element mapping shows elevated signals from Fe, Cr and Ni.

- Mapping 21*30 Points
Investigation of Inclusions in a Polymer Surface

- A detailed look shows that the particles show differences in their composition
Spot Analysis of Single Particles

- The spot analysis of single particles can be used for a quantification of the composition
  - 180 s per spot

- A material identification is possible based on the analysis results

<table>
<thead>
<tr>
<th></th>
<th>1.8550 specification in %</th>
<th>Spot analysis using SPECTRO MIDEX in %</th>
<th>1.2379 specification in %</th>
<th>Spot analysis using SPECTRO MIDEX in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.5 - 1.8</td>
<td>0.8759</td>
<td>11.0 - 12.0</td>
<td>9.95</td>
</tr>
<tr>
<td>Cr</td>
<td>0.85 - 1.15</td>
<td>0.17</td>
<td>&lt;</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.15 - 0.25</td>
<td>0.18</td>
<td>0.6 - 0.8</td>
<td>0.20</td>
</tr>
<tr>
<td>Mo</td>
<td>0.4 - 0.7</td>
<td>0.64</td>
<td>0.15 - 0.45</td>
<td>0.41</td>
</tr>
<tr>
<td>Other (C, Al, Si, ...)</td>
<td>max. 2.03</td>
<td>max. 2.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Summary**

- XRF is a useful analysis technique for the elemental analysis of polymers
  - for various elements
  - in various matrices
  - in concentration ranges from a ppm to % levels

<table>
<thead>
<tr>
<th></th>
<th>Best suited</th>
<th>Well suited</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compliance screening</td>
<td><img src="image1.png" alt="Image" /> <img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Process control</td>
<td><img src="image4.png" alt="Image" /> <img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Process control incl. light elements</td>
<td><img src="image7.png" alt="Image" /> <img src="image8.png" alt="Image" /></td>
<td></td>
</tr>
<tr>
<td>Process control incl. trace elements</td>
<td><img src="image9.png" alt="Image" /> <img src="image10.png" alt="Image" /></td>
<td></td>
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<tr>
<td>Inclusions</td>
<td><img src="image11.png" alt="Image" /> <img src="image12.png" alt="Image" /></td>
<td></td>
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</tbody>
</table>
Visit http://www.spectro.com


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