Screening Consumer Products for Toxic Substances
X-ray Fluorescence and Reducing Compliance Risk

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Consumer Products White Paper

ABSTRACT
The passage of the Consumer Product Safety Improvement Act (CPSIA) of 2008, H.R. 4040, reduces the permissible levels of lead (Pb) in paint, sets allowable levels of lead in all other materials, implements an alternative standard for measuring lead in surface coatings, and permits the use of x-ray fluorescence (XRF) analyzers for screening purposes.

An effective screening program using handheld XRF analysis greatly reduces the chances that lead-containing materials will enter the manufacturing process or accidentally end up on store shelves. This starts with a process that includes rapid screening of metals, polymers, and components at the (subcontractor's) receiving dock, in the warehouse, during product assembly, and even at vendor sites, including testing through packaging to save time.

Thermo Scientific Niton XL3t 700 Series XRF consumer goods analyzers provide quick and easy screening of toys, apparel, and other consumer goods for lead, cadmium (Cd), mercury (Hg), and other toxic metals. Using these analyzers, importers, brand owners, retailers, and regulators can implement a standardized inspection protocol for incoming shipments to verify compliance. XRF testing provides nondestructive, "Go/No Go" determination, complementing other analytical techniques. Other analyzers in the Niton® XL3t Series use x-ray fluorescence to analyze the elements present in materials for applications such as alloy analysis, RoHS compliance, mining exploration, and environmental testing.

Standard Convention: Parts per million (ppm) and milligrams/kilogram (mg/kg) are used interchangeably in this document.

Keywords: CPSIA, H.R. 4040, lead screening, consumer products, XRF, x-ray fluorescence, x-ray analyzer, XRF analyzer

INTRODUCTION
In recent years, a startling number of lead-laden children's toys and other child-accessible products such as jewelry, apparel, and furniture found their way to retailers' shelves, resulting in millions of recalled items. With this reality as the backdrop and an ultimate goal of keeping our children safe, the Consumer Product Safety Improvement Act (CPSIA) of 2008, H.R. 4040, was signed on August 14, 2008. This legislation reduces the permissible levels of lead (Pb) in paint, sets allowable levels of lead in all other materials, implements an alternative standard for measuring lead in surface coatings, and permits the use of x-ray fluorescence analyzers for screening purposes[1].

With civil penalties growing to a maximum of US$100,000 per individual violation and US$15 million for ongoing violators, and states attorneys general permitted to enforce federal law, the need for manufacturers, importers, distributors, and retailers to rapidly identify lead-containing products has never been greater.

MORE THAN JUST LEAD – MORE THAN CPSIA
Though lead has been the main focus of the toy recalls and CPSIA, it is only one of eight elements that are regulated in toys designed for children under the age of 12 (ASTM F963[2]). The other elements that require monitoring are arsenic (As), selenium (Se), cadmium (Cd), antimony (Sb), barium (Ba), mercury (Hg), and hexavalent chromium (CrVI). Niton XL3t 700 Series instruments, now available with geometrically optimized large area drift detector (GOLDD™) technology, are uniquely capable of analyzing these elements, providing superior detection limits with a handheld device.

Handheld XRF instruments have already proven their worth in helping manufacturers comply with complementary regulations such as the European Union (EU) Restriction of Hazardous Substances (RoHS) directive (2002/95/EC), which is aimed at 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 Hg, Pb, CrVI, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE), or more than 100 ppm Cd. Since the regulations took effect on July 1, 2006, manufacturers in many countries have sought a cost-effective analytical sample testing solution that will ensure the materials they use are RoHS compliant.

Similar regulations have been or are being promulgated in many countries and areas outside the EU. China's "Administrative Measure on the Control of Pollution Caused by Electronic Information Products" legislation, or "China RoHS," has a broader scope and provides fewer exemptions than the EU's regulations. As of March 1, 2007, all products sold in China or imported into China must meet new product labeling requirements detailed in the first phase of the directive. California's Proposition 65, which took effect on January 1, 2007, and is similar in restrictions and scope to the EU directive, sets the stage for an ever-expanding trend toward laws promoting "green" manufacturing.

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[1] CPSIA, Sec 235 (a) (16) – Children's Product, p. 59
[2] ASTM F963 - 08 Standard Consumer Safety Specification for Toy Safety, revised December 1, 2008)

Also falling under the "green" umbrella is the move toward halogen-free products. Halogens are the elements found in Group 17 of the Periodic Table of Elements – fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). Typically, consumer goods manufacturers are concerned with Cl and Br. Chlorine is a major component of polyvinylchloride (PVC), but Cl and Br also are found in many flame retardants. Ultimately, halogens are a potential problem because incineration of plastic materials containing chlorine and bromine can lead to the production of toxic materials like dioxins and furans, which are released into the environment and can have negative health and ecological effects.

Therefore, following RoHS, electronic manufacturers and suppliers are paying greater attention to reducing halogens in consumer electronics and other products, such as furniture. As a result, there is an industry-sponsored effort underway to provide halogen-free flame retardants. The transition to reduced halogen content in consumer products consequently will decrease the amount of material that may undergo improper incineration, helping to moderate the formation of dioxins and furans.

Clearly, the further back in the supply chain that screening and testing take place, the easier it is to prevent toxic substances from entering the hands of a child or entering into the waste stream – regardless of the regulations or corporate initiatives driving the testing program. For all the stakeholders, the challenge is balancing compliance, cost efficiency, and productivity. Screening with a handheld XRF analyzer is vital to achieving this balance and effective control in the supply chain.

CPSIA AND XRF ANALYSIS
The Consumer Product Safety Improvement Act of 2008 adds new regulations for lead in all base materials, which are commonly referred to as "substrates," and not just paint on the surface. These substrates include plastic, wood, metal, and ceramics.

The new lead limits will be phased in and only apply to children's products, but it is important to realize that they apply to *total lead content by weight,* not just accessible or bioavailable lead[3]:

> For surface paint:
> - <90 ppm
>
> For substrates:
> - <600 ppm, effective February 10, 2009
> - <300 ppm, effective August 14, 2009
> - <100 ppm, effective August 14, 2011 (if technologically feasible)

Under CPSIA, XRF analysis can be used for screening lead in small painted areas[4] if:
- Total weight of the paint or coating is ≤ 10 mg
- Or if the coating is ≤ 1 cm^2

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[3] CPSIA, Sec. 101 (a) (2) (A), (B), and (C), p. 2
[4] CPSIA, Sec. 101 (f) (3), p. 5

As of this writing, XRF technology can be used to support general conformity certification (GCC) for lead paint or lead content limits. According to the Consumer Product Safety Commission (CPSC) website, "Where third-party testing by an accredited laboratory is required as the basis for certification, that testing cannot be based on XRF technology at this time; however, XRF testing, either by a manufacturer or by a laboratory, may serve as the basis for general conformity certification. Manufacturers are cautioned, however, to be careful in their use of XRF for this purpose given the difficulties in screening for lead in paint with that technology.[5]"

XRF analyzers have the ability to quickly, reliably, and cost-effectively provide rapid screening solutions, which accrue from the instruments' portability, ease of use, speed, and non-destructive nature. XRF complements rather than replaces lab testing, allowing for an optimized two-stage process for finding problem toys, apparel, and other consumer products.

Screening vs. Testing

All parts of a product should be screened for restricted elements. The primary goal of screening is not necessarily to accurately analyze the chemical composition of all components or parts of the product, but to weed out and eliminate from the market products containing prohibited elements.

In fact, the CPSIA endorses the screening concept when it states, "Nothing in this subsection shall be construed to affect the authority of the Commission or any other person to use alternative methods for detecting lead as a screening method to determine whether further testing or action is needed.[6]"

XRF analysis is nondestructive, which is a clear advantage over traditional laboratory methods not only because all samples remain intact while screened, but also because so many more samples can easily be included in the analyzed lot. It is only logical, then, to start screening the product "as is," without disassembly. This is particularly true of products that are painted because many of the toxic elements – especially lead – are typically found in paint.

Subsequently, selected samples can be analyzed using lab techniques for confirmatory analysis, or when necessary, to resolve vendor disputes. Increased screening permits manufacturers, distributors, and retailers to "trust but verify," resulting in better compliance at lower cost than other available methods.

XRF and ICP

When literally hundreds of thousands of child-accessible products must be tested in a short period of time, speed and expense are key considerations. Traditional methods of

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[5] CPSC website, Consumer Product Safety Improvement Act, "FAQs for Section 101: Children's Products Containing Lead; Lead Paint Rule," <http://www.cpsc.gov/about/cpsia/faq/101faq.html> April 2009

[6] CPSIA, Sec. 101 (f) (7), p. 6

testing rely on Inductively Coupled Plasma (ICP), which is generally accepted as accurate, but also destructive and time consuming. Ultimately, this makes the method inefficient.

Illustrating the drawbacks of ICP is the following scenario. A toy manufacturer, or an importer, distributor, or retailer, has 5,000 small plastic trucks made from a variety of plastic and metallic parts, all painted in attractive colors. Based on an unsubstantiated report in the media, they know that these toys may be contaminated, most likely by lead in paint used during their manufacture. The manufacturer has to make sure contaminated toys will not get to market and decides to send one toy truck to an accredited lab for testing.

The lab calls back to say that there is not enough of one kind of paint on a toy to scrape off for ICP analysis. They say that at least 10, or, better yet, 20 toys would be necessary for a successful test. Why? The ASTM Standard F963-03, "Standard Consumer Safety Specification for Toy Safety" calls for 100 mg of sample for ICP analysis, with an absolute minimum of 10 mg. It is quite difficult to get 100 mg of paint scraped off any one toy.

Therefore, our manufacturer sends 19 more toys to the lab, and, after several days, receives the results back from the lab. Depending on the result of the testing, there are four possible scenarios, as shown in Table 1, which will affect the owner's decision about what to do with his toy trucks.

Lab Result [mg/kg] Pb	Owner's Decision	Was the Decision Correct?
ND (not detected, <0.1) < **600**	Toys are clean and can be put on the market	**No**
210 < **600**	Toys are clean and can be put on the market	**No**
3250 > **600**	Toys are contaminated, scrap the whole batch (what a loss!)	**No**
650 >? **600**	Toys are contaminated, scrap the whole batch (however, since 650 is so close to 600, maybe there was an error and more tests would "fix" the problem?)	**No**

Table 1. Four lab testing scenarios showing results and decisions

In all four cases, the decision was wrong because it was based on some tacit assumptions, which may not be valid given the actual manufacturing process. First, they assumed that all the toys in the particular batch are identical, i.e., they all underwent the same manufacturing process…all were painted with the same paints, during the same shift, made of the same batch material, etc. Based on such assumptions, the owner came to the wrong conclusions, followed by the wrong decisions, in all four scenarios.

Scenario 1 – In the first scenario when the reported result was "ND," lead not detected, the owner assumed that *all* the toys were fine. He forgot, however, that the lab analyzed paint scraped from just 20 toys and analyzed the material as *one* sample. What he does know is that none of 20 toys tested had leaded paint. However, he cannot be certain

whether this statement applies to any of the other remaining 4,980 toys. He assumes that is the case, but does not know for sure. This means that some toys could have lead in paint and could slip undetected onto the market. In other words, *the ICP test does not really give us enough information about lead content of all the toys in the batch. Another way to put it is that the ICP test relies on the assumption that all 5000 toys are identical, and ignores the potential impact that may occur from rework and/or subcontractors.*

Scenario 2 – In the second scenario when the reported result was 210 mg/kg, our owner assumed that since the result was less than the regulatory level of 600 mg/kg the toys were fine to release. Again, he has forgotten that the lab scraped their sample from 20 toys and analyzed the material as *one* sample. Therefore, the reported value of 210 mg/kg is an average of 20 toys. Now, it may be that all 20, a few, or just one toy had leaded paint. We do not know. Regardless, there is a very high probability that some of the tested toys had lead in paint at much higher level than 600 mg/kg. This means then that some toys would get onto the market with elevated levels of lead. In short, *the ICP approach failed to indicate the real problem, and actually masked it by "diluting" bad with good.*

Scenarios 3 and 4 – In the third and fourth scenarios, the results are above the regulatory level. At least the manufacturer does not make a mistake of releasing contaminated toys to the market. But, again, he makes another mistake by assuming that *all* the toys are bad. This may not be the case. Therefore, he might be disposing of a large number of compliant products. But how can he be sure? Only by testing – but not with a destructive technique, such as ICP, especially if he wants to test all toys. Testing all of them destructively is pointless since even if some turn out "clean," they are no longer saleable. In addition, he will have incurred the cost of excessive lab testing.

Defining the Real Problem
The real problem is lack of knowledge and control of the manufacturing processes, which then forces us to perform massive amounts of testing of the final products, rather than the materials and components, i.e., paint, and substrates before they enter production.

At this point, it should be obvious that ICP is not the right technique for quickly, positively, inexpensively, and nondestructively screening large numbers of toys (or any other goods for that matter) for compliance, especially if they all have to be tested. Further, even if we did embrace the abstract idea of testing all products using ICP, the test would make little sense since it is by definition destructive; we would end up with product that would be compliant, but could never be sold!

Selective use of ICP to characterize a large batch of product makes sense and is justified ONLY if we have total control over the production process. This means that we know the exact quality of the materials used in the production and know of any variations from the approved and tested processes. It is only then that we can characterize the whole batch of products by the sacrificial testing of selected numbers of them. When we have no control of the process, we are forced to test every item of the product, which is impossible to

achieve with any classical laboratory instrumental method such as ICP, AAS, GC, and so forth.

Given the many contractors and sub-contractors involved in today's supply chain manufacturing, we often have limited control, or even the knowledge, of the manufacturing processes that take place on a global scale.

An Alternative Solution

For an immediate and long-term solution to the problems just discussed, we need to identify and implement a method that would make possible rapid, positive, and economically feasible identification of bad product within a large pool of products. In brief, we are primarily looking for a nondestructive screening tool to provide a "Go/No Go" (or compliant/non-compliant) answer with which to sort toys (or apparel or jewelry or furniture) into "bad" and "good" categories. In parallel, we must work diligently on gaining control of manufacturing processes to prevent bad products from being made in the first place, which would lead to a permanent solution to the entire problem.

Screening with XRF

X-ray fluorescence is the best tool available today for Go/No Go screening for lead and other restricted elements (see Figure 1). As a technique, XRF offers a unique combination of features:

- High sensitivity to the elements of interest
- Field-proven method used in harsh industrial environments for more 30 years
- Robust calibration via fundamental parameters (FP)
- Simultaneous multi-element analysis
- Truly nondestructive to the sample and to the analyzed object
- Instantaneous, "on-the-spot" results for very high throughput
- Ease of use – shift personnel can learn testing in a matter of minutes
- Environmentally friendly – does not generate waste; requires no special maintenance
- Comparatively inexpensive – the cost of the instrument is justified (amortized) in a very short time
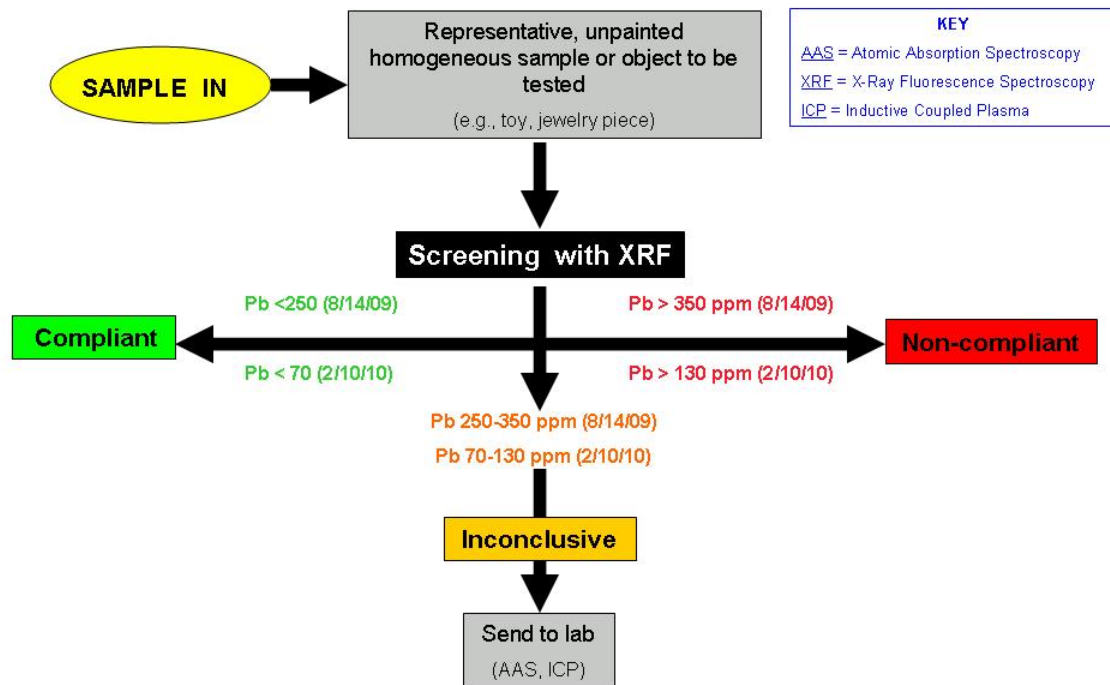
Screening Scenario

Figure 1. XRF screening scenario showing possible results

A HISTORY OF INNOVATION

Founded more than 20 years ago, we are the world's leading producer of handheld XRF analyzers, with more than 21,000 units installed worldwide.

A culture of innovation and a distinguished history of breakthrough achievements have defined our instruments since we introduced the first handheld XRF analyzer in 1994. Many "firsts" have followed, including the:

- First use of miniaturized x-ray tubes in one-piece handheld analyzers
- First and only isotope-based handheld XRF analyzer that never requires source replacement
- First handheld analyzer equipped with an He purge for direct analysis of Mg, Al, Si, P, and S in metal alloys
- First handheld small-spot XRF analyzer
- First and only handheld XRF analyzer to feature a 50kV x-ray tube
- First geometrically optimized large area drift detector

The company has been awarded numerous patents and has received many honors and awards, including three R&D 100 awards.

Thermo Scientific Niton XRF instruments provide you with rapid, reliable, nondestructive, on-site sample analysis. They not only are used for screening for lead in toys and consumer goods, but also are used for identification and analysis of metal alloys; compliance testing for RoHS, WEEE, and ELV regulations; mining exploration and geochemical analysis; environmental site assessment, monitoring and clearance testing; lead-based paint testing; catalyst recycling; coating thickness testing; forensic analysis; and other applications. We are committed to making the highest performance, easiest to use, most economical handheld XRF analyzers in the world; to giving you the tools that help you work more productively than ever before; and enabling you to make the world healthier, cleaner, and safer.

Niton XL3t SERIES CONSUMER GOODS ANALYZERS

The Niton XL3t Series, the winner of both the 2008 R&D 100 Award for technological innovation and a 2008 Product of the Year Award in the Product Safety category from *Creative Child Magazine*, provides a fast, dependable, and nondestructive means of screening toys, painted parts, plastic and metal jewelry, crystal and gemstone settings, soldered chain links, ceramics, apparel, and furniture as well as electronic components for restricted substances such as lead and cadmium.

Using the XRF technique, these instruments offer numerous features and benefits:
- Easy-to-use, intuitive software – rapid screening of incoming shipments and existing inventory, providing significant savings in both time and costs compared to exclusive reliance on lab testing

- Wireless Bluetooth™ or USB data transfer – direct data transfer to PC or networked storage device
- Variable spot size and integrated CCD camera – isolate areas of interest and store the test area image along with the analysis data for regulatory due diligence documentation
- TestAll™ (patent pending) technology – automatically selects the correct analytical mode for the best analytical results

With dual modes of operation – either as a handheld tool or from a fixed position (optional test stand) run from a PC – the Niton XL3t portable XRF analyzer provides quantitative analysis of lead and other toxic metals in seconds (see Figures 2 and 3).

Figure 2. Screening result shows almost instantaneously on the tilting, color, touch-screen display

Figure 3. The SmartStand™ portable test stand provides users a safe platform for analyzing small and irregularly shaped objects

More Power in the Palm of Your Hand

In a complex regulatory environment, Niton XL3t Series analyzers give you, and all stakeholders – component manufacturers, distributors, OEMs, and others – the fast, accurate, easy-to-use analytical tools you need to test parts and finished goods for compliance.

The x-ray tube-excited Niton XL3t features a 50 kV, 2-watt miniaturized x-ray tube with multiple multi-layer primary filters – the most versatile x-ray tube ever placed in a commercially available handheld XRF analyzer. Detection limits for all banned substances are improved over lower voltage instruments.

Now, the power of the Niton XL3t is taken to an even higher level with our groundbreaking GOLDD technology (see Figure 4). Because of its faster analysis, higher precision, and the ability to measure light elements without helium or vacuum purge, it is the instrument of choice when you require extreme speed, accuracy, precision, and ease of use.
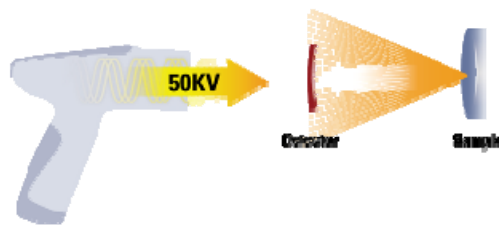

Figure 4. Larger drift detector and optimized geometry in the Niton XL3t GOLDD mean more x-ray counts for faster, more precise readings for prohibited substances

For example, Figure 5 shows measurements taken with a Niton XL3t XRF analyzer with GOLDD technology on paint primer containing barium (Ba), titanium (Ti), and calcium (Ca), which was applied over pine wood. The measurements were taken at 50 kV and 40 kV. At 40 kV, the Ba K-lines are barely visible, while at 50 kV, they are strong. Estimating from these spectra, indications are that 50 kV excitation yields at least 25 to 30 times better limits of detection (LODs) for Ba than 40 kV, all other conditions being identical.

Excitation of K-series X-Rays of Barium from Typical Paint at 40 and 50 kV High Voltage
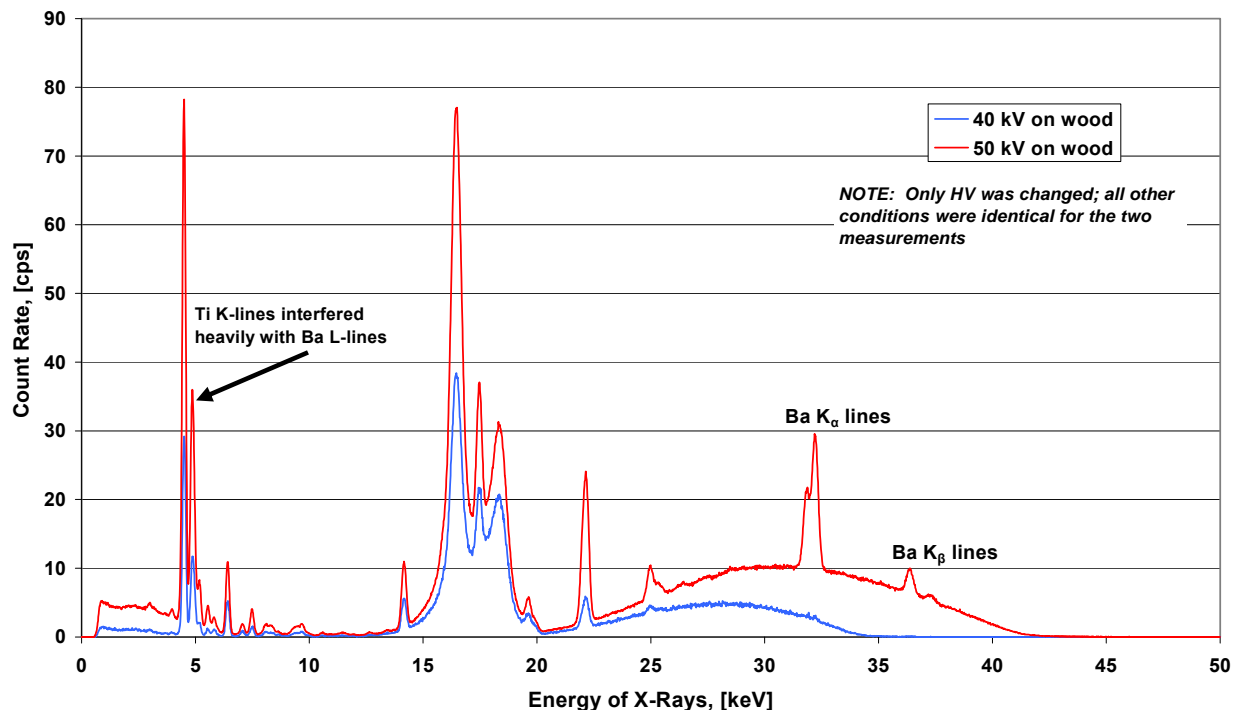
Figure 5. Analyses using 50 kV Niton XL3t analyzers with GOLDD technology demonstrate the increased accuracy and precision over 40 kV instruments, illustrated by the strong Ba K lines

Eliminating the Guesswork with TestAll Technology

TestAll technology, with its automatic mode selection, determines whether lead is present on the surface of the sample undergoing testing, or is in the base material/substrate. It then applies the appropriate analysis mode, helping to eliminate guesswork for faster, more efficient screening and allowing non-technical users to easily perform measurements with minimal training.

Of greater importance, this unique software, along with the Painted Products mode, makes the Niton XL3t 700 Series the only handheld XRF analyzer capable of differentiating lead on the surface of an object, such as paint or glaze, from lead in the substrates, such as plastic, metal, or wood.

TestAll Technology for Consumer Goods Screening	
Mode	**Description**
Metal	Bulk, unpainted metals & metallic alloys. Will display the alloy grade match
Painted Metal	Painted metal toys, die cast objects, and other painted metal surfaces
Thin Metal	Thin metal materials, e.g., foils
Plastic	Non-PVC plastics and, because of their similar x-ray signature, also wood, cardboard, and fibers
PVC Plastic	All PVC type plastics regardless of thickness. Since the PVC assignment is based on Cl content, any material with a high Cl signal will use the PVC calibration
Thin Plastic	Thin polymers (non-PVC type)
Layered Materials	Layered non-metals, not necessarily painted, e.g., glazed ceramics. Outer layer is thick enough to modify spectrum in such a way that two layers of different materials sandwiched together are identified.
Non-Metal	Bulk, non-metallic and non-plastic materials, e.g., soil, minerals, ceramics, concrete, and sheetrock
Other	Similar to non-metal, but the algorithm cannot classify the measured material into any of the other types

Table 2. TestAll technology automatically selects the correct mode.

If lead is detected in a surface coating, it is reported in micrograms per square centimeter ($\mu g/cm^2$), enabling a direct pass/fail comparison against the new CPSIA alternative standard of 2 $\mu g/cm^2$ for Pb in surface paint (see Figure 6). This method allows the XRF instrument to be used to its full advantage, namely as a rapid and nondestructive tool. XRF has already been widely used for determining the lead content in painted surfaces for years with the acceptance of OSHA, EPA, and HUD[7] for leaded paint testing in homes and other buildings.

With TestAll technology, you benefit by not having to determine and then manually select the proper calibration to use (see Figure 7). Upon starting the analysis sequence, the program will automatically select between the following modes: metal, painted metal, thin metal, plastic, PVC plastic, thin plastic, layered materials, and non-metal (see Table 2). The test results are evaluated for Pass/Fail based on the results for each element, or organizations can optimize the criteria based on specific limits (see Figure 8).

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[7] U.S. Department of Labor – Occupational Safety & Health Administration, U.S. Environmental Protection Agency, and U.S. Department of Housing and Urban Development.
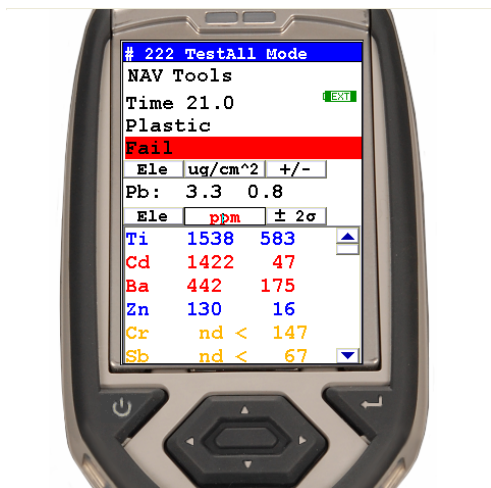
Figure 6. Shown here are the results from screening a yellow toy telephone using TestAll mode, which classified the sample as Plastic.

Figure 7. When unsure of which mode is suitable for the sample analysis, TestAll technology determines the best mode for the best analytical results.

Figure 8. Using TestAll technology, test results are evaluated as Pass/Fail (left), or you can optimize the criteria based on specific limits that you set yourself (right).

Find It, See It, Save It – Small Spot and CCD Camera

Rapid nondestructive analysis of small areas – the eye of a rubber duck, a plastic button – on child-accessible products is challenging for any size analytical instrument: individual components are hard to isolate from adjoining materials, making them difficult to analyze, and are themselves often heterogeneous in composition. Niton XL3t consumer goods analyzers can meet and even exceed expectations with regard to this challenge.

Adding significant analysis capability is our exclusive option of a variable analysis small-spot feature, which allows you to collimate the x-ray beam on individual areas as small as 3 mm in diameter. The small-spot analysis feature lets you switch "on the fly" between normal focus (8 mm) for analyzing larger, homogeneous materials, and small-spot focus for locating, isolating, and measuring individual small areas and components (see Figure 9).

Further, an optional, color CCD camera and sample imaging system, the first CCD camera ever integrated into a handheld XRF analyzer, allow you to visually identify, locate, specify, and save the image of the analysis area together with elemental analysis results (see Figure 10).

The small-spot feature, combined with the CCD camera, is ideal for positioning, isolating, analyzing, and documenting the analytical results of small components – something previously only achievable with benchtop XRF analyzers. The CCD camera not only displays a picture of the sample on the instrument screen, but also stores it along with the analysis data for easy reference, data management, and data integrity.
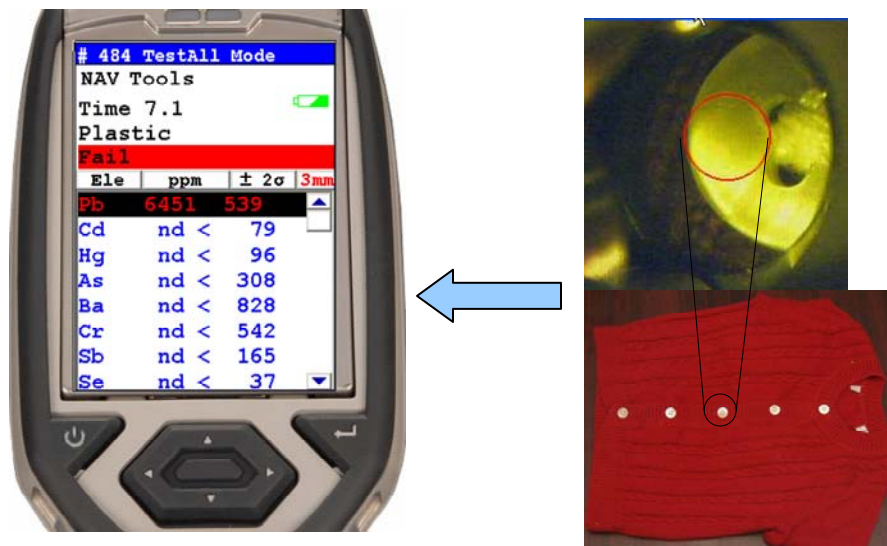
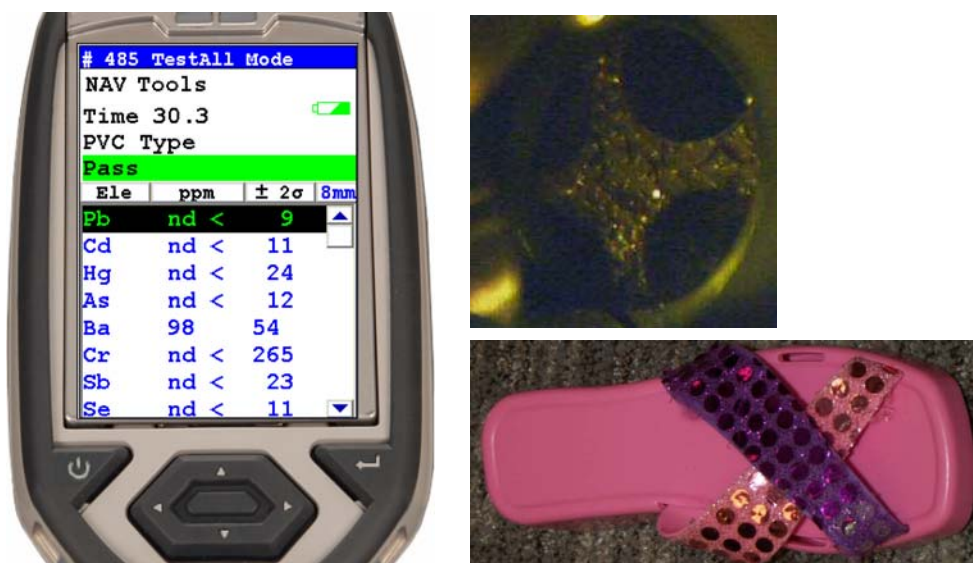Figure 9. Small-spot feature; analysis of a plastic button

Figure 10. CCD Camera provides live video of the sample on the analyzer screen, for perfect sample alignment prior to initiating a measurement

CONSUMER GOODS APPLICATIONS – TOYS, JEWELRY, APPAREL, AND FURNITURE

In light of the CPSIA, an effective program using handheld XRF analysis to screen toys, jewelry, apparel, and furniture for toxic metals greatly reduces the chances that lead containing materials will enter the manufacturing process, or accidentally end up on store shelves. This starts with a process that includes rapid screening of metals, plastic, wood, fabrics, and paints:

- At the receiving dock
- In the warehouse
- During product assembly
- Even at vendor sites, including testing through packaging to save time

As stated previously, all stakeholders can implement a standardized inspection protocol for incoming shipments to verify compliance, while simultaneously requiring supply chain documentation based on empirical testing. It is important to reiterate that the further back in the supply chain that the lead testing takes place, the easier it is to prevent lead from entering the marketplace.

The glare of the spotlight has been placed primarily on toys and fashion jewelry, so there is, perhaps, less familiarity with what is included in the law under the umbrellas of apparel and furniture.

For apparel, the test for lead in children's clothing includes:
- Fabric
- Appliqués
- Buttons, zippers, and other fasteners
- Footwear

Also, according to the new law, testing children's furniture for lead expands pre-existing paint regulations to include substrate material, and includes:
- Beds/cribs
- Bookcases/shelves
- Chairs
- Chests
- Tables
- Dressers
- Desks

Using the Niton XL3t consumer goods analyzer, you can confidently screen all CPSIA cited materials from toys to furniture for lead – quickly, accurately, precisely.

CONCLUSION

Handheld x-ray fluorescence analyzers provide a real solution to the problem of screening of paint and plastics for CPSIA compliance. They are robust, easy to use, and less expensive than their laboratory counterparts. Further, they are completely nondestructive with negligible maintenance costs. The XRF method is the only technique that can screen numerous samples in a relatively short time, yet with minimal expense. It narrows the pool of samples for potential lab testing to the bare minimum, contributing to large savings of time and money.

Major toy and consumer goods manufacturers, retailers, Internet shopping sites, and most importantly, the Consumer Product Safety Commission itself, have all chosen and trust the handheld Thermo Scientific Niton XRF consumer goods analyzer. It is the smart choice for consumer product screening and helping to meet the requirements of CPSIA. Additionally, the European Union's Product Safety Enforcement Forum of Europe (PROSAFE), through one of the joint market surveillance actions between several member states from the European Economic Area, has utilized Niton analyzers for XRF screening of certain toys.

The vast majority of toys and child-accessible products comply with existing regulations. But even if less than 1 out of 100 contains non-compliant levels of lead, is that a chance you are willing to take with your business? Help reduce your risk with XRF analysis…the path to a fast and nondestructive way to cost-effectively screen existing inventory as well as incoming materials.

How XRF Works

To understand how x-ray fluorescence works, a basic understanding of the structure of an atom is necessary. The nucleus of an atom is made up of both positively charged particles called protons and electrically neutral particles called neutrons. Orbiting around the nucleus are negatively charged electrons. These electrons can have different orbits, called shells, which are labeled sequentially starting with K, L, M, N, O, P, etc.
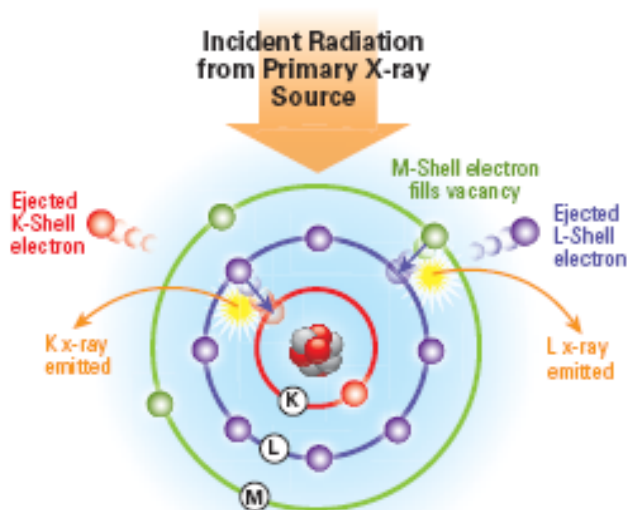

Figure A.1. X-rays are emitted when higher energy electrons move to an inner shell

The electrons of the K shell are of the lowest energy; therefore, the bond to the nucleus is the greatest. The electrons of the L shell, M shell, etc. are of higher energy and are therefore not as tightly bound to the nucleus. X-rays form part of the electromagnetic (EM) spectrum and have similarities to other forms of EM radiation, such as infrared and radio waves. However, because of their high energy, x-rays can knock an atom's electrons out of orbit. This radiation is generated within the instrument by an x-ray source, either an x-ray tube or radiation emitted by the natural decay of a radioactive isotope. When an electron is ejected from its shell, the vacancy is filled by an electron from another shell in a step-wise fashion. When an outer shell electron jumps to an inner shell less energy is required to maintain that lower energy orbit, and thus the left over energy is emitted by the atom as a characteristic x-ray (see Figure A.1). These are the x-rays that are analyzed by the detector within the XRF analyzer.
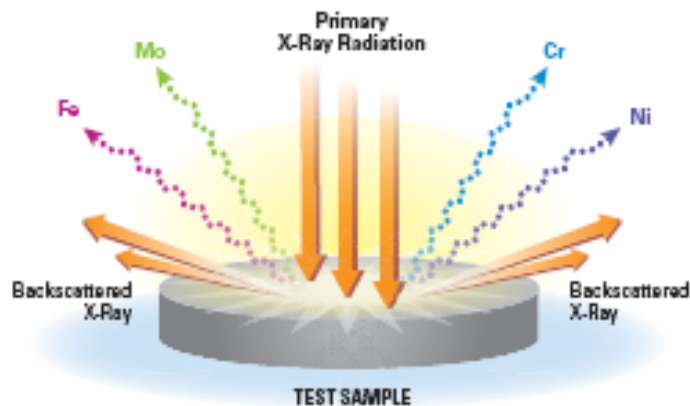
Figure A.2. XRF analysis can determine the concentration of specific elements

For example, when a K shell electron is ejected, an L shell electron jumps into its place and creates a subsequent vacancy in the L shell. Similarly, the L shell vacancy is filled by an M shell electron, with the simultaneous emission of the characteristic L x-ray of that element. This process continues to the outer shells in such a way that when K x-rays are generated, L, M, N (and so on) x-rays are also emitted. The process of excitation by one high energy x-ray, followed by emission of characteristic lower energy x-rays, is called x-ray fluorescence.

Each element in the periodic table has a characteristic x-ray fluorescence spectrum that is unique, rather like a fingerprint. These unique x-rays are detected in the handheld analyzer, measuring both the energy of the incoming signal (which identifies the element), and the number of x-ray events detected over time at that particular energy (which defines the concentration of the element within the sample). Since each x-ray represents the presence of a specific element such as chromium (Cr), iron (Fe), or nickel (Ni), the specific element and its percentage concentration within the sample can be calculated by the instrument's internal computer (see Figure A.2).
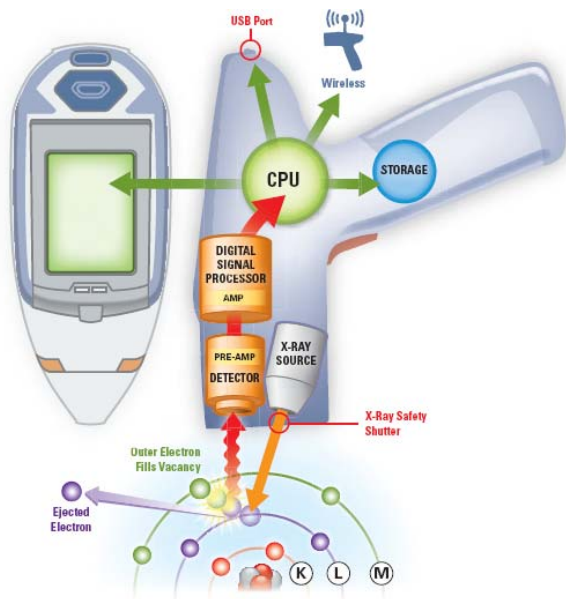
Figure A.3. Niton analyzers incorporate real-time digital signal processing and dual state-of-the-art embedded processors for computation, data storage, and communication

In the case of determining alloy grade, once the analyzer has determined the elemental composition, it references an onboard alloy grade library to give specific grade information for the sample. The information may also be stored for future reference, including downloading to a PC (see Figure A.3).

Results can always be verified by inspecting the spectrum generated by the sample. Whenever lead is detected, the spectrum will show two peaks of lead, approximately the same size, one at 10.5 keV and another at 12.6 keV. If lead is not detected, the spectrum will show no lead peaks. The spectra in Figure A.4 below are examples of the two situations described.
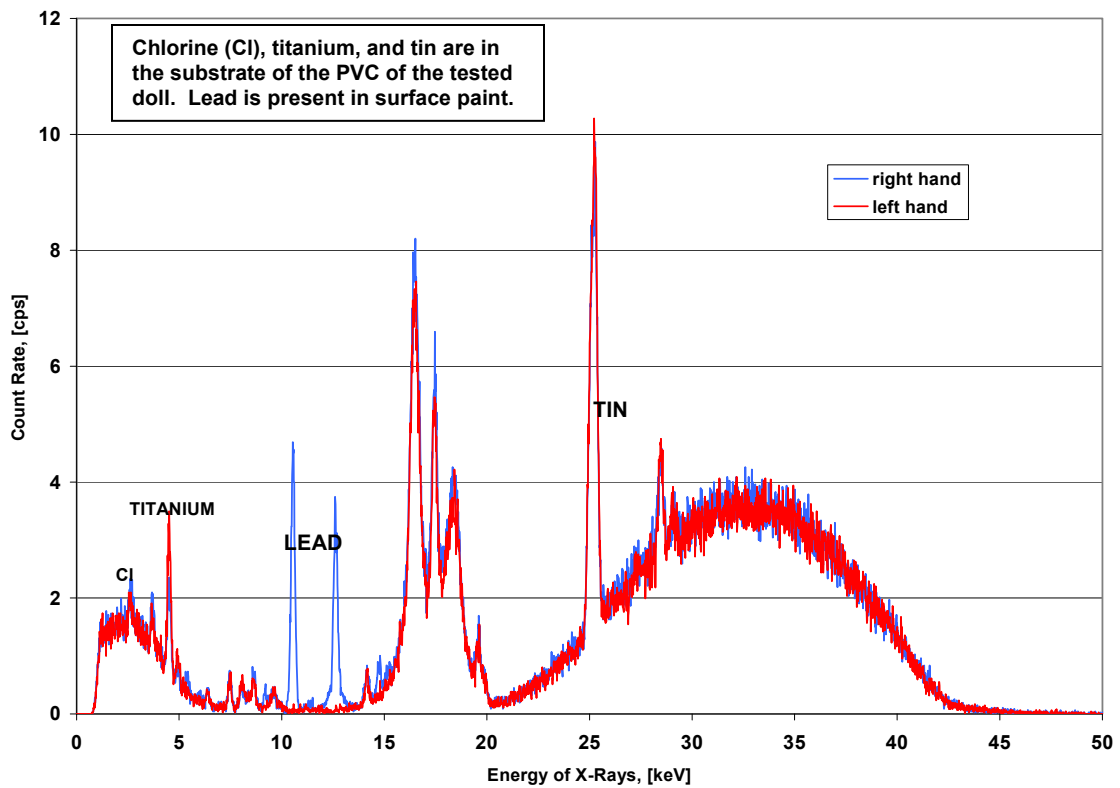
Figure A.4. Spectra of paint as measured directly on the same color on two separate areas of a doll. One part is painted with leaded paint (blue spectrum). The other part containing the same color paint, shown with red spectrum, does not show any lead. This can be caused by separate parts being painted on separate production lines, or may be due to rework of a cosmetic defect.

APPENDIX B
Fundamental Parameters, Empirical Calibration, and Compton Normalization

Based on our experience and extensive research, we determined that the best analytical approach to XRF analysis of plastics and polymers is the fundamental parameters (FP) method, also known as "standardless" analysis. Long-used for metal alloy analysis, this method of calibration uses the fact that the measured characteristic x-ray intensities of the elements in a sample can be fully described by a complete set of equations that are based on the physics of the interaction of x-rays with matter and sample composition.

Alternatives to the FP-based method are a classical empirical calibration and the so-called Compton Normalization (CN) method. An empirical calibration has the advantage of being the most accurate of all methods within a defined range of element concentration. However, its distinct disadvantage is its requirement for the availability of an extensive set of analyzed samples with compositions as close as possible to those of unknown samples. Given the number of various plastic materials, this requirement is practically impossible to satisfy. The CN method, on the other hand, while being less demanding regarding availability of standards, is not capable of handling the wide concentration ranges encountered in analysis of plastics. The detailed result of the research to develop the optimum calibration for this application has been published earlier[8], while an excellent, in depth discussion of the calibration methods mentioned here can be found in reference 9, as noted[9]. Our mission is to provide real solutions for the real-life analytical problems that users encounter. This is why we have focused our development efforts on the FP-based method as most appropriate for the task.

The FP method has the unique ability to address wide and unexpected concentration ranges observed in actual samples of plastics and polymers. Alloys, despite their great number of grades, are, nevertheless, a very well-defined group of materials with standardized compositions. Unlike alloys, we found the compositions of plastics to be non-standardized and quite different, even when manufactured repeatedly for the same application by the same compounder. The FP method allows both quantitative and qualitative screening of plastics for compliance with regulatory requirements. In addition, this approach comes without the need for the laborious, time consuming, and destructive sample preparation necessary with other instrumental methods.

Tables B.1 and B.2 show the performance that can be expected from a portable XRF analyzer using the FP method. Table B.1 shows the limits of detection (LODs) obtained using the Niton XL3t 700 Series analyzer, while Table B.2 shows the LODs obtained using the faster, even more accurate and precise Niton XL3t 700 GOLDD instrument.

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[8] Piorek S., "Feasibility of Analysis and Screening of Plastics for Heavy Metals with Portable X-ray Fluorescence Analyzer with Miniature X-ray Tube", presented at GPEC 2004, February 18-19, 2004, Detroit, Michigan, published in Conference Proceedings.
[9] Van Grieken, R. E. and Markowicz A., Handbook of X- Ray Spectrometry, Marcel Dekker, New York, (2002)

The LODs are detailed for specific plastic matrices as the density of a matrix directly influences the detection limits. Detection limits are specified following the U.S. EPA protocol of 99.7% confidence level[10]. Individual LODs improve as a function of the square root of the testing time. All detection limits listed are in parts per million (ppm).

Niton XL3t 700 Series Limits of Detection for Restricted Elements in Polymers All values below are represented in ppm (mg/kg)				
Element	PE blank	PE+2% Sb	PE+5%Br	PVC
Ba	120	220	240	N/A
Sb	25	N/A	65	30
Cd	15	25	35	15
Pb	4	10	50	10
Br	3	5	N/A	10
Se	3	5	40	15
As	3	10	20	10
Hg	6	15	30	20
Cr	20	20	25	40
Cl	200	250	350	N/A
Cl*	120	140	160	N/A

Table B.1. Niton XL3t 700 Series for restricted elements in polymers – polyethylene (PE) and polyvinylchloride (PVC) – using the 8 mm aperture; 180-second total analysis time, 120 seconds for the main filter and 60 seconds for the low filter.

Lower chlorine detection limits achieved using optional Cl calibration on light filter. These detection limits achieved in 60 seconds on light filter instead of low filter.

Niton XL3t 700 GOLDD Limits of Detection for Restricted Elements in Polymers All values below are represented in ppm (mg/kg)				
TIME	PE blank	PE+2% Sb	PE+5%Br	PVC
Element	30 Sec/filter	30 Sec/filter	30 Sec/filter	30 Sec/filter
Ba	110	200	200	N/A
Sb	25	N/A	50	25
Cd	12	16	30	12
Pb	3	8	45	15
Br	3	5	N/A	8
Se	3	12	30	12
As	3	8	15	15
Hg	4	10	22	25
Cr	12	20	15	30
Cl	50	60	50	N/A

Table B.2. Niton XL3t 700 Series with GOLDD technology for restricted elements in polymers – polyethylene (PE) and polyvinylchloride (PVC) – using the 8 mm aperture; 90-second total analysis time.

When analyzing plastics with XRF, the thickness of the measured object should be considered because plastics are generally very weak absorbers of x-rays. A thin object may transmit part of the x-ray beam, and therefore, the results will depend not only on the

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[10] *Definition and Procedure for the Determination of the Method of Detection Limit,* 40 CFR, Part 136, Appendix B. Revision 1.11. U.S. Environmental Protection Agency. U.S. Government Printing Office: Washington, DC, 1995

concentration of the element, but also on the thickness of the sample. Typically, the thicker the object the better; for a plastic object only a few mm thick, a correction will be required. This condition is dependent on the instrument design and may be different for different analyzers. The Niton XL3t 700 Series allows you to make an accurate correction for the thickness, by letting you input the known sample thickness.

APPENDIX C
Acronym List

$\mu g/cm^2$	Micrograms per square centimeter
AAS	Atomic absorption spectroscopy
CCD	Charged coupled device
CN	Compton Normalization
CPSC	Consumer Product Safety Commission
CPSIA	Consumer Product Safety Improvement Act
ELV	End of Life Vehicles (directive)
EM	Electromagnetic
EPA	U.S. Environmental Protection Agency
EU	European Union
FP	Fundamental Parameters
GC	Gas chromatography
GCC	General Conformity Certification
GOLDD	Geometrically optimized large area drift detector
HUD	U.S. Department of Housing and Urban Development
ICP	Inductively coupled plasma
kg	Kilogram
kV	Kilovolt
LOD	Limits of Detection
mg	Milligram
mm	Millimeter
MHz	Megahertz
OSHA	Occupational Safety & Health Administration
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ethers
PE	Polyethylene
ppm	Parts per million
PVC	Polyvinylchloride
RoHS	Restriction of Hazardous Substances (directive)
USB	Universal Serial Bus
WEEE	Waste Electronic and Electrical Equipment (directive)
XRF	X-ray fluorescence

List of Elements

As	Arsenic
Ba	Barium
Br	Bromine
Cd	Cadmium
Cl	Chlorine
Cr	Chromium
CrVI	Hexavalent chromium

F	Fluorine
Fe	Iron
Hg	Mercury
Ni	Nickel
Pb	Lead
Sb	Antimony
Se	Selenium
Ti	Titanium