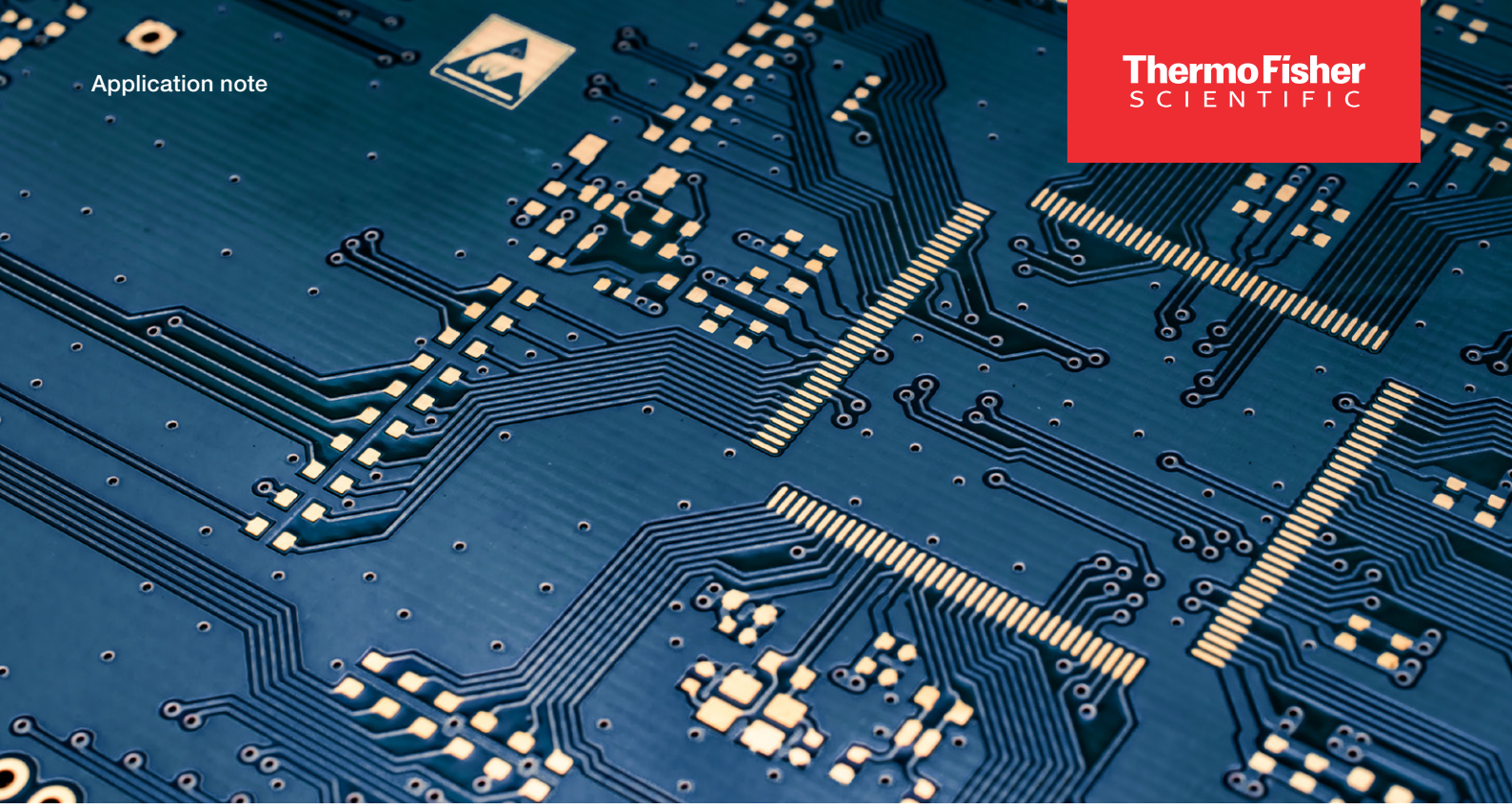

Application note

RoHS compliance and halogen screening with handheld XRF analysis

Author

Mathieu Bauer,
Senior Application Scientist

Key terms

Niton XL5 Plus, RoHS compliance, XRF Analyzer, TestAll Mode, regulatory compliance, analytical sensitivity

RoHS compliance screening

The European Union's initial Restriction of Hazardous Substances (RoHS) Directive (2002/95/EC) was instituted with the aim of limiting pollution caused by electrical and electronic equipment. It prohibits manufacturers from using materials, parts, and subassemblies that contain more than 1000 ppm each of mercury (Hg), lead (Pb), hexavalent chromium (CrVI), polybrominated biphenyls (PBB), or polybrominated diphenyl ethers (PBDE), or more than 100 ppm of cadmium (Cd). The RoHS II directive (2011/65/EU) expanded upon the initial regulation to cover additional products such as medical devices and monitoring or control instruments. The RoHS II directive was later amended (2015/863/EU) to prohibit four more substances: Bis(2-Ethylhexyl) phthalate (DEHP), Benzyl butyl phthalate (BBP), Dibutyl phthalate (DBP), and Diisobutyl phthalate (DIBP), at levels above 1000 ppm. The RoHS directive is related to the Waste Electrical and Electronic Equipment Directive (2012/19/EU), which regulates the recycling of all types of electrical goods.

Similar regulations have been promulgated in many countries outside of the European Union (EU). This includes the Chinese Measures for Administration of the Pollution Control of Electronic Information Products (Chinese RoHS); the Japanese standard JIS C 0950 (Japanese RoHS); and the Korean Act for Resource Recycling of Electrical and Electronic Equipment and Vehicles (Korean RoHS). In the US, California has passed the Electronic Waste Recycling Act of 2003 (EWRA). This law prohibits the sale of electronic devices, including LCDs and CRTs, that are non-RoHS-compliant. Also, the California Lighting Efficiency and Toxics Reduction Act applies RoHS to lighting products. Several US states do ban heavy metals such as mercury or PBDE.

Since these regulations took effect, manufacturers in many countries have sought a cost-effective analytical sample testing solution to ensure the raw materials they use are RoHS compliant.

Halogens under review

In addition to monitoring the compounds covered by RoHS, electronic manufacturers and suppliers are paying greater attention to reducing halogens in consumer electronics and other consumer goods. Electric and electronic equipment can contain chlorinated or brominated flame retardants in cable jackets, connectors, printed circuit boards, tapes, or adhesives. When end-of-life equipment is burnt or exposed to heat, dioxins and furans can form as unwanted byproducts of combustion; this can lead to health and environmental issues. As a result, an industry-sponsored effort is underway to provide halogen-free flame retardant products.

Several standards, such as the JPCA-ES-01, the IEC 61249-2-21, or the IPC 4101, propose a definition of halogen-free components as follows:

- 900 ppm maximum chlorine (Cl)
- 900 ppm maximum bromine (Br)
- 1,500 ppm maximum total halogens

X-Ray fluorescence analysis

Compliance with RoHS regulations (2011/61/EU) is achieved when every homogeneous part of a product contains less than 100 ppm Cd and less than 1000 ppm Pb, Hg, Cr (VI), PBB, and PBDE.

X-ray fluorescence spectrometry (XRF) can screen for Cd, Pb, Hg, Cr, and Br according to the international standard IEC 62321 [1]. Figure 1 shows the screening logic with XRF analysis for a sample of a homogenous product part. Depending on the level of the detected element, the samples are classified as compliant (pass), non-compliant (fail), or inconclusive.

Compliant: If the pass criteria are met for all elements (less than 70 ppm Cd and less than 700 ppm Pb, Hg, Cr(VI), PBB, and PBDE), then the sample passes and is compliant with the RoHS directive.

Inconclusive: If any one of the elements does not meet the pass criteria, then the sample cannot be considered compliant. If the element(s) that don't pass have data in the inconclusive range, the sample needs further testing with laboratory instrumentation, as it may yet be compliant. The inconclusive range is less than 130 but more than 70 ppm Cd, less than 1300 but more than 700 ppm for Pb and Hg, more than 700 pm Cr(VI), and more than 300 ppm Br (equivalent to 700 ppm PBB or PBDE).

Fail: If the measurement of any one of the elements falls into the fail range, then the entire sample is non-compliant.

Because XRF is a method of elemental analysis and does not detect molecules, it can't provide information about the presence or concentration of phthalates. Therefore, further screening of the plastic product parts should be conducted using infrared spectrometry[2] or gas chromatography coupled with mass spectrometry[3].

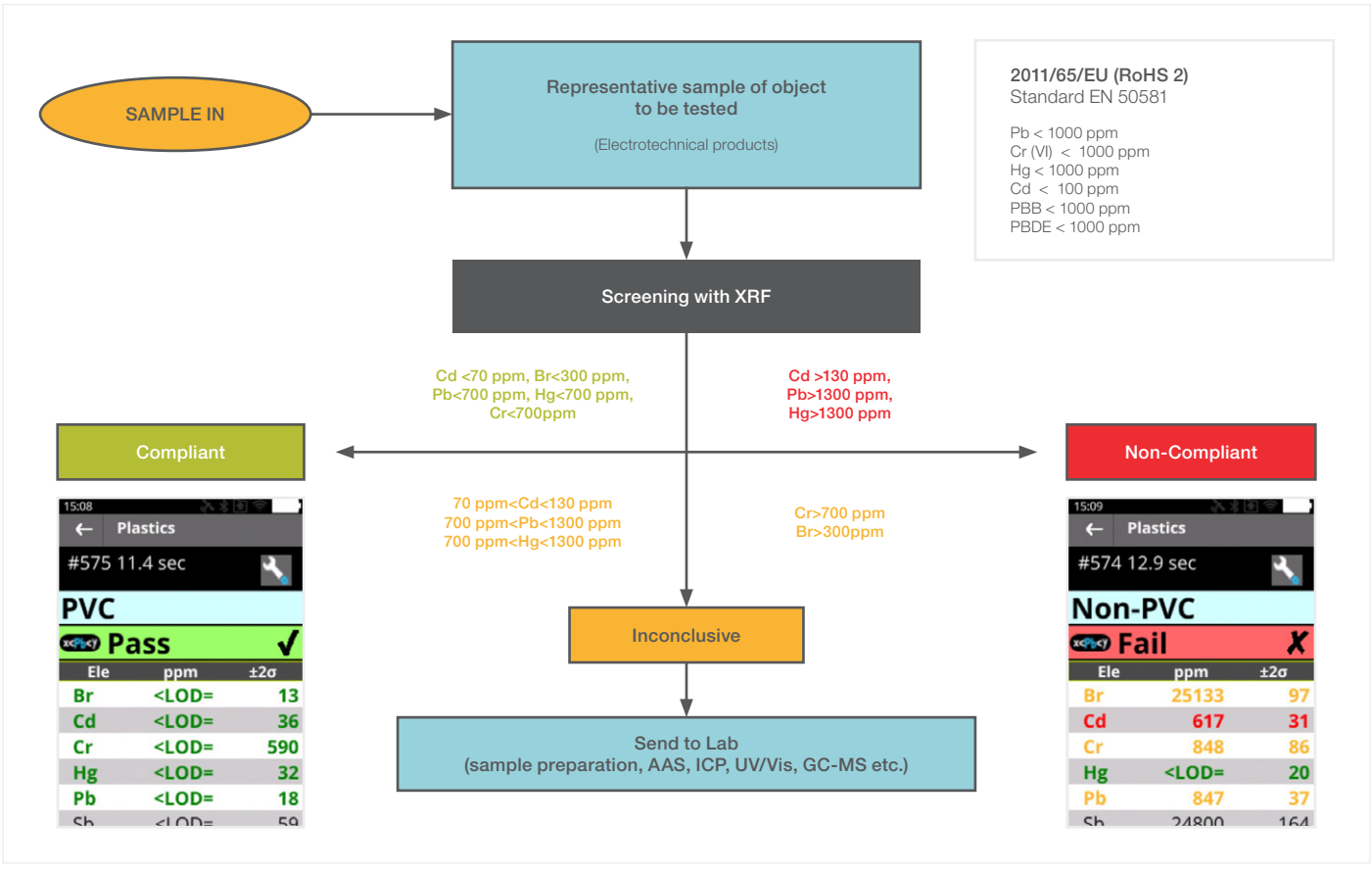

Figure 1. XRF analysis screening logic, according to standard IEC 62321.

Niton XL5 Plus Handheld XRF Analyzers

With a 5W proprietary miniaturized X-ray tube and a large area silicon drift detector with a graphene window, the Thermo Scientific™ Niton™ XL5 Plus XRF Analyzer belongs to the latest generation of handheld XRF instruments, providing enhanced analytical performance for fast, reliable and nondestructive screening of a large variety of materials used in electronic and electric products.

The Niton XL5 Plus analyzer is available with fit-for-purpose applications, called modes, to analyze all types of materials used in electronic and electric products. The Electronic Metals and Plastics Modes use proprietary fundamental parameter (FP)-based standardless calibrations that account for variations in the sample composition to deliver accurate results. Metals, alloys, ceramics, and glass are analyzed using the Electronic Metals Mode, whereas all types of plastics and polymers are analyzed using the Plastics Mode. The user can operate the Niton XL5 Plus analyzer and fulfill requirements from the standards IEC 62321-3-1 [4] or ASTM F2617-15 [5] for the analysis of heavy metals and bromine in every type of material covered by the respective standards.

The Niton XL5 Plus analyzer operates the X-ray tube at a variable current, which is automatically ramped up to maximize the count rate recorded by the detector. This way, the analytical sensitivity is optimized for every measurement, and best-in-class detection limits can be obtained, as reported in Table 1.

	PVC	PE	Sn-base	Cu-base	Fe-base	Al-base
Pb	4	1	79	44	63	3
Hg	7	1	150	74	51	7
Cd	8	4	140	19	13	3
Br	3	1	24	14	9	1
Cr	13	4	48	29	66	28
Cl	N/A	6	N/A	N/A	N/A	N/A

Table 1. Niton XL5 Plus analyzer limits of detection in ppm (mg/kg). Three sigma criterion, 60-second analysis times per filter (120 seconds total analysis time).

The Niton XL5 Plus analyzer delivers outstanding analytical performance and has numerous features to enhance the ease of use, productivity, and traceability of RoHS screening analyzes.

- TestAll™ Mode is an extra measurement mode that automatically recognizes the type of material and picks the correct analysis. An example is shown in Figures 2a, 2b, and 2c: the analyzer accurately identifies the specimens as metal (solder), non-metal (glass), and plastic (PVC). TestAll Mode considerably simplifies the workflow of users analyzing various types of materials.
- A micro camera allows users to locate and precisely position the analyzer in the area of interest and to capture a picture of the measurement spot, which is stored along with the analysis data for easy reference, data management, and data integrity.
- The small spot feature, combined with the micro camera, makes it possible to focus the analysis on an area of 3 mm in diameter. This can be done as needed for isolating and measuring individual small components, such as leads or terminations on a populated PCB. Reverting to a standard spot size of 8mm is more suitable for large homogenous specimens.
- A macro camera and the tag feature capture a visual record of the item and spot to be analyzed with a tag.
- A wide range of threshold types allows users to adapt their analyzes to any situation where targeted elements must be monitored and clear pass/fail/inconclusive results must be displayed. Default threshold settings are available for RoHS and halogen screening multiple profiles can be set up and stored on the same instrument to set the measurement parameter according to different standards such as ASTM F963, IEC 62321, IEC 61249, etc.
- The thickness correction feature improves accuracy in analyzing plastic samples with thicknesses down to 0.5 mm. Without such a feature, there is a risk of underestimating concentrations of heavy elements and missing non-compliant items.

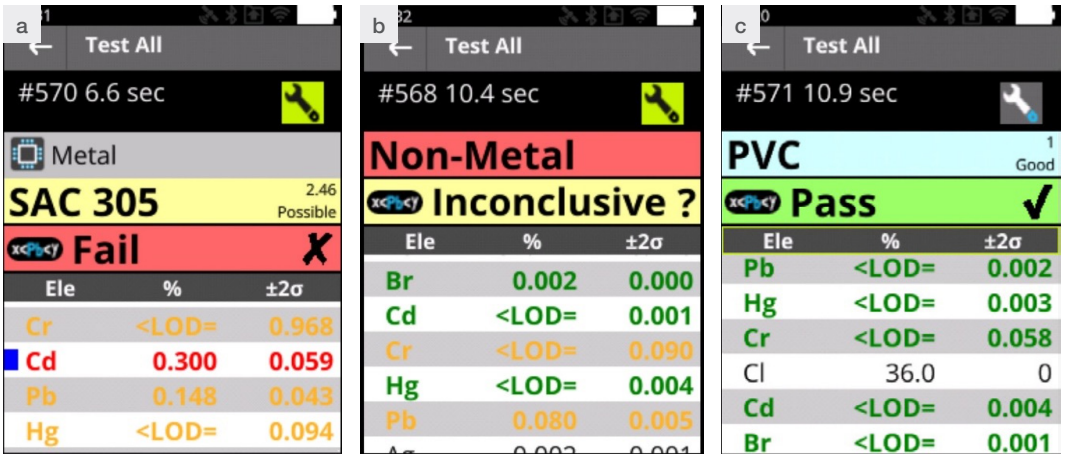

Figure 2. Analysis results using TestAll Mode, where the analyzer automatically selects the appropriate measurement mode to analyze a) a tin solder; b) a part made of glass; and c) a part made of plastic.

Electronic and electric equipment

Rapid, nondestructive analysis of heterogenous samples from small electronic components, such as populated circuit boards, can be challenging. This is especially true when individual components are small and mounted close together, making them difficult to analyze, and are themselves typically heterogeneous in composition. The Niton XL5 Plus analyzer meets and can even exceed such a challenge.

When a homogenous measurement spot of the material is isolated, the Niton XL5 Plus analyzer can be used directly to analyze the specimen without sample preparation (see Figure 3a). In some cases, when regulations or standards require analyzing homogeneous units, as in the RoHS II directive and the related Standard IEC 62321, thin or very small parts may have to be dismantled from the product before analysis. For better ergonomics, small-sized samples or electronic parts such as printed circuit boards (PCBs) can also be analyzed using the Thermo Scientific™ XL5 Portable Test Stand™ (Figure 3b), which converts the analyzer into a small benchtop unit and provides laboratory-like conditions.

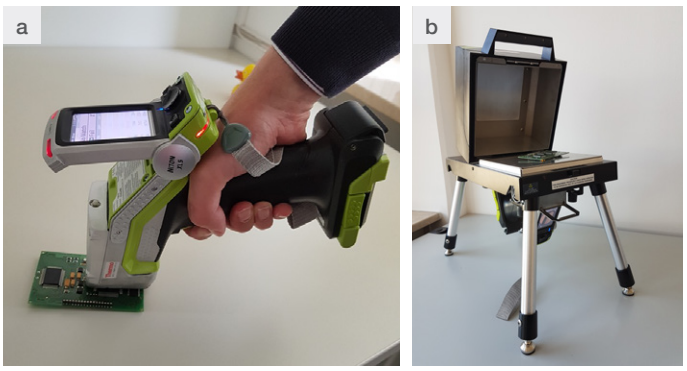

Figure 3. a) Niton XL5 Plus analyzer aiming at PCB; b) analyzer mounted in a portable test stand.

To illustrate the screening process according to IEC 62321-3-1, homogeneous units were analyzed for RoHS compliance.

Figure 4a shows the results of analyzing a PCB substrate made of plastics. It contains high levels of Br, which is generally used as a flame retardant. XRF analysis cannot determine PBB or PBDE, but it can detect the total level of Br, which could be related to a non-compliant level of PBB or PBDE. The instrument displays “inconclusive,” according to IEC 62123; further analysis needs to be done in a laboratory to determine whether the Br compound is PBB or PBDE.

Figure 4b shows the analysis results of a solder point analysis using the small spot feature. The solder point is not compliant with the RoHS directive because the measured value of Pb is higher than the threshold of 1300 ppm (defined in the standard IEC 62321). Hence, the analyzer displays “Fail.”

Figure 4c shows the analysis results of polyethylene pellets screened for halogens. The measured content of Br and Cl are respectively below the threshold of 500 ppm for each element set in the standard IEC 61249. The sum of Cl+Br is above the threshold of 1500 ppm; hence, the polyethylene pellets are not halogen-free, and the instrument displays “Fail.”

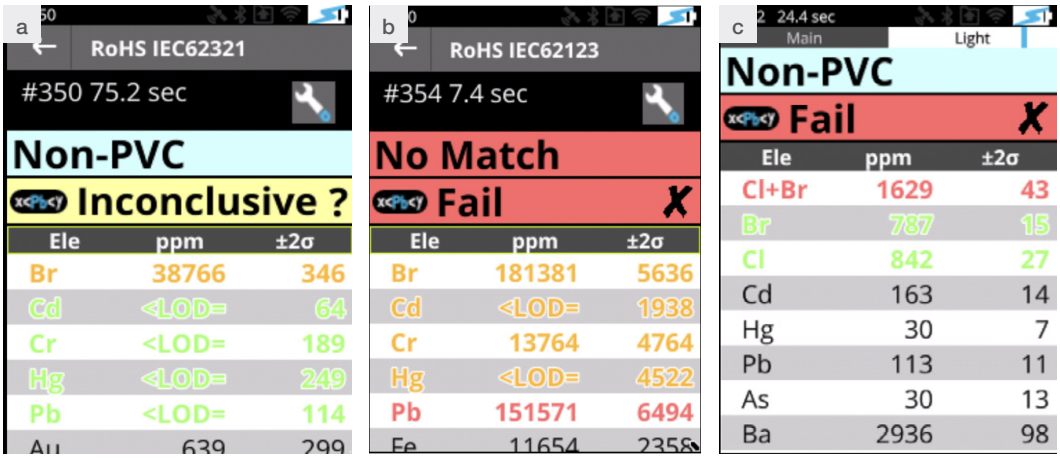

Figure 4. a) screening of PCB substrate according to IEC62321-3-1; b) screening of solder point according to IEC62321-3-1; c) screening for halogens in plastics: Cl, Br, and sum Cl+B.

Conclusion

Numerous regulation authorities worldwide, such as the US's Consumer Product Safety Commission (CPSC), use handheld XRF analyzers as on-site screening tools for heavy metals and halogens to complement traditional lab analysis. Several of those same authorities encourage manufacturers also to use handheld XRF analyzers in their processes to ensure compliance.

Many manufacturers, importers, and retailers of electrical and electronic products have incorporated handheld XRF testing into their workflows as additional insurance and due diligence to ensure regulatory compliance. In this way, handheld XRF assists in a "trust but verify" philosophy.

Handheld XRF analyzers are easy to use and provide nondestructive point-and-shoot analysis of heavy metals and halogens across the entire supply chain. Furthermore, a handheld XRF analyzer is designed to provide accurate measurements regardless of the user's skill level. After a manufacturer implements the handheld XRF analysis method, the total number of samples analyzed increases dramatically. In contrast, the number of samples sent to the lab and the average cost of analysis decreases significantly.

With improved sensitivity and portability, the Niton XL5 Plus is among the most powerful and advanced handheld XRF analyzers. It helps users further increase sample throughput while preserving analytical sensitivity, which reduces the probability of non-compliant items falling through the cracks and resulting in product recalls.

References

1. Standard IEC 62321-1:2013 Determination of certain substances in electrotechnical products
2. Enhanced Sensitivity to Detect Phthalates by FT-IR, https://assets.thermofisher.com/TFS-Assets/MSD/Application-Notes/AN52157-enhanced-sensitivity-detect-phthalates-ftir.pdf
3. Rapid determination of phthalates in polymers, https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-73587-gc-ms-phthalates-polymers-an73587-en.pdf
4. Standard IEC 62321-3-1: Determination of certain substances in electrotechnical products Part 3-1: Screening — Lead, mercury, cadmium, total chromium, and total bromine by X-ray fluorescence spectrometry
5. Standard ASTM F2617-15: Test Method for Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometer

Learn more at **thermofisher.com/xl5plus**