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Analysis of Recycled Materials: Capabilities and Limitations of XRF

XRF is widely used for rapid screening, but its effective application to recycled materials requires a clear understanding of its limitations and material complexity

The analysis of recycled materials – such as solar panels, printed circuit boards (PCBs), black mass and other complex recycling streams – is a growing analytical challenge. In this context, analysis primarily refers to the quantitative determination of the elemental composition. Recycled materials are not only highly heterogeneous, but also inherently variable in composition between batches, depending on their origin, processing history, and degree of contamination. As a result, no single analytical technique can provide a complete and reliable characterization.

Outline

For routine screening of stable production processes, X-ray Fluorescence (XRF) techniques are widely applied. This application note explains why XRF is a valuable tool for the initial screening of recycled materials but should not be considered a standalone analytical solution. The focus is on the main XRF techniques – WDXRF and EDXRF – and their strengths and limitations in recycling analysis. In addition, complementary analytical techniques are briefly reviewed, including LIBS, ICP, IGA, IC, XRD and SEM, which are essential for comprehensive characterization and for closing elemental mass balances. Above all, we address the importance of sampling and sample preparation.

Critical Role of Sampling and Sample Preparation

The most important – and often underestimated – part of the analysis of recycling materials is sampling and sample preparation. If these steps are poorly executed, any subsequent analytical result becomes meaningless, regardless of how advanced the analytical technique may be.

First, the sample supplied by the recycler must represent the entire batch. Poor sampling introduces systematic errors that cannot be corrected analytically. Once in the lab, the sample undergoes splitting to reduce mass while maintaining representativeness, followed by shredding and grinding to achieve homogeneity. The obtained homogeneous powder must then be prepared for further analysis. Preparation depends on the analytical technique applied, for example pressing pellets for XRF or performing acid digestion for Inductively coupled Plasma (ICP) based techniques. During sample preparation, multiple pitfalls can occur, such as oxidation of metals, loss of volatile elements, contamination originating from grinding media, and incomplete homogenization.

Figure 1. Example of a mixed stream of e-waste

Key takeaway: investing time and resources in proper sampling and sample preparation is essential. An unrepresentative or inadequately prepared sample will always generate results, but the results will be unreliable. *"Poor sample in, poor results out."*

XRF as a Screening Tool

Once a representative and well-prepared sample is available, analytical measurements can start. XRF techniques are generally classified into two main measurement principles: wavelength-dispersive XRF (WDXRF) and energy-dispersive XRF (EDXRF).

Wavelength-Dispersive XRF (WDXRF)

WDXRF uses wavelength-dispersive optics (crystals) to separate X-ray wavelengths prior to detection. WDXRF is capable of measuring elements from fluorine (F) to uranium (U). It offers excellent spectral resolution, allowing accurate separation of closely spaced elemental peaks. Depending on the element, detection limits can reach the low µg/g range, particularly for heavy elements. As a result, WDXRF is well suited for the analysis of major and minor elemental concentrations.

Energy-Dispersive XRF (EDXRF)

EDXRF measures X-ray energies directly using an energy-dispersive detector. The theoretical elemental range extends from magnesium (Mg) to uranium (U). However, light elements such as aluminum, silicon, phosphorus and sulfur are difficult to measure unless they are present at relatively high concentrations. Typical detection limits are in the order of 100 µg/g.

While XRF is a powerful and versatile technique, the accuracy and reliability of quantitative results strongly depend on matrix composition and material properties, including particle size effects, variable density, and the presence of mixed phases such as metals and metal oxides. In addition, spectral line overlaps for certain elements can further complicate accurate quantification.

Reliable quantification therefore requires appropriate calibration using representative, matrix-matched reference materials. In complex recycling streams, these are often not available, making accurate calibration challenging and potentially limiting the reliability of quantitative results. In such cases, fundamental parameter (FP) approaches can be applied, although these often come with reduced accuracy for highly complex and heterogeneous matrices.

In addition to these challenges, a fundamental limitation of XRF is that a significant fraction of the material is "invisible" to the technique. In WDXRF, elements such as hydrogen (H), lithium (Li), boron (B), carbon (C), nitrogen (N) and oxygen (O), cannot be detected, while EDXRF is even more limited in its ability to measure light elements. Because XRF only reports concentrations for detectable elements, the results are normalized to this incomplete elemental set. This normalization can lead to artificially high reported concentrations, apparent inconsistencies between batches, and incorrect interpretation of elemental mass balances.

Limitations of Handheld XRF (HHXRF)

Handheld XRF (HHXRF) instruments are based on EDXRF technology and are often considered attractive due to their speed and ease of use. However, their suitability for reliable quantitative characterization of complex and heterogeneous recycling materials remains limited.

Key limitations include spectral interferences (which are generally more pronounced than in conventional EDXRF instruments due to lower spectral resolution), relatively high detection limits, and the inability to detect certain light or critical elements, resulting in an inherently incomplete measured composition.

In addition, the small measurement spot of HHXRF further limits representativeness. In highly heterogeneous recycling streams, individual measurements may reflect only local variation rather than the true bulk composition, leading to substantial variability between measurements and poor correlation with laboratory-based bulk analysis. This can result in misleading conclusions when assessing material composition and value.

Furthermore, accurate calibration remains challenging due to the lack of suitable matrix-matched reference materials. As a result, while HHXRF is well suited for rapid screening and sorting, it generally lacks the accuracy and analytical robustness required for quantitative analysis, process optimization, and informed decision making in recycling applications.

Table 1. Strengths and Limitations of WDXRF vs Handheld EDXRF for Heterogeneous Materials

	WDXRF	HH-EDXRF
Accuracy	✓	✗
Detection limits	✓	✗
Spectral resolution	✓	✗
Light elements	✓	✗
Representativeness	✓	✗ small spot, local variation
Speed	✗	✓
Portability	✗	✓
Screening	⚠ overqualified	✓ simple, homogeneous material
Quantification	✓	⚠ limited

Limitations of Handheld XRF

- Many critical elements are not detectable.
- Small spot size limits representativeness.
- Limited spectral resolution for overlapping peaks.
- Relatively high detection limits.
- Accurate calibration is extremely challenging.

The Need for Complementary Analytical Techniques

XRF cannot function as a standalone analytical technique for complete elemental characterization of complex recycled materials. To close elemental mass balances, additional techniques are required, providing complementary information.

Elemental Composition

For bulk elemental analysis, Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) enable accurate quantification of major, minor and trace elements. However, these techniques generally require complete sample dissolution, which can be challenging for heterogeneous recycled materials.

Depending on the matrix, tailored mixed-acid or multi-step microwave-assisted digestion protocols may be required. Such approaches can increase method complexity and turnaround times. These procedures frequently involve aggressive reagents such as hydrofluoric acid (HF) or perchloric acid, introducing additional safety concerns. Refractory phases and halogen-containing fractions (Cl, Br, F) may further lead to the formation of corrosive acids and volatile species.

Combustion and fusion elemental analysis (often referred to as IGA) is essential for the determination of light elements such as H, O, C and N, which are not detectable by XRF. Ion chromatography (IC) is particularly suited for the analysis of halogens such as F, Cl and Br.

Beyond Elemental Composition: Chemical Form and Structural Information

In addition to determining elemental concentrations, it is equally important to understand how these elements are present within recycled materials. For example, fluoride can occur in various chemical states and matrices, including incorporation within polymeric materials (e.g. as PFAS compounds), within glass matrices, or as residual inorganic species (e.g. LiF) originating from electrolyte components in recycled battery material. Aluminum may originate from different sources or exist in multiple chemical forms. Likewise, metals may be present as pure metals, oxides or other compounds, each of which can significantly influence material behavior and processability.

Techniques such as X-ray Diffraction (XRD) provide insight into the crystalline phase composition, while Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation ICP-MS (LA-ICP-MS) enable spatially resolved elemental and chemical analysis. Scanning Electron Microscopy with Energy-Dispersive X-ray (SEM-EDX) further supports this by linking elemental distribution to microstructure. Together, these techniques provide a deeper understanding of phase composition, elemental distribution, and chemical form.

Morphology and Physical Properties

Beyond chemical composition, material characteristics such as particle morphology and size distribution are relevant. SEM enables visualization of particle morphology, while particle size distribution and specific surface area measurements provide insight into bulk physical properties. In addition, thermogravimetric analysis (TGA) can support the evaluation of material composition and thermal stability. These parameters are often critical for understanding process performance and overall material quality.

Conclusion

For routine screening of stable production processes, a single analytical technique such as XRF can be highly effective. However, complete and reliable characterization of complex and heterogeneous recycled materials requires generally a multi-technique approach.

Equally important, the reliability of any analytical result fundamentally depends on representative sampling and proper sample preparation.

When applied within its capabilities, XRF remains a powerful and efficient tool. In particular, WDXRF provides robust, high-throughput quantification of many major and minor elements with minimal preparation. However, its results must be interpreted with a clear understanding of its limitations and supported by additional analytical methods.

Contact

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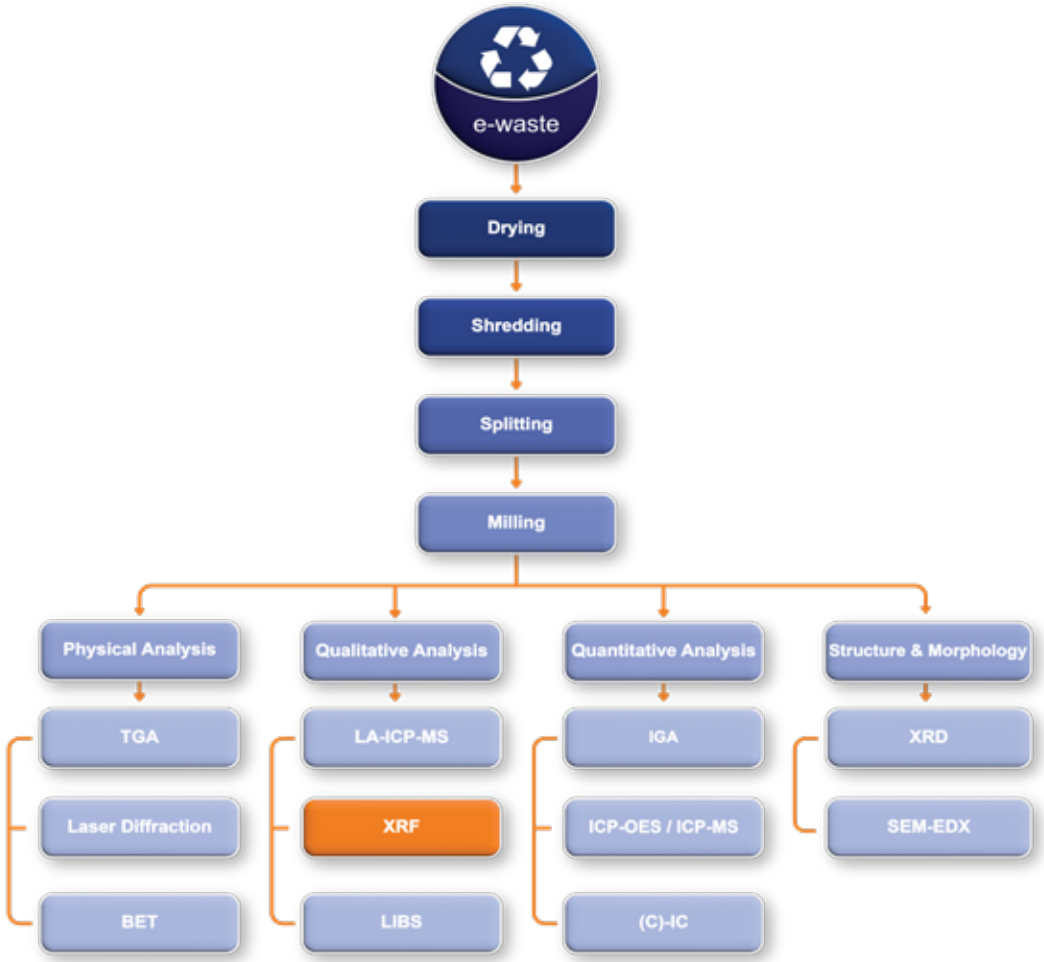

Figure 2. Illustrative workflow showing common pre-treatment steps and selected analytical techniques for e-waste characterization