JOINT MARKET SURVEILLANCE ACTION ON TOYS

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Guidance Document

HAND-HELD XRF SCREENING EQUIPMENT

PROSAFE
PRODUCT SAFETY ENFORCEMENT FORUM OF EUROPE

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1 INTRODUCTION

Special Thanks go to Thermo Fisher Scientific for giving this Joint Action permission to utilise certain photos and information found within some of their technical documents.

1.1 Purpose

The purpose of this document is to try to bring together the experience and lessons learnt from the joint action in purchasing and using XRF hand-held equipment as a preliminary screening tool before laboratory tests on migration of heavy metals is performed. Any market surveillance authority which might be interested to know some basic information about this handheld XRF equipment as well as perhaps are interested in purchasing such equipment should find this document useful. However, it is important to note that this is a generic guide and thus it is expected that the respective market surveillance authority will perform additional research of its own to arrive at any final conclusions on what needs to be done

1.2 Coordination with EMARS II

Coordination between this joint action and EMARS II has also been established, in particular with Task A of EMARS II, within which various guidance documents are being developed for market surveillance authorities. Some members within this Joint Action as well as the Project Coordinator are also directly involved in Task A. This has ensured that a coordinated approach whilst also bringing together various ideas and considerations when developing such guidance documents. Indeed, the current pocket guide being developed by Task A – EMARS II has been taken into account when developing this guidance document.

1.3 Coordination with TOY-ADCO Members

The Joint Action on Toys has periodically during the TOY-ADCO meetings updated the members of the developments and findings of this joint action. It is hoped that these guidance document will possibly serve as a basis for further discussions and improvement to this guidance document so that it is widely accepted and utilised by various market surveillance authorities.

1.4 Suitability

XRF can only be used for screenings. It measures content, and not the migration of elements. So in the EEA no enforcement can take place based in the results of the XRF.

2 GENERAL INFORMATION

Toys must not contain dangerous substances or preparations in amounts that may harm the health of children using them. In all cases, it is not allowed to include dangerous substances or preparations (in a toy if these are accessible when the toy is being used) which exceed the legal limit

In order to assess whether a toy is safe or not, different legislations across the world adopt different methodologies. To take an example, in the case of the United States, there are direct limits on the *content* of heavy metals. On the other hand, in the case of the legislation within the European Economic Area (EEA), the limits are not directly related to the *content* but rather to the *migration* of heavy metal.

A simple way of initially determining the *content* of heavy metals within a toy is to use XRF handheld equipment. In the case of surveillance activities within the EEA, XRF analysis is used as an initial screening tool, upon which further testing is needed in accredited laboratories to determine the level of migration of heavy metals within that particular toy.

Before proceeding, it is important to have a good understanding of what XRF means and how it actually works.

2.1 What is XRF and how does it work

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and other materials.

X-ray Fluorescence and Reducing Compliance Risk

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 labelled sequentially starting with K, L, M, N, O, P, etc.

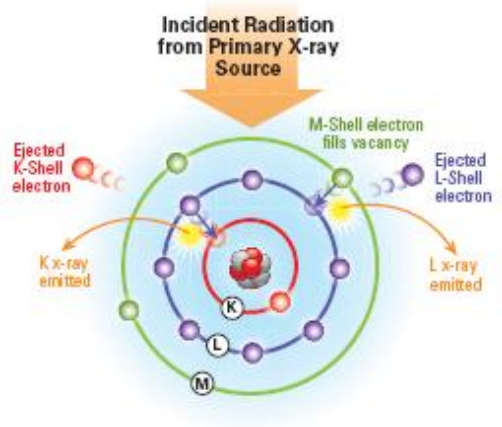

Figure 1.1 X-rays are emitted when higher energy electrons move to an inner shell

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 1.1). These are the x-rays that are analyzed by the detector within the XRF analyzer.

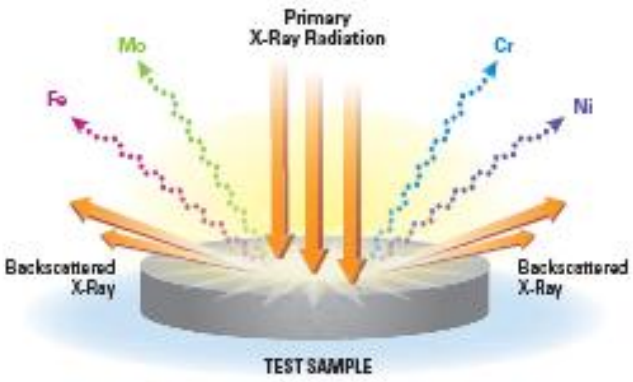

Figure 1.2 XRF analysis can determine the concentration of specific elements

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 1.2).

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 1.3).

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 1.4 below are examples of the two situations described.

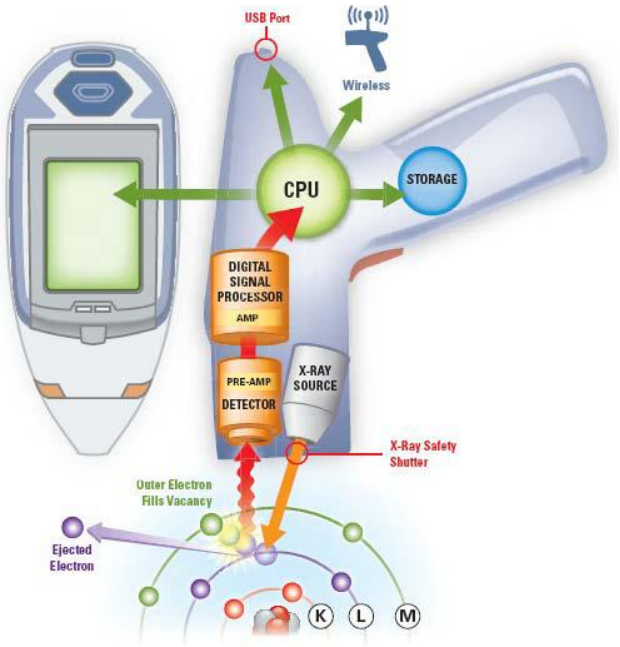

Figure 1.3 Certain XRF analyzers *incorporate* real-time digital signal processing and dual state-of-the-art embedded processors for computation, data storage, and communication

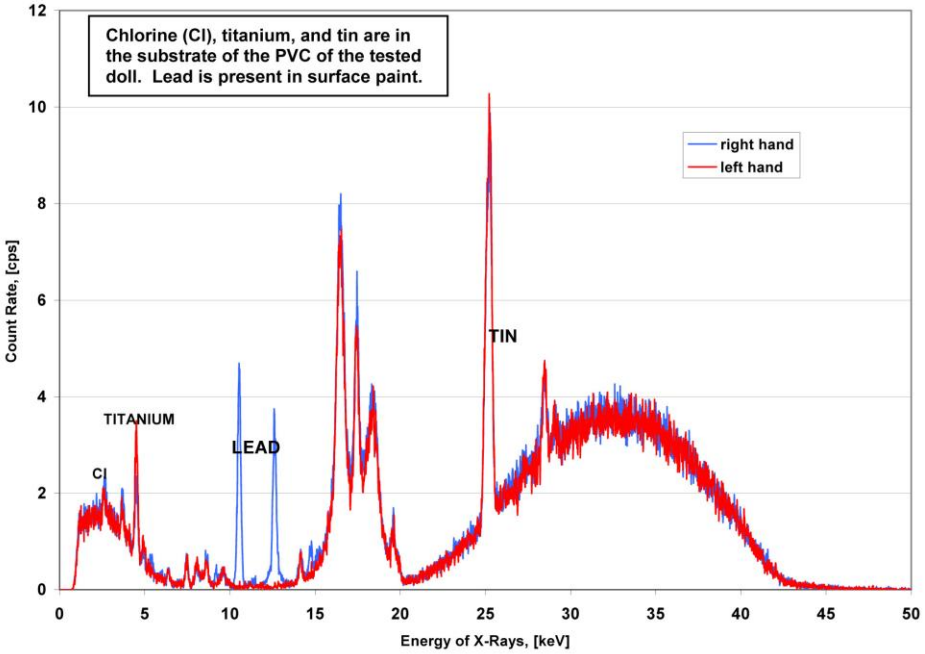

Figure 1.4 Spectra of paint as measured directly on the same colour on two separate areas of a doll. One part is painted with leaded paint (blue spectrum). The other part containing the same colour paint, shown with red spectrum, does not show any lead. This can be caused by separate parts being painted on separate production lines, or may be due to rework of a cosmetic defect.

All the above mentioned processes can thus be summarised into these three main steps:

1) **Fluorescence -** Source X-rays strike a homogenous sample causing elements in sample to fluoresce signature x-rays.
2) ***Spectral Capture*** - Detector within analyzer captures these X-rays as an energy spectrum which represents the chemical make-up of the sample
3) ***Compositional Analysis*** - A calibrated algorithm processes the energy spectrum - steps include identifying & measuring each peak as a unique element ***(qualitative result);*** calculating height of peak / (area under curve), correcting for elemental interference & finally determining the concentration of each element ***(quantitative results)***

2.2 XRF Instrumentation

There is a variety of XRF systems in the market place with highly varied power levels, filter systems, and analysis algorithms for converting raw data to useful output information. For any analytical equipment and technique, it is critical for the analyst to understand the capabilities, principles and settings of the particular instrument and technique especially with regard to the particular application and sample in question. XRF analyzers are generally classified as being either

- **Energy Dispersive (EDXRF) or**
- **Wavelength Dispersive (WDXRF),**

with some additional sub categories within these two systems which go beyond the scope of this guidance document.

WDXRF systems are generally slower, more expensive, and require more sample preparation than EDXRF systems, but generally have increased sensitivity and lower detection limits. The EDXRF systems are usually smaller, simpler in design and have fewer engineered parts. They can also use miniature X-ray tubes or gamma sources. This makes them cheaper and allows miniaturization and portability. The type of instrument is commonly used for portable quality control screening application, such as testing toys for Lead (Pb) content, sorting scrap metals, and measuring the lead content of residential paint.

2.2.1 Different types of XRF hand-held detection devices

There are also two main types of XRF hand-held heavy metals detection devices: those that use **radioisotopes** and those that use **x-ray tubes**.

An XRF analyzer consists of three major components: (1) a source that generates x-rays (a radioisotope or x-ray tube); (2) a detector that converts x-rays emitted from the sample into measurable electronic signals; and (3) a data processing unit that records the emission or fluorescence energy signals and calculates the elemental concentrations in the sample.

Both XRF hand-held devices are relatively simple to use and operate. They are placed on the area where heavy metal is suspected to be present. Depending on the type of device and the depth of analysis required, the results can be viewed in seconds. Companies that sell or rent these devices provide onsite training and technical support.

2.2.2 Radioisotope Devices

Radioisotope devices for identifying the presence of lead and other heavy metals are the older of the two types of heavy metal detection devices. One advantage of the radioisotope device is its ability to read large or heavy concentrations of heavy metals accurately. The radioisotope device may possibly perform a better job of detecting heavy metals buried under numerous layers of paint than the x-ray tube device.

One disadvantage of the radioisotope device is that as the cadmium radioisotope loses strength, readings take longer. Because the half-life of the cadmium radioisotope is about 15 months, it takes twice as long to get a reading after 15 months, 4 times as long to get a reading after 30 months, and so forth.

Security is another issue. Both the radioisotope and the x-ray tube devices use radioactivity, but the radioisotope is radioactive all the time. The radioisotope device requires special licensing and may pose travel issues. In addition, when a radioisotope device reaches the end of its service life or is broken or damaged, it must be disposed of as hazardous material. Check with the appropriate State agencies to determine how to dispose properly of a radioisotope device.

2.2.3 X-Ray Tube Devices

The x-ray tube devices are the latest generation of XRF hand-held heavy metals detection devices. Although the x-ray tube devices offer numerous advantages, radioisotope devices may still be the best choice for some users. For instance, x-ray tube devices find it difficult to accurately detect lead-based paint that is covered by 10 or more coats of paint unless fitted with enough power to be able to do this.

X-ray tube devices cost more to purchase than radioisotope devices, but because components of x-ray tube devices do not break down as rapidly, they do not need to be serviced as frequently as the radioisotope devices. In addition, because the x-ray tube device's components do not suffer from half-life issues, they provide quicker, more constant readings.

Another advantage of the x-ray tube devices is that their radioactive components are not "on" all the time. These devices only need to be registered, not licensed in most Member States. No special requirements apply when travelling with x-ray tube devices, nor do x-ray tube devices require special hazardous materials handling or disposal.

2.2.4 Benefits of handheld XRF analyzers

1. They are handheld and can be used to screen toys and other consumer goods anywhere, any time.
2. Are easy to use. Very easy to learn how to operate the equipment quickly and safely.
3. Are fast, with screening results coming in minutes and not days.
4. Are non-destructive, so the product is not damaged or affected in any way.

2.2.5 Advantages of Using XRF for Paint Analysis:

If one is assessing the content only of heavy metals, the main advantages of utilizing XRF over the current digestion/ICP method are:

1. XRF is often non-destructive and the paint can be tested *in situ* on the item.
2. Little to no sample preparation is required which greatly reduces the analysis time and cost. Sample times for XRF *in situ* are typically less than 2 minutes. It takes several hours to collect paint scrapings, digest and analyze using the current test method.
3. XRF can be utilized more easily to test small painted areas. It can be difficult to remove enough paint from a small area to quantitatively analyze using the current digestion and ICP method. Small painted areas generally require the compositing of like paints from multiple items of a sample lot to obtain sufficient material for analysis. XRF analyzers equipped with video cameras can be used to analyze spot sizes of a few millimeters.
4. Hand held XRF analyzers are portable, allowing for field-screening of products.

2.2.6 Limitations in Paint Film Analysis:

In situ analysis of paint films on children's products by XRF has the following limitations:

1. XRF instruments do not readily measure heavy metals in thin paint films in mass per mass units such as weight %, mg/kg, or ppm. XRF methods typically report the amount of analyte in a thin layer such as a paint film in mass per unit area, e.g. ~g/cm^2 because energetic xrays are typically measured for a known spatial area and the count rate of x-rays is a function of both mass fraction and thickness of the specimen layer. The source radiation can travel through a thin paint film and into the underlying substrate. For example, if paint films of different film thickness, containing the same lead concentration by weight were analyzed by XRF, the thicker film would yield a higher measurement count rate. Paint film thicknesses on children's products vary considerably, which makes it difficult to quantitatively analyze and compare to calibration

standards on a mass per mass unit basis. (For PVC material there is a possibility for thickness correction)

2. The source radiation can travel through the paint film into the underlying substrate, leading to a measurement result that has contributions from both. Special care needs to be taken in ascertaining the source of lead in any measurement.
3. XRF is matrix sensitive. Spectral and matrix interferences must be taken into account during analysis, especially from the underlying substrates. X-ray fluorescence measurements are typically particularly susceptible to errors from metal substrates.
4. There are currently no consensus industry standard test methods for quantifying heavy metals in paint films on a mass per mass unit basis.

2.2.7 XRF and ICP

When literally hundreds of thousands of child-accessible products must be tested for the level of content of heavy metals in a short period of time, speed and expense are key considerations. Traditional methods of testing rely on Inductively Coupled Plasma (ICP), which is generally accepted as accurate, but also destructive and time consuming.

However, if the migration (and not the content) of heavy metals needs to be analysed, this cannot be done by XRF handheld systems since these only measure the content of heavy metals. In that case, ICP systems are needed to analyse this.

2.3 Screening versus Testing

XRF analysis is non-destructive, 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. 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.

All parts of a product should ideally be screened for restricted elements. The primary goal of screening done by a market surveillance authority within the European Economic Area (EEA) is not necessarily to accurately analyze the chemical composition of all components or parts of the product, but to weed out and identify from the market products which have considerable concentrations of lead or other heavy metals. These in turn would still need to be ultimately tested within an (accredited) laboratory in accordance to the European Standard EN71-3 (migration of heavy metals) in order to ascertain that the level of migration of heavy metal is higher than the limits indicated within EN71-3.

2.4 Regulatory Aspects

One has to note that there are considerable differences in legislation between various parts of the world.

In the case of the legislation within the European Economic Area, the new Toys Directive (2009/48/EC) which came into force in July 2009, replacing Directive 88/378/EEC, must be applied within all Member States as from 20 July 2011, except for Annex II, (chemical requirements) which will come into force on 20 July 2013. During this transitional period, in the case of chemicals, part III of annex II of Directive 88/378/EEC will continue to apply.

In accordance to the essential requirements as per part III of Annex II of the Toys Directive 88/378/EEC, toys must be so designed and constructed that, when used as specified in Article 2 (1) of the Directive, they do not present health hazards or risks of physical injury by ingestion, inhalation or contact with the skin, mucous tissues or eyes. They must in all cases comply with the relevant Community legislation relating to certain categories of products or to the prohibition, restriction of use or labelling of certain dangerous substances and mixtures . In particular, for the protection of children's health, bioavailability resulting from the use of toys must not, as an objective, exceed the following levels per day:

0,2 µg for antimony,
0,1 µg for arsenic,
25,0 µg for barium,
0,6 µg for cadmium,
0,3 µg for chromium,fs
0,7 µg for lead,
0,5 µg for mercury,
5,0 µg for selenium,

or such other values as may be laid down for these or other substances in Community legislation based on scientific evidence.

The bioavailability of these substances means the soluble extract having toxicological significance.

Ultimately, one has to remember that in the case of European legislation, the respective limits are thus NOT related to the *content* of heavy metals but rather on the *migration* of heavy metals.

In the case of the United States, the CPSIA (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:

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 if:
• Total weight of the paint or coating is ≤ 10 mg
• Or if the coating is ≤ 1 cm^2

2.5 The European Standard EN71

Although the appropriate harmonised standard or normative document provides a presumption of conformity with the essential requirements, it must be remembered that the market surveillance authority must ultimately check for compliance with the essential requirements, not the harmonised standard or normative document.

The European Standard EN71 has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports the essentials requirements of the respective Toys Directive 88/378/EEC. This Directive has been superseded by a new Directive 2009/48/EC as mentioned above. However, the chemical requirements within Annex II of the Directive will not come into force until July 2013 by which time the existing standard is assumed to be updated accordingly.

The way bioavailability is defined within the Toy Safety Directive led to the test methods in the standard addressing the amount of soluble element migration from a toy material.

The table on the next page shows the limits of element migration according to the respective parts of the European Standard EN71-3 and EN71-7. The part of the table highlighted in yellow shows the analytical correction needed after the laboratory performs the initial element migration test.

Therefore, in order to explain this better, an example is being reproduced below:
The analytical result of lead within modelling clay is ***120mg/kg****. The analytical correction from table above is 30%.*

$$\textit{Adjusted analytical result} = 120 - \frac{120 \times 30}{100} = 120 - 36 = \mathbf{84mg/kg}.$$

Table 1. Limits of migration of metals as per EN71 standard & Analytical correction needed of the initial test results BEFORE comparing with the limits below									
Element		As Arsenic	Hg Mercury	Se Selenium	Cr Chromium	Sb Antimony	Pb Lead	Cd Cadmium	Ba Barium
Maximum migrated element in mg/kg toy material	Any toy material except modelling clay and finger paint according to EN71-3	25	60	500	60	60	90	75	1000
	Modelling clay and finger paint according to EN71-3	25	60	500	35	60	90	50	250
	Finger paints according to En71-7	10	10	50	25	10	25	15	350
Analytical correction needed after initial test results of the sample (in %)		60%	60%	30%	30%	30%	30 %	50%	60%

In other words, although the initial migration test result was over the limit (120mg/kg), when one corrects the figure in accordance to the percentage analytical correction indicated within the standard, the final result would be that this particular sample is deemed as complying with the requirements of the standard since the limit for modelling clay is 90mg/kg as shown in the table 1 above.

Although any accredited laboratory for EN71-3 and EN71-7 testing is fully aware of this analytical correction, it may be of particular interest to any market surveillance authority be aware of this too, ensuring that the final results given by the laboratory are those that have taken into account the respective analytical corrections.

IMPORTANT NOTE: *The information within the section is only given for indicative purposes only. Ultimately, it is strongly recommended that each market surveillance authority purchases the respective standards so that the market surveillance officials are fully trained and aware of the details within the standard.*

3 OVERVIEW & PROPER USE OF HAND-HELD EQUIPMENT

3.1 Radiation and General Safety

WARNING! Always treat radiation with respect

At a minimum all operators of the XRF should be familiar with the instructions provided by the manufacturer. Manufactures recommends that instrument users participate in a radiation safety and operational training class. Many states demands a radiation safety officer as a supervisor for using a XRF

The x-rays emitted from the XRF are capable of passing straight through many different materials (such as wood) without loosing strength. Therefore it is very important to be mindful of where the device is aiming whenever performing an analysis. The beam is capable of passing through the sample material and tables upon which the samples are placed. A small amount of the X-rays are scattered back towards the unit. Therefore it is important to keep hands away from the sample window and the metal frontal portion of the unit.

Proper use includes holding the units by the handle and analyzing materials only when they are lying on the floor or a table. The devices should never be used to analyze material that is being held in a person's hand. Always be certain that the beam is not pointed at anyone and assume that the beam may pass through testing material and any table the testing material upon which it is placed.

Various recommendations are given by the companies themselves offering these products. One needs to carefully assess and ensure that all the users are fully informed of all risks.

THE XRF SHOULD NOT BE POINTED AT ANYONE OR ANY BODY PART, ENERGIZED OR DE-ENERGIZED

These instruments produce ionizing radiation and should ONLY be operated by individuals, who have been properly trained. A market surveillance authority should check before purchasing equipment that full training is provided by the company offering this XRF handheld equipment, ensuring that they are also trained in radiation safety.

3.2 General Safety Precautions and Information

Retain and follow all product safety and operating instructions. Observe all warnings on the product and in the operating instructions. To reduce the risk of bodily injury, electric shock, fire and damage to the equipment, observe all safety precautions issued by the respective company.

3.3 Recommended Radiation Safety Training Components

The purpose of the recommendations below is to provide generic guidance for an ALARA - best practice- approach to radiation safety. These recommendations do not replace the requirement to understand and comply with the specific policies of any state organization.

a. Proper Usage. Never point the instrument at another person. Never point the instrument into the air and perform a test. Never hold a sample in your hand and test that part of the sample.

b. Establish Controlled Areas. The location of storage and use should be of restricted access to limit potential exposure to ionizing radiation. In use, the target should not be hand held and the area at least three paces beyond the target should be unoccupied.

c. Specific Controls. The instrument should be stored, in a locked case, or locked cabinets when not in use. When in use, it must remain in the direct control of a factory trained, certified operator.

d. Time - Distance - Shielding Policies. Operators should minimize the time around the energized instrument, maximize the distance from the instrument window, and shoot into high density materials whenever possible. Under no circumstances should the operator point the instrument at themselves or others.

e. Prevent Exposure to Ionizing Radiation. All reasonable measures, including labeling, operator training and certification, and the concepts of time, distance, & shielding, should be implemented to limit radiation exposure to as low as reasonably achievable

f. Personal Monitoring. Radiation control regulations may require implementation of a radiation monitoring program, where each instrument operator wears a film badge or TLD detector for an initial period of 1 year to establish a baseline exposure record. Continuing radiation monitoring after this period is recommended, but may be discontinued if accepted by radiation control regulators.

3.4 Additional Safety Features

The XRF units themselves have some built in safety features to protect against accidental exposure. XRF handheld analyzers are predominantly very safe when used correctly. However the analyzer does emit radiation through the analyzer window, and all precautions must be taken to reduce exposure to this radiation. In order to minimize the possibility of accidental exposure, the following safety features should be followed:

4 ANALYSIS OF SAMPLES

Toys and the majority of consumer products represent a wide variety of composition, shapes, and functionality. Each XRF Analyzer might have different modes that need to be utilised according to the substrate being analysed. In most of the cases, one would get better result if the appropriate mode is selected according to the type of material being analysed. Thus, it is very important that the user is fully aware of all the software options and capabilities and restrictions of the XRF handheld equipment.

4.1 General Testing Protocol

Disclaimer: *These testing protocols are based on the Thermo Scientific Niton XL3t Analyzer bought by a number of market surveillance authorities involved in the joint action on toys carried out between 2009-2011. However, one can easily adopt similar protocols of other handheld XRF equipment too.*

4.1.1 Large Objects

These are the objects that can easily cover the measuring window of the analyzer and are typically at least as large as the analyzer.

1. Select the areas or fragments of the sample that is to be tested.

2. Based on the type of material, select appropriate analytical mode: Plastic Mode for all non-metallic materials and combinations of Non-metallic and metallic Alloy Mode for all metallic materials

3. Place the measuring window of the analyzer flush within the area identified on the toy or product for analysis and pull the trigger to start measurement.

4. Continue the measurement until the display says PASS or FAIL.

5 When testing larger surfaces, it is advisable to take several measurements at different locations. This is especially important if the surface tested is partially painted, plated, or otherwise appears different from location to location. This will help in identifying the location of the analytes, whether in the substrate, paint, or both. (figure 2 and 3)

6. Interpret the results. Again, it is very important that one is well informed on how to interpret the actual results given by the Analyzer.

7. Continue measurements as planned.

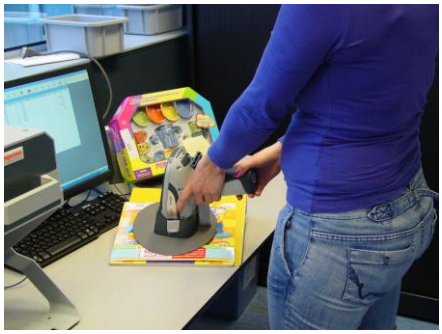

Figure 2. Screening with use of a backscatter shield

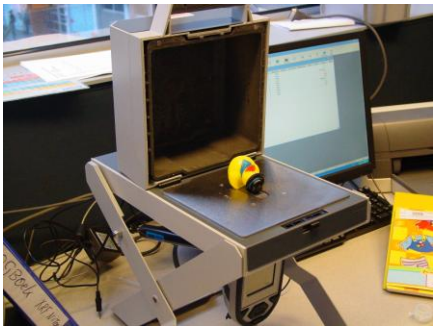

Figure 3. Screening with use of a stand

4.1.2 Small Objects

These are objects that are typically smaller in size than the analyzer, but still large enough to cover the measuring window of the analyzer.

1. Select the areas or fragments of the object that are to be tested.

2. Mount the analyzer in a test stand and connect the analyzer to a PC (via Serial Cable, USB Cable, or via Bluetooth). Start the respective software program on PC.

3. Stretch taut a piece of Mylar film over the measuring aperture of analyzer and secure it with tape.

4. Place the object in a test stand in such a way that the area selected for testing covers the measuring aperture of the instrument as much as possible. If the toy cannot be manipulated into a position suitable for measurement, one may need to use some small objects to support the object in proper position. Common, small rubber erasers were found suitable and convenient for such task. Care must be taken to not allow any part of the support to be within the perimeter of the measuring window of the analyzer. Figures 4 through 14 show examples of how the object can be manipulated into proper testing position.

5. Based on the type of material, select appropriate analytical mode: Plastic Mode for all non-metallic materials and combinations of non-metallic and metallic Alloy Mode for all metallic materials

6. Start the measurement, preferably via a PC using the respective software program.

7. Continue the measurement until the display says PASS or FAIL.

8. If possible, take more than one measurement of the sample, preferably in a different location.

9. Interpret the results. Again, it is very important that one is well informed on how to interpret the actual results given by the Analyzer.

10. Continue measurements as planned.

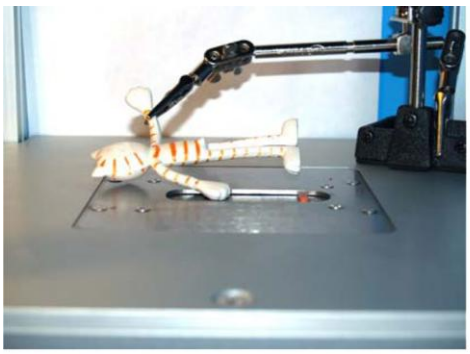

Figure 4. The figure is positioned so that the paint on the palm of its hand is as close to the window as possible. A "helping hand" is used to assist positioning. Note: Clamps should be at least 1 inch from window.

Figure 5. The figure is balanced with its arm positioned for analysis. Not all samples will require "helping hand" or other devices.

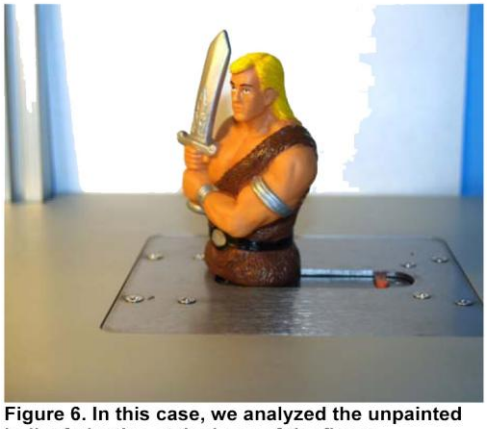

Figure 6. In this case, we analyzed the unpainted bulk of plastics at the base of the figure.

Figure 7. Here the figure is positioned to analyze its back.

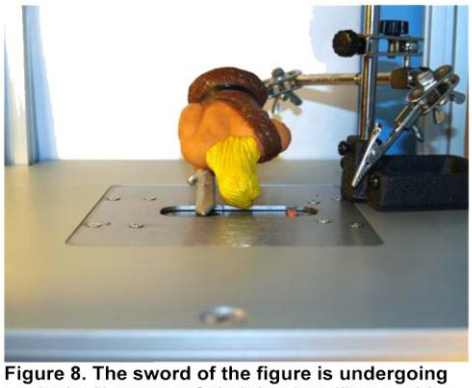

Figure 8. The sword of the figure is undergoing analysis. Note use of "helping hand" to position the sword.

Figure 9. Again with the aid of the "helping hand," the silver arm band on the right arm is screened.

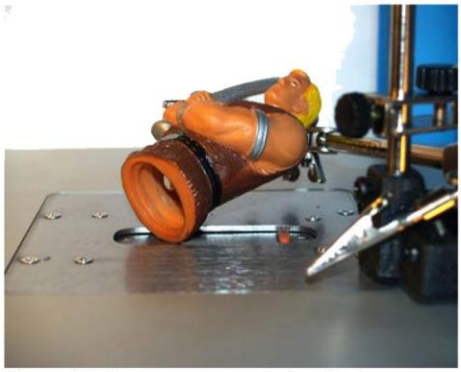

Figure 10. Here, we are analyzing the brown paint on the figure's clothing.

Figure 11. Propped on the "helping hand," the yellow hair on the figure undergoes screening.

Figure 12. The stripes of the cat's back present a challenge. The width of the stripe is smaller than the window.

Figure 13. Here we are analyzing the stripes on the cat's back. Multiple readings may be required. Move the cat to position with the window over both the striped and non-striped area to determine presence of any elements in the stripes.

Figure 14. The figure's eyes are smaller than the window opening. Longer sample times may be required on small samples.

4.1.3 Very Small Objects

These are objects that are not large enough to cover the analyzer measuring window, typically less than 10 mm in any dimension, e.g., beads, small jewelry pieces, chains, etc.

1. Mount the analyzer in a test stand and connect it to PC (via Serial Port, USB port, or Bluetooth). Start the respective software program on user's PC.

2. Stretch taut a piece of Mylar film over the measuring aperture of the analyzer and secure it with tape.

3. Place the object in a test stand in such a way that it resides in the center of the measuring window of the analyzer. If available, it is possible to take more than one identical small item and pile a small quantity of them over the measuring window of the analyzer. However, one must be certain that these individual items are identical in composition.

4. Based on the type of material, select appropriate analytical mode: Plastic Mode for all non-metallic materials and combinations of non-metallic and metallic Alloy Mode for all metallic materials

5. Start the measurement, preferably using the respective software program.
6. Continue the measurement until the display says PASS or FAIL.

7. Interpret the results. Again, it is very important that one is well informed on how to interpret the actual results given by the Analyzer.
8. Continue measurements as planned.

4.1.4 Thin Objects, Such as Plastic, Foils, or Films

1. Mount the analyzer in a test stand and connect it to PC (via Serial Port, USB port, or Bluetooth). Start the software program on user's PC.

2. Stretch taut a piece of Mylar film over the measuring aperture of analyzer and secure it with tape.

3. Place the film/foil object in a test stand in such a way that it covers the measuring window of the analyzer. If possible, take more than one layer of film and stack as many of them as are available over the measuring window of the analyzer. It is recommended the thickness of the stack be at least 5 mm. However, either
single layers or stacks can be analyzed as long as they are not less than 1 mm in thickness.

4. Based on the type of material, select appropriate analytical mode: Plastic Mode for all non-metallic materials and combinations of non-metallic and metallic Alloy Mode for all metallic materials

5. If Plastic Mode has been selected, set the thickness correction on the instrument to the actual thickness of the sheet or stack of film in [mm].

6. Start the measurement, preferably using the software programme.

7. Continue the measurement until the display says PASS or FAIL.

8. Interpret the results. Again, it is very important that one is well informed on how to interpret the actual results given by the Analyzer.
9. Continue measurements as planned.

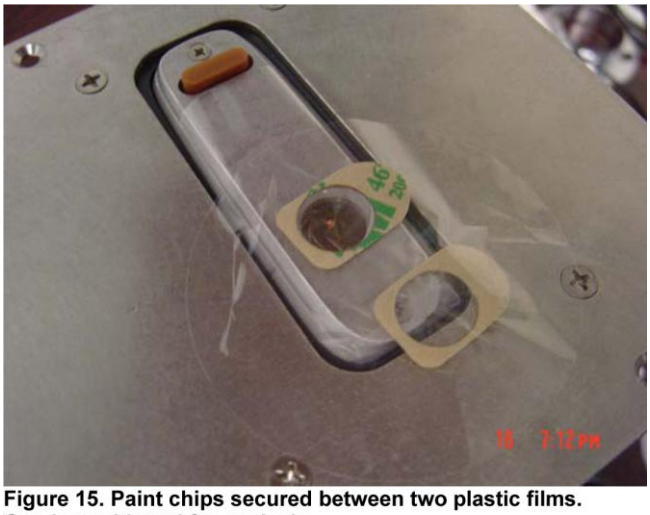

Figure 15. Paint chips secured between two plastic films. One is positioned for analysis.

4.1.5 Paint Chips

Some objects may have painted surfaces that will not be accessible for direct x-ray scan. In such circumstances, it is possible to scrape a small sample of paint and analyze it directly by placing it over the measurement window of the analyzer.

1. Mount the analyzer in a test stand and connect it to PC (via Serial Port, USB port, or Bluetooth). Start the software program on user's PC.

2. Stretch taut a piece of Mylar film over the measuring aperture of the analyzer and secure it with tape.

3. Take a Mylar film and spread it on a clean, flat surface.

4. With a sharp razor blade or Exacto knife, scrape paint from the area to be tested and place it over the Mylar film. Use caution during this step so as not to disturb the substrate material.

5. Take a Prolene window used for helium flush instruments and cover the chip of paint. Now the paint chip is secured between two thin plastic films and ready for analysis (see Figure 15).

6. Select the Plastic Mode of analysis. Set thickness correction to OFF.

7. Place the paint sample over analyzer window and perform a measurement. Typically, a 30-second analysis time is sufficient to ascertain the presence or absence of lead in the paint.

8. Continue the measurement until the display says PASS or FAIL.

9. Interpret the results. Again, it is very important that one is well informed on how to interpret the actual results given by the Analyzer

10. Continue measurements as planned.

4.1.6 Apparel

Screening and analyzing apparel items – fabric, appliqués, buttons, zippers, footwear –for toxic elements using XRF can pose some challenges. While these challenges can be met, it is important to keep some key concepts in mind to successfully perform the screenings and interpret the results. By nature, fabrics, in particular, are a very low-density sample. This means that the XRF instrument effectively "sees" less sample-per-unit area than with a metallic specimen, for example. One way to compensate for the lower density is to increase the analysis time, thereby allowing the instrument to gather more data. Another option is to increase the apparent mass of the sample "seen" by the instrument by folding the fabric several times. Using the latter technique may mitigate having to significantly increase the analysis time, though increasing the time still could be necessary.

Another consideration when analyzing fabrics is that the incident x-ray beam will penetrate the material relatively unimpeded, meaning that x-rays generated from the sample-support-medium beneath the fabric can pass back up through the fabric sample to the analyzer. Simply pressing the analyzer on the garment while it is being supported on a tabletop is a common temptation. As expedient as this appears, it is possible to get erroneous results if there are elements in the table that are the same as those elements being tested for in the sample material. In addition, there may be elements present in the table that interfere with the detection of the elements of interest in the sample material. In all cases, the composition of the tabletop should be non-metallic. Analyzing fabrics in one of the supplied test stands is always preferable, however, that may not always be practical because of the size of the sample undergoing screening or some other circumstance. If sample analysis on a tabletop is necessary, then the tabletop itself should be screened first with the analyzer to determine if it contains contaminate elements or if it contains significant concentrations of an element that could interfere with the target elements within the sample material. If the user determines, after screening, that tabletop does not pose an impediment to the analysis of the test specimens, then the fabric should be folded several times before subjecting it to analysis.

Proper x-ray safety procedures should be followed, which includes avoiding having any body parts under the tabletop where the analysis is being performed. The Niton XL3t used during the joint action on toys can also be used to analyze garments on a hanger, though the user may find that it is impractical to support the weight of the instrument for the entire analysis time. Please note that when undertaking this type of analysis, it is imperative that the user give proper consideration to radiation safety procedures, ensuring that no one could possibly be exposed to the x-ray beam after it passes through the hanging garment. Garment fasteners, such as buttons and zippers, should be centred as closely as possible over the analysis aperture of the instrument. If a signal is detected for any of the elements of concern, then the adjacent fabric should be tested to determine from where the signal is coming. Alternatively, the fastener of interest can be removed and screened separately, or the test specimen can be isolated using the 3 mm small-spot feature, if the analyzer is equipped with this option. Appliqués, such as decals or silk screens, can be screened directly. As in the above example,

the adjacent fabric material should be screened separately if an element of concern is detected to determine whether the signal is coming from the appliqués or the fabric.

Mount the analyzer in a test stand, if used, and connect it to PC (via serial port, USB port, or Bluetooth™). Start NDTr software program on the user's PC.

1. Place the object in a test stand in such a way that it is centred in the measuring window of the analyzer. If enough material is available, fold it over on itself several times.

2. Based on the type of material, select appropriate analytical mode:
    a. Plastic Mode for all non-metallic materials and combinations of non-metallic and metallic
    b. Alloy Mode for all metallic materials

3. Start the measurement, preferably using the respective software program.

4. Continue the measurement until the display says PASS or FAIL.

5. Interpret the results. Again, it is very important that one is well informed on how to interpret the actual results given by the Analyzer .

6. Continue measurements as planned.

5 CONCLUSION

Handheld x-ray fluorescence analyzers provide an effective way of screening a huge number of products to determine the content of heavy metals. The respective legislation within the European Economic Area and the respective European Standard (EN71-3) specify the importance of ultimately performing full laboratory testing for ***migration*** of heavy metals .Although there is no scientific direct correlation between the content of heavy metals and the migration of heavy metals, one may utilise XRF screening to minimise extensively the number of products sent for laboratory testing.

One needs to remember that having large quantities of content within a toy product does not necessarily mean that it will also result in migration of heavy metal too. However, from even the experience gathered from this particular joint action on toys itself, the probability increases substantially that a product will be found to have migration of heavy metals if the content is relatively high.

6 REFERENCES

- Screening Consumer Products for Toxic Substances X-ray Fluorescence and Reducing Compliance Risk
  (White Paper) August 2009

- Screening Toys, Children Jewelry, and Consumer Products for Lead (Pb) and Other Heavy Metals Using
  the Thermo Scientific Niton XL3t or Niton XLt 700 Series X-Ray Fluorescence (XRF) Analyzer with SoftwareVersion 6.2b and Higher(Standard Operating Procedure, January 2009)

- Information and direct experience gathered from the Joint Action on Toys (2009-2011)

APPENDIX A. BASIC GUIDE TO PURCHASING OF XRF HAND-HELD EQUIPMENT

The price of XRF hand-held equipment can vary considerably, ranging in price quite substantially, depending on the type of XRF bought and the accessories accompanying it. Indeed, in view of technological advances made and also due to the increase in usage of such equipment, the prices in the future may be considerably lower. At the same time, in view of the investment needed, it is very important that the market surveillance authority interested to purchase such equipment takes considerable care on how to choose such equipment.

The specifications shown below give a breakdown of the most important considerations that a market surveillance authority might wish to consider when analysing different XRF hand-held equipment. These are not comprehensive and only highlight some of the most important aspects that one may need to consider.

Having a number of interested market surveillance authorities issue a joint tender will usually make the business more interested in giving special packages since they would know that they are reaching a much more wider area of the EEA and also due to economies of scale. For this reason, it is highly recommended that PROSAFE is contacted in order to check whether there may be other surveillance authorities who currently might be interested to also purchase XRF equipment and so that PROSAFE could also share any other lessons learnt from the issuing of such joint tenders.

Specifications

1. System

1.1 Lightweight, compact and convenient for transport and to reach samples in difficult situations.

1.2 Splash and dust proof.

1.3 No effect of temperature, humidity and dust on the measurement.

1.4 Battery should be of quality to measure for longer periods without recharging.

1.5 Automatic detection of matrix (metal, plastic) should be possible.

1.6 Detection of heavy metals should be possible for textiles, plastic and wooden toys, jewellery and packaging material.

1.7 Internal calibration of the instrument for a wide range of elements from the periodical system is necessary. Additional information should be applied for which elements this is possible.

1.8 Reliable results at low concentrations should be available within a few seconds and traceable.

1.9 Hands-free use should not influence the confidence in the results.

1.10 Available assay and grade libraries.
1.11 X-ray tube should be minimally 40 kV.
1.12 The equipment should possibly also have the possibility to equip with small spot focus

2. Software

2.1 Easy to use.
2.2 Possible to program series of analysis including alarm limits and test criteria.
2.3 Option to show only the elements of interest or all detected elements.

2.4 Input sample names by touch screen or by barcode reader.

2.5 Easy transfer of data to PC.
2.6 Software compatible with Microsoft Windows.

2.7 Excel compatible and possibility to generate quality control (QC) reports.
2.8 Possibility to add information to existing libraries or edit an existing library or create a new library.

3 General

3.1 It should be possible to conclude a service level agreement (SLA). In this SLA intervention time for technical malfunctions should be included.

3.2 A comprehensible instruction manual should be available in the English language.

4 Safety

4.1 The handheld XRF should be marked with a CE label and should therefore comply with all regulations mentioned in the Health and Safety at Work Act.

4.2 The user should not be exposed to radiation during normal use.

4.3 For mobile use, there should be the possibility to use a radiation shield for protection against scattered radiation.

5 Installation and implementation

5.1 After installation the instrument should be demonstrable comply with all specifications declared by the supplier

6. Handling

6.1 Easy handling for mobile use: results of screening with variation should possibly be visible during measurement.